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THE REACTION OF ATOMIC OXYGEN

WITH ORGANIC COMPOUNDS

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Arthur Mosher

7/25/68

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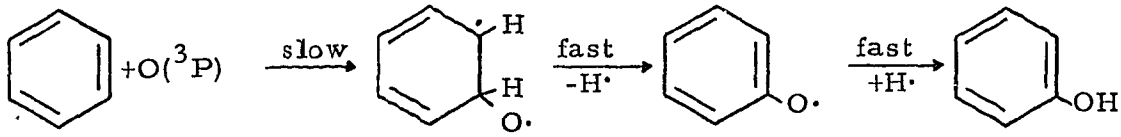
SUMMARY

The purpose of this research was to study the reaction of hydrocarbons with atomic oxygen; the major emphasis was placed on product determination and reaction rates. The majority of work concerned the oxidation of aromatic compounds with ground state atomic oxygen, $O(^3P)$. The experimental technique of choice was the mercury photosensitized decomposition of nitrous oxide at 2537Å; a flow system at atmospheric pressure and 30°C was found to be convenient for most aromatic compounds studied. The compounds successfully oxidized were: benzene, toluene, ethylbenzene, tert-butylbenzene, ortho-, meta-and para-xylene, mesitylene, 1, 2, 3-trimethylbenzene, anisole, fluorobenzene, benzotrifluoride and nitrobenzene. In every case the main products were phenols. When ortho-methyl groups were present, methyl cleavage (resulting in phenols) became an important reaction. No evidence for formation of anisoles was found in the most favorable case, that of 1, 2, 3-trimethylbenzene.

After the identity of the primary volatile addition products had been established, kinetic analysis of the relative reactivity (and attendant partial rate factors) was made. The logarithm of the partial rate factors gave a satisfactory Hammett relationship when plotted versus $\sigma+$ constants; this confirms the electrophilic nature of oxygen atoms.

It was also found that the logarithm of the partial rate factors gave a fair straight line when plotted against the calculated ground state electron densities of the aromatic hydrocarbons. This was interpreted as good evidence for an early rate-determining transition state in the $O(^3P)$ oxidation of hydrocarbons. The activating effect of methyl groups was found to be a function of their position and number. A plot of calculated reactivity (based upon toluene) versus the experimental reactivity of the polymethylbenzenes as ordinate gives a straight line with a fall-off factor (slope) of 0.84. Linear free energy correlations with related reactions were also found.

A kinetic isotope effect ($\frac{k_H}{k_D}$ of 1.14) was determined for an equimolar mixture of benzene and deuterobenzene. This is in agreement with the mechanism of $O(^3P)$ oxidation of benzene shown below:



σ-complex

Since the partial rate factors for $O(^3P)$ correlate well with calculated electron densities of the ground state hydrocarbon, the reaction is believed to have an early transition state. The absence of anisoles argues for two fast steps following σ-complex formation rather than an intramolecular hydrogen shift. However, a one-step rearrange-

ment from the σ-complex to the product phenol is not ruled out.

Oxidation of aromatics via a microwave glow discharge through CO_2, O_2 or N_2O gave substantially different product distributions than did the mercury-nitrous oxide technique. Although benzene and benzotrifluoride gave only phenols, toluene and para-xylene gave large amounts of side chain oxidation as well as substantial amounts of methyl cleavage. Thus the side chain in toluene was oxidized to give benzaldehyde and benzyl alcohol as well as cleaved to produce phenol. Attempts to determine the side-chain oxidant in the discharge were made; excited aromatic substrate, ozone, $O(^1D)$ and $O(^3P)$ were considered. The best rationale at this time is that $O(^3P)$, reacting at a high temperature, is responsible for the observed products.

The action of ozone on toluene and cyclohexane received brief attention as did the reaction of $O(^1D)$ with cyclohexane. The photodecompositions of various substrates as toluene, nitrobenzene, anisole, chlorobenzene and bromobenzene are also discussed. The possibility of nitrobenzene photolysis as a source of $O(^3P)$ was investigated; preliminary results imply that $O(^3P)$ is not the sole oxidizing agent generated.

CHAPTER I

INTRODUCTION AND HISTORICAL BACKGROUND

During the past fifteen years, the reactions of atomic oxygen with organic compounds have received increased attention. The majority of work concerns the reaction of ground state atomic oxygen (^3P) with olefins, only five papers dealing with O(^3P) and aromatic or saturated hydrocarbons have been thus far published. Of the electronically excited states of atomic oxygen, only O(^1D) has received much attention. The majority of work on atomic oxygen has been done by physicists and physical chemists; the generation, deactivation and kinetic analysis of reaction rates are the prime topics. These aspects will not be covered here, save a few of the more pertinent references for our work.

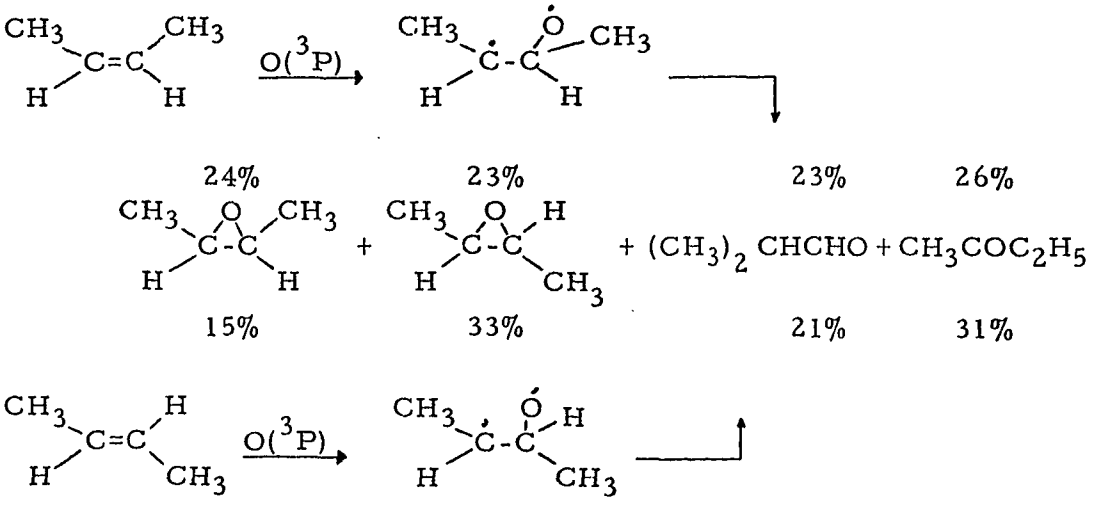
The purpose of this research is to study the reactions of atomic oxygen with aromatic compounds since this class of hydrocarbons has been essentially ignored to date. This study is primarily concerned with mechanistic implications based upon the oxidation products and relative rates of reaction.

Ground State Atomic Oxygen, O(^3P)

The man who put the reactions of atomic oxygen with organic

compounds "on the map" is R. J. Cvetanović. The products, relative and absolute rates, stereochemistry and postulated mechanism of $O(^3P)$ oxidation of olefins and alkanes are among his credits[1]. His usual method of generating atomic oxygen is the mercury photosensitized decomposition of nitrous oxide in a static system (50-600 mm pressure) at room temperature.

The oxidation of olefins is believed to proceed through an intermediate bi-radical from preferential attack of oxygen at the less substituted sp^2 carbon of the olefin. This bi-radical then rearranges to a carbonyl compound or collapses to an epoxide. The case of <u>cis</u> and <u>trans</u>-2-butene[2] is of interest since it sheds some light on the postulated bi-radical intermediate. Here, if the bi-radical has a sufficient lifetime, identical product distributions should be obtained.



1 R. J. Cvetanović, <u>Advan. Photochem.</u>, <u>1</u>, 115 (1963)
2 R. J. Cvetanović, <u>Can. J. Chem.</u>, <u>36</u>, 623 (1958)

Obviously, equilibrium between the bi-radicals is only partially achieved before conversion to the final products. Hence the bi-radical has a lifetime of the same magnitude as rotation around the 2-3 carbon-carbon bond.

Due to the large exothermicity of these oxidations, fragmentation of the olefins can be a disruptive side reaction. This is seen in the extreme case of ethylene where at high pressures[3] the main products are ethylene oxide and acetaldehyde. However, at low pressure[4], cleavage to formaldehyde and hydrogen is observed; presumably $\dot{C}H_3$ and $\dot{C}HO$ radicals are the primary products. High pressures, heavier olefins (increased degrees of freedom), and lower reaction temperatures can greatly decrease the extent of fragmentation.

The most recent work on the reaction of $O(^3P)$ with olefins has been done by Klein and Sheer[5, 6]. Their work was done at much lower temperatures (90°K - liquid oxygen) than Cvetanović used; $O(^3P)$ was generated via the dissociation of molecular oxygen on a rhenium ribbon heated to 2300°K[7]. The olefins studied were dissolved in propane; propane was found inert to $O(^3P)$ at temperatures below 150°K[8].

---

3 R. J. Cvetanović, J. Chem. Phys., 23, 1375 (1955)
4 J. T. Herron and R. D. Penzhorn, J. Phys. Chem., 73, 191 (1969)
5 R. Klein and M. D. Sheer, J. Phys. Chem., 73, 597 (1969)
6 R. Klein and M. D. Sheer, J. Phys. Chem., 73, 1398 (1969)
7 A. N. Hughes, M. D. Sheer and R. Klein, J. Phys. Chem., 70, 798 (1966)
8 R. Klein and M. D. Sheer, J. Phys. Chem., 72, 616 (1968)

The unsymmetrical olefin 2-methyl-2-pentene[6] was used to determine the migratory aptitudes of alkyl versus hydrogen and illustrate a subtle difference in mechanism. Instead of oxygen attacking perpendicular to the plane of the olefin to form Cvetanović's bi-radical, the oxygen is considered to attack the double bond in the plane of the olefinic structure. This allows interaction between the oxygen and the nearest neighbor hydrogens bonded to the sp^2 carbon earlier in the transition state. Of course, this results in preferential attack at the least substituted carbon.

Some interesting work with halo-olefins has appeared within the last four years. Saunder and Heicklen[9, 10] found that $O(^3P)$ with C_2F_4 gave CF_2O and $\ddot{C}F_2$ (isolated as cyclo-C_3F_6), but no C_2F_4O. Mitchell and Simons[11] verified the above and also found that when CF_2CCl_2 was oxidized with $O(^3P)$ the primary reaction was the formation of CF_2O and $\ddot{C}Cl_2$ (isolated as CCl_2CCl_2).

Tyerman followed the oxidation of C_2F_4 by spectroscopy and believes that $\ddot{C}F_2$ is in its triplet ground state[12]. When O_2 is present, small amounts of C_2F_4O can be identified. Although C_2F_4 reacts with $O(^3P)$ about as fast as C_2H_4, partial substitution of CF_3 lowers the

9 D. Saunders and J. Heicklen, J. Phys. Chem., 70, 1950 (1966)
10 D. Saunders and J. Heicklen, J. Am. Chem. Soc., 87, 2088 (1965)
11 R. C. Mitchell and J. P. Simons, J. Chem. Soc., Sect. B, 1005 (1968)
12 W. J. R. Tyerman, Trans. Faraday Soc., 65, 163 (1969)

relative rate appreciably[13]. Thus the relative rate of 2-trifluoromethylpropene to 1-butene is 0.077. The final halide studied was CCl_4. The reaction products[14] were $COCl_2$, Cl_2, CO and CO_2.

$O(^3P)$ oxidation of compounds other than olefins has received limited study only. Wright studied iso-butane[15] and neopentane[16] via the nitric oxide titration method.

$$N_2 \xrightarrow[\text{discharge}]{\text{microwave}} N\cdot \xrightarrow{NO} N_2 + O(^3P)$$

It is noteworthy that photolysis of NO_2 and Hg^*, N_2O[a] gave the same major products as the nitric oxide titration. Iso-butane gave CO, CO_2, H_2 and H_2O as the major products. The more interesting products were CH_4, CH_3COCH_3, $(CH_3)_2CHCHO$ and $(CH_3)_2C=CH_2$. Small amounts of t-BuOH, H_2CO, CH_3CHO and C_3H_6 were also obtained. It should be noticed that no i-BuOH or butane dimers were formed; this appears to rule out hydrogen abstraction as a primary reaction. The postulated mechanism includes three major eliminations. The first gives water and iso-butylene, the second gives hydrogen and iso-butraldehyde and the third gives methane and acetone.

Most other references[17] alluding to $O(^3P)$ with alkanes do not

---

a Abbreviation for mercury-photosensitized decomposition of N_2O.

13 S. J. Moss and K. R. Jennings, Trans. Faraday Soc., 64, 686 (1969)
14 A. Y-M. Ung and H. I. Schiff, Can. J. Chem., 40, 486 (1969)
15 F. J. Wright, J. Chem. Phys., 38, 950 (1963)
16 F. J. Wright, Tenth Symposium (International) on Combustion, 387 (1965)
17 W. K. Stuckey and J. Heicklen, J. Chem. Phys., 46, 4843 (1967)

identify the products, but just measure rates of reaction assuming hydrogen abstraction as the primary step. The only paper concerning alkyl halides with atomic oxygen is quite recent[18]. Hydrogen abstraction is again considered to be the first reaction. As usual, no product analysis was done.

In justification of the hydrogen abstraction reaction of $O(^3P)$ with alkanes, Cvetanović found[19] that a shift to secondary radicals occured when $O(^1D)$ was deactivated to $O(^3P)$. It was found that $O(^1D)$ with propane gave (in addition to other products) the following hexane distribution:

2-Methylpentane	2, 3-dimethylbutane	n-hexane
47%	23%	30%

The addition of an efficient electronic deactivator as xenon, changed this distribution to:

2-Methylpentane	2, 3-dimethylbutane	n-hexane
44%	45%	11%

This shift toward iso-propyl radicals was viewed as a change in atomic oxygen from (^1D) to (^3P). Thus, the more selective $O(^3P)$ generates secondary radicals in preference to primary radicals.

Oxidation of acetylenes via $O(^3P)$ has been limited to acetylene itself. When in a solid matrix (20^oK), ketene was the sole product[20].

---

18 J. T. Herron and R. E. Huie, J. Phys. Chem., 73, 1327 (1969)
19 H. Yamazaki and R. J. Cvetanović, J. Chem. Phys., 41, 3703 (1964)
20 I. Haller and G. C. Pimentel, J. Am. Chem. Soc., 84 2855 (1962)

$O(^3P)$ with gaseous C_2H_2 gives no ketene[21] but rather carbon monoxide, hydrogen, allene, propyne and tar. The proposed mechanisms for these two reactions are analogous to those for ethylene and $O(^3P)$. In one study[22] diacetylene was also found as a product.

The reaction of $O(^3P)$ with aldehydes, alcohols and ethers, results in α-hydrogen abstraction. Formaldehyde gives CO, H_2O, H_2 and CO_2; acetaldehyde[23, 24] gave H_2O and biacetyl presumably via hydrogen abstraction from the alpha position of the aldehyde by $O(^3P)$ and $\dot{O}H$, then dimerization of the organic radicals.

This preferential hydrogen abstraction gives rise to acetone and pinacol when iso-propyl alcohol[25] is oxidized. Dimethyl ether[26] gives $CH_3OCH_2CH_2OCH_3$ as a main product in addition to H_2O, CH_3OH, H_2CO and CH_3OCH_2OH.

The reaction of $O(^3P)$ with aromatics has received pertinent study only from Cvetanović. Benzene[27] gave phenol as the only addition product; H_2O, CO and tar were also formed. About 80% of the benzene consumed could be accounted for; tars accounted for 60%, CO

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21 D. G. Williamson and K. D. Bayes, J. Phys. Chem., 73, 1232 (1969)
22 C. A. Arrington et al., J. Chem. Phys., 43, 525 (1965)
23 R. J. Cvetanović, Can. J. Chem., 34, 775 (1956)
24 H. E. Avery and R. J. Cvetanović, J. Chem. Phys., 43, 3727 (1965)
25 A. Kato and R. J. Cvetanović, Can. J. Chem., 46, 235 (1968)
26 H. Kawasaki and Y. Takezaki, Bulletin of the Institute of Chemical Research; Kyoto University, 42, 378 (1964)
27 G. Boocock and R. J. Cvetanović, Can. J. Chem., 39, 2436 (1961)

accounted for 7% and phenol for about 13%. Toluene[28] gave the expected cresols as well as polymer, CO and water. The cresols accounted for 15 to 20% of the oxygen atoms produced, water accounted for about 7% and polymer was present in approximately 60%. Thus about 20% of the oxygen atoms were unaccounted for. The product distribution of cresols was 80 ± 10% ortho, 15 ± 5% para and less than 5% meta. The relative rates of reaction of both aromatics was measured relative to cyclopentene. Combination of these two values gives the relative rate of reaction of toluene to benzene as 2.7 ± 0.5 at 120°C.

Other work with aromatics is much less definitive due to the experimental technique used. Thus, the photo-oxidation of alkylbenzene-nitrogen dioxide mixtures in air was studied in 1964[29]. However, the reaction was allowed to proceed to such an extent that the primary reactions were obscure. All the aromatics studied gave unidentified aldehydes, CO, CO_2, formic acid, peroxyacetyl nitrate and polymer. Ring cleavage rather than substitution was the main reaction. Even though $O(^3P)$ was generated, subsequent radical reactions made any interpretation of $O(^3P)$ with aromatics impossible. Further complications involve ozone produced when nitrogen dioxide is photolized in air.[30]

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28 G. R. H. Jones and R. J. Cvetanović, Can. J. Chem., 39, 2444 (1961)

29 S. L. Kopczynski, International Journal of Air and Water Pollution, 8, 107 (1964)

30 P. L. Hanst, E. R. Stephens and W. E. Scott, Journal of the Air Pollution Control Association, 5 (Feb.), 219 (1956)

Excited Atomic Oxygen, $O(^1D)$

In contrast to $O(^3P)$, the reactions of $O(^1D)$ are in a state of infance; only olefins and alkanes have been studied thus far. In 1958, Cvetanović[31] initiated the study of $O(^1D)$ with olefins by photolyzing NO_2 at different wavelengths; the differences in product distribution from the substrate, 1-butene, allowed a distinction between $O(^3P)$ and $O(^1D)$. At long wavelengths, (3261Å), $O(^3P)$ is the principal species and the resulting ratio of ∝-butene oxide to butanal is about 1.2. At shorter wavelength, (2288Å), this ratio is 2.6; here $O(^1D)$ is the principal species. The relative increase in oxide formation is presumed due to the spin-allowed addition of $O(^1D)$ directly to the double bond of the olefin to give the oxide in one step. Due to the reaction of NO_2 with the oxide product, only trends in product distribution could be reproduced. As expected from the above interpretation, as the total pressure (adjusted with N_2) is increased at 2288Å, the product distribution is shifted to that gotten from the longer wavelength. Thus, collisional deactivation of $O(^1D)$ to $O(^3P)$ is demonstrated. As seen earlier in this survey, NO_2 photolysis is among the least attractive methods of studying any species of atomic oxygen due to secondary reactions.

The most recent paper[32] on $O(^1D)$ and olefins utilized the photolysis of ozone at 2537Å; in this technique the fast reaction between O_2 and

---

31 S. Sato and R. J. Cvetanović, Can. J. Chem., 36, 1668 (1958)
32 W. B. DeMore, J. Phys. Chem., 73, 391 (1969)

$O(^3P)$ to give ozone will eliminate competitive oxidation by $O(^3P)$. The rate of reaction of O_3 compared to $O(^1D)$ was negligible with both ethylene and tetrafluoroethylene. However, ozonolysis was more rapid for higher olefins and a quantitative study of $O(^1D)$ oxidation could not be made. Although C_2F_4 reacts as fast as C_2H_4 with $O(^3P)$, only a small amount of reaction took place between C_2F_4 and $O(^1D)$. Infrared spectroscopy was used to identify CF_2O; CF_3CHO, C_2F_4O and cyclo-C_3F_6 could not be detected.

In the presence of added oxygen[32], ethylene and $O(^1D)$ gave 18% acetaldehyde, 14% ethylene oxide, 6% hydrogen and 2% acetylene based on the decomposed ozone. When oxygen was not present, the reaction was ethylene with $O(^3P)$; here acetaldehyde and ethylene oxide accounted for 85% of the decomposed ozone. The three reactions postulated for ethylene and $O(^1D)$ were elimination of water to give acetylene, C-H insertion to give the corresponding enol which rearranged to acetaldehyde and addition to the double bond to give excited ethylene oxide which then was either stabilized or rearranged to acetaldehyde.

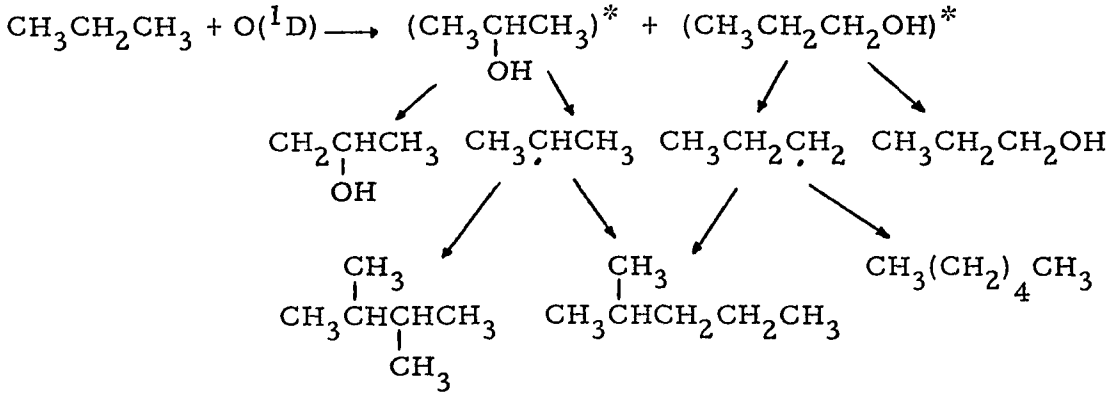
The reaction of $O(^1D)$ with alkanes was initiated between 1957 and 1959 by Noyes[33] and then left fallow until 1964. Noyes found nine products from ethane and $O(^1D)$ and postulated[34] that a major pathway

33 G. A. Castellion and W. A. Noyes, Jr., J. Am. Chem. Soc., 79, 290 (1957)

34 E. Murad and W. A. Noyes, Jr., J. Am. Chem. Soc., 81, 6405 (1959)

was a one-step dehydrogenation to give ethylene and water; the $O(^1D)$ then preferentially attacked the product olefin.

Cvetanović investigated the oxidation of propane[19] and found that the propyl alcohols and propyl dimers were principal products. The ratio of n-propyl alcohol to iso-propyl alcohol was about three; this statistical distribution was expected for C-H insertions by the energetic $O(^1D)$ atoms. The postulated mechanism was:



Some fragmentation to n-pentane, 2-methylbutane, n-butane, ethane and methane was also found.

More recently, Cvetanović investigated the reaction of $O(^1D)$ with iso-butane[35]. Again, indiscriminate C-H insertion analogous to propane was observed. The ratio of iso-butyl alcohol to tert-butyl alcohol is 12.6 at 82 torr but decreases to 9.4 at high pressures. This change is attributed to the excited iso-butyl alcohol being more easily

35 G. Paraskwapoulos and R. J. Cvetanović, J. Chem. Phys., 50, 590 (1969)

stabilized at lower pressures. As expected, the relative amounts of alcohol plus dimer to fragmentation products is higher for iso-butane than propane. This is due to the increase in degrees of freedom in iso-butane.

W. B. DeMore co-workers have also studied $O(^1D)$ with alkanes via ozone photolysis at 90°K. Methane[36], ethane[37], propane[37] and isobutane[32] were studied. For methane, three paths were postulated; the first was elimination of hydrogen to give formaldehyde. The other paths were formation of "hot" methanol which either was stabilized or dissociated to methyl and hydroxyl radicals.

With ethane and propane, no radicals were produced as expected from the increase in degrees of freedom. Propane[32] gave a ratio of n-propyl to iso-propyl alcohol of 3.2 ± 0.3 while iso-butane gave a ratio of iso-butyl to tert-butyl alcohol of 8.7 ± 0.4. The relative rates of oxidation of hydrogen, methane, ethane and propane were: 1.0, 1.16, 1.9 and 2.5 The energy of activation for $O(^1D)$ attack on C-H bonds was found to be zero.

At this time, no work on the reactions of $O(^1D)$ with acetylenes, aromatics, alcohols, carbonyl compounds or ethers has been published. Since the work of DeMore implies that the atomic oxygen of Avramenko

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36 W. B. DeMore and O. F. Raper, J. Chem. Phys., 46, 2500 (1967)

37 W. B. DeMore and O. F. Raper, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Florida, April (1967) No. R 028

may be in the (^{1}D) state, Avramenko's work is discussed next.

The reactions of atomic oxygen (state unspecified) with alkanes, olefins, alcohols, aromatics and carbonyl compounds have been studied by Avramenko and co-workers for some time. Since their product analysis does not agree with other workers, I believe that they may actually be using excited atomic oxygen, such as O(^{1}D). The passage of oxygen[38] (or water vapor) through a high voltage electrical discharge gave phenol when benzene was subsequently added to the gas stream; CO, CH_2O and unidentified material was also found. Ethane[39] gave mainly formaldehyde and CO with smaller amounts of acetaldehyde and ethanol. Olefins[40] gave mainly formaldehyde as did alkanes.

Acetaldehyde[39] gave glycolic acid, ketene, formic and acetic acids. In more recent work[41] with n-octane; formaldehyde, and unidentified aldehydes and acids were obtained. Also, both cis and trans-2-butene[41] gave formaldehyde, methyl ethyl ketone, "acid"and possibly acetaldehyde. Ethanol[42] gave formaldehyde, acetaldehyde,

38 L. I. Avramenko, I. I. Ioffe and R. V. Lorentso, Doklady Akad. Nauk SSSR, 66, 111 (1949); Chem. Abstr. 43, 7922h (1949)

39 L. I. Avramenko and R. V. Kolesnikova, Advan. Photochem., 2, 25 (1964)

40 L. I. Avramenko, R. V. Kolesnikova and G. I. Savinova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, No. 1, 36 (1963); Chem. Abstr., 58 10770e (1963)

41 L. I. Avramenko, R. V. Kolesnikova and G. I. Savinova, Izv. Akad. Nauk SSSR, Ser. Khim. No. 2, 253 (1967); Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 2, 247 (1967)

42 L. I. Avramenko, R. V. Kolesnikova and G. I. Savinova, Izv. Akad. Nauk SSSR, Ser. Khim. No. 1, 22 (1967); Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 1, 19 (1967)

carbon monoxide and traces of "acid".

As stated previously, Avramenko must have a different form of atomic oxygen than that obtained by Cvetanović. One cannot help but wonder what role, if any, ozone plays in Avramenko's system.

Atomic Oxygen from Electrical Discharge

Oxidation of organic compounds via electrical discharges is still in a descriptive stage of development; useful references are few far between. Electrical discharges (usually 2450 MHz) in carbon dioxide, oxygen or air produce atomic oxygen; unfortunately reactive species other than $O(^3P)$ are produced. Thus $O_2\ (^1\Delta_g)$[43,44], $O_2\ (^1\Sigma_g^-)$[45], $O(^1D)$[46,47,48], $O(^1S)$[49], $O(^5S_o)$[50], O_3[51] as well as ionic species[47,52] are known in electrical discharges through oxygen. The ground state of atomic oxygen has been considered to be the only active species resulting from a microwave discharge in oxygen when the sub-

43 R. P. Wayne, Advan Photochem., 7, 311 (1969)
44 E. J. Corey and W. C. Taylor, J. Am. Chem. Soc., 86 3881 (1964)
45 R. L. Brown, J. Phys. Chem., 71, 2492 (1967)
46 F. J. LeBlanc, O. Oldenberg and N. P. Carleton, J. Chem. Phys., 45, 2200 (1966)
47 C. W. Nutt and A. J. Biddlestone, Trans. Faraday Soc., 58, 1368 (1962)
48 W. D. McGrath and J. J. McGarvey, Planetary and Space Science 15, 427 (1967)
49 G. Kvifte and L. Vegard, Geofysiske Publikasjoner, Utgitt av det Norske Videnskaps Akademi i Oslo, 17, 3 (1947)
50 G. O. Brink, J. Chem. Phys., 46, 4531 (1967)
51 L. Elias, E. A. Ogryzlo and H. I. Schiff, Can. J. Chem., 37, 1680 (1959); L. Elias and H. I. Schiff, ibid, 38, 1657 (1960)
52 E. A. Ogryzlo and H. I. Schiff, J. Chem. Phys., 32, 628 (1960)

sequent reaction with organic molecules has been investigated[1, 18]. The wisdom of this assumption is quite questionable in my mind. Recalling the work of Avramenko, DeMore, and Noyes on $O(^1D)$ with ethane to give complicated product mixtures, it seems reasonable that a microwave discharge technique could indeed provide $O(^1D)$ as well as $O(^3P)$ and ozone. Due to the different experimental conditions such as pressure, temperature and extent of oxidation, it is difficult to draw any firm conclusions on the type of atomic oxygen resulting from a discharge[48].

Jarvie and Cvetanović[53] studied the oxidation of 1-butene via a 2450 MHz discharge in pure oxygen or dilute oxygen in helium. They decided that $O(^3P)$ was responsible for the products at low oxygen pressures and that ozone was responsible at high oxygen pressures. The ratio of α-butylene oxide to butanal was 1.3 ± 0.3 at low oxygen pressures; this is within experimental error of the ratio of 1.2 given previously for the Hg^*, N_2O technique. The primary products, (α-butylene ozonide, butanal and methyl ethyl ketone) became less significant when the pressure of the discharge was less than 10 torr. This behavior was attributed to less collisional stabilization of the initial "hot" products at low pressures but it could well be due to less collisional deactivation of other active species as $O(^1D)$ and $O(^1S)$ as the pressure of the discharge decreases. The presence of HCHO, CH_3CHO and C_2H_5CHO in

53 J. M. S. Jarvie and R. J. Cvetanović, Can. J. Chem., 37, 529 (1959)

Cvetanović's work partially coincides with Avramenko's work on propene[39] which gave H_2CO, CH_3CHO and CO in addition to other products. Of course ozone reacts with 1-butene to give HCHO and CH_3CH_2CHO; this leads us to the possibility of ozone in Avramenko's system.

Other interesting notes on the type of atomic oxygen from a microwave discharge in oxygen can be seen in the work of Kaufman[54]. He postulated $O(^3P)$ only since the addition of hydrogen did not give a rapid reaction as expected if $O(^1D)$ was present. However, Elias[55] used an electric discharge to study the rate of reaction of ethylene with atomic oxygen and disagreed with the value of the energy of activation obtained by Cvetanović. In repeating his work, using the NO titration technique, Elias could not resolve the differences. Fontyn and Ellison[56] used the NO titration of Elias to obtain $O(^1S)$. Apparently, the identity of atomic oxygen generated by electrical discharge is open to question.

The oxidation of benzene to phenol by the use of an electrical discharge in oxygen[39] or air is well known. When a mixture of benzene and air is passed through a silent electrical discharge, phenol is formed[57]. The reactive species was considered to be atomic oxygen; the consumption of atomic oxygen by benzene inhibited ozone formation[58]. This technique with toluene gave 28% benzyl alcohol, 17% benzaldehyde,

54 F. Kaufman, Proc. Roy. Soc., London, A247, 123 (1958)
55 L. Elias, J. Chem. Phys. 38, 989 (1963)
56 A. Fontijn and R. Ellison, J. Phys. Chem., 72, 3701 (1968)
57 K. Sugino and E. Inoue, Bull. Chem. Soc., Japan, 24, 93 (1951)
58 E. Inoue and K. Sugino, Advan. Chem. Ser., 21 313 (1959)

3% benzoic acid, 27% ortho-cresol and 25% tars, (meta and para cresols possibly included with the ortho-cresol). Cyclohexane gave 63% cyclohexanol, 22% cyclohexanone, 3% adipic acid and 15% tars. Although the type of atomic oxygen is never mentioned, it appears to me that $O(^1D)$ could be present as well as $O(^3P)$. The mechanism of Sugino and Inoue, involves hydrogen abstraction to give the cyclohexyl radical; this then reacts with molecular oxygen and eventually is found as cyclohexanol and cyclohexanone.

In the same vein, Sonoda and co-workers[59] passed a mixture of cyclohexene and air through a silent electrical discharge to obtain 14% cyclohexanol, 16% cyclohexanone, 28% cyclohexenol, 21% cyclohexenone, 12% cyclohexene oxide and 9% of saturated and unsaturated cyclohexyl dimers. Their postulated mechanism involved cyclohexyl radicals reacting with molecular oxygen; atomic oxygen was not mentioned.

Since Cvetanović[27] found that $O(^3P)$ with cyclohexene gave cyclohexanone, cyclohexene oxide and cyclopentane carboxaldehyde (no per cent distribution given), the interpretation of Sonoda's work may not include $O(^3P)$ at all. However, $O(^1D)$ cannot be ruled out as the principal reactive species.

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59 N. Sonoda et al., Advan. Chem. Ser., 76, 352 (1968)

CHAPTER II

REAGENTS AND MATERIALS

Organic Substrates

The hydrocarbons studied are listed in Table I. All were of purity equal to or greater than 99% by our glc analysis[a] and gave one peak unless otherwise noted. Purification was accomplished by distillation through a N/F column[b]. This column is of the spinning band variety; the magnetically driven band is constructed of a stainless steel spiral screen having 300 teeth per inch. The band contacts the walls of the still and provides 28 plates. The column has an 8 mm bore, and is 24 in tall.

Table I Hydrocarbons Used

Substrate	Source	Purification[c]
Benzene	Fisher Chemical, 99 mole %	distilled at 80°
Toluene	Baker Analyzed	distilled at 109°
o-Xylene	Phillips '66, 99+%	distilled at 141°, three peaks on glc, 99. min%
p-Xylene	Phillips '66, Research grade	used as is
m-Xylene	Phillips '66, 99+%	used as is
Mesitylene	Columbia chemical "puriss" grade	distilled at 161°
1,2,3-Trimethylbenzene	Aldrich Chemical	distilled four times at 173-4° four peaks on glc, 99.5 min %

a glc is abbreviation for gas-liquid chromatography (chromatograph).
b N/F is abbreviation for Nester-Faust column described.
c Boiling points are quoted in uncorrected centigrade degrees and at atmospheric pressure unless otherwise noted.

continuation of Table 1

Substrate	Source	Purification
Ethylbenzene	Matheson, Coleman and Bell	distilled twice at 134°, glc showed 99.4 min %
t-Butylbenzene	Phillips '66, 99 mole %	distilled at 168°
Fluorobenzene	Aldrich Chemical	distilled at 84°
Benzotrifluoride	Aldrich Chemical	used as is
Nitrobenzene	Eastman White Label	distilled at 39° (200u)
Anisole	Eastman White Label	distilled at 149-150°
Chlorobenzene	Fisher Certified (mono)	used as is
Bromobenzene	Eastman White Label	used as is
Pyridine	Eastman White Label	distilled at 113°
Cyclohexane	Baker Analyzed, G.C.-Spectrograde	distilled at 80°
Cyclohexene	Phillips '66, 99+ mole %	distilled at 82°, added 0.02% 2,6-di-t-butyl-p-cresol as inhibitor

Gases

All gases in this work were used as received without further purification. Table 2 lists the nine gases which were used, the source and the manufacturer's statement of purity.

Table 2 Gases

Gas	Source	Purity
Butane	The Matheson Co.	99.5%
Propane	The Matheson Co.	99.5%
Nitrous Oxide	The Matheson Co.	98.% (2% air)
Nitrogen	American Cryogenics	99.999%[a]
Oxygen	American Cryogenics	99.9%
Carbon Dioxide	Marks Oxygen Co.	99.98%
Air	American Cryogenics	-
Helium	The Matheson Co., ultra-pure grade, Gold Label	99.995%
Nitrogen Dioxide	The Matheson Co.	99.5%

a The actual purity is probably no better than 99.9%.

Products of Oxidation

The compounds used as qualitative or quantitative standards are listed in Table 3 according to the parent substrate oxidized. Unless otherwise noted, all distillations were done using the N/F column. All sublimations were done in an ordinary sublimation apparatus with a Welch vacuum pump where necessary. The procedures for compounds not obtained from commercial sources are given at the conclusion of Table 3.

Table 3 GLC Standards

Compound	Source	Purification[a]
Phenol	Baker Analyzed	used as is
Biphenyl	Paragon Chemical	" " "
o-Cresol	Eastman Practical Grade	dist at 185°, then at 51° (4 torr)
m-Cresol	Eastman Practical Grade	dist at 60° (4 torr)
p-Cresol	Matheson, Coleman and Bell	dist at 48° (300μ)
Benzyl Alcohol	Fritzsche Bros. Inc.	dist[b] at 199°
Benzaldehyde	Fisher Certified	used as is
Anisole	Eastman White Label	dist at 149-150°
Bibenzyl	" " "	used as is
o-Ethylphenol	" " "	dist at 35-38° (60μ)
m-Ethylphenol	Eastman Yellow Label	dist at 100° (200μ)
p-Ethylphenol	" " "	subl at 60° (50μ)
Phenetole	Georgia Tech Stock	used as is
Methyl Benzyl Ether	" " "	" " "
Acetophenone	" " "	" " "
Phenylacetaldehyde	Matheson, Coleman and Bell	" " "
α-Methylbenzyl Alcohol	Georgia Tech stock	" " "
Phenethyl Alcohol	Eastman White Label	" " "
Styrene Oxide	Georgia Tech stock	" " "
2, 3-Dimethylphenol	Aldrich	recryst from toluene, m p 73-75°
3, 4-Dimethylphenol	Aldrich	used as is
o-Tolualdehyde	K & K Chemical Co.	" " "

continuation of Table 3

Compound	Source	Purification
o-Methoxytoluene	Aldrich	used as is
o-Methylbenzyl Alcohol	Alfred Bader Chemicals	" " "
2, 6-Dimethylphenol	Aldrich	recryst from $CHCl_3$, m p 43-45°
2, 4-Dimethylphenol	Columbia, Puriss grade	dist at 68° (1 torr)
3, 5-Dimethylphenol	Eastman White Label	used as is
m-Tolualdehyde	Aldrich	" " "
2, 5-Dimethylphenol	"	subl at 100°
p-Tolualdehyde	"	dist at 73° (4 torr)
1, 2-di-p-tolylethane	"	used as is
p-Methylbenzyl Alcohol	Benzol Products Co.	recryst from toluene
p-Methoxytoluene	Eastman White Label	used as is
2, 4, 6-Trimethyl-phenol	Aldrich	subl at 80°
1, 2, 3-Trimethyl-phenol	Alfred Bader Chemicals	used as is
2, 3, 4-Trimethyl-phenol	Aldrich	used as is
3, 5-Dimethylanisole	Aldrich	used as is
2, 6-Dimethylanisole	"	" " "
2, 3-Dimethylanisole	"	" " "
o-t-Butylphenol	Eastman Yellow Label	dist at 56° (1 torr)
m-t-Butylphenol	Aldrich	dist at 61-63° (200μ)
p-t-Butylphenol	Eastman Yellow Label	subl at 50° (35μ) then resubl at 75° (200μ)
t-Butyl Alcohol	Georgia Tech stock	used as is
Neophyl Alcohol	Prepared in this laboratory	
o-Methoxyphenol	Eastman White Label	dist at unrecorded conditions
m-Methoxyphenol	Eastman Yellow Label	dist at unrecorded conditions
p-Methoxyphenol	Eastman White Label	subl at 110° (atm)
1, 2-Diphenoxyethane	Aldrich	used as is
o-Methoxybiphenyl	K & K Laboratories	" " "
o-Methoxydiphenyl Ether	" " " "	" " "
o-Fluorophenol	Aldrich	dist at 40° (1 torr)
m-Fluorophenol	"	dist at unrecorded conditions
p-Fluorophenol	Aldrich	used as is
o-Trifluoromethyl-phenol	Pierce Chemical	" " "

continuation of Table 3

Compound	Source	Purification
m-Trifluoromethyl-phenol	Pierce Chemical	dist at unrecorded conditions
p-Trifluoromethyl-phenol	Pierce Chemical	used as is
Benzoyl Fluoride	Peninsular Chemresearch	used as is
Trifluoromethyl Phenyl Ether	Pierce Chemical	" " "
o-Nitrophenol	Georgia T h stock	subl at 130° (atm)
m-Nitrophenol	Eastman W te Label	subl at 160° (atm)
p-Nitrophenol	" " "	used as is
Nitrosobenzene	Aldrich	" " "
p-Nitrosophenol	"	" " "
p-Nitrobiphenyl	Eastman White Label	" " "
o-Chlorophenol	Georgia Tech stock	" " "
m-Chlorophenol	Aldrich	" " "
p-Chlorophenol	Eastman White Label	" " "
o-Chlorobiphenyl	K & K Laboratories	" " "
m-Chlorobiphenyl	" " " "	" " "
p-Chlorobiphenyl	Aldrich	" " "
o-Bromophenol	Eastman White Label	" " "
m-Bromophenol	" " "	" " "
p-Bromophenol	Georgia Tech stock	" " "
m-Bromobiphenyl	K & K Laboratories	" " "
p-Bromobiphenyl	" " " "	" " "
Pyridine N-oxide	Aldrich	" " "
2-Hydroxypyridine	"	" " "
3-Hydroxypyridine	"	" " "
4-Hydroxypyridine	"	" " "
Cyclohexanol	Eastman White Label	dist[b] at 159°
Cyclohexanone	Georgia Tech stock	dist[b] at unrecorded conditions
2-Cyclohexen-1-ol	Aldrich	used as is
2-Cyclohexen-1-one	"	" " "
3-Cyclohexen-1-ol	Prepared in this laboratory	
Cyclohexene Oxide	Aldrich	used as is
Cyclopentane-carboxaldehyde	Prepared in this laboratory	
Bicyclohexyl	Aldrich	used as is
1-Butanol	Georgia Tech stock	" " "
2-Butanol	Eastman White Label	dist at 98°
Butanal	Georgia Tech stock	used as is
Methyl Ethyl Ketone	" " "	" " "

continuation of Table 3

Compound	Source	Purification
n-Octane	Aldrich	used as is
3-Methylheptane	"	" " "
3,4-Dimethylhexane	Georgia Tech stock	" " "
1-Propanol	" " "	" " "
2-Propanol	Atlanta Solvents	" " "
Propanal	Eastman White Label	dist at 47-48°
Acetone	Atlanta Solvents	used as is
n-Hexane	" "	" " "
2-Methylpentane	Aldrich	" " "
2,3-Dimethylbutane	Phillips '66	" " "
Acetaldehyde	Georgia Tech stock	" " "
Diethyl Ether	Baker Analyzed	" " "
Oxepane	Aldrich	" " "

a Abbreviations used are "dist" for "distilled", "subl" for "sublimed", "recryst" for "recrystallized", "atm" for "atmospheric pressure", "m p" for "melting point" and "μ" for "micron".

b One foot N/F column used.

Neophyl Alcohol

The Grignard reagent corresponding to neophyl chloride[a] was prepared, oxygenated and hydrolyzed to give neophyl alcohol. The procedure for the Grignard compound was approximately that used for cyclohexyl chloride[60].

The reaction flask was degassed with nitrogen but was not flame-dried to remove water. To 6.33 g of magnesium in a 500 ml three-necked flask, 50 ml of the chloride solution (40.0 g neophyl chloride in 150 ml anhydrous ether) was added. A small crystal of iodine was added to initiate the reaction. This failed to initiate the reaction; the ether was distilled off by warming until the Grignard formation did start. The remaining chloride solution was added in twenty minutes and the mixture refluxed gently for one hour. Oxygen was slowly bubbled underneath the solution for one hour and the mixture was stirred for an additional three hours to convert any peroxidic material to the alkoxy magnesium species.

One hundred milliliters of saturated sodium chloride solution was added and stirring continued for thirty minutes. The ethereal layer was decanted and the aqueous layer washed twice with 100 ml aliquots of ether. The ethereal washes were combined and dried overnight with Drierite. The ethereal washes were decanted from the

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a Obtained from Y. M. Cheng.

60 H. Gilman and W. E. Catlin, Org. Syn., Coll. Vol. 1, 188 (1948)

Drierite and the ether removed at atmospheric pressure, on a one-foot column. Distillation of the residue gave 11 g of tert-butylbenzene at 30° (100u). Further distillation at 70° (100u) gave two cuts of the desired alcohol. The first cut of 2.26 g was 92% pure by glc and the second cut of 2.7 g was 85% pure; the total yield was 14% of theory. The ir and nmr of the 92% alcohol were taken and agreed with the desired product.

The ir spectrum was taken on a Perkin-Elmer model 237-B instrument. The expected shift[61] from bonded (3475 cm^{-1}) to free OH stretching modes (3590 and 3630 cm^{-1}) was found as the concentration of the alcohol in carbon tetrachloride was decreased from 5% to 0.25%. Also the 1500 to 2000 cm^{-1} region was in agreement with a monosubstituted benzene.

The nmr of the neophyl alcohol was taken in 50% CCl_4 with tms[a] as the standard. A Varian A-60 spectrometer gave the following data.

Proton Assignment	Multiplicity	Intensity	τ value
C_6H_5-	complex	5.0	2.65
$C(CH_3)_2$	sharp singlet	6.0	8.75
-CH_2-	singlet	1.8	6.55
-OH	singlet	1.0	7.55

a The abbreviation used for tetramethylsilane is tms.

61 J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N.J., 1965, p 36

Cyclopentanecarboxaldehyde

The procedure used was that of Grummitt[62] et al. for preparation and subsequent hydrolysis of cyclohexene-mercuric sulfate complex. To a solution of 24 ml of concentrated H_2SO_4 in 1 liter of H_2O, 222 g of $HgSO_4$ was added. The solution was stirred under nitrogen and heated to 55°, 24.6 g of cyclohexene was added all at once and the solution mixed for one hour at 55-68°. The reaction flask was then adapted for steam distillation and, with nitrogen bubbling through, distillate collected for 90 minutes. The organic layer was separated from the distillate and the aqueous layer washed twice with 15 ml portions of ether. The ethereal solutions were combined with the organic layer and dried overnight with anhydrous sodium sulfate. The ether was removed at atmospheric pressure and the product distilled at 42-49° (31 torr) on the two foot spinning band column. The first cut was 95% pure by glc; the nmr spectrum was taken on this cut. Total yield of 95% pure product was 17% (50% expected yield). The following nmr data were observed.

Proton Assignment	Multiplicity	Intensity	τ value
$-CH_2CH_2CH_2CH_2-$	Complex	8.1	8.3
CHC=O	broad doublet	1.5	7.4
-CHO	very sharp doublet	1.0	0.4

62 O. Grummitt, J. Liska and G. Gruell, Org. Syn., 44, 26 (1964)

3-Cyclohexen-1-ol

Procedure used was reconstructed from the incomplete data of Gogek et al.[63] for the dehydration of 1, 4-cyclohexanediol. To 52.8 g of the solid diol in a one liter reaction flask, 0.2 ml of 65% H_2SO_4 was added. The flask was heated to 190° by plunging into an oil bath. The flask was equipped with a short adapter which led to a collection flask at 0°; the product was then able to be distilled out of the reaction vessel as quickly as possible. The reaction flask was heated for two hours at 190-210° although the majority of the product had distilled over within 30 minutes.

The organic layer of the distillate was separated and the aqueous layer saturated with NaCl. The organic layer which separated was collected and combined with the original organic layer. These were then dried overnight with $MgSO_4$. The crude product, together with the ether washes of the $MgSO_4$, was distilled on the N/F column. The ether was removed at atmospheric pressure and the product alcohol distilled at 70-76° (17 torr).

The forerun of the distillation contained 1.3 g of material believed to be cyclohexadienes; the remaining fractions were found to be $\geqslant$ 99% pure 3-cyclohexen-1-ol by glc. The total yield was 17.3 g (46%); the original reference gave a yield of 38%. With tms as a standard,

63 C. J. Gogek, R. Y. Moir and C. B. Purves, Can. J. Chem., 29, 946 (1951)

a 50% solution of alcohol in CCl_4 gave the following nmr analysis.

Proton Assignment	Multiplicity	Intensity	τ value
$-CH_2-$, $-CH_2CH_2-$	Complex	6.2	7.9
-CH=CH-	Sharp complex	1.9	4.4
O-CH-	Complex	1.0	6.2
OH	Sharp singlet	1.0	5.4

Solvents

Toluene

Atlanta Solvents stock toluene was distilled at 109° on the N/F column. One peak other than toluene was observed by glc; the purity was 99%. This grade of toluene was used for preparing standard glc solutions and recrystallizing phenols.

Acetone

This solvent was used to rinse the reaction cells and traps as well as occasional use as solvent for standard glc solutions. Atlanta Solvents stock was distilled at 55° on a four-foot glass-helices column at a reflux ratio of 50:1. The major impurity of iso-propyl alcohol was thus removed to give 97% pure acetone by glc.

Chloroform

This solvent was used for preparation of glc columns. Mallinkrodt Reagent Grade was distilled at 58° on the two-foot annular teflon column. One per cent ethyl alcohol was added as stabilizer.

Carbon Tetrachloride

This solvent was used for preparation of glc columns. Atlanta Solvents stock was distilled at 75° on the two-foot annular teflon column. When used for ir and nmr samples, Baker Analyzed Spectrophotometric Grade was used as received.

Benzene

Benzene was used for silane solutions in glc work and as solvent in preliminary standard glc solutions. Baker Analyzed Reagent (thiophene free) was distilled on the N/F column at 80°. Gas chromatography gave 99% purity with one peak of retention time greater than benzene.

Cyclohexane

Cyclohexane was used for glc standards and solvent for the determination of the ir spectrum of phenol. Fisher Certified 99 mole % Reagent Grade was distilled on the N/F column at 80°; glc showed 99 min % purity.

Ethyl Alcohol

Ethanol was used for the ir spectrum of phenol. Georgia Tech stock grade was distilled on the N/F column at 77°.

Diethyl Ether

Baker Analyzed Anhydrous Reagent Grade ether was used as received for the preparation of suspected oxidation products.

GLC Columns

The glc columns used for qualitative and quantitative purposes are given in Table 4. The code name, substrate, solid phase, column dimensions, maximum temperature and source are as shown below. Procedures for columns prepared in this laboratory are given at the end of the table. All columns were 6 feet by 1/4 inch unless otherwise noted. All solid phases except the glass beads were acid washed and treated with dichlorodimethylsilane; all solid phases were 60 to 80 mesh unless otherwise noted.

Table 4 GLC Columns Used

Code Name	Liquid Phase (per cent coating)	Solid Phase	Maximum Temp. (°C)	Source
1-ApL	Apiezon L grease (10%)	Chromosorb G	300	F&M[a]
2-ApL	(20%)	GC-22[b]	300	P. E.[c]
1-DEGS	Diethylene glycol	Chromosorb G	180	F&M
2-DEGS	succinate (10%)	Diataport S	180	F&M
1-Phos	Tris (2, 4-xylenol)	Chromosorb W[d]	148	AJM[e]
2-Phos	phosphate (5%)	Chromosorb W	140	AJM
1-PPE	Polyphenyether-6 ring	Chromosorb W	300	AJM
2-PPE	(5%)	Chromosorb P[f]	300	AJM
SE-30	Silicone gum rubber, GE SE-30 (10%)	Chromosorb G	350	F&M
1-Acid	DEGA(0.10%), H_3PO_4(0.05%)[g]	glass beads	150	AJM
2-Acid	DEGA(0.15%), H_3PO_4(0.06%)	glass beads	180	AJM
3-Acid	DEGA(0.05%), H_3PO_4(0.09%)	glass beads	180	AJM
4-Acid	DEGA(0.08%), H_3PO_4(0.05%)	glass beads	150	AJM

continuation of Table 4

Code Name	Liquid (per cent coating)	Solid Phase	Maximum Temp.(°C)	Source
Carbo	Carbowax 20M Polyethylene glycol (10%)	Chromosorb G	190	F&M
1-Ucon	Ucon oil 50HB-5100	Chromosorb G	200	F&M
2-Ucon	Polypropylene glycol (10%)	Chromosorb W	180	F&M
ApH	Apiezon H grease (15%)	Chromosorb W	300	ASL[h]

a F&M Division of Hewlett Packard
b column dimensions were 10' x 1/8"
c Perkin-Elmer Corp.
d column dimensions were 3' x 1/4"
e prepared in this laboratory by A. J. M.
f 80-100 mesh; column dimensions were 4' x 1/4"
g DEGA is the abbreviation for diethylene glycol adipate
h Applied Science Laboratories

Preparation of "Phos" Columns

While investigating different column materials, it was found that Chromosorb W was far superior to either Chromosorbs P or G. For this reason, Chromosorb W was the solid phase used in the majority of "homemade" columns. The Chromosorb W was acid-washed and silanized in this laboratory as follows.

Three hundred grams of crude packing[a] was washed overnight with 600 ml of concentrated HCl; the packing was filtered and washed five times with 500 ml aliquots of water. The packing was then back-washed in a 3"x5' column to remove the "fines". Water was allowed to fill the liquid chromatography column through the usual exit end, the

a Crude packing obtained from F&M.

fine mesh packing being carried out of the top of the column. After drying the packing for 24 hours at 130°, it was mixed with two liters of 4% dichlorodimethylsilane in benzene to remove polar surface groups. This suspension was mixed for one hour and the packing filtered off. The packing was dried at 130° for 24 hours and sieved thru 100 and 50 mesh screens. The yield of packing was 180 grams.

The tris(2, 4-xylenyl) phosphate[a] was dissolved in 100 ml of CCl_4 and then mixed with 36 g of Chromosorb W in 100 ml CCl_4 [64]. This was shaken and let stand for 30 minutes after which the CCl_4 was removed with a rotating evaporator. The packing was dried for two hours at 120° and a column filled. After curing the column in the oven compartment of the glc overnight (100°, N_2 at 15 ml/min), the columns were connected to the detector block and were ready to use. The column was filled by plugging one end with a 1/4" wad of glass wool and pumping on the column while the packing was added to the other end. After agitation to settle the packing, the pump was turned off and the open end of the column plugged with glass wool. It is worthy to note that the glass wool must <u>not</u> be tightly tamped down or the flow through the column will be quite slow. Since a high carrier gas flow is essential to good separations, this must not be overlooked.

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a Obtained from Aldrich Chemical Company.

64 J. R. Lindsay Smith, R. O. C. Norman and G. K. Radda, <u>Journal of Gas Chromatography</u>, <u>3</u>, 146 (1964)

Preparation of "PPE" Column

It was found that both homemade PPE on chromosorb P and commercially available[a] PPE columns were inferior to the 1-PPE column prepared in this laboratory. The technique was analogous to the Phos column and is described below.

To 30 g of chromosorb W in 90 ml of $CHCl_3$, a solution of 1.6 g PPE[a] in 40 ml of $CHCl_3$ was added and this swirled for 15 minutes. The solvent was removed and the packing dried for 5 hours at 150°. A 6'x1/4" stainless steel column was filled and cured for 12 hours at 240°. The column was then ready to use.

Preparation of "Acid" Columns[64]

A total of eight columns were prepared with varying amounts of DEGA and H_3PO_4. It was found that only high concentrations of H_3PO_4 gave good peak shapes for meta and para-nitrophenols. Lower concentrations of H_3PO_4 gave good results for phenol, ortho-nitrophenol and methoxyphenols. The solid phase and DEGA were obtained through Applied Science Laboratories; Baker Analyzed 85% H_3PO_4 was used as it was. The smooth glass beads were in the 60-80 mesh range and treated with an unspecified silicone. The preparation of the column labeled 3-Acid is described below.

To 50.0 g of glass beads in 20 ml of $CHCl_3$, a solution of 0.0452 g DEGA in 40 ml of $CHCl_3$ was added. Three drops of H_3PO_4(~0.075g)

a F&M was the source of both the PPE columns and "raw" PPE.

was then added and this mixture shaken for 10 minutes. The solvent was removed and the packing dried overnight at 140°C. The column was filled as in previous techniques but it must be done very fast. As the packing cools from 140° to room temperature, it absorbs water and becomes a viscous mass with no resolving power. Hence, the column was filled with hot packing (direct from 140° oven) and used immediately with no curing. The column could be used to analyze meta and para-nitrophenols for about four hours before resolution was lost. Unpacking the column and treating the packing at 140° for 2-3 hours would regenerate the packing. Under optimum conditions, less than 1 μg of the para-nitrophenol could be detected on the F&M 810 glc.

CHAPTER III

EXPERIMENTAL TECHNIQUES

Mercury Photosensitized Decomposition of N_2O

The generation of ground state atomic oxygen was carried out using the mercury photosensitized decomposition of nitrous oxide[a] at 2537 Å. The flow system used can be conveniently divided into five parts; flow controllers, radiation source, reactant bubblers, reaction cell and trap. A brief description of each follows.

A Matheson model 665 gas proportioner was used to regulate the flow of N_2O; below flows of 100 ml/min, it was also used as a flowmeter to measure the flow of N_2O. When high flows of N_2O were desirable, a bubblemeter (converted 50 ml burette) and stopwatch were combined to monitor the exact flow. The bubblemeter could be conveniently used to measure the flow of the trap exit gases.

The heart of our radiation source was a custom made Hanovia low pressure mercury lamp of the Z-1400-019 variety. The pressure of mercury inside the lamp was 10^{-3} torr; 10 torr of argon and neon were also present. At 120 ma and a temperature of 57°C, the lamp was capable of supplying 10 watts at 2537 Å. The power supply was a 5000

a Hereafter abbreviated as Hg^*, N_2O.

volt transformer; this was also purchased from the Hanovia Company. For relative reactivity runs the primary lamp voltage was attenuated to 25 volts with a Variac; this was the lowest potential capable of allowing stable operation of the lamp.

This lamp was fabricated of Supracil quartz to allow us to use the 1849 Å line (2 watts at 120 ma) if desirable. Since the 1849 Å line was not desired in our $O(^3P)$ runs, it was removed with a Vycor 7913 filter. This Corning Glass was 23 cm x 38 mm O.D.; it has a cutoff wavelength of approximately 2200 Å and is 80-90% transparent[a] at 2537 Å. In early runs, a Hanau low pressure mercury lamp was used. No specifications for this lamp available, but it presumably emits 7 watts at 2537 Å.

The final considerations on the radiation source include cooling techniques and the screening used to decrease the intensity of the lamp. Air from the house line, passed through a CO_2-acetone condenser, was fed to the Vycor well at a rate sufficient to maintain the temperature of the reaction cell wherever desired (below 50°). For the more reactive substrates, fine mesh screening[b] was used to decrease the intensity of the lamp and hence decrease the extent of substrate oxidation. The 60 and 150 mesh screens used were coiled to fit between the lamp and inner wall of the Vycor filter. Two turns of the 150 mesh provided ap-

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a Measured with a Cary Model 14 spectrophotometer.

b Supplied through the courtesy of Mr. Carmody of SWECO in Marietta, Georgia; these screens were made of stainless steel.

proximately the same decrease in light intensity as three turns of 60 mesh screen.

Mercury and the aromatic substrate were introduced into the reaction cell by bubbling N_2O through each. The mercury bubbler was simply a tube leading to a fine-sintered glass frit immersed in a pool of mercury. This N_2O-Hg vapor was then passed through an analogous bubbler (open tube of 6 mm O. D.) of the organic substrate which was joined to the reaction cell. In a few runs where the temperature of the aromatic bubbler was less than 20°, the order of the bubblers was reversed to avoid excessive condensation of the mercury in the organic substrate.

The reaction cell was a cylindrical vessel made of Pyrex glass. The dimensions were 7.8 cm I. D. by 24 cm high (excluding the ground glass joints); with the Vycor filter in place, it had a volume of 850 ml. Two of the four joints were for introduction and withdrawal of the reaction mixture; the entrance joint was located on the bottom of the vessel to insure mixing of the reagents before passage to the trap via the outlet at the top of the reaction cell. The remaining two joints allowed introduction of a thermometer and the Vycor well. For runs above 50°, heating tape was used to maintain the desired temperature. Figure 1 is a sketch of the reaction cell, trap and bubblers used in Hg^*, N_2O runs.

An acetone-scrubber trap was developed to eliminate the loss of hydrocarbons due to non-condensation of dilute hydrocarbon solutions

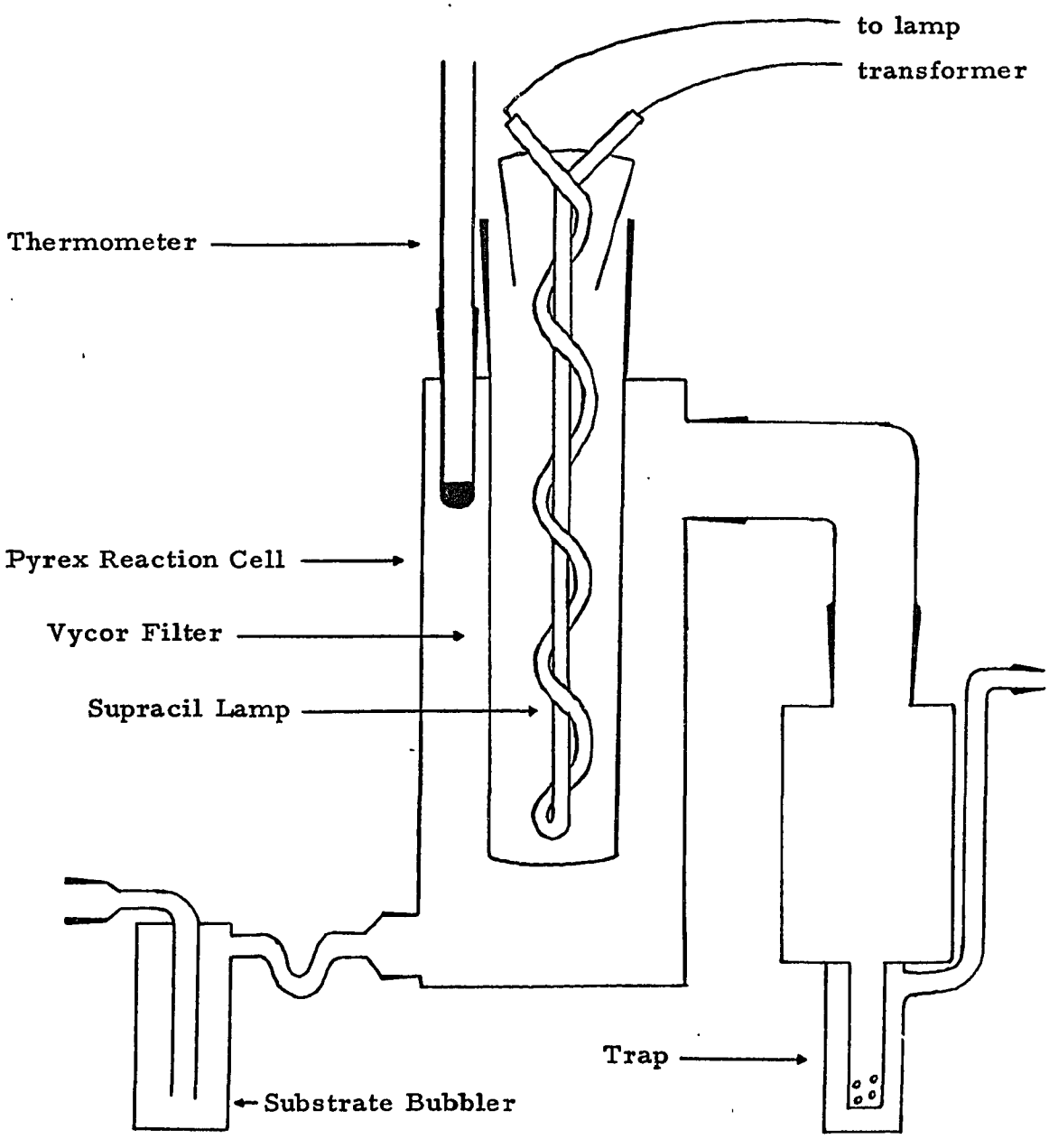

Figure 1 Experimental Apparatus for Hg^*, N_2O Runs (not to scale)

from the gas phase. This non-condensation occurred when the "usual" traps were maintained at liquid nitrogen temperatures! The acetone-Scrubber trap contains two chambers; the first is 12 cm x 5 cm O. D. and is to trap out as much material as possible from the gas phase as an ordinary trap. The second chamber is an 8 mm O. D. tube with pin-holes in the bottom; this is immersed in acetone to remove the organic materials via solubility. The entire trap was immersed in a CO_2-acetone Dewar.

A typical photolysis required four hours from start to end, excluding purification of starting reagents, cleanup of apparatus and analysis of products. After the system was assembled, the trap Dewar was filled with CO_2-acetone and the organic bubbler cooled to -78°C also (or -20° if the organic material crystallized at -78°). The system was then de-gassed with 6 to 10 liters of N_2O in one hour to remove about 99.9% of the air[65]. If the run was to be made above 30°, the temperature of the reaction cell was brought to 10° below the desired temperature during the degassing period.

After de-gassing, the bubbler was rapidly brought to the desired temperature and the lamp ignited. The cooling air inside the Vycor well

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65 This calculation was made assuming complete mixing of the sweep gas. This leads to the equation $X/X_o = e^{-V/Vo}$ where X and V are the moles of gas to be swept out and the volume of sweep gas at any time. See the Ph. D. Thesis of D. A. Gordon, Georgia Institute of Technology, Atlanta, Georgia p 143 (1953)

was adjusted to maintain the proper temperature as measured inside the reaction cell. The actual photolysis time was usually two hours during which checks of the flow, temperature, and lamp were made every twenty minutes. At the end of the run, the lamp was extinguished, the substrate bubbler again cooled as low as possible, and the flow decreased to about 40 ml/min. The reaction cell was then degassed for 10-15 minutes removing[65] about 50% of the reactant gases remaining in the reaction cell.

Since much N_2O remains dissolved in the acetone scrubber, the trap Dewar was removed and the trap allowed to warm up to 0^o at its pleasure. Attempts to hasten this warm-up would produce only bumping and consequent acetone shower. While the trap warmed up, the organic bubbler was cleaned and reweighed to determine the amount of substrate passed through the reaction cell. When at 0^o, the trap was emptied into a weighed vial; three to four acetone washes of the reaction cell and trap were subsequently added to this vial in order to give the total reaction products. The vial was warmed to room temperature and alternately shaken and opened to release most of the dissolved N_2O. The reaction solution was then stored in the freezer (-20^o) until it was to be analyzed.

Microwave Glow Discharge

Microwave glow discharges[a] were carried out on CO_2, O_2 and

a Hereafter abbreviated as mgd.

N_2O at 2450 MHz in efforts to generate atomic oxygen. The low pressure (4-30 torr) system used can be divided into four sections for descriptive purposes; these are flow-pressure controls, microwave generator, reaction apparatus and trap. Figure 2 shows the central portion of the discharge apparatus.

The flow was measured with a Matheson model 665 gas proportioner. A line filter, Hoke A443 needle valve and tooled brass fitting (for 24/40 ⅀ female joint) made up the regulatory device for the pressure inside the discharge zone. A short closed-end mercury manometer was used to measure the pressure. The pump used was a Welch Duo-Seal, model 1405H. The gas used was fed through the gas proportioner (and flowmeter) to the Hoke valve; this valve was allowed to leak against a constant pump speed. The amount of the leak determined the pressure of the system.

The microwave power was supplied by a Raytheon model PGM-10 microwave generator; a coaxial cable coupled the generator to the waveguide (Raytheon #FC-7097-1001 G1). This waveguide accepted a 13 mm O.D. tube very nicely and this set the specifications for both the discharge zone and the reaction zone of the reaction apparatus. Rubber tubing (5/8") could also be slipped into the waveguide to cool the discharge. A small air compressor was used to pump laboratory air through 0° and -78° cooling wells; this air was then focused on the discharge zone.

The glass apparatus leading from the brass fitting to the trap is

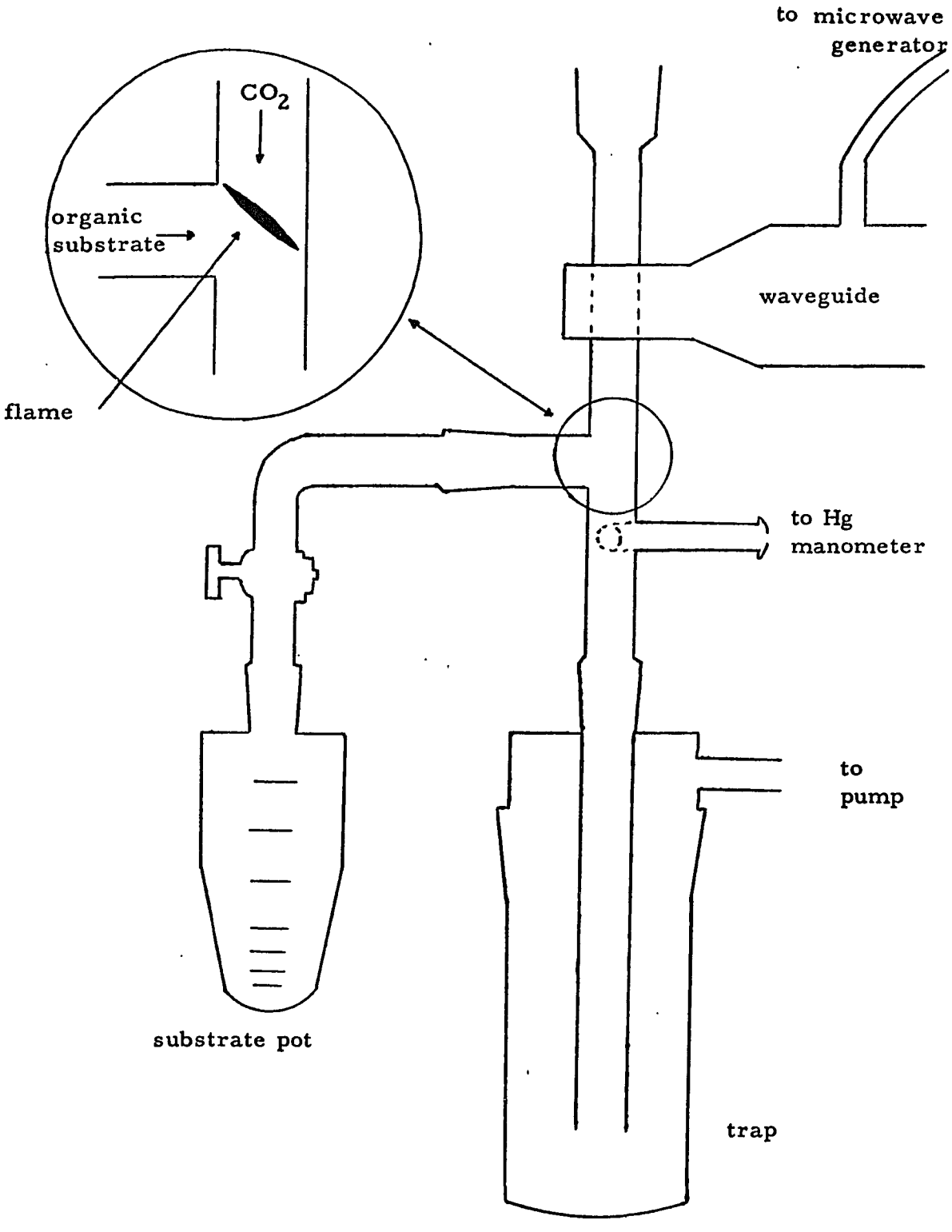

Figure 2 Experimental Apparatus for Microwave Glow Discharge Runs (not to scale)

designated as the reaction apparatus. It is essentially a 12 mm O. D. tube of length 19 cm; two "arms" are also present, one for introduction of organic substrate(s) and the other leading to the mercury manometer. The waveguide would be positioned above the organic inlet so that the organic substrate could be swept into the stream of discharged gases. The reaction distance was defined as the distance from the bottom of the waveguide to the top of the organic inlet. The reaction zone is the distance from the top of the organic inlet to the top of the trap. The waveguide was mounted on a Labjack; this arrangement enabled us to alter the reaction distance at will.

The trap usually consisted of a wide tube (24 cm x 2 cm O. D.) leading into a well of dimensions 30 cm x 4. 8 cm O. D. This was immersed in a CO_2-acetone Dewar and connected to the pump. For substrates which were liquid at -78° (as toluene), the internal part of the trap was a 6 mm O. D. coil of four turns (4cm O. D.); this was used to provide a greater surface area for condensation.

Most mgd runs were of two hours duration. The system was pumped down to one torr pressure before the Hoke valve was opened to insure that no gross leaks were present. After the trap Dewar was filled with CO_2 and acetone, the CO_2 flow was adjusted to the desired pressure and the substrate well was cooled and pumped down to the desired pressure. The system was then degassed for thirty minutes to obtain an atmosphere of CO_2 only.

The discharge was ignited by selecting the desired operating power (usually 90% of the maximum 85 watts) and allowing a tesla coil to touch the discharge zone. Due to the ever-present possibility of the generator overheating and automatically shutting down, the run needed constant supervision during the two hour run. The cooling air was kept at the greatest flow possible (one l/min) in order to cool the discharge zone. This was quite necessary lest the heat generated allow atmospheric pressure to collapse the Pyrex walls of the discharge zone. The pressure, flow and per cent power of the generator were observed and adjusted every 15 minutes. The organic substrate well was kept at a temperature which allowed a "boil over" of about 4 ml/hour.

At the end of the run, the pump was stopped and the system allowed to approach atmospheric pressure before air was admitted. The trap was quickly warmed to 0^{o} and decanted into a tared vial. The acetone washes of the trap were put into the same vial and this stored in the freezer as the reaction solution until it was analyzed. Acetone washes of the reaction zone removed most of the tars but contained a negligible amount of volatile products. For this reason, these acetone washes were simply allowed to evaporate in order to find the weight of tars formed.

Photolysis of Nitrogen Dioxide

The generation of $O(^3P)$ via photolysis of NO_2 at wavelengths

greater than 3000 Å is a well known process[31]. For this reason, the 450 watt Hanovia lamp equipped with a Pyrex filter, was used to irradiate a solution of NO_2 and an organic substrate in the gas phase. The above mentioned mercury lamp was of the high pressure variety; it was capable of generating 26 watts at 3660 Å. The lamp and filter were housed in double wall quartz well; the lamp could be cooled by either water or air, in this work air was usually used. Runs were done at atmospheric pressure and 70°C.

The NO_2 was introduced into the reaction cell (35 cm x 6.5 cm O.D.) at a slow rate of one to two ml/min; the entry tube led to the bottom of the reaction cell and was shielded from the lamp with teflon film. A stream of N_2 bubbling through the organic substrate was used to introduce the substrate into the reaction cell via a separate entry tube. The gases were then mixed and irradiated as they passed to the top of the reaction cell and then through a CO_2-acetone trap. At the end of the run the trap was warmed to 0° while a slow (10 ml/min) stream of helium passed through the trap to remove NO_2. A few drops of mercury were added to the trap at 0° to remove any remaining NO_2. The reaction mixture was then stored over this mercury at -20° until it was analyzed.

Photolysis of Ozone

Since photolysis of ozone is known to give $O(^1D)$, several attempts at ozone photolysis were made. Ozone was generated via a

homemade ozonizer; this consisted of a high voltage transformer[a] and a triple wall glass apparatus which allowed a silent electrical discharge to be maintained through oxygen. The central well was a static $CuSO_4$ (0.71M) electrode, the middle well contained the oxygen flowing through to the photolysis cell and the outer sleeve contained the cooling water. This outer well also functioned as the other electrode. The maximum output of this generator was 400 mg of ozone per hour at an oxygen flow of 65 ml/min. The irradiation source was the Hanovia 450 watt mercury lamp described earlier; at 2537 Å, 5.8 watts were generated. The lamp was equipped with a Vycor filter to eliminate the lines below 2200 Å. The reaction apparatus was identical to that used for NO_2; the runs were done at atmospheric pressure and 25°C.

A solution of ozone in oxygen was mixed with a solution of the organic substrate in nitrogen so that only gas phase oxidation was possible. The resulting mixture was then irradiated and the products trapped out at CO_2-acetone temperatures. At the end of the run, the trap was quickly warmed to 0° and helium used to degas the substrate until the odor of ozone could not be detected. The reaction solution was then stored at -20° until it was analyzed.

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a This transformer may be used but possesses a maximum secondary voltage in excess of 10,000 volts. Since the transformer was partially shorted to its housing, extreme caution was required.

Photolysis of Nitrous Oxide

The direct photolysis of N_2O was carried out in a flow system at either 70° or 85°C. The Hanovia 450 watt lamp was used with no filter (quartz double well only) since the lines around 2000 Å are responsible for the decomposition of N_2O to N_2 and $O(^1D)$[34]. The experimental setup was much simpler than that of the Hg^*, N_2O system since the Vycor filter and mercury bubbler were absent.

The reaction cell was again that used in the NO_2 runs; a glass stopcock led from the flowmeter to the organic substrate bubbler and then to the reaction cell. The solution of organic substrate was irradiated and then passed through a CO_2-acetone trap. At the end of the run, the trap was warmed to 0° and the contents of the trap saved for analysis.

Kinetic Isotope Effect

Equimolar mixtures of benzene and deuterobenzene were oxidized by the Hg^*, N_2O technique at 30°C and atmospheric pressure. The experimental apparatus and technique was as that described earlier in this chapter. The trap solution was not diluted with acetone but simply warmed to 0°, weighed and prepared for mass spectral analysis as outlined below.

Capillary tubes containing 10% DEGS on Chromosorb G were filled with 60 ul of the trap solution and the benzene solvents removed with a pump and vacuum dessicator. The tubes contained approximately

one tenth of a milligram of each phenol; this was sufficient for mass spectral analysis. A 10 atomic mass unit sweep[a] at 70 eV and 20 μamp, with a pressure of 1×10^{-6} torr was sufficient to produce full scale pen deflection and yet give a stable baseline for optimum analysis. After correction for the pressure loss while sweeping the spectrum and ^{13}C contributions, the intensities of the phenols were used to calculate the kinetic isotope effect.

In the first run, a mixture of 4.28 g benzene and 4.33 g of deuterobenzene was oxidized. A 115 ml/min N_2O flow through a 19° substrate bubbler swept 2.1 g/hr of the mixture through the reaction cell; this gave 8.3 mg/hr of volatile products, tars were not measured. Mass spectral analysis of the resulting phenols and reactant hydrocarbons gave a value of k_H/k_D of 1.14 ± 0.04 for the two runs done with the benzene-deuterobenzene system. A sample calculation of this value is given in Appendix 1.

Product Analysis

All analyses were done on an F&M model 810 gas chromatograph. Although equipped for dual column operation, in all cases only one column was used. The detection system was flame ionization with nitrogen as the carrier gas. The usual operating parameters were: injection port, 250°; detector block, 275°; hydrogen and air flows, 50 and

a Mass spectral analysis done on a Varian model M-66 mass spectrograph by George Turner.

350 ml/min respectively. The column used, oven temperature and carrier gas flow are the only variable operation parameters.

Each sample to be analyzed was injected into the glc with a weighed 10 ul syringe (Hamilton, model 701N). Standard phenol solutions were prepared from the phenols, given in Chapter 2, dissolved in pure toluene. Acetone was used as a co-solvent in the few cases where solubility was a problem. When analysis of reactant concentrations were made, the standard solutions were prepared from the pure hydrocarbons with distilled acetone as the solvent.

Duplicate standard solutions were prepared in all cases and duplicate injections made for all samples and standard solutions. Multiple integrations of each peak were done in every analysis, agreement to two per cent was considered satisfactory on all peaks. A Gelman planimeter (serial number 45 458) was used to integrate the majority of peaks. In a few rare cases, where the peak was too sharp to integrate, peak heights were used to calculate the amount of material present. A sample calculation for toluene is given in Appendix 2.

A summary of the columns and operating conditions used for the glc analyses of hydrocarbons is given in Table 5.

Table 5 Separation of Parent Hydrocarbons

Hydrocarbon Mixture	Column	Temperature (°C)	Nitrogen Flow (ml per min)
Benzene + Toluene	1-ApL	66	35
Benzene + Ethylbenzene	ApH	90	35
Benzene + o-Xylene	1-ApL	65	32
Benzene + p-Xylene	1-ApL	66	29
Benzene + m-Xylene	1-ApL	66	27
Benzene + Fluorobenzene	Carbo	52	47
Benzene + Benzotrifluoride	SE-30	48	37
p-Xylene + Anisole	1-ApL	91	31
p-Xylene + 1, 2, 3-Trimethylbenzene	1-ApL	110	34
p-Xylene + Mesitylene	1-ApL	90	32
p-Xylene + t-Butylbenzene	ApH	130	35
Nitrobenzene + Benzotrifluoride	1-ApL	93	44
Nitrobenzene + Anisole	1-ApL	91	40
Nitrobenzene + p-Xylene	1-ApL	110	40
Nitrobenzene + p-Xylene + Mesitylene	1-ApL	110	30

CHAPTER IV

THE REACTION OF $O(^3P)$ WITH AROMATICS AT 30°C

Product Distributions in Neat Hydrocarbons

The majority of work with $O(^3P)$ and aromatic compounds was conducted at 30°C and atmospheric pressure. All oxidations done in this chapter were via the Hg^*, N_2O technique (Supracil lamp) unless otherwise specified. All per cent compositions are based on total millimoles of volatile product; any single run was reproducible to seven per cent[a] unless otherwise noted. The weight of substrate is in grams per hour while that of the volatile products and tar is in units of milligrams per hour. The flow of all gases is given in milliliters per minute. All product identifications are based upon identical retention times on two or more glc columns of different polar characteristics; if a compound was found on only one column, it is considered to be tentatively identified. The glc column used for analysis, operating conditions[b], and relative retention time for each component analyzed are also given; unidentified peaks are listed in order of increasing retention time and designated by

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a Per cent agreement is based upon the difference between two values divided by the average value and then multiplied by 100. This is used for both duplicate analyses and the agreement between different runs.

b Column conditions are given in the order of temperature and nitrogen flow. For example the column used to analyze the benzene run was the 1-Phos column at 148°C with a nitrogen flow of 56 milliliters per minute. Column flows are reproducible to 20% only.

the letter U.

Benzene

A 120 ml/min N_2O flow through a 7° benzene bubler swept 2.2g of benzene through the reaction cell; this gave 7.4 mg and approximately 10 mg of volatile products and tar respectively. The product composition was 98.5% phenol, 1.5% of an unidentified product and less than 0.3% biphenyl. The 1-Phos column, (148-56), gave retention times for U-1 (0.26) and phenol (1.00) while the 1-DEGS column, (181-40), gave retention times of phenol (1.0) and biphenyl (1.5). A duplicate run agreed with the above product composition to within 2%.

Toluene

A 115 ml/min N_2O flow through a 21° toluene bubbler swept 0.85g of toluene through the reaction cell; this gave 22 mg and approximately 8 mg of volatile products and tar respectively. The product composition was 1% benzaldehyde, 2.2% benzyl alcohol, 59.4% o-cresol, 13.2% m-cresol, 14.9% p-cresol, 7.7% phenol, 1.6% of two unidentified products and less than 0.03% bibenzyl. The 1-Phos column (142-44), gave the following relative retention times; benzaldehyde (1.0), U-1 (1.4), U-2 (1.7), benzyl alcohol (2.1), phenol (3.7), o-cresol (4.3) and m and p-cresols (5.8). The 2-DEGS column, (200-50), gave retention times for benzaldehyde (1.0) and bibenzyl (3.4). The ApH column, (140-40), gave retention times for p-cresol (1.00) and m-cresol (1.16). A duplicate run agreed with the above product composition to within 10%.

Attempts to photolyze toluene in a helium atmosphere at 40°C (no mercury present) gave less than 5% of the quantity of volatile products of an analogous Hg^*, N_2O run. Thus a 110 ml/min He flow through a 19° toluene bubbler swept 1.8 g of toluene through the reaction cell; this gave 1 and 7 mg of volatile products and tar respectively. The product composition resulting from this Supracil photolysis was 36% benzyl alcohol, 64% bibenzyl and less than 3% benzaldehyde, cresols and unidentified products. When the Hanau low pressure lamp (no mercury present) was used under the same reaction parameters, the yield of volatile products and tars were 0.3 and 2 mg respectively. The product composition was 64% benzyl alcohol, 36% bibenzyl and less than 3% of cresols, benzaldehyde and unidentified products. The 2-DEGS column, (200-50), gave the following relative retention times for both runs given above; benzaldehyde (1.0), benzyl alcohol (2.0) and bibenzyl (3.4).

When nitrogen was the carrier gas, the Hanau lamp was used as the radiation source. In a mercury free run, a 100 ml/min N_2 flow through a 20° toluene bubbler swept 1.5 g of toluene through the reaction cell to give 2.2 and 2 mg of volatile product and tar respectively. The product composition was 12% benzaldehyde, 66% benzyl alcohol, 5% o-cresol, 1% m and p-cresols, 13% bibenzyl and 3% of two unidentified products. The 1-DEGS column, (182-60), gave the following relative retention times; benzaldehyde (1.0), U-1 (1.5), U-2 (1.8), benzyl alcohol (2.2), o-cresol (2.6), m and p-cresols (3.4) and bibenzyl (3.9).

A duplicate run using mercury, nitrogen and the Hanau lamp agreed with the values quoted above to within 25%.

Ethylbenzene

A 200 ml/min N_2O flow through a 25° substrate bubbler swept 0.65 g of ethylbenzene through the reaction cell. The yield of volatile product was 30 mg per hour; tars were not measured. The product composition was 3.5% phenetole[a] or benzyl methyl ether[a], 0.4% phenylacetaldehyde or styrene oxide, 4.4% acetophenone, 6.5% ∝-methylbenzyl alcohol, 0.5% phenethyl alcohol, 10.0% phenol, 49.7% o-, 11.9% m- and 10.3% p-ethylphenol and 2.8% of five unidentified products. The 1-Phos column at (149-50), gave the following relative retention times: U-1 (0.26), U-2 (0.29), phenylacetaldehyde and styrene oxide (0.42), acetophenone (0.47), ∝-methylbenzyl alcohol (0.53), U-3 (0.67), phenethyl alcohol (0.81, phenol (1.00), U-4 (1.2), U-5 (1.4), o- (1.8), m- and p- ethylphenol (2.5). The ApH column, (150-42) gave the following retention times: phenetole and benzyl methyl ether (0.50), phenol (1.00), p-ethylphenol (1.9) and m-ethylphenol (2.3). No duplicate run was made.

A run using a 270 ml/min flow of He through a 25° substrate bubbler swept approximately 0.4 g of ethylbenzene through the reaction cell. Irradiation of this ethylbenzene-helium-mercury mixture with the Supracil lamp gave less than one mg of ethylphenols. The probable

a These products tentatively identified.

presence[a] of diphenylbutanes was established but in less than 5 mg. The 1-ApL column (210-37) gave the following relative retention times: biphenyl (1.0), bibenzyl (1.4), U-1 (1.5), U-2 (1.7), U-3 (1.8) and 1,2-di-p-tolylethane (2.4). No duplicate run was made.

t-Butylbenzene

A 215 ml/min N_2O flow through a 25° substrate bubbler swept 0.18 g of t-butylbenzene through the reaction cell. The yield of volatile products was 11 mg per hour, tar formation was not measured. The product composition was 12% t-butyl alcohol (tentative), 13% phenol, 41, 19 and 12% of o, m, and p-t-butylphenol, 1% neophyl alcohol and 2% of one unidentified product. The ApH column, (168-50), gave the following relative retention times; t-butyl alcohol (0.12), phenol (1.00), neophyl alcohol (1.6), o- (1.8), p- (2.6) and m-t-butylphenol (3.0) and U-1 (4.0). No duplicate run was made.

o-Xylene

A 150 ml/min N_2O flow through a 23° xylene bubbler swept 0.35 g of o-xylene through the reaction cell. This gave 27 mg of volatile product; tars were not collected for this substrate. The product composition was 1% o-methoxytoluene (tentative), 1% o-tolualdehyde, 5% o-methylbenzyl-alcohol, 34% o-cresol, 32% 2,3-dimethylphenol, 22% 3,4-dimethylphenol and 6% of seven unidentified products. The 1-Phos column (150-47), gave

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a Presence established from the retention times of biphenyl, bibenzyl and 1,2-di-p-tolylethane listed above.

gave the following relative retention times; o-methoxytoluene (0.42), U-1 (0.77), o-tolualdehyde (1.00), U-2 (1.2), U-3 (1.4), U-4 (1.8), U-5 (2.0), o-methylbenzyl alcohol (2.3), o-cresol (2.8), U-6 (3.3), U-7 (4.1), 2,3-dimethylphenol (5.3) and 3,4dimethylphenol (6.7). No duplicate run was made.

m-Xylene

The neat m-xylene run was made at 35° rather than 30° due to cooling problems. A 120 ml/min N_2O flow through a 26°C xylene bubbler swept 0.75 g of m-xylene through the reaction cell. The yield of volatile products was 136 mg; tars were not measured. The product composition was 0.2% m-tolualdehyde, 0.9% m-methylbenzyl alcohol[a], 3.8% m-cresol, 41.7% 2,6-dimethylphenol, 49.0% 2,4-dimethylphenol, 1.6% 3,5-dimethylphenol and 2.8% of five unidentified products. Less than 2% 1,2-di-m-tolylethane[a] was found. The 1-DEGS column, (180-40) gave the following relative retention times: m-tolualdehyde (1.0), U-1 (1.2), U-2 (1.4), U-3 (1.5), 2,6-dimethylphenol (1.8), p-methylbenzyl alcohol (2.3), 2,4-dimethylphenol (2.6), m-cresol (2.8), U-4 (3.3), 3,5-dimethylphenol (3.5), U-5 (3.9) and 1,2-di-p-tolylethane (5.1). The 1-PPE column, (120-40), gave the following relative retention times: m-cresol (0.89), m-tolualdehyde (0.95), and 2,6-dimethylphenol (1.00). No duplicate run was made.

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a Based on retention time of corresponding para-isomer.

p-Xylene

A 115 ml/min N_2O flow through a 27° xylene bubbler swept 0.64 g of p-xylene through the reaction cell; this gave 60 mg of volatile product. Tar formation was not measured. The product composition was 3% p-tolualdehyde, 4% p-methylbenzyl alcohol, 11.6% p-cresol, 78% 2,5-dimethylphenol, less than 1% 1,2-di-p-tolylethane and 3.4% of six unidentified products. The 1-PPE column, (130-47) gave the following relative retention times; U-1 (0.39), U-2 (0.54), U-3 (0.58), U-4 (0.71), p-cresol (0.85), p-tolualdehyde (1.00), 2,5-dimethylphenol (1.2), U-5 (1.4), p-methylbenzyl alcohol (1.5), 1,2-di-p-tolylethane (1.8), U-6 (2.0). No duplicate run was made.

Mesitylene

No neat run at 30° was done. The data following was obtained from a benzene-mesitylene relative reactivity run. A 200 ml/min N_2O flow through a 22° substrate bubbler swept 0.11 g of mesitylene through the reaction cell. The yield of tar was not measured; the low yield of 3.1 mg of volatile products is due to attenuation of the usual lamp intensity to prevent large per cent oxidation in the relative reactivity run.

The product composition was 95.6% 2,4,6-trimethylphenol, 2.2% 3,5-dimethylphenol and 2.2% of one unidentified product. It was found that 3,5-dimethylanisole was present in less than 1% and that an interfering peak from p-xylene had an identical retention time as 3,5-

dimethylphenol. Hence the per cent composition and partial rate factor for 3, 5-dimethylphenol may be twice as large as it should be. The 1-DEGS column, (183-45), gave the following retention times; U-1 (0.56), 2, 4, 6-trimethylphenol (0.88), and 3, 5-dimethylphenol (1.00). A duplicate run agreed with the above data to within 5%.

1, 2, 3-trimethylbenzene

A 200 ml/min N_2O flow through the 29° substrate bubbler swept 0.17 g of 1, 2, 3-trimethylbenzene through the reaction cell. The yield of volatile product was 20 mg; tar formation was not measured. The product composition was 25% 2, 6-dimethylphenol, 13% 2, 3-dimethylphenol, 46% 2, 3, 4-trimethylphenol, 2% 3, 4, 5-trimethylphenol and 14% of eight unidentified products. The 1-Acid column, (121-37), gave the following retention times: U-1 (0.61), U-2 (0.67), U-3 (0.78), 2, 6-dimethylphenol (1.00), U-4 (1.4), U-5 (1.7), 2, 3-dimethylphenol (2.2), U-6 (2.5), U-7 (2.9), U-8 (3.2), 2, 3, 4-trimethylphenol (3.8), and 3, 4, 5-trimethylphenol (5.4). The eight unidentified products did not include either 2, 6- or 2, 3- dimethylanisoles, both of which were present in less than 0.2% if at all. The 1-Acid column (81-34), gave retention times of 0.12 and 0.21 for 2, 6- and 2, 3-dimethylanisole relative to 2, 6-dimethylphenol. No duplicate run was made.

Anisole

A 140 ml/min N_2O flow through a 30° anisole bubbler swept 0.20 g of reactant through the reaction cell. The yield of volatile product was 40 mg; tars were not measured. The product composition

was initially thought to be 5.7% phenol, 55.5% o-, 3.8% m- and 30.6% p-methoxyphenol and 4.4% of three unidentified products. One of the unidentified products, (U-2), is tentatively identified as o-methoxybiphenyl; less than 0.2% of 1, 2-diphenoxyethane was found. The 1-Acid column (120-28) gave the following relative retention times: o-methoxyphenol (0.70), phenol (1.00), U-1 (2.6), U-2 (3.5), m- (4.5) and p-methoxyphenol (5.2) and U-3 (6.2). No duplicate run was made.

A discrepancy in the product distribution quoted above was found when the relative reactivity of anisole was determined at 30° and 100°. p-Methoxyphenol was found to be 30.6% of the total volatile products at 30° in the neat run but only 20% in the neat run at 100°. Comparison of the relative reactivity runs shows that the para isomer was present in 16% at both 30° and 100°. Hence the neat anisole run at 30° does not agree with any other run and a better product distribution would be that from relative reactivity runs at 30°. This more accurate distribution would be 9.1% phenol, 72.5% ortho, 2.4% meta and 16.0% para-methoxyphenol.

Benzotrifluoride

A 120 ml/min N_2 flow through a 24° substrate bubbler swept 2.9 g of benzotrifluoride through the reaction cell. The yield of volatile product was 20 mg, tar formation was not measured. The product composition was 2.0% phenol, 20.1% o-, 34.0% m- and 27.3% p-trifluoromethylphenol and 16.6% of four unidentified products. The

1-Acid column (112-32) gave the following relative retention times: U-1 (0.45), o-trifluoromethylphenol (0.55), U-2 (0.71), phenol (1.00), U-3 (1.1), m- (1.5) and p-trifluoromethylphenol (2.0) and U-4 (3.4). The largest unidentified product was U-4 at 15.1%; this is believed not to be 1,2-diphenyletrafluoroethane, since the relative retention times of biphenyl and bibenzyl were 1.1 and 1.8 relative to phenol. The presence or absence of either benzoyl fluoride or trifluoromethyl phenyl ether could not be established on any glc column tested. A duplicate run agreed within 10% for the trifluoromethylphenols and component U-4 but only 67% for phenol itself.

Attempts to photolyze benzotrifluoride in a nitrogen atmosphere at 50°C, with the Hanau lamp and mercury, gave 2 to 10% of the quantity of volatile products observed in a Hg^*, N_2O technique. In one run, a 105 ml/min N_2 flow through a 24° substrate bubbler swept 1.6 g of benzotrifluoride through the reaction cell; this gave 0.10 and 1 mg of volatile products and tar respectively. The product composition was 37% phenol, 15% o-, 18% m and 18% p-trifluoromethylphenol and 12% of four unidentified products. Less than 5% of 1,2-diphenyltetrafluoroethane was formed based on the retention time of bibenzyl. The 1-DEGS column (180-47), gave the following relative retention times; o-trifluoromethylphenol (0.45), U-1 (0.53), U-2 (0.59), U-3 (0.70), U-4 (0.73), phenol (1.00), m- (1.1) and p-trifluoromethylphenol (1.3) and bibenzyl (1.4). A similar run (but no mercury present) gave 0.8 mg of volatile product.

The product composition agreed within 25% for the trifluoromethylphenols but the yield of phenol was only 7%. Again, less than 5% of 1,2-diphenyltetrafluoroethane was formed.

Fluorobenzene

A 100 ml/min N_2O flow through an 18° substrate bubbler swept 5.0 g of fluorobenzene through the reaction cell. The yield of volatile product was 8.6 mg; tars were not measured. The product composition was 2.6% phenol, 44.8% o-, 26.3% m- and 26.3% p-fluorophenol and 0.1% of two unidentified products. The 1-Phos column, (148-56), gave the following retention times: U-1 (0.24), U-2 (0.28), phenol (1.00), o- (0.39), p- (1.6) and m-fluorophenol (2.0). No duplicate run was made.

Chlorobenzene

A 120 ml/min N_2O flow through an 27° substrate bubbler swept 0.67 g of chlorobenzene through the reaction cell. The yield of volatile product was 11 mg; tars were not measured. The product composition was 13.7% biphenyl, 45.8% o-, 16% m- and 19.6% p-chlorobiphenyl, 4.9% of one unidentified product and less than 3% of phenol or any chlorophenol. The 1-DEGS column (180-40), gave the following relative retention times; biphenyl (1.0), phenol (0.92), o- (1.4), m- (2.1), and p-chlorobiphenyl (2.2). The unidentified product, U-1, had a relative time of 2.5 while that of o-chlorophenol was 0.65.

A 160 ml/min He flow through a 25° substrate bubbler swept 0.95 g of chlorobenzene through the reaction cell. The yield of volatile

product was 6.0 mg; tars were not measured. No mercury bubbler was used and the Supracil lamp was the radiation source. The product composition was 15.7% biphenyl, 41.7% o-, 20.4% m- and 20.4% p-chlorobiphenyl, 1.8% U-1 and less than 2% o-chlorophenol. The relative retention times were as those given for the previously described run. No duplicate runs of either N_2O or N_2 carrier gases were made.

Bromobenzene

A 170 ml/min N_2O flow through a 27° substrate bubbler swept 0.48 g of bromobenzene through the reaction cell. The yield of volatile products and tar was not determined. The product composition based on glc peak areas was 2.6% biphenyl, 15.8% o-bromobiphenyl, 22% p and m-bromobiphenyl, 59.6% of five unidentified products, less than 1% phenol and less than 10% of any bromophenols. The 1-Acid column, (140-40), gave the following retention times; biphenyl (1.0), phenol (0.75), p-bromophenol (5.8), o-bromobiphenyl (4.3), m- and p-bromobiphenyl (4.5), U-1 (2.4), U-2 (6.9), U-3 (8.5), U-4 (10.0) and U-5 (11.3). No duplicate run was made.

A 133 ml/min He flow through a 29° substrate bubbler swept 0.59 g of bromobenzene through the reaction cell. The yields of volatile product and tar were not determined. No mercury bubbler was used and the Supracil lamp was the radiation source. The product composition of 8% biphenyl, 16% o-bromobiphenyl, 16% m and p-bromobiphenyl, 60% of two unidentified products and less than 10% of

any phenols was based upon total glc peak area. The 1-Acid column, (140-40), gave the following retention times; biphenyl (1.0), U-1 (1.4), U-2 (2.3), o-bromobiphenyl (4.0), m and p-bromobiphenyl (4.2). No duplicate run was made.

Pyridine

A 110 ml/min N_2O flow through a 25° substrate bubbler swept 1.4 g of pyridine through the reaction cell. This gave less than 1 mg of volatile products and an undertermined amount of tars (tars estimated at 50 mg). The product composition was less than 15% of any hydroxypyridines or pyridine N-oxide. The sole volatile component had a retention time of 0.83 relative to ∝-hydroxypyridine on the 1-ApL column, (160-37). A duplicate run using a 125 ml/min N_2O flow through a 12° substrate bubbler swept 0.94 g of pyridine through the reaction cell; again no hydroxypyridines were found.

Relative Reactivity Runs And Partial Rate Factors

The experimental techniques for relative reactivity runs were identical to those for oxidation of neat hydrocarbons with two exceptions. The substrate bubbler contained a mixture of the two compounds to be oxidized and analysis of the unreacted hydrocarbons was always completed within six hours after the run was completed. The latter precaution was necessary since the reaction solution vials were not capable of preventing some evaporation of the volatile hydrocarbons

over an extended period of time. Table 6 gives the initial weight of hydrocarbons in the substrate bubbler, the per cent change in the mole fraction of the substrate bubbler (change in mole fraction divided by the initial mole fraction) and the per cent of each substrate oxidized (weight of volatile products divided by the weight of substrate vaporized from the liquid substrate bubbler). The derivation of the relative reactivity equation is given in Appendix 3; this equation shows why both the fore-mentioned percentages of Table 6 had to be kept as low as possible.

Table 7 lists the relative reactivities, product compositions and partial rate factors[a] of the monosubstituted benzenes studied at 30°C. The relative reactivities refer to phenols only and are relative to benzene. The product composition is based on the total millimoles of phenolic products as determined by glc. The partial rate factors refer to the positional reactivity of each compound relative to benzene. A sample calculation of these quantities for toluene is given in Appendix 3. The quantity Z_f is the partial rate factor for removal of Z to give phenol as the observed product.

Data for polymethylbenzenes is given in Tables 8 and 9. Table 8 is entirely analgous to that for monosubstituted benzenes (Table 7). The prf's of toluene can be used to calculate the reactivity of the polymethylbenzenes towards C-H insertion. These calculations are shown in Table 9, the graphical form of which will be given in Chapter 8.

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a Partial rate factors will be hereafter abbreviated as prf.

These calculations are based upon the additivity principle[66] of substituent effects and are illustrated below for p-xylene.

All positions in p-xylene are identical and activated by an ortho- and a meta-methyl group. Assuming that the methyl groups activate a position in p-xylene as they do in toluene, the reactivity of one position would be given by the product of the ortho and meta partial rate factors of toluene. Hence the total reactivity of p-xylene is given by the equation shown in Table 9.

66 L. M. Stock and H. C. Brown, Advan. Phy. Org. Chem., 1, 35, (1963)

Table 6 Experimental Quantities At 30°C For Relative Rate Equation

Compound A	Compound B	Initial Weight in Bubbler (grams) A	Initial Weight in Bubbler (grams) B	Per Cent Change in Mole Fraction of Bubbler A	Per Cent Change in Mole Fraction of Bubbler B	Per Cent of Substrate Oxidized A	Per Cent of Substrate Oxidized B
Toluene	Benzene	46.27	38.48	2.9	-2.9	1.3	0.3
		45.09	35.38	2.6	-2.8	1.5	0.3
Ethylbenzene	Benzene	40.58	16.05	5.6	-10.6	1.6	0.3
		39.94	13.41	7.0	-15.4	0.8	0.1
t-Butylbenzene	p-Xylene	71.08	16.71	0.4	-1.4	0.7	1.9
		70.54	16.27	0.5	-1.6	0.9	2.5
Anisole	p-Xylene	36.43	19.61	0.6	-1.1	2.7	1.8
		36.08	19.10	0.6	-1.1	4.0	2.5
Fluorobenzene	Benzene	35.74	15.10	0.4	-0.8	0.3	0.5
		33.69	19.66	0.6	-0.8	0.2	0.3
Benzotrifluoride	Benzene	60.01	5.01	1.0	-6.7	0.3	1.0
		80.56	4.45	0.9	-8.7	0.2	0.8

continuation of Table 6

Compound A	Compound B	Initial Weight in Bubbler (grams) A	B	Per Cent Change in Mole Fraction of Bubbler A	B	Per Cent of Substrate Oxidized A	B
o-Xylene	Benzene	40.43	12.12	4.2	-10.4	1.4	0.1
		39.73	15.98	8.2	-15.0	1.6	0.1
m-Xylene	Benzene	61.7	40.0	11.0	-0.5	1.5	1.6
		56.8	39.5	6.5	-0.3	1.9	2.0
		56.8	57.6	1.2	-0.5	4.8	3.5
p-Xylene	Benzene	65.19	37.3	4.5	-5.7	0.6	0.08
		64.56	33.3	5.5	-7.9	0.8	0.09
Mesitylene	p-Xylene	13.87	7.28	15.0	-18.5[a]	1.5	0.2
		36.28	35.77	1.8	-1.6	2.4	0.3
1,2,3-Trimethyl-benzene	p-Xylene	55.04	18.07	0.9	-2.4	6.0	1.9
		77.16	17.40	0.4	-1.6	3.6	1.2

a This change in the mole fraction of the substrate bubbler was the largest observed. The relative reactivity from this run was in excellent agreement with the duplicate run.

Table 7 Relative Rate Data For Monosubstituted Benzenes at 30°C

Substrate C_6H_5Z	Relative Reactivity[a]	Percent Composition ortho	meta	para	phenol	Partial Rate Factors O_f	M_f	P_f	Z_f
$Z=CH_3$	4.33	58.0	15.8	18.2	8.0	7.5	2.05	4.7	2.09
	4.43	59.6	15.2	17.1	8.1	7.9	2.01	4.6	2.15
average	4.4					7.7	2.03	4.65	2.1
$Z=C_2H_5$	5.4	54.9	18.5	14.4	12.2	8.8	3.0	4.6	3.9
	4.5	62.7	13.3	11.9	12.1	8.5	1.8	3.2	3.3
average	4.9					8.65	2.4	3.9	3.6
$Z=C(CH_3)3$	3.55	54.5	18.0	14.4	13.1	5.8	1.9	3.07	2.8
	3.67	56.2	19.3	14.1	10.4	6.2	2.1	3.09	2.3
average	3.6					6.0	2.0	3.08	2.55
$Z=OCH_3$[b]	12.9	80.1	2.8	17.1		30.9	1.08	13.2	
	13.6	79.5	2.5	18.0		32.4	1.02	14.7	
average	13.2					32.	1.05	14.	
$Z=F$	0.69	41.4	27.2	29.4	2.0	0.85_5	0.56	1.21	0.082
	0.63	46.4	27.0	24.6	2.0	0.88_4	0.51	0.94	0.076
average	0.66					0.87	0.54	1.1	0.08
$Z=CF_3$	0.30	26.5	40.0	31.6	1.9	0.24	0.36	0.57	0.034
	0.28	28.2	41.1	28.8	1.9	0.24	0.36	0.48	0.032
average	0.29					0.24	0.36	0.53	0.033

a Relative to Benzene.

b Methyl cleavage not calculated due to anisole photolysis to give phenol.

Table 8 Relative Rate Data for Methylbenzenes at 30° C

Substrate	Rel. Reactivity	Per Cent Composition				Partial Rate Factors			
		Dimethylphenols			o-Cresol	(O_fM_f)	(M_fP_f)	Z_f	
		2,3-		3,4-					
o-Xylene	10.0	34.3		31.4	34.3	10.3	9.45	10.3	
	10.1_5	35.7		30.4	33.9	10.9	9.25	10.0_5	
average	10.1					10.6	9.35	10.2	
		Dimethylphenols			m-Cresol	O_f^2	(O_fP_f)	M_f^2	Z_f
		2,6-	2,4-	3,5-					
m-Xylene	22.4	46.2	46.8	2.6	4.4	62	31.4	3.5	3.0
	24.7	50.3	45.2	1.0	3.5	74	33.5	1.5	2.6
	21.3	47.8	47.5	1.3	2.4	61	30.3	1.3	2.4
average	22.8					66	32.	2.	2.7
		2,5-Dimethylphenol			p-Cresol	(O_fM_f)		Z_f	
p-Xylene	9.5_1	89.4			10.6	12.8		3.02	
	10.1_5	88.5			11.5	13.5		3.50	
average	9.8					13.1		3.3	
		Polymethylphenols				$(O_f^2P_f)$		Z_f	
		2,4,6-		3,5-					
Mesitylene	79.4	96.5		3.5		153		5.6	
	80.2	97.7		2.3		157		3.7	
average	80.					155		4.6	
		Polymethylphenols				$(O_fM_fP_f)$	$(M_f^2P_f)$	$(Z_f^oZ_f^m)$	$(Z_f^o)^2$
		2,3,4-	3,4,5-	2,3-	2,6-				
1,2,3-Tri-	25.4	55.2	2.6	14.8	27.4	42.1	3.97	11.3	41.9
methylbenzene	25.2	54.0	2.8	15.1	28.1	40.9	4.30	11.4	42.5
average	25.3					41.5	4.1	11.3_5	42.2

Table 9 Total Reactivity as Calculated from Toluene for C-H Insertion Only

Compound	Relative Reactivity Formula	Calculated $\frac{k_X}{k_B}$	Calculated log $\frac{(k_X)}{(k_B)}$	Experimental $\frac{k_X}{k_B}$	Experimental log $\frac{(k_X)}{(k_B)}$
Toluene	$k_{Me} = 1/6[2O_f + 2M_f + P_f]$	4.02 ± 0.08	0.60 ± 0.01	4.02 ± 0.05	0.604 ± 0.01
o-Xylene	$k_o = 1/6[2(O_f M_f) + 2(M_f P_f)]$	8.4 ± 0.2	0.92 ± 0.01	6.65 ± 0.07	0.82 ± 0.01
m-Xylene	$k_m = 1/6[(O_f)^2 + 2(O_f P_f) + (M_f)^2]$	22.5 ± 0.9	1.35 ± 0.02	$22.7 \pm 2.$	1.36 ± 0.04
p-Xylene	$k_p = 1/6[4(O_f M_f)]$	10.4 ± 0.4	1.02 ± 0.02	8.75 ± 0.25	0.94 ± 0.01
Mesitylene	$k_s = 1/6[3(O_f)^2 P_f]$	$138. \pm 10.$	2.14 ± 0.03	$77.5 \pm 1.$	1.89 ± 0.01
1, 2, 3-Tri methylbenzene	$k_H = 1/6[2(O_f M_f P_f) + (M_f)^2 P_f]$	27.4 ± 1.4	1.44 ± 0.02	14.5 ± 0.2	1.16 ± 0.01

CHAPTER V

THE REACTION OF $O(^3P)$ WITH AROMATICS AT 100°C

Product Distribution in Neat Hydrocarbons

Several substrates were oxidized at atmospheric pressure and 100°C. This temperature was convenient for high boiling substrates but since relative reactivity ratios are depressed at 100°, only nitrobenzene and a few other substrates were studied at this temperature. Nitrobenzene is considered in a separate section at the end of this chapter; the other substrates studied by the $H\overset{*}{g}$, N_2O technique are given below. The presentation of data is entirely analogous to that used previously.

Benzene

A 110 ml/min N_2O flow through a 14° substrate bubbler swept 3.0 g of benzene through the reaction cell; this gave 22.4 and 12 mg of volatile products and tar respectively. The product composition was 98% phenol and 2% of two unidentified products. The 2-DEGS column, (200-53), gave the following relative retention times: U-1 (0.70), phenol (1.00) and U-2 (1.4). No duplicate run was made.

Toluene

A 125 ml/min N_2O flow through a 25° substrate bubbler swept 1.4 g of toluene through the reaction cell; this gave 17 and 23 mg of

volatile products and tar respectively. The product composition was 1% benzaldehyde, 2.5% benzyl alcohol, 57% o-, 13% m- and 14% p-cresol, 10% phenol, 1.5% bibenzyl and 1% of an unidentified peak. The 2-DEGS column, (200-53), gave the following retention times: benzaldehyde (1.0), U-1 (1.2), benzyl alcohol (2.0), phenol and o-cresol (2.3), m- and p-cresol (3.0) and bibenzyl (3.4). The 2-ApL column, (163-60), gave the following relative retention times: benzaldehyde (1.0), phenol (1.2), benzyl alcohol and o-cresol (1.6), and m- and p- cresol (1.9). The ApH column, (140-40), gave the relative times of p- and m- cresol as 1.00 and 1.16 respectively. A duplicate run agreed with the aforementioned product distribution to within 5%.

p-Xylene

Since no neat p-xylene run was done at 100°, the product distribution of a relative reactivity run with benzene will be given here. A 200 ml/min N_2O flow through a 20° substrate bubbler swept 0.40 g of p-xylene through the reaction cell. The yield of volatile products was 3.6 mg; tars were not measured. The product composition was 5.8% p-tolualdehyde, 9.5% p-cresol, 72.8% 2,5-dimethylphenol, 11.3% p-methylbenzyl alcohol and 0.6% 1,2-di-p-tolylethane. The 1-PPE column (128-37) gave the following relative retention times: p-cresol (1.0), p-tolualdehyde (1.2), 2,5-dimethylphenol (1.3_5), p-methylbenzyl alcohol (1.7) and 1,2-di-p-tolylethane (2.1). A duplicate run agreed with that give above to within 10%.

Mesitylene

A 110 ml/min N_2O flow through a 80° substrate bubbler swept 1.3 g of mesitylene through the reaction cell. This gave 76 mg of volatile product; tars were visually estimated at less than 5 mg. The product composition was 95.7% 2,4,6-trimethylphenol, 2.2% 3,5-dimethylphenol and 2.1% of four unidentified products. The 1-Phos column, (147-37), gave the following relative retention times: U-1 (0.26), U-2 (0.30), U-3 (0.40), U-4 (0.44), 2,4,6-trimethylphenol (0.62) and 3,5-dimethylphenol (1.00). No duplicate run was made.

1,2,3-Trimethylbenzene

A 115 ml/min N_2O flow through an 80° substrate bubbler swept 0.32 g of 1,2,3-trimethylbenzene through the reaction cell. The yield of volatile product was 23 mg; tar was not measured. The product composition was 32.0% 2,6-dimethylphenol, 19.8% 2,3-dimethylphenol, 39.7% 2,3,4-trimethylphenol, 1.5% 3,4,5-trimethylphenol and 7.0% of five unidentified products. The 1-DEGS column, (188-40), gave the following retention times: U-1 (0.51), U-2 (0.77), U-3 (0.91), 2,6-dimethylphenol (1.00), U-4 (1.2), U-5 (1.4), 2,3-dimethylphenol (1.8), 2,3,4-trimethylphenol (3.4). No duplicate run was made.

Benzotrifluoride

A 110 ml/min N_2O flow through a 40° substrate bubbler swept 3.4 g of benzotrifluoride through the reaction cell. The yield of volatile product was 15 mg; tars were not measured. The product composition

was 2.8% phenol, 25.0% o-, 41.2% m- and 28.8% p-trifluoromethylphenol and 2.2% of four unidentified products. The 2-Acid column, (110-32), gave the following retention times: U-1 (0.45), U-2 (0.50), U-3 (0.71), U-4 (1.1), phenol (1.00), o- (0.55), m- (1.5) and p-trifluoromethylphenol (2.0). A duplicate run gave agreement within 5% for the trifluoromethylphenols.

Anisole

A 200 ml/min N_2O flow through an 85° substrate bubbler swept 2.0 g of anisole through the reaction cell. The yield of volatile product was 28 mg; tar was not measured. The product composition was 10.0% phenol, 65.8% o-, 3.9% m- and 20.3% p-methoxyphenol. The 1-Acid column, (120-38), gave the following retention times: phenol (1.00), o- (0.70), m- (5.5) and p-methoxyphenol (4.6). No duplicate run was made.

Attempts to photolyze anisole in a helium atmosphere gave phenol as the sole identifiable product. The Supracil lamp was used as the radiation source; no mercury bubbler was used but mercury was most probably present since the apparatus was not thoroughly cleaned with nitric acid. A 200 ml/min He flow through an 87° substrate bubbler swept 0.95 g of anisole through the reaction cell. The yield of volatile product was 14 mg; tar was not measured. The product composition was 86.5% phenol, 0.1% o-methoxybiphenyl, 0.3% of o-methoxydiphenyl

ether, less than 1% 1,2-diphenoxyethane, less than 0.5% o-methoxyphenol and 13.1% of four unidentified products. The 4-Acid column (100-40) gave the following retention times: U-1 (0.67), U-2 (0.78), and phenol (1.00). The 1-Acid column (120-40) gave the following relative retention times: phenol (1.00), U-3 (1.4), o-methoxybiphenyl (3.4), U-4 (4.2) and o-methoxydiphenyl ether (4.7). No duplicate run was made.

Relative Reactivity Runs and Partial Rate Factors

Techniques for determining relative reactivities at 100° were identical to those at 30°. Table 10 lists the pertinent relative rate data obtained using the Hg^*, N_2O method at 100°, and is analogous to Tables 7 and 8 in Chapter 4. The given relative reactivities are for all phenolic products relative to benzene; anisole and nitrobenzene are exceptions to the above owing to direct photolysis of the substrate to the product phenol. The notation used for partial rate factors is straightforward, Z_f referring to cleavage of the aromatic substituent to give a phenol.

Nitrobenzene

Hg^*, N_2O technique

Due to analytical difficulties with this highly polar reactant and even more polar products, the reproducibility of product composition was good to only 20% in duplicate runs. In a typical run, a 200 ml/min N_2O flow through a 80° substrate bubbler swept 0.40 g of nitrobenzene through the reaction cell. The yield of volatile product was 32 mg; tar

Table 10 Relative Rate Data for Aromatics at 100°C

Substrate	Rel. Reactivity	Per Cent Composition				Partial Rate Factors			
		ortho	meta	para	phenol	O_f	M_f	P_f	Z_f
Toluene	3.48	53.3	15.9	22.6	8.2	5.5_6	1.7	4.7	1.7
	2.98	54.9	15.3	21.6	8.2	4.9_2	1.4	3.9	1.5
average	3.2					5.2	1.5	4.3	1.6
Anisole	4.75	80.9	3.7	15.4	-	11.5	0.53	4.4	-
	5.42	79.5	3.8	16.7	-	12.9	0.62	5.4	-
average	5.1					12.	0.57	4.9	-
Benzotri-	0.47	25.0	43.1	29.1	2.8	0.35_5	0.61	0.83	0.079
fluoride	0.45	23.3	42.2	31.7	2.8	0.32_5	0.59	0.88	0.074
average	0.46					0.34	0.60	0.85	0.076
Nitrobenzene[a]	4.4	29.6	6.1	64.3	-	1.7	0.36	7.6	-

		2,5-Dimethylphenol	p-Cresol	$O_f M_f$	Z_f
p-Xylene	5.36	88.4	11.6	7.1	1.87
	5.67	87.0	13.0	7.4	2.21
average	5.5			7.2_5	2.0

		Polymethylphenols			
		2,4,6	3,5-	$O_f^2 P_f$	Z_f
Mesitylene	28.9	97.0	3.0	56.1	1.73
	24.2	96.3	3.7	46.6	1.79
average	26.6			51.	1.76

a The values for nitrobenzene are only approximate as discussed in the text.

was not measured. The product composition was 0.3% nitrosobenzene, 4.6% phenol, 13.4% o-, 5.4% m- and 74.0% p-nitrophenol and 2.3% of two unidentified products. The 1-ApL column, (100-44), gave the following retention times: U-1 (0.56), nitrosobenzene (0.61), U-2 (0.73), phenol (1.00) and o-nitrophenol (2.3). The 3-Acid column, (190-44), gave relative retention times for m- and p-nitrophenol of 1.0 and 1.6 respectively.

Direct Photolysis

In addition to the oxidation of nitrobenzene by $O(^3P)$ via the Hg^*, N_2O technique, a substantial amount of work was done with direct photolysis of nitrobenzene. Since there is some indication that $O(^3P)$ may play an important role in the photodecomposition of nitrobenzene, this data will be given here. No mercury bubbler was used in these runs; the radiation source was the 200 watt Hanovia lamp[a] and the carrier gas was helium. It should be mentioned that the use of the Supracil lamp and mercury did not change the product composition given below.

In a typical run, a 200 ml/min He flow through a 93° substrate bubbler swept 0.52 g of nitrobenzene through the reaction cell. The yield of volatile product was 14.5 mg; tars were not measured. The

a The 200 watt lamp was a high-pressure mercury-arc lamp; its spectral characteristics were analogous to the 450 watt lamp described in Chapter 3.

product composition was 30.0% nitrosobenzene, 47.5% phenol, 3.3% o-, 1.1% m- and 12.6% p-nitrophenol and 5.5% of four unidentified products. The 1-ApL column, (108-40), gave the following retention times: nitrosobenzene (0.68), U-1(0.77), phenol (1.00). The 4-Acid column, (100-40), gave the retention time of o-nitrophenol as 0.73 relative to phenol at 1.00. The 3-Acid column, (180-44), gave the following relative retention times: m-nitrophenol (1.00), U-2 (1,2), U-3 (1.36), U-4 (1.44) and p-nitrophenol (1.6).

Relative Reactivity Runs

Since the distribution of nitrophenols was identical whether Hg^*, N_2O or direct photolysis techniques were used, relative reactivity runs were made via these techniques. The runs of chief interest are p-xylene plus mesitylene, nitrobenzene plus benzotrifluoride and nitrobenzene plus p-xylene. Table 11 lists the experimental data for the above-mentioned runs. This table is analogous to that given for relative reactivity runs at 30°C, Table 6. The relative reactivity of mesitylene relative to p-xylene was found to be 4.8 ± 0.5 by the Hg^*, N_2O technique and $4. \pm 1$ by the direct photodecomposition of nitrobenzene. The relative reactivity of nitrobenzene relative to benzotrifluoride[a] was found to be 10 ± 1 by the Hg^*, N_2O method and 88 ± 15 by the direct photodecomposition of nitrobenzene. It should be noted that the large change in the

a Deviation given is estimated error only since only one determination of these values was made.

composition of the bubbler makes the relative reactivity values for nitrobenzene approximate at best.

Relative reactivity runs between p-xylene and nitrobenzene were also made. In these runs, no nitrophenols were found and hence no relative rates could calculated regardless of which technique of oxidation was used. The Hg^{*}, N_2O technique gave 6.4 mg of p-cresol and 2,5-dimethylphenol with 8.5 mg of phenol; the corresponding direct photolysis of nitrobenzene gave 1.3 and 11.8 mg of the same products.

Table 11 Experimental Data For Nitrobenzene Runs at 100°C

Technique[a]	Initial Weight[b] in Bubbler		Total Weight[b] Vaporized		Per Cent Change in Mole Fraction of Bubbler		Per Cent[c] of Substrate Oxidized	
	Benzotrifluoride	Nitrobenzene	Benzotrifluoride	Nitrobenzene	Benzotrifluoride	Nitrobenzene	Benzotrifluoride	Nitrobenzene
$\overset{*}{Hg}$, N_2O	6.8	101.93	4.25	0.53	-61	+ 3.4	0.3	4.5
$C_6H_5NO_2 \xrightarrow{hv}$	9.15	101.4	5.52	0.26	-59	+ 4.5	0.03	7.4
	p-Xylene	Mesitylene	p-Xylene	Mesitylene	p-Xylene	Mesitylene	p-Xylene	Mesitylene
$\overset{*}{Hg}$, N_2O	31.89	35.83	2.26	1.00	-1.9	+ 2.1	0.4	2.
$C_6H_5NO_2 \xrightarrow{hv}$ [d]	1.79	2.27	0.53	0.37	-27	- 13	0.1	0.3
	p-Xylene	Nitrobenzene	p-Xylene	Nitrobenzene	p-Xylene	Nitro benzene	p-Xylene	Nitrobenzene
$\overset{*}{Hg}$, N_2O	1.04	33.28	0.61	1.66	-54	+ 1.9	1.0	0.40
$C_6H_5NO_2 \xrightarrow{hv}$	1.25	31.62	0.65	0.94	-52	+ 2.3	0.17	1.0

a Abbreviation used in tables for the direct photodecomposition of nitrobenzene is $C_6H_5NO_2 \xrightarrow{hv}$.

b Weight given in grams.

c Percent nitrobenzene oxidized includes phenol.

d The per cent change in mole fraction of nitrobenzene in the substrate bubbler was + 2.6% (0.37 g of 33.0 g vaporized).

CHAPTER VI

MISCELLANEOUS OXIDATIONS OF AROMATIC COMPOUNDS

Microwave Discharge

The dissocitation of CO_2 or O_2 by an electrical discharge is a well known method of producing atomic oxygen.[43, 52] The main experimental parameters involved in electrical discharges are the frequency and intensity of the radiation, pressure and temperature of the discharge, and the reaction distance. The gases passed through the discharge and the temperature of the reaction zone can also be varied; CO_2, O_2 and N_2O were the gases used in this work. A set of standard microwave glow discharge parameters was chosen to allow comparison between the various organic substrates oxidized. Unless otherwise noted, these conditions were, 2450 MHz at 85 $\pm$ 10% power (70 watts), 13.5 $\pm$ 0.5 torr at a reaction distance of 20 $\pm$ 1 mm. The products of oxidation of benzene, toluene, p-xylene and benzotrifluoride via electrical discharge follow. The retention times are all relative and are given in the same format as those in the preceding chapters. The weights of substrate and products are given in grams and milligrams per hour and the per cent composition is based on total millimoles of volatile product.

Benzene — CO_2

The oxidation of 6.8 g of benzene with 3.8 liters of CO_2 gave 15 and 11 mg of volatile products and tar respectively. The product composition was 95.3% phenol and 4.7% of three unidentified products. The Carbo column, (190-60) gave the following relative retention times: U-1 (0.14), U-2 (0.19), U-3 (0.22) and phenol (1.00). No duplicate run was made.

Benzene — O_2

The oxidation of 9 g of benzene with 3.2 liters of O_2 gave 100 and 10 mg of volatile products and tar respectively. The product composition was 93.6% phenol and 6.4% of thirteen unidentified products. The Carbo column, (190-60) gave the following retention times: U-1 (0.14), U-2 (0.17), U-3 (0.19), U-4 (0.22), U-5 (0.26), U-6 (0.32), U-7 (0.36), U-8 (0.39), U-9 (0.45), U-10 (0.52), U-11 (0.68), U-12 (0.82), phenol (1.00), U-13 (1.3). No duplicate run was made.

Benzene — N_2O

The oxidation of 6.2 g of benzene with 4.6 liters of N_2O gave 1.6 and 5 mg of volatile products and tar respectively. The product composition was 90% phenol and 10% nitrobenzene. The 1-DEGS column, (200-56), gave relative retention times of 1.0 for phenol and 0.80 for nitrobenzene. No duplicate run was made.

Toluene — CO_2

The oxidation of 7.7 g of toluene with 3.7 liters of CO_2 gave 15

and 9 mg of volatile products and tar respectively. The product composition was 23.3% benzaldehyde, 9.3% benzyl alcohol, 20.5% o-cresol, 16.7% phenol, 22.3% m- and p-cresols, 0.9% bibenzyl and 7.0% of four unidentified products. The Carbo column, (190-60), gave the following retention times: U-1 (0.82), benzaldehyde (1.00), U-2 (1.4), U-3 (1.6), benzyl alcohol (2.6), U-4 (3.3), phenol and o-cresol (3.6), m- and p-cresol (4.9) and bibenzyl (5.6). The 2-ApL column, (155-60), gave a retention time of 1.2 for phenol relative to benzaldehyde. The ApH column, (140-40), gave relative times of 1.00 and 1.15 for p- and m-cresol respectively. A duplicate run agreed with the product composition given above to within 10%.

Toluene —O_2

The oxidation of 6.7 g of toluene with 3.7 liters of O_2 gave 80 mg of volatile products and 7 mg of tar. The product composition was 22.2% benzaldehyde, 12.6% benzyl alcohol, 29.8% phenol, 10.6% o-cresol, 17.0% m- and p-cresol, 4.5% bibenzyl and 3.3% of six unidentified products. The Carbo column, (190-60), gave the following relative retention times: U-1 (0.75), U-2 (0.89), benzaldehyde (1.00), U-3 (1.4), U-4 (1.6), U-5 (1.9), U-6 (2.1), benzyl alcohol (2.5), phenol and o-cresol (3.6), m- and p-cresol (4.8) and bibenzyl (5.5). The 2-ApL column, (155-60), gave a retention time of 1.2 for phenol relative to benzaldehyde. No duplicate run was made.

Toluene — N_2O

The oxidation of 3.5 g of toluene with 2 liters of N_2O gave 4.7 and 10 mg of volatile products and tar respectively. The product composition was 28.2% benzaldehyde, 55.7% benzyl alcohol, 4.2% o-cresol, 2.0% bibenzyl, less than 1% phenol or m- and p-cresol and 9.9% of three unidentified products. The 1-DEGS column, (200.56), gave the following relative retention times: benzaldehyde (1.0), U-1 (1.6), U-2 (1.9), U-3 (2.1), benzyl alcohol (2.4), o-cresol (2.9) and bibenzyl (4.4). No duplicate run was made.

p-Xylene — CO_2

The reaction distance was 18 mm and the pressure 18 torr for both the p-xylene runs given in this chapter. The oxidation of 5.7 g of p-xylene with 1.5 liters of CO_2 gave 6 and 12 mg of volatile products and tar respectively. The product composition was 42% p-tolualdehyde, 18% p-methylbenzyl alcohol, 14% p-cresol, 21% 2,5-dimethylphenol, 3% p-methylanisole (tentative) and 2% of one unidentified product; the presence of 1,2-di-p-tolylethane was not established. The 2-PPE column, (130-40), gave the following retention times: p-methylanisole (0.50), U-1 (0.71), p-cresol (0.86), p-tolualdehyde (1.00), 2,5-dimethylphenol (1.2) and p-methylbenzyl alcohol (1.4). No duplicate run was made.

p-Xylene — O_2

The oxidation of 3.9 g of p-xylene with 2.4 liters of O_2 gave 18 and 8 mg of volatile products and tar respectively. The product composition

was 9% p-methylanisole (tentative), 21% p-cresol, 33% p-tolualdehyde, 13% 2,5-dimethylphenol, 17% p-methylbenzyl alcohol and 7% of three unidentified products; the presence of 1,2-di-p-tolyethane was not established. The 2-PPE column, (130-40), gave the following retention times: p-methylanisole (0.50), U-1 (0.71), p-cresol (0.86), p-tolualdehyde (1.00), 2,5-dimethylphenol (1.2), p-methylbenzyl alcohol (1.4), U-2 (1.6) and U-3 (1.8). No duplicate run was made.

Benzotrifluoride — CO_2

The oxidation of 4.7 g of benzotrifluoride with 6 liters of CO_2 gave 18 and 39 mg of volatile products and tar respectively. The product composition was 24.1% o-, 56.1% m- and 14.0% p-trifluoromethylphenol, 2.3% phenol and 3.5% of two unidentified products. The 1-DEGS column, (166-56) gave the following relative retention times: U-1 (0.28), U-2 (0.50), phenol (1.00), o- (0.43), m- (1.1), and p-trifluoromethylphenol (1.3). No duplicate run was made.

Benzotrifluoride — O_2

The oxidation of 3.7 g of benzotrifluoride with 7.3 liters of O_2 gave 27 and 180 mg of volatile products and tar respectively. The product composition was 16.8% o-, 51.5% m- and 26.3% p-trifluoromethylphenol, 2.3% phenol and 3.1% of five unidentified products. The relative retention times of all products was identical to those given previously for the CO_2 run.

Product Distribution of Toluene at Various Reaction Distances

Toluene was studied extensively with respect to changes in the reaction distance and consequent change in travel time. From the pressure, volume flow of gas, reaction distance and volume of the discharge system, the travel time of atomic oxygen from the waveguide to the toluene inlet can be calculated. Hence in run T-XIII, the flowmeter reading of 30 mm gives a volume flow of CO_2 of 26 ml/min or 0.43 ml/sec at STP. Since we are operating in a partial vacuum, the pressure of which is 13 torr, a correction factor of 760/13 torr is applied to obtain a volume flow of 25 ml/sec in our discharge system. The linear flow rate equals the volume flow divided by the product of π times the square of the tube radius. Since the discharge tube is 10 mm I.D., the linear flow is 32.2 cm/sec. The travel time is simply the reaction distance divided by the linear flow rate; for run T-XIII, this reaction distance is 5.0 cm giving a travel time of 0.155 seconds.

Table 12 gives the change in product yield as a function of the travel time using CO_2 as the carrier gas. The graphical summation of this data and the subsequent conclusions based upon it will be given in Chapter 8. It is to be noted that the temperature of the discharged gas stream is strongly dependent upon the reaction distance. Thus, as the reaction distance decreases, the temperature of the discharged gases at the substrate inlet increase; this change in temperature is also given in Table 12. It should be noted that the temperature is that of CO_2 as the

Table 12 Toluene Yields at Different Travel Times

Run (T-)	Pressure (torr)	Reaction Distance (mm)	Travel Time (sec)	Temperature (^{o}C)	Total millimoles of product	log (total millimoles x 100)
VI	12.0	5	0.010	200	0.96	1.98
VII	12.5	10	0.019	150	0.68	1.84
VIII	12.0	20	0.036	105	0.62	1.79
XVI	13.0	20	0.041	105	0.46	1.66
IX	12.0	30	0.055	85	0.26	1.41
XV	11.5	30	0.059	85	0.33	1.52
X	12.5	40	0.074	75	0.21_5	1.33
XIV	13.0	40	0.101	75	0.19	1.28
XIII	13.0	50	0.155	65	0.085	0.93

discharged gas. When O_2 was the discharged gas, the temperature was higher by about 50%; thus at a reaction distance of 20 mm, the temperature of an O_2 gas stream was 155°C. The temperature of N_2O as the discharged gas was not measured.

Identification of Phenol from Discharge Runs

In order to provide a better identification of the products resulting from a mgd[a] oxidation of an aromatic compound, preparative glc was done on a combination of benzene runs. A 12 foot by 1/2 inch SE-30 column was used to separate the product phenol from the benzene solvent, the column temperature was 150° and the flow of nitrogen 250 ml/min. Ten injections of 0.20 ml were used to collect the phenol in a simple cold trap; this trap was supplied by the F&M Corporation. The trap was rinsed out with CCl_4 and the resulting solution found to contain 6.2% phenol by weight when subjected to glc analysis.

This solution was diluted to 1.6% phenol and its i r spectrum compared to an authentic sample of 1.9% phenol in CCl_4. A Perkin-Elmer model 237-B grating infrared spectrometer gave spectra which were superimposable except for an absorption at 1700 cm^{-1} for the suspected phenol. Removal of the CCl_4 solvent followed by vacuum sublimation of the phenol residue gave a solution of phenol which was completely superimposable on an authentic sample. The main absorptions of interest were those at 3600 cm^{-1} (free O-H stretch), 3460 cm^{-1}

a The abbreviation for microwave glow discharge is mgd.

(hydrogen bonded O-H stretch) and 3040 cm^{-1} (aromatic C-H stretch).

The u v spectra of a benzene-CO_2 run and a benzene-O_2 run were obtained in 15% methanol and iso-octane solutions. The benzene solvent from the discharge runs was removed at 0° and the residue dissolved in either the aqueous alcohol or the hydrocarbon solvent. The Cary, Model 14, uv spectrometer was used with 1.0 cm cells to obtain the data given below; the wavelengths obtained were only reproducible to 5 Å units due to the rapid sweep used.

When aqueous methanol was the solvent the benzene-CO_2 run gave an absorption maxima at 2700 Å while the benzene-O_2 run gave an absorption maxima at 2695 Å. Since the authentic sample of phenol in aqueous methanol absorbed at 2700 Å, both mgd runs are in agreement with phenol as the major product.

The use of iso-octane gave even more striking evidence for phenol; an authentic sample of phenol in this hydrocarbon gave three maxima, 2775 Å, 2708 Å and 2645 Å. The benzene-CO_2 run showed maxima at 2775 Å, 2708 Å, and 2643 Å. Finally the benzene-O_2 run gave analogous peaks at 2775 Å, 2710 Å, and 2645 Å.

Photolysis of NO_2

Toluene was oxidized by NO_2 in both dark and photolytic runs to unidentified products and small amounts of side chain oxidation products. A dark reaction using 1 g of toluene in 7 liters of N_2 and approximately

100 ml NO_2 gave 13 mg of volatile product per hour. The solution of toluene in N_2 was mixed with NO_2 at atmospheric pressure in a gas phase reaction; aluminum foil was used to eliminate room light. Analysis of the resulting products gave 88% unidentified products, 10% benzaldehyde and two % benzyl alcohol. Less than five % of m- and p-cresols were formed; the same was true for bibenzyl. The amounts of phenol and o-cresol were less than 1% of the volatile products. Tars were not measured. The 1-DEGS column, (192-56), gave the following relative retention times: benzaldehyde (1.0), U-1 (1.4), U-2 (1.9), benzyl alcohol (2.1), U-3 (2.3), U-4 (2.6) and U-5 (3.7).

An analogous run using the Hanovia 450 watt lamp gave 2.1 mg of volatile product and 70 mg tars per hour. Again the unidentified products accounted for most of the reaction, being present in 81%. Benzaldehyde and benzyl alcohol were formed in 15 and 4% respectively; bibenzyl and the phenolic products were absent within the same limits as the dark reaction. The 1-DEGS column, (192-56), gave the following relative retention times: benzaldehyde (1.0), U-1 (1.9), benzyl alcohol (2.0), U-2 (2.2) and U-3 (2.5). Duplicate runs were not made for either the dark or photolytic systems. It should be pointed out that the reason for more product in the dark reaction than in the photolytic run is most probably due to a mistake in labeling the two runs.

Photolysis of O_3

A total of 15 runs with toluene and O_3 were made using four different ozonizers under a variety of conditions. Since these various conditions do not easily lend themselves to comparison, only the pertinent blank, dark and photolytic runs will be given here. The blank run was a mixture of toluene and O_2 irradiated for two hours in an atmospheric flow system. The yield was only 0.3 mg of volatile product and 3 mg of tar; benzaldehyde was present in 61%, benzyl alcohol in 9% and the m and p - cresols in 10%. Phenol and o - cresol were not separated under the glc conditions used but together were present in 18%. One unidentified product accounted for two per cent while bibenzyl was present in less than 10%. The 1-DEGS column, (200-56), gave the following relative retention times: benzaldehyde (1.0), U-1 (1.4), benzyl alcohol (2.0), phenol and o-cresol (2.3), m- and p-cresol (2.9).

After the above blank run, a dark reaction between toluene and O_3 was made. This run, utilizing 0.75 g of toluene in 6 liters N_2 and 260 mg of O_3 in 6.0 liters O_2, gave 0.8 mg of volatile products per hour; the tar was not collected but was visually estimated as less than 10 mg. The product composition was 55% benzaldehyde, 5% benzyl alcohol and 20% each of two unidentified peaks. The 1-DEGS column, (192-56), gave the following relative retention times: U-1 (0.70), benzaldehyde (1.00), U-2 (1.4) and benzyl alcohol (2.1).

Repetition of the toluene—O_3 run using the Hanovia 450 watt lamp

(quartz cell) to irradiate the reaction mixture gave 4.1 mg of volatile product and 60 mg tar per hour. To obtain these products, 1.0 g of toluene in 6 liters N_2 was mixed with 260 mg of O_3 in 6 liters O_2. The product composition was 48% benzaldehyde, 1% benzyl alcohol, 51% of four unidentified products and less than 2% of any phenols or bibenzyl. The 1-DEGS column, (192-56), was used to obtain the following relative retention times: U-1 (0.65), benzaldehyde (1.00), U-2 (1.4), U-3 (1.9), benzyl alcohol (2.1) and U-4 (2.6). The unknown products U-1 and U-2 again accounted for the majority of the unidentified material. No duplicate runs were done.

CHAPTER VII

OXIDATION OF ALIPHATIC COMPOUNDS

Cyclohexene

Hg^*, N_2O Technique

Cyclohexene was the only olefin studied with atomic oxygen. Due to air oxidation of this olefin, 2,6-di-t-butyl-4-methylphenol was used as an inhibitor in order to study the reaction of atomic oxygen. This inhibitor was non-volatile and hence not present in the gas phase oxidations studied. The use of the Hanau mercury lamp with the usual Hg^*, N_2O apparatus at atmospheric pressure and 50°C allowed us to oxidize cyclohexene to five known products. A 130 ml/min N_2O flow[a] through a 20° substrate bubbler swept 1.8 g of cyclohexene through the reaction cell; this gave 120 and 4 mg of volatile products and tar respectively. The product composition was 45.0% cyclohexene oxide, 16.6% cyclopentanecarboxaldehyde, 14.6% cyclohexanone, 1.8% 2-cyclohexen-1-ol, 2.0% of a mixture of 2-cyclohexen-1-one, 3-cyclohexen-1-ol and 3-cyclohexene-1-one[b] and 20% of two unidentified products. The 1-DEGS column, (132-60), gave the following relative retention times: U-1 (0.41), cyclohexene oxide and

a All data in this chapter are given in the same manner of the previous three chapters.

b This product is only tentatively identified since no authentic sample is available. Its identification is based upon the retention times of the remaining unsaturated alcohols and ketone.

cyclopentanecarboxaldehyde (0.49), U-2 (0.62), cyclohexanone (1.00), and 2-cyclohexen-1-ol (1.7). The 1-ApL column, (61-69), gave the relative time for cyclopentanecarboxaldehyde of 0.88 relative to cyclohexene oxide. The 1-DEGS column, (88-70), gave retention times of the unsaturated alcohols and ketones as follows: 2-cyclohexen-1-ol (0.92), 2-cyclohexen-1-one (1.00), suspected 3-cyclohexen-1-ol and 3-cyclohexen-1-one (1.1). No duplicate run was made.

Direct Photolysis of N_2O

The Hanovia 450 watt lamp was used to irradiate a mixture of N_2O and cyclohexene in the gas phase. Mercury was not present and a quartz reaction well was used. The oxidation of 2.1 g of cyclohexene with 11 liters N_2O gave 2.2 and 2 mg of volatile products and tar respectively. The product distribution was 10% cyclohexene oxide, 3.8% cyclopentanecarboxaldehyde, 9.8% cyclohexanone, 4.2% cyclohexanol, 50.6% 2-cyclohexen-1-ol, 19.2% of a mixture of 2-cyclohexen-1-one, 3-cyclohexen-1-ol and 3-cyclohexen-1-one[a] and 2.4% of five unidentified products. The relative retention times of all products were within 10% of those given for cyclohexene oxidation by the Hg^*, N_2O technique. No duplicate run was made.

Microwave Discharge on CO_2

The standard set of discharge conditions given in Chapter 6 were used in the cyclohexene work cited here. The oxidation of 12 g of

a This product is only tentatively identified since no authentic sample is available. Its identification is based upon the retention times of the remaining unsaturated alcohols and ketone.

cyclohexene with 3.1 liters CO_2 gave 56 and 8 mg of volatile products and tar respectively. The product composition was 25.2% cyclohexene oxide, 25.2% cyclopentanecarboxaldehyde, 22.1% cyclohexanone, 9.9% cyclohexanol, 5.7% 2-cyclohexen-1-ol, 8.4% 2-cyclohexen-1-one, 3.3% 3-cyclohexen-1-ol and 3-cyclohexen-1-one and 0.2% of seven unidentified products. The 1-DEGS column, (110-56), gave cyclohexanol with a relative retention time of 1.1 relative to cyclohexanone. The Carbo column, (101-60), gave the following relative retention times: 2-cyclohexen-1-one (1.0), 2-cyclohexen-1-ol (1.1), 3-cyclohexen-1-ol and 3-cyclohexen-1-one (1.2). The 1-ApL column, (61-69), gave the relative time for cyclopentanecarboxaldehyde of 0.90 relative to cyclohexene oxide. Since each unidentified product was present in less than 0.05% on the 1-DEGS column, (80-44), their relative times will not be given. A duplicate run agreed within 20% to the run given above.

Microwave Discharge on O_2

The oxidation of 7.0 g of cyclohexene with 3.4 liters O_2 gave 60 and 8 mg of volatile product and tar respectively. The product composition was 14.5% cyclohexene oxide, 24.0% cyclopentanecarboxaldehyde, 7.3% cyclohexanone, 3.6% cyclohexanol, 12.5% 2-cyclohexen-1-ol, 28.8% 2-cyclohexen-2-one, 1.6% 3-cyclohexen-1-ol and 3-cyclohexen-1-one and 7.7% of two unidentified products. The 1-DEGS column, (120-50), gave the following relative retention times: cyclohexanone (1.0), cyclohexanol (1.2), U-1 (1.3), U-2 (1.5), 2-cyclohexen-1-ol (1.8) and 2-cyclohexen-

1-one (2.0). The Carbo column, (101-60), gave the following retention times: 2-cyclohexen-1-one (1.0), 2-cyclohexen-1-ol (1.1), 3-cyclohexen-1-ol and 3-cyclohexen-1-one (1.2). The 1-ApL column, (61-69), gave cyclopentanecarboxaldehyde a retention of 0.90 relative to cyclohexene oxide. No duplicate run was made.

Cyclohexane

Hg^*, N_2O Technique

Four runs of interest were done in relation to the oxidation of cyclohexane with the Hg^*, N_2O technique. The first used the Hanau mercury lamp under the usual $O(^3P)$ conditions at 50°C. A 130 ml/min N_2O flow through a 13° substrate bubbler swept 2.9 g of cyclohexane through the reaction cell. This gave 150 and 8 mg of volatile products and tar respectively. The product composition was 15.8% cyclohexene oxide, 57.5% bicyclohexyl, 7.3% cyclohexanone, 18.2% cyclohexanol and 1.2% of two unidentified products. The 1-DEGS column, (90-60), gave the following relative retention times: U-1 (0.35), cyclohexene oxide (0.42), U-2 (0.55), bicyclohexyl (0.70), cyclohexanone (0.89) and cyclohexanol (1.00). No duplicate run was made.

Nitrogen was substituted for N_2O and a run analogous to that above made. A 130 ml/min N_2 flow through a 13° substrate bubbler swept 3.0 g of cyclohexane through the reaction cell; this gave 60 and 1 mg of volatile products and tar respectively. The product composition

was 0.5% cyclohexene oxide, 80.4% bicyclohexyl, 3.5% cyclohexanone, 6.8% cyclohexanol and 8.8% of five unidentified products. The 1-DEGS column, (90-50), gave the following relative retention times: U-1 (0.17), U-2 (0.26), U-3 (0.31), cyclohexene oxide (0.37), U-4 (0.50), bicyclohexyl (0.63), cyclohexanone (0.82), cyclohexanol (1.00) and U-5 (1.1). A duplicate run agreed with the forementioned product distribution within 10%.

In the third run of interest, the Hanovia 450 watt lamp in the quartz reaction well was the radiation source, no mercury bubbler was present and the temperature of the run was 75°C. A 100 ml/min N_2 flow through a 0° substrate bubbler swept 1.3 g of cyclohexane through the reaction cell. The yield of volatile product was 0.4 mg; tars were not measured. The product composition was based on total glc peak area; about 5% cyclohexanone, 5% cyclohexanol and 90% of three unidentified products was observed. The 1-DEGS column, (110-47), gave the following retention times: U-1 (0.16), U-2 (0.22), U-3 (0.39), cyclohexanone (0.85) and cyclohexanol (1.00). No duplicate run was made.

The fourth run was analogous to the third run except that air was the carrier gas rather than N_2. A 100 ml/min air flow through a 0° substrate bubbler swept 1.3 g of cyclohexane through the reaction cell; this gave 1.3 and 1.5 mg of volatile products and tar respectively. The product composition was 54% cyclohexanol, 46% cyclohexanone and less than 1% cyclohexene oxide, bicyclohexyl or unidentified material. The

1-DEGS column, (110-47), gave the following retention times: cyclohexanone (0.90), cyclohexanol (1.00) and bicyclohexyl (0.68). No duplicate run was made.

Direct Photolysis of N_2O

Two runs at atmospheric pressure were done using the Hanovia 450 watt lamp to irradiate a N_2O-cyclohexane mixture at 75°C. The first run used a 100 ml/min flow of N_2O through a 0° substrate bubbler to sweep 2.7 g of cyclohexane through the reaction cell. The yield of volatile product was 3.1 mg; tars were not measured. The product composition was 9.5% cyclohexanone and 90.5% cyclohexanol. The duplicate run used a 130 ml/min flow of N_2O through a 5° substrate bubbler to sweep 2.6 g per hour of cyclohexane through the reaction cell. Volatile product and tar were formed in 8 and 4 mg per hour respectively; cyclohexanol was the sole volatile product, less than 5% cyclohexanone was formed. The 1-DEGS column, (100-60), gave a relative retention time of 0.91 for cyclohexanone relative to cyclohexanol. It was found that less than 1% bicyclohexyl or cyclohexene oxide was formed in either run.

Photolysis of NO_2

The reaction apparatus and technique used for the cyclohexane-NO_2 system was identical to the toluene-NO_2 system previously described. It was established that a dark reaction between NO_2 and cyclohexane took place both in the gas and liquid phases; to facilitate

comparison with other techniques of oxidation only the gas phase work will be presented here. A dark reaction using 2.4 g of cyclohexane in 6.5 liters of N_2 and approximately 100 ml NO_2 gave 0.3 mg of volatile products per hour. Analysis of the resulting products gave 5% cyclohexanol, 33% cyclohexanone, less than 10% bicyclohexyl and 62% of two unidentified products. The 1-DEGS column, (92-70) gave the following retention times: U-1 (0.20), cyclohexanone (0.90), cyclohexanol (1.00) and U-2 (3.5).

An analogous run, with the Hanovia 450 watt lamp and Pyrex filter, used 2.4 g of cyclohexane in 6.5 liters N_2 and approximately 100 ml NO_2. This gave 4.7 and 1 mg of volatile products and tar respectively; the product composition was 6% cyclohexanol, 5% cyclohexanone and 89% of four unidentified products. The 1-DEGS column, (92-70), gave the following relative retention times: U-1 (0.20), U-2 (0.64), cyclohexanone (0.86), cyclohexanol (1.00), U-3 (1.2) and U-4 (3.4). No duplicate run was made in either the dark or photolytic reaction.

Photolysis of O_3

The techniques used in these runs were as previously described for the toluene-O_3 system. Wherein photolysis of cyclohexane-air mixtures gave essentially no product, the mixing of cyclohexane with O_3 gave products whether they were irradiated or not. The dark reaction utilized 3.6 g of cyclohexane in 6 liters N_2 and 260 mg of O_3 in 6 liters O_2. This gave 1.6 mg of volatile product. Tars were not collected but

visually estimated at less than 10 mg. The product composition was 59% cyclohexanol, 31% cyclohexanone and 10% of an unidentified product. The 1-DEGS column, (90-70), gave the following retention times: cyclohexanone (0.87), cyclohexanol (1.00) and U-1 (1.3).

An analogous run using the 450 watt Hanovia lamp with a Vycor filter was made to determine if $O(^1D)$ could be generated. This run used 6 g of cyclohexane in 12 liters N_2 and 260 mg of O_3 in 6 liters O_2 to give 67 mg of volatile product. The composition of the products was 69.8% cyclohexanone, 28.9% cyclohexanol and 1.3% of five unidentified products. The glc analysis of the dark reaction gave the following relative retention times: U-1 (0.27), U-2 (0.32), U-3 (0.39), U-4 (0.60), U-5 (0.75), cyclohexanone (0.85) and cyclohexanol (1.00). No duplicate runs were made for the dark or photolytic systems.

Microwave Discharge on CO_2

The standard set of discharge conditions given in Chapter 6 were used. The oxidation of 12 g of cyclohexane with 3.6 liters CO_2 gave 30 and 5 mg of volatile products and tar respectively. The product composition was 3.3% cyclohexene oxide (tentative), 43.8% cyclohexanol, 42.2% cyclohexanone, 3.5% 2-cyclohexen-1-ol, 1.4% 2-cyclohexen-1-one, 0.3% 3-cyclohexen-1-ol and 3-cyclohexen-1-one and 5.5% of three unidentified products; bicyclohexyl was present in less than 0.2% if at all. The 1-DEGS column, (80-44), gave the following retention times: U-1 (0.35), U-2 (0.45), U-3 (0.56) and cyclohexene oxide (1.00). The 1-DEGS column,

(111-56), gave cyclohexanone a retention time of 0.87 relative to cyclohexanol. The Carbo column, (101-60), gave the following retention times: 2-cyclohexen-1-one (1.0), 2-cyclohexen-1-ol (1.1), 3-cyclohexen-1-ol and 3-cyclohexen-1-one (1.2). A duplicate run agreed with the above product distribution to 40%.

Microwave Discharge on O_2

Only one run was made with O_2; the reaction distance was 30 mm while all other parameters were standard. The oxidation of 10 g of cyclohexane with 3.5 liters O_2 gave 40 and 10 mg of volatile products and tar respectively. The product composition was 9.4% cyclohexene oxide, 20.4% cyclohexanol, 20.3% cyclohexanone, 1.3% 2-cyclohexen-1-ol, 1.9% 2-cyclohexen-1-one, 0.5% 3-cyclohexen-1-ol and 3-cyclohexen-1-one and 46.2% of five unidentified products. Bicyclohexyl was present in less than 0.2% if at all. The 1-DEGS column, (80-34), gave the following relative retention times: U-1 (0.39), U-2 (0.48), U-3 (0.57), U-4 (0.76), U-5 (0.88) and cyclohexene oxide (1.00). The 1-DEGS column (120-50) and Carbo column (101-60), gave retention times as those found in the CO_2 system to within 10%. No duplicate run was made.

Microwave Discharge on N_2O

As with O_2, only one run was made, this using the standard discharge conditions. The oxidation of 4.3 g of cyclohexane with 6 liters N_2O gave 8 and 15 mg of volatile product and tar respectively. The product composition was 7.8% cyclohexanone, 24.2% cyclohexanol, 20.2%

bicyclohexyl and 47.8% of eight unidentified products. The 1-DEGS column, (110-47), gave the following relative retention times: U-1 (0.23), U-2 (0.31), U-3 (0.38), U-4 (0.41), U-5 (0.51), U-6 (0.57), U-7 (0.63), cyclohexanone (0.87), cyclohexanol (1.00), bicyclohexyl (1.1) and U-8 (1.3). No duplicate run was made.

Propane and n-Butane

Microwave Discharge on CO_2 or O_2

A total of three runs were made with these low molecular weight alkanes, these were propane-CO_2, propane-O_2, and n-butane-CO_2. Both CO_2 runs were made at the standard conditions while the O_2 run utilized a reaction distance of 30 mm rather than 20 mm. The butane run utilized approximately 600 ml or n-butane with 6 liters CO_2 during a 3 hour run; tars were not measured and the actual yield of volatile products not calculated due to extreme separation difficulties encountered during glc analysis. The per cent composition of the butane run using glc peak areas follows: 10% acetaldehyde, 6% propanal, 15% acetone, 6.5% butanal, 25% methyl ethyl ketone, 6% 2-propanol, 12.5% 2-butanol, 4% 1-propanol and 15% of four unidentified peaks. The presence of 1-butanol could not be established due to the large excess of ethylbenzene solvent employed in the reaction trap. The Carbo column, (75-28), gave the following relative retention times: U-1 (0.37), acetaldehyde (0.57), U-2 (0.70), propanal (0.89), acetone (1.00), butanal (1.4), methyl ethyl ketone (1.6), 2-propanol

(1.9), U-3 (2.4), U-4 (2.6), 2-butanol (3.3) and 1-propanol (3.6).

The oxidation of 15 g of propane with 6 liters CO_2 during a 2 hour run gave about 2.3 mg of volatile product; tars were not measured. The product composition based on total glc peak area was found to be 13.2% acetaldehyde, 5.6% propanal, 14.4% acetone, 16.0% 2-propanol, 24.4% 1-propanol and 26.4% of six unidentified products. The Carbo column, (75-28), gave the following relative retention times: acetaldehyde (0.55), U-1 (0.68), propanal (0.87), acetone (1.00), U-2 (1.3), U-3 (1.4), U-4 (1.6), 2-propanol (1.8), U-5 (1.9), U-6 (2.4) and 1-propanol (3.5).

The oxidation of 2 g of propane with 400 ml O_2 during a 2 hour run gave about 7.2 mg of volatile product; tars were not measured. The product composition based on total glc peak area was found to be 15.7% acetaldehyde, 6.7% propanal, 23.8% acetone, 13.7% 2-propanol, 15.4% 1-propanol and 24.7% of five unidentified products. The Carbo column, (75-28), gave the following retention times: acetaldehyde (0.56), U-1 (0.67), propanal (0.87), acetone (1.00), U-2 (1.3), U-3 (1.6), 2-propanol (1.8), U-4 (2.0), U-5 (2.4) and 1-propanol (3.5). Oxetane and the three hexanes expected by hydrogen abstraction from propane were formed in less than 5% if at all.

CHAPTER VIII

DISCUSSION

Reaction Of $O(^3P)$ With Aromatic Compounds At 30°C

Product Distribution of Neat Hydrocarbons

In all the aromatic compounds studied, phenols accounted for more than 82% of the volatile products. Oxidation of the substituent was observed only with alkyl groups. Cleavage of the substituent was observed with all substrates but was of importance only with particular polymethylbenzenes. Unidentified products usually possessed retention times between the substrate and phenol and were largely ignored; low molecular weight products of retention time less than or equal to the substrate were also ignored. Tar formation was infrequently measured and found to be dependent upon the reactivity of the substrate; thus the weight ratio of tar to volatile product was 0.2 for anisole and 2 for benzotrifluoride. No effort was made to determine the composition of the tar. The possible presence of H_2O, CO, CO_2 and other products will be discussed in Chapter 9.

The three non-alkyl substituents gave more than 97% phenols; thus a discussion of non-phenolic products can be made for alkylbenzenes only. Benzene gave phenol as the sole identifiable product while toluene

gave approximately 3% of side chain oxidation to benzaldehyde and benzyl alcohol. The o-, m- and p-xylenes gave about 6, 1 and 7% of side chain oxidation to the corresponding benzyl alcohols and tolualdehydes.

The lack of benzyl hydrogens in t-butylbenzene conferred extra stability on this compound with respect to side chain oxidation. Only 1% of neophyl alcohol was formed and probably less than 2% of phenyldimethylacetaldehyde (this compound was not available for glc identification). The opposite behavior was exhibited by ethylbenzene which gave 12% of side chain oxidation; preliminary considerations would have predicted the 3% oxidation found for toluene. This four-fold increase in side chain oxidation could be ascribed to the extra stability of the α-methylbenzyl free radical with respect to the benzyl radical after hydrogen abstraction by $O(^3P)$. However, the known reaction[67] of triplet mercury with alkanes possessing gem C-H groups to give free radicals is probably the best explanation. Toluene, t-butylbenzene and the polymethylbenzenes would be largely immune from hydrogen abstraction by excited mercury atoms; ethylbenzene would be the only aromatic compound studied which would be expected to possess this side reaction.

The side chain oxidation products expected from 1, 2, 3-trimethylbenzene and mesitylene were not available commercially, hence they were not identified. By analogy with m-xylene, where only 1% of side

67 H. E. Gunning and O. P. Strausz, Advan. Photochem. 1, 209 (1963)

chain oxidation was observed, mesitylene would be expected to give less than 5% side chain oxidation. No glc peaks for side chain oxidation products were observed where they would have been expected in the mesitylene run. By analogy with o-xylene, the numerous unidentified glc peaks from the 1, 2, 3-trimethylbenzene run suggest that both 2, 6 and 2, 3-dimethylbenzyl alcohols and benzaldehydes are formed. The presence or absence of benzoyl fluoride from benzotrifluoride could not be established under the glc conditions used due to lack of separation of benzotrifluoride from the benzoyl fluoride.

A search for carbon-carbon insertion to give anisoles was unsuccessful. Due to the similarities in volatility and polar nature of the anisoles with the parent hydrocarbon, glc separation of a small quantity of an anisole in the presence of a large excess of the hydrocarbon is almost impossible. Thus, anisole from toluene, p-methylanisole from p-xylene, m-methylanisole from m-xylene and phenyl trifluoromethyl ether from benzotrifluoride were not confirmed as to their presence or absence. The substrates ethylbenzene, o-xylene, mesitylene and 1, 2, 3-trimethylbenzene were able to be used to determine the amounts of the corresponding anisoles formed. Ethylbenzene gave a tentative yield of 3.5% phenetole and/or methyl benzyl ether while o-xylene gave a tentative yield of 1% o-methylanisole. Mesitylene gave less than 0.8% of 3, 5-dimethylanisole and 1, 2, 3-trimethylbenzene gave less than 0.2% of either 2, 6 or 2, 3-dimethylanisole. The presence of phenyl t-butyl ether

from t-butylbenzene was not checked.

Since the intermediate leading to anisoles would be expected to be the same as that leading to cleavage, the ortho activation effect would predict that 1, 2, 3-trimethylbenzene would give the best yield of anisoles. The absence of anisoles from this substrate strongly implies that overall carbon-carbon insertion is not an important process in $O(^3P)$ oxidation of aromatic hydrocarbons.

Substituent cleavage to a phenol was observed with all compounds studied but was important only for o-xylene and 1, 2, 3-trimethylbenzene. Since anisole is known to give phenol from reaction with triplet mercury atoms[68], the presence of this product in the Hg^*, N_2O runs cannot be ascribed solely to $O(^3P)$. However, the remaining substrates do appear to give substituent cleavage from interaction with $O(^3P)$. Most substrates gave less than 13% substituent cleavage. Thus toluene gave 8% phenol, a product which was not found by the pioneer in reactions of $O(^3P)$[28]. The exceptions were o-xylene (34% o-cresol) and 1, 2, 3-trimethylbenzene (38% of 2, 3 and 2, 6-dimethylphenols). The large ortho activation effect seen above was found for both C-H and C-C cleavage.

As stated earlier in this chapter, the fate of the substituent after cleavage was usually ignored. Toluene could give either methyl radical or methylene upon oxidation to phenol. The case of t-butylbenzene

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68 J. G. Calvert and J. N. Pitts, "Photochemistry", John Wiley and Sons, Inc., New York, 1966, p 106

is of interest here since a tentative yield of 12% t-butyl alcohol was found; this corresponds well with the yield of 13% phenol. The implication of this substrate is that the substituent is cleaved as a free radical in the rest of the substrates. The possible fates of the substituent upon cleavage will be discussed further in the following chapter.

Chlorobenzene and bromobenzene were not able to be studied with $O(^3P)$ using the Hg^*, N_2O technique because of ready photolysis to phenyl radicals. As seen from the photolytic studies of Kharasch[69], p-fluorobiphenyl is most resistant of the p-halobiphenyls toward homolytic cleavage to aryl radicals upon irradiation with 2537 Å light. A similar result was obtained by us in our efforts to study fluoro-, chloro- and bromobenzene with $O(^3P)$.

Since the total amount of biphenyls formed was small, only the product distribution of chlorobiphenyls was determined in our work. The average area per cent of the chlorobiphenyl glc peaks from a Hg^*, N_2O and helium blank run were 53 ± 2% ortho, 22 ± 2% meta and 25 ± 1% para-chlorobiphenyl. This is in fair agreement with other work[70] on the phenylation of chlorobenzene where 50% ortho, 32% meta and 18% para-chlorobiphenyl was found at 80°C.

Pyridine gave only tars when subjected to the Hg^*, N_2O technique.

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69 N. Kharasch, R. K. Sharma and H. B. Lewis, Chem. Commun., 418 (1966)

70 G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, Oxford (1960)

It was not established if this was direct or mercury photosensitized decomposition of the substrate. Since mercury plays no noticeable role in the photodecomposition of toluene or nitrobenzene, the process is probably direct photodecomposition of pyridine.

Relative Reactivity Runs and Partial Rate Factors

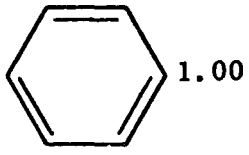
The total reactivity series for phenol formation relative to benzene is given below. The value includes substituent cleavage except for anisole. The order is: mesitylene[a] (80), 1,2,3-trimethylbenzene (25), m-xylene (22), anisole (13), o-xylene (10), p-xylene (9.0), ethylbenzene (4.9), toluene (4.4), t-butylbenzene (3.6), benzene (1.00), fluorobenzene (0.66) and benzotrifluoride (0.29).

Table 13 gives the prf's[b] observed for the aromatic compounds studied at 30°C relative to benzene. It must be stressed that all partial rate factors are used under the assumption that the non-volatile products do not affect the prf's; that is tars are formed non-selectively and not preferentially from attack on any one position of the aromatic[71]. The monalkylbenzenes show a reasonably constant prf series; the only surprise being the prf for removal of the ethyl group being larger than that of toluene and t-butylbenzene. As mentioned previously, the mer-

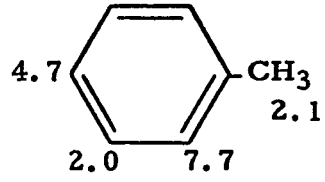
a Numerical value given in parenthesis following the substrate.
b prf is abbreviation for partial rate factor.
71 D. H. Hey, M. J. Perkins and G. H. Williams, Chem. Ind., London, 83 (1963); R. T. Morrison, J. Cazes, N. Samkoff and C. A. Howe, J. Am. Chem. Soc., 84, 4152 (1962)

Table 13 Partial Rate Factors from $O(^3P)$ at 30°C

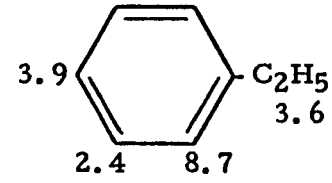
Benzene



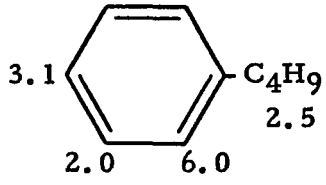
Toluene



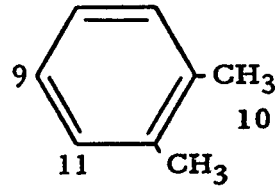
Ethylbenzene



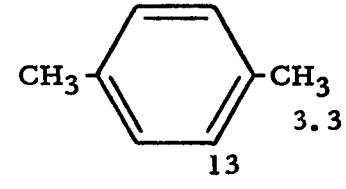
t-Butylbenzene



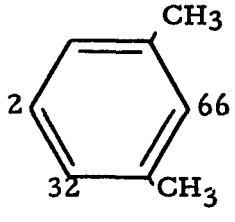
o-Xylene



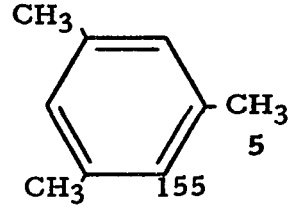
p-Xylene



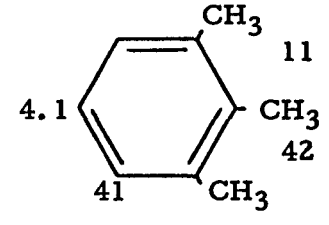
m-Xylene



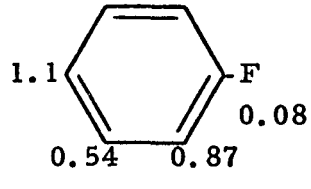
Mesitylene



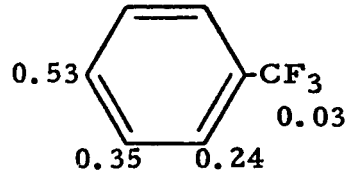
1, 2, 3-trimethylbenzene



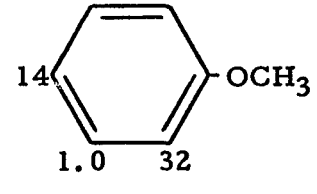
Fluorobenzene



Benzotrifluoride



Anisole[a]



a The partial factor for methoxy cleavage cannot be determined because of concurrent photolysis to produce phenol.

cury photosensitized hydrogen abstraction reaction is possible only for ethylbenzene. The postulated precursor of phenethyl alcohol and phenylacetaldehyde is the phenethyl free radical; this could eliminate ethylene to give phenyl radical which could give rise to phenol. This reaction or others might account for the increase in the prf for ethyl cleavage.

The constancy of the ratio of ortho to para prf's (O_f/P_f) in the monoalkylbenzene series provides a strong argument for the absence of appreciable steric factors in the oxidation of t-butylbenzene. For toluene, ethylbenzene and t-butylbenzene[a], O_f/P_f is $1.66 \pm .06$, 2.04 ± 0.15 and $1.9_5 \pm .05$ respectively. Hence $O(^3P)$ is a reagent of low steric requirement. The fact that $O_f > P_f > M_f$ can be explained by the order of hyperconjugative and inductive effects expected for electrophilic attack on these hydrocarbons. The ratio of O_f/P_f is usually less than one for electrophilic attack by a charged species[b]; however aromatic substitution by free radical attack is well documented[72] in having an O_f/P_f ratio greater than unity. The possible reasons for this fact will be given in the discussion of anisole prf's.

The prf's of the polymethylbenzenes are in fair accord with those calculated from toluene[c]. o-Xylene is surprising in that the ratio of

---

a Ratio given is average of two runs and deviation from this average.

b In Brown's review (reference 66), only 5 or 54 examples of electrophilic attack on toluene possessed a ratio O_f/P_f greater than one.

c See Table 9.

72 R. Itô, T. Migita, N. Morikawa and O. Simamura, Tetrahedron, 21, 955 (1965)

prf's of the 3 position to that of the 4 position is calculated to be 1.64; the observed value is 1.22. Since the glc separation of the meta and para-cresols used to calculate the above ratio and of the 2, 3- and 3, 4-dimethylphenols used for the observed value of the above ratio are not complete, this discrepancy may be due to analytical errors.

The 1, 2, 3-trimethylbenzene system is also surprising in that the prf at the 5 position is calculated to be five times larger than experimentally observed. This discrepancy cannot be solely traced to analytical errors in either the observed prf or the calculated prf. Linear free energy correlations for the polymethylbenzenes will be given later in this chapter.

The order of prf's for non-alkyl substituents is also of interest. Benzotrifluoride shows an effect $P_f > M_f > O_f$; a similar order is obtained from attack of phenyl radicals[73]. This order is best explained by a pure inductive effect. This view is reinforced by the constant increase in reactivity as the distance from the trifluoromethyl group increases; thus the ratios M_f/O_f and P_f/M_f are 1.5 ± 0.15 and 1.5 ± 0.2 respectively. This is acceptable agreement with literature[74] values of 1.67 for these ratios as predicted by direct field and inductive effects. The inductive control exhibited here also rules out any double bond no-bond

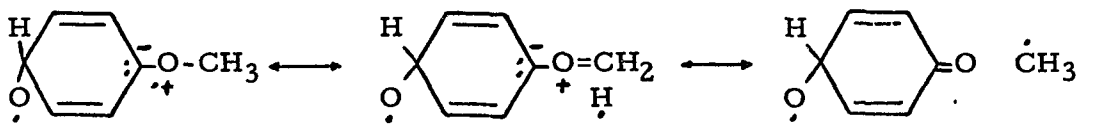
73 J. Hine, "Physical Organic Chemistry" 2nd ed., McGraw-Hill, New York, 1962, p 471

74 K. Bowden, Can. J. Chem. 41, 2781 (1963)

resonance[75] for the trifluoromethyl group.

Fluorobenzene shows the order $P_f > O_f > M_f$. The order expected from inductive control of orientation would be $P_f > M_f > O_f$. Phenyl radicals (which presumably have little or no polar characteristics) exhibit an order $O_f > M_f > P_f$ when attacking fluorobenzene[73]. For $O(^3P)$, the enhanced reactivity of the ortho position relative to the meta- position could be due to stabilization by a resonance structure which cannot be drawn for the meta- position. This structure is analogous to "A" given in the next paragraph for anisole.

Inductive effects are clearly of little import in the anisole case since the series of prf's is $O_f > P_f > M_f$; this is analogous to the order found[72] with substituted (H, p-NO_2, p-Cl, p-CH_3, p-OCH_3) phenyl radicals reacting with anisole. Resonance structures can be used to rationalize the prf's.



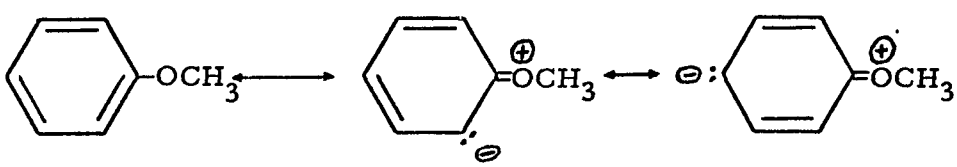
A B C

The ability of the methoxyl group to stabilize free radical attack at the ortho and para positions is analogous to the enhancement in reactivity of the α-position observed for $O(^3P)$ oxidation of ethyl

75 C. L. Liotta and D. F. Smith, Jr., Chem. Commun., 416 (1968); also private communication.

alcohol[25].

Since we believe that the O(^{3}P) oxidation of most aromatic compounds has a very early transition state, resonance structures shown for fluorobenzene and anisole do not provide a wholly satisfactory explanation of the observed prf's. Anisole in particular is difficult to explain since both field and inductive effects would tend to make the <u>para</u> prf larger than the <u>ortho</u> prf. If the ground state anisole molecule is considered, the electron density would be expected to be greatest in the <u>ortho</u> position since there is no solvent to interact with the charged species. Since the <u>para</u>- structure has the largest separation of charge, the lack of a solvent would diminish the contribution of this structure more than that of the <u>ortho</u> structure. These structures are shown below; the order of prf of anisole appears reasonable in this light and are to be expected for a reaction with a very early transition state.



For fluorobenzene, analogous resonance structures as shown above are of less importance due to the greater electronegativity of fluorine. This being the case, a combination of resonance and inductive effects explain the observed order of $P_f > O_f > M_f$. The use of σ_p^+ constants, developed for liquid phase systems, would predict a larger prf

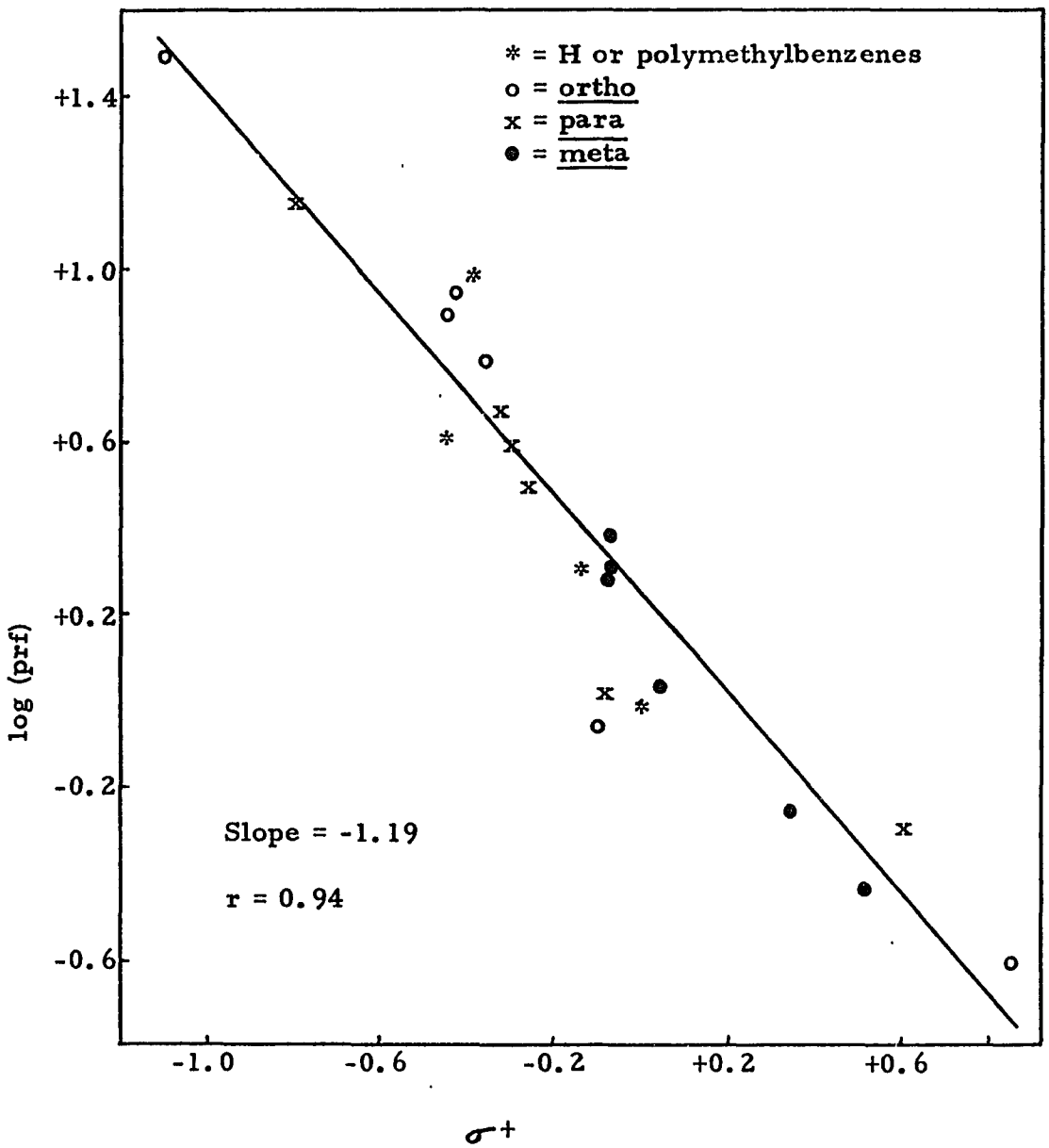
than was observed for our gas phase oxidations; consequently the p-F point deviates from the Hammett plott shown in the next section.

Correlation of Partial Rate Factors with σ^+

Benzene, the six monosubstituted benzenes and three of the polymethylbenzenes can be used to generate sixteen experimental points for a Hammett correlation of the data. Due to the high reactivity of the para position of anisole, a better correlation is gotten with σ^+ constants. Figure 3 shows the logarithm of the observed prf for meta, para or a combination of meta and para attack plotted versus the appropriate σ^+ constants. The use of all sixteen points gives a slope of -1.19 ($r = 0.94$)[76]. The use of benzene and the six monosubstituted benzenes gives a slope of -1.15 ($r = 0.95$), while subsequent elimination of the p-trifluoromethyl group gives a slope of -1.28 ($r = 0.97$). The ortho prf's included in Figure 3 were not used to calculate the slope; these values will be discussed in the following section.

Regardless of which plot is considered best, the ramifications are that $O(^3P)$ is a slightly electrophilic reagent with a transition state which involves some charge separation, the partial negative charge being on the attacking oxygen atom. Since the slope, ρ, is small compared with other electrophilic reactions (ρ is -12 for nitration), the ring possesses only a small amount of positive charge in the rate determining

76 H. H. Jaffé, Chemical Reviews, 53, 191 (1953); r is the correlation coefficient.



Logarithm (partial rate factors) versus σ^+ constants

Figure 3 Hammett Plot at 30°C

transition state. This is to be expected for an uncharged reagent as $O(^3P)$ and is in line with the Hammett plots of the other free radical reagents[72]. Unfortunately, all the other free radicals involved in aromatic substitution are doublets while $O(^3P)$ may lead to either a triplet or singlet transition state; this could lead to large differences in the polar characteristics of the transition state. The agreement of prf's with the substituent constants to give the observed Hammett plot is considered to be a reflection of the electron density of various positions in the ground state of the aromatic substrate.

Ortho Partial Rate Factors

A recent evaluation of polar ortho substituent[77] constants has appeared in the literature. The technique utilized the previously reported association constants of substituted benzoic acids with 1, 3-diphenylguanidine in benzene solution at 25°C. The ratio of the association constants of the para-substituted acid to benzoic acid was plotted as the ordinate against the ratio of association constants of the ortho-substituted acid to benzoic acid. The straight line observed was interpreted as illustrating the absence of steric and solvation effects. Thus the slope (0.71) of the above mentioned plot gave the relative magnitude of para to ortho polar effects.

Our data can be treated in the same manner, (Figure 4), to obtain a slope of 0.66 ($r = 0.99$) when the logarithm of the para prf is

77 C. L. Liotta, Chem. Commun., 388 (1968); also private communication.

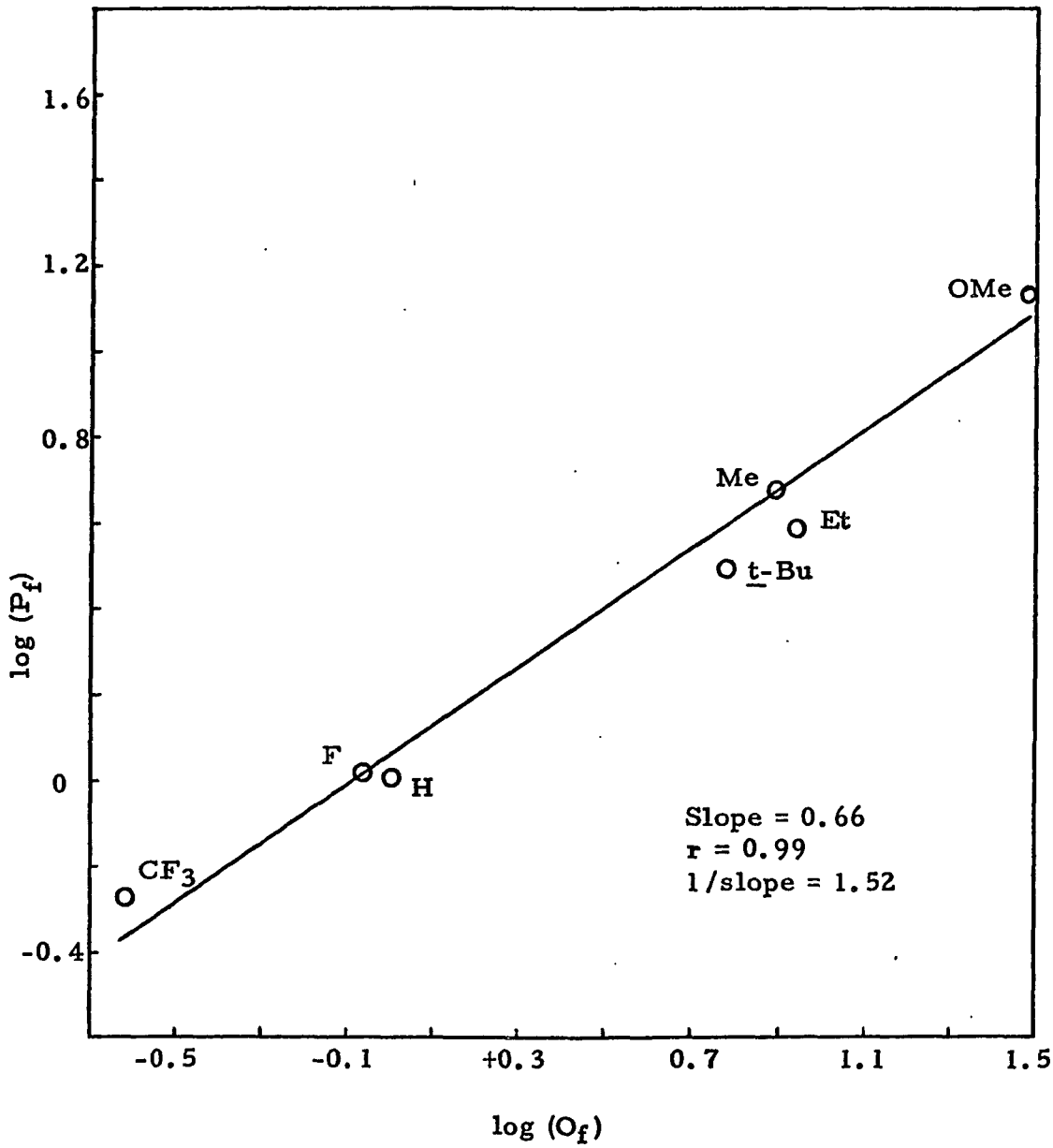


Figure 4 Logarithm (para prf) versus Logarithm (ortho prf)

plotted versus the logarithm of the ortho prf for our six monosubstituted benzenes. Steric and solvation interactions are negligible which is to be expected since $O(^3P)$ shown no steric demands and a gas phase reaction would be expected to be free of solvation problems.

The slope of Figure 4 can be used to calculate σ_o^+ constants, all of which will be 1.5 times larger than the corresponding σ_p^+ values. This is quite contrary to the usual notions[78] of the enhanced ability of a para-substituent to transfer substituent effects with respect to an ortho substituent. As discussed in preceeding sections, this is believed to be a natural consequence of our gas phase system. Since it would be virtually impossible to test this hypothesis with a charged electrophile in a gas phase system, only the comparisons such as made with phenyl radicals in non-polar solvents tend to verify this interpretation. The σ_o^+ constants calculated by multiplication of σ_p^+ by 1.52 are shown in Figure 3.

Test of Additivity Principle for Polymethylbenzenes

Further investigation of the polymethylbenzene series shows that the logarithm of the calculated[a] versus the observed relative rates and partial rate factors give good straight lines when plotted against each other. Figures 5 and 6 exhibit this point for C-H insertion of $O(^3P)$. In Figure 5 for the relative rates, the slope of the line is 0.84 ($r = 0.98$).

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a See Table 9 in Chapter 3.

78 M. Charton, J. Org. Chem., 34, 278 (1969)

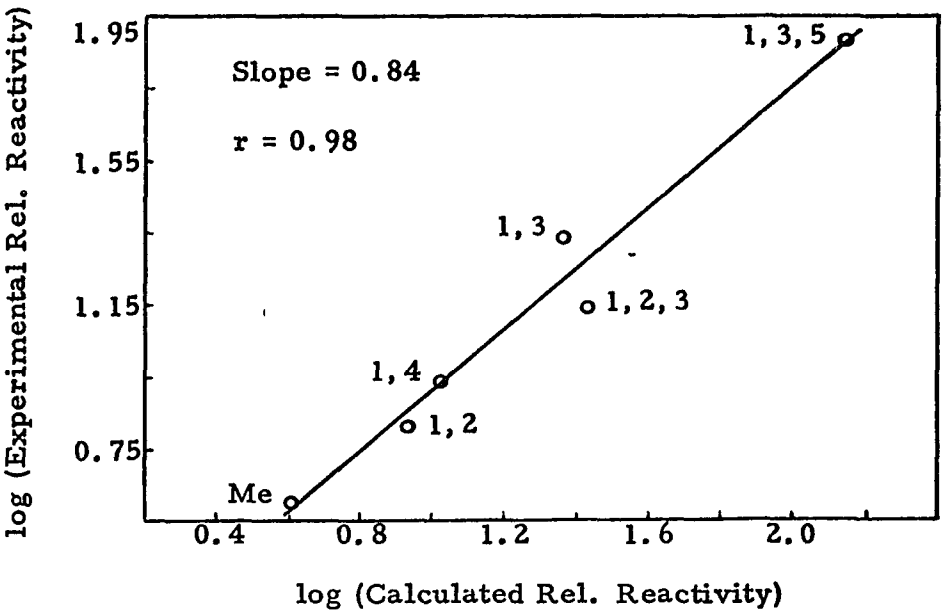

Figure 5 Log. [Experimental vs. Calculated Relative Reactivity for $O(^3P)$]

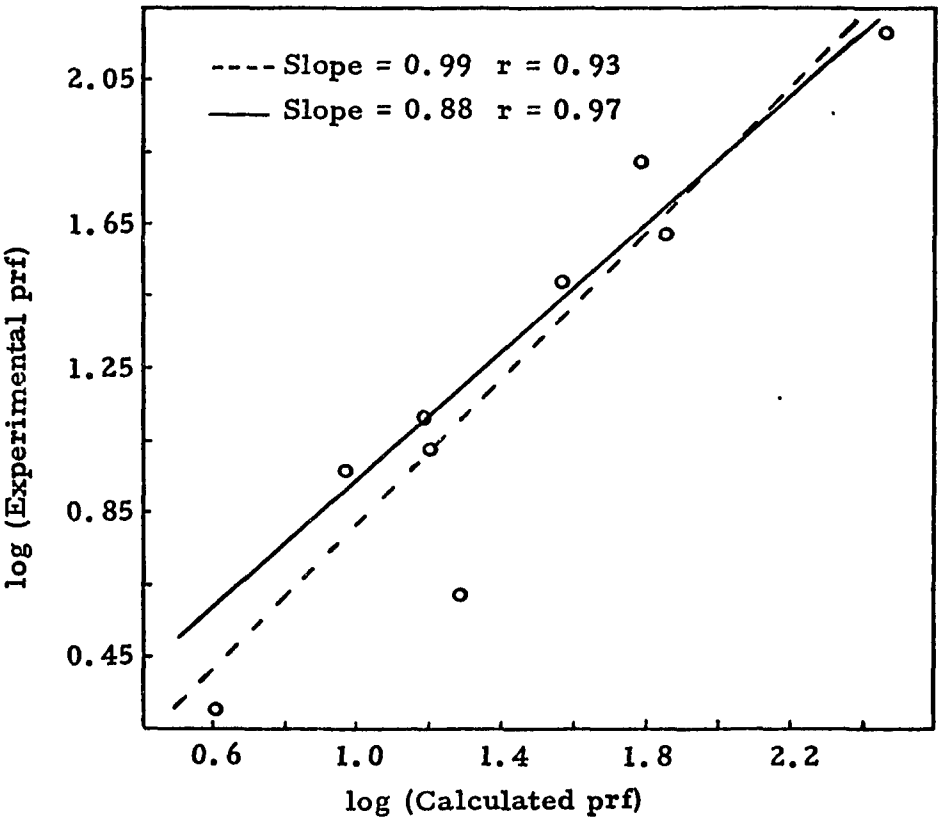

Figure 6 Logarithm [Experimental vs. Calculated prf's for $O(^3P)$]

This slope may be considered the fall-off factor for substitution of a benzene nucleus with the addition of each subsequent methyl group. In principle, this slope would be expected to be unity barring any steric effects; this is true in a reaction such as chlorination[79] in acetic acid. However, other electrophilic aromatic substitutions do exhibit slopes less than unity; thus for benzoylation and sulfonation slopes of 0.76 and 0.56 can be calculated from data in the literature[79].

Figure 6 is a much more demanding plot in that the individual partial rate factors must be known as well as the relative reactivity in order to obtain a correlation coefficient equal to that of the previous plot. Since the glc peaks do overlap each other in almost all the substrates studied, it is not surprising that Figure 6 has much more scatter than Figure 5. By analogy with Figure 5, the slope of the prf plot should be 0.84 if all positions are behaving perfectly. The large deviations in the five position of both m-xylene and 1,2,3-trimethylbenzene give a slope of 0.994 (r = 0.93). Both of these points are experimentally difficult to determine since the respective phenols are present in less than 3% of the total volatile products, however this alone cannot explain the large deviations of these points. Elimination of these two points gives a slope of 0.88 (r = 0.97), thus the agreement with Figure 5 is good for the majority of prf's.

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79 E. Baciocchi and G. Illuminati, Prog. Phys. Org. Chem., 5, 1 (1967)

Free Energy Correlations with Related Reactions

Numerous free energy correlations between our relative rate data with $O(^3P)$ and other electrophilic aromatic substitution rate data were attempted. Since the ratio O_f/P_f is less than 0.8 for most electrophilic substitutions, only overall rate ratios were used in these correlations. The polymethylbenzenes were most often used in the free energy correlation due to the facts that reviews on aromatic substitution are primarily concerned with polymethylbenzenes and our choice of substituents (F, CF_3) are used only infrequently by other investigators.

Good correlations were found with reactions involving both σ and π complexes. Those reactions involving σ complexes were relative basicity[80], iodination[81], bromination[82] and chlorination[82, 83] in acetic acid; an example is chlorination (Figure 7). Those reactions involving π-complexes were the $FeCl_3$ catalyzed chlorination[83] in nitromethane and the relative stability of aromatic-HCl complexes[84]; an example is the stability of aromatic-HCl complexes (Figure 7). It should be noted that since the xylenes have very similar stabilities[80] when complexing with Br_2, I_2, ICl, IBr and SO_2, no correlation is

80 From the compilation of E. Berliner, Prog. Phy. Org. Chem., 2, 253 (1964), in his superior review on aromatic electrophilic substitution.

81 J. McKelvey, private communication.

82 P. B. D. De la Mare and J. H. Ridd, "Aromatic Substitution, Nitration and Chlorination", Acedemic Press, Inc., New York, 1959

83 G. A. Olah, S. J. Kuhn and B. A. Hardie, J. Am. Chem. Soc., 86, 1055 (1964)

84 H. C. Brown and J. D. Brady, J. Am. Chem. Soc., 74, 3570 (1952)

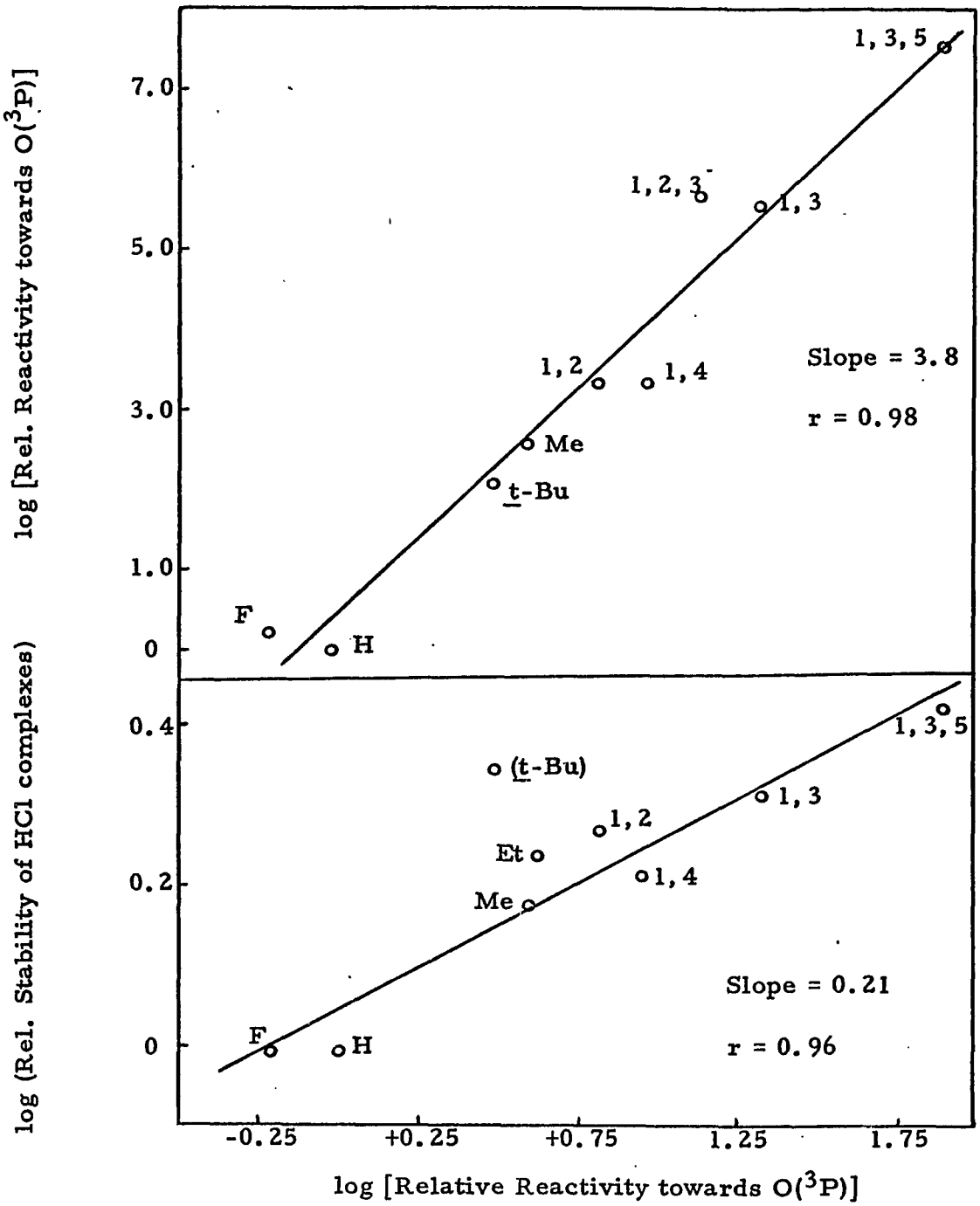

Figure 7 Logarithm (Relative Reactivity towards Cl_2) vs. Logarithm [Relative Reactivity towards $O(^3P)$]

Logarithm (Relative Stability of HCl complexes) vs. Logarithm [Relative Reactivity towards $O(^3P)$]

found with these π-complexes.

The relative importance of σ or π-complexes in aromatic substitution is somewhat tenuous at the present time. Most investigators[80] accept σ-complexes as intermediates in the substitution scheme and consider these structures as close to that of the rate determining transition state. However, the effect of substituents upon both σ and π-complexes is expected to be similar leading to difficulty in stating which is most important. This difficulty is reflected in our work, where correlations can be made with either σ or π-complexes.

Possible correlations of $O(^3P)$ with an analogous free radical substitution reagent is limited to phenyl radicals. Although both phenyl (Figure 8) and p-nitrophenyl radicals show the same general order of prf's, neither of these correlate well with our data for $O(^3P)$. Less direct correlations were attempted with other free radicals. No correlation was found with the hydrogen abstraction from phenols with 2,2-diphenyl-1-picrylhydrazyl[85]; six experimental points were used. Fair correlation was found with the relative rates of dissociation of di-substituted benzoyl peroxides[86]; the meta-methoxy substituent was the major deviation of the five points used.

The relative rates of hydrogen abstraction from substituted

85 J. S. Hogg, D. H. Lohmann and K. E. Russell, Can. J. Chem., 39, 1588 (1961)

86 C. Gardner Swain, W. H. Stockmayer and J. T. Clarke, J. Am. Chem. Soc. 72, 5426 (1950)

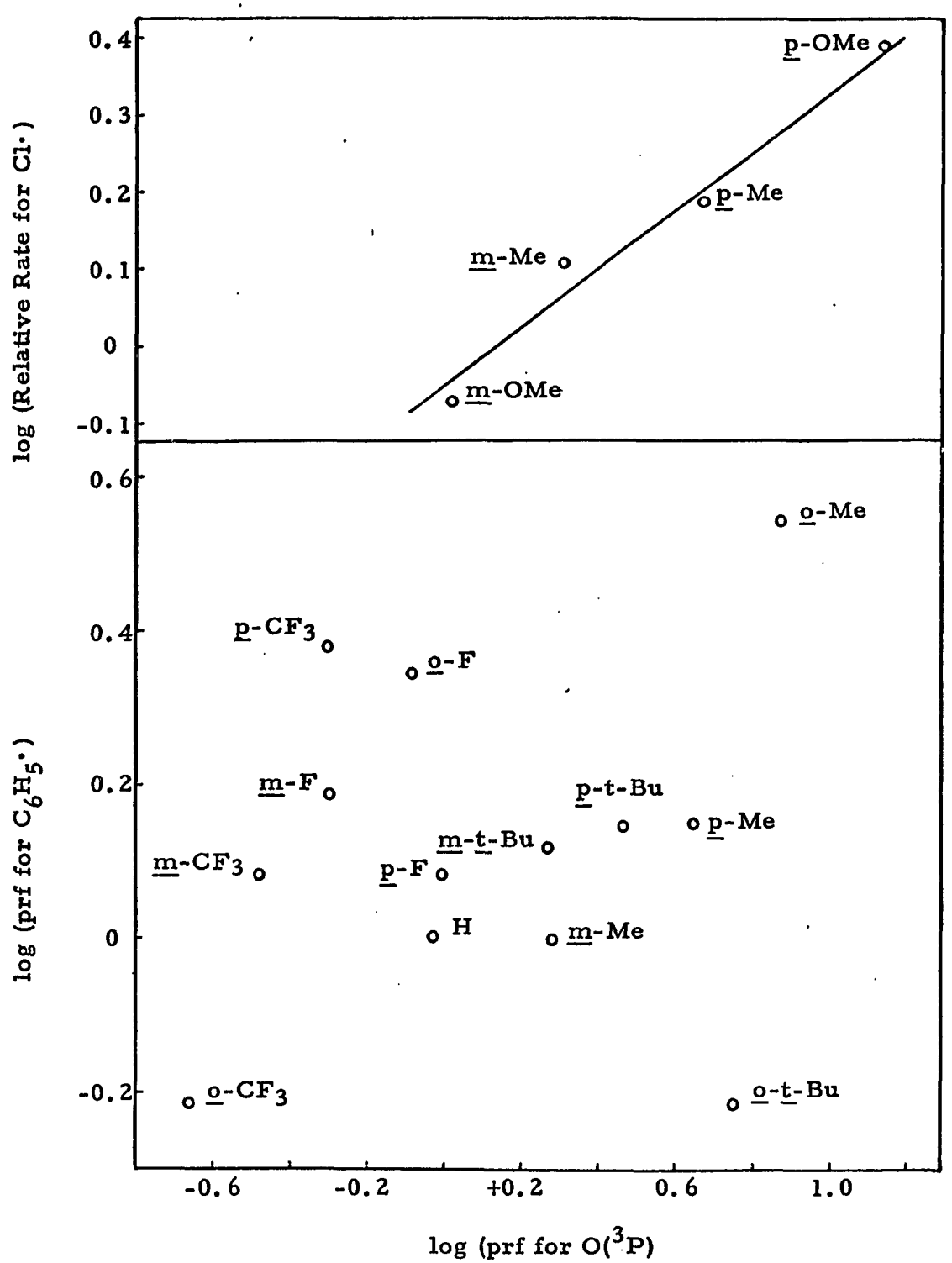

Figure 8 Logarithm (Relative Rate for Cl·) vs. Logarithm [prf for O(^{3}P)]
Logarithm (prf for C_6H_5·) vs. Logarithm [prf for O(^{3}P)]

toluenes also gave linear free energy correlations with $O(^3P)$ oxidation. The substituents common to both reactions were meta-methyl, para-methyl, meta-methoxy and para-methoxy in all examples. The free radicals used were styrylperoxy[87], trichloromethyl[88] and chlorine atoms[89]; all gave good correlations. The free energy plot for chlorine atoms is shown in Figure 8.

Molecular Orbital Calculations

The CNDO II approximation[a] was used to estimate the ground state electron density of various ring carbons of the aromatic compounds studied. This program was written by G. A. Segal and modified for use in the Burroughs 5500 computer by J. McKelvey[b]. The calculated electron density of the various aromatic compounds is listed in Table 14. It was found that a fair correlation existed between the logarithm of the prf's from $O(^3P)$ at 30°C and the electron density of the various ring carbons. This relationship is shown graphically in Figure 9. The omission of certain points improves the correlation coefficient noticeably; thus omission of p-F, o-F, o-OMe and m-CF_3 changes the correlation coefficient from 0.64 to 0.91. These four points were omitted from the calculation of the least square slope of Figure 9.

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a CNDO is the standard abbreviation for complete neglect of differential overlap.

b Mr. McKelvey is in no small way responsible for the use of CNDO calculations in this thesis.

87 J. A. Howard and K. U. Ingold, Can. J. Chem., 41, 1744 (1963)

88 E. S. Huyser, J. Am. Chem. Soc., 82, 394 (1960)

89 G. A. Russell and R. C. Williamson, Jr. ibid, 86, 2357 (1964)

Table 14 Calculated Electron Density[a] of Aromatics

Substrate	Position	Electron Density	Substrate	Position	Electron Density
Mesitylene	1	+0.051	Toluene	1	+0.039
"	2	-0.036	"	2	-0.105
			"	3	+0.012
m-Xylene	1	+0.048	"	4	-0.001
"	2	-0.025			
"	4	-0.021	Ethylbenzene	1	+0.042
"	5	+0.014	"	2	-0.016
			"	3	+0.016
Anisole	1	+0.179	"	4	-0.005
"	2	-0.048			
"	3	+0.025	t-Butylbenzene	1	+0.043
"	4	-0.013	"	2	-0.017
			"	3	+0.013
1,2,3-tri-	1	+0.028	"	4	-0.008
methylbenzene	2	+0.005			
"	4	-0.012	Benzene	1	+0.007
"	5	+0.010			
			Fluorobenzene	1	+0.228
p-Xylene	1	+0.004	"	2	-0.050
"	2	-0.0055	"	3	+0.028
			"	4	-0.010
o-Xylene	1	+0.022			
"	3	-0.0045	Benzotrifluoride	1	-0.046
"	4	+0.005	"	2	+0.030
			"	3	+0.004
			"	4	+0.019

a The convention adopted is minus for more than 4 valence elctrons and positive for less than 4 electrons on the designated carbon.

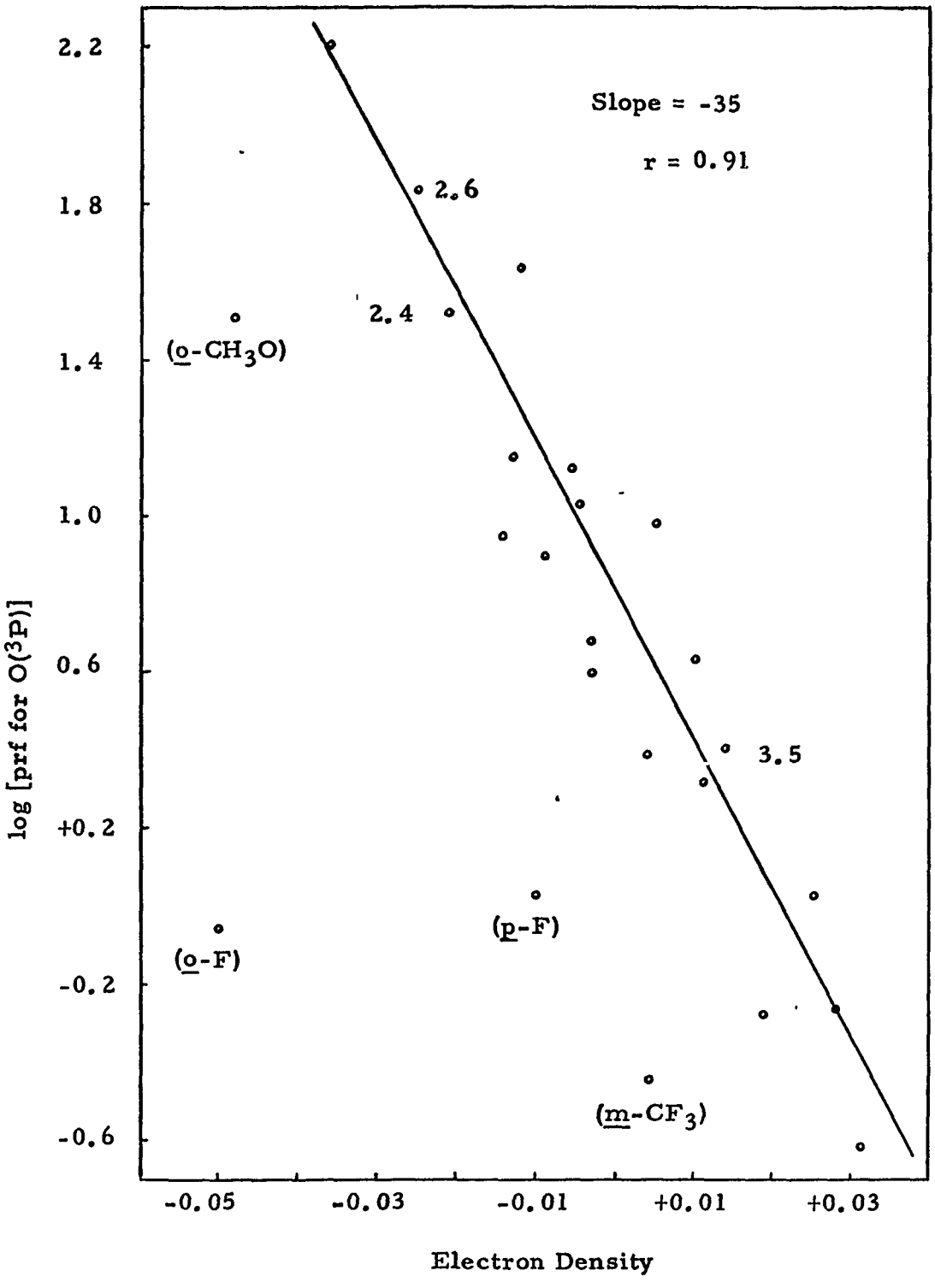


Figure 9 Logarithm [prf for $O(^3P)$] versus Calculated Electron Density

Table 14 shows that the CNDO calculation predicts that the prf's for alkyl cleavage would be less than unity; this is not borne out be experiment (Table 13). Systematic deviations also occur for the meta and ortho - para positions of the monosubstituted benzenes. All meta positions are more reactive than predicted from the CNDO electron density while all ortho and para positions are less reactive than the CNDO predictions. A least squares treatment of data for the ortho and para positions of alkylbenzenes gives a slope of -36 and no improvement of the correlation coefficient.

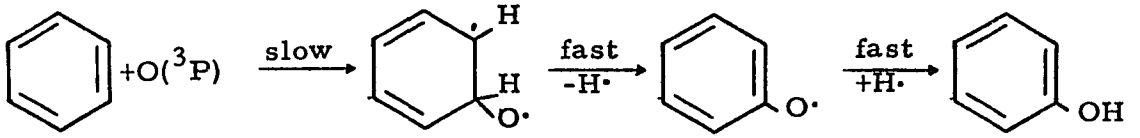
This agreement between the ground state electron density and the prf's from $O(^3P)$ provides good evidence for a very early rate-determining transition state in the $O(^3P)$ oxidation of aromatic hydrocarbons. Since this transition state would be expected to occur later along the reaction coordinate as the reactivity of the aromatic compound decreased, it is not surprising that fluorobenzene and benzotrifluoride provide major deviations from the slope of Figure 9. However, incorrect parameters for fluorine and oxygen could also explain why a poor correlation was gotten for molecules with atoms other than carbon and hydrogen.

Kinetic Isotope Effect and Postulated Mechanism

Special relative reactivity runs involving benzene and deuterobenzene were made to determine the intermolecular kinetic isotope effect

for hydrogen. The value of k_H/k_D was found to be 1.14 ± 0.04[a]; this may be considered to be either a very small primary isotope effect or a secondary isotope effect. The essential fact is that there is little C-H bond breaking in the rate-determining transition state. It should be noted that this is an intermolecular isotope effect and does not imply the lack of an intramolecular kinetic isotope effect; this will be further explored in the following chapter.

The kinetic isotope effect is in agreement with the first step of a mechanism tentatively proposed by Cvetanović[27] for the $O(^3P)$ oxidation of benzene. The slow step of this mechanism was not postulated but our data dictates that the first step is rate determining. Our proposed mechanism is:



σ-complex

The intermediate biradical is the σ-complex believed present in most electrophilic aromatic substitution reactions. The kinetic isotope effect[b] is considered a secondary isotope effect[90] due to hyperconjugation of the

a This value is the average of two determinations, the precision of which was ± 0.01, the given deviation is the estimated error.

b It should be noted that the kinetic isotope effect could be a small primary isotope effect.

90 G. A. Olah, S. J. Kuhn and S. H. Flood, J. Am. Chem. Soc., 84, 1688 (1962)

carbon-hydrogen bond which is to be broken with the aromatic electrons; this would tend to decrease the zero point energy and cause the protium compound to react faster than the deuterium compound. This hyperconjugation apparently is strong enough to overcompensate the increase in zero point energy due to out-of-plane vibrations of the aromatic C-H bond.

For all substrates except nitrobenzene, which will be dealt with later, the reaction is considered to have an early transition state. The detailed structure of this activated complex is thought to be a very loosely bound σ-complex or an oriented π-complex. To keep the situation simple, only a σ-complex will be considered. This mechanism thus embraces the small kinetic isotope effect as well as the agreement between the prf's and the CNDO total electron density of the aromatic compound. The fast portion of the above mechanism could be considered as two steps, loss of a hydrogen atom to form a phenoxyl radical and then abstraction or combination with a hydrogen atom. This is postulated, rather than an intramolecular hydrogen shift, since anisoles were not obtained from the "favorable" case of 1, 2, 3-trimethylbenzene. A one step process from the σ-complex to the product phenol cannot be ruled out at this time.

Reaction Of $O(^3P)$ with Aromatic Compounds At 100°C

Product Distribution in Neat Hydrocarbons

The product distributions found at 100°C were within experimental errorof those found at 30°C for C-H insertion to phenols. The amount of side chain oxidation and substituent cleavage was increased by a factor of 2-3. For toluene and p-xylene small amounts of dimers were found at 100°; thus toluene gave 1.5% bibenzyl and p-xylene gave 0.6% 1,2-di-p-tolylethane. The p-xylene runs showed 11.4% of p-methylbenzyl alcohol at 100° and only 4% of this alcohol at 30°; likewise the per cent of p-tolualdehyde increased from 3 to 5.8% upon raising the temperature from 30° to 100°. Since no neat p-xylene run was made at 100°, the data quoted here is from relative reactivity runs. Consequently, the per cent distribution may be in error due to unknown products arising from the presence of the other substrate (benzene) or from the low per cent conversion of p-xylene to volatile products and the attendant analytical difficulties. Toluene did not show an increase in benzaldehyde or benzyl alcohol but the presence of bibenzyl would give a two-fold increase in total side chain oxidation when the temperature is increased from 30° to 100°.

Mesitylene, 1,2,3-trimethylbenzene and benzotrifluoride agreed well in product distribution of phenols at 30° and 100°. Analysis of the anisole system shows a discrepancy in the data reported for the neat compound; this was discussed in Chapter 4. When the anisole relative

reactivity runs are compared, the methoxyphenol composition is constant. However the yield of phenol increases from 10% at 30° to 28% at 100°; apparently because of the higher activation energy for phenol formation relative to formation of methoxyphenols.

Relative Reactivities and Partial Rate Factors

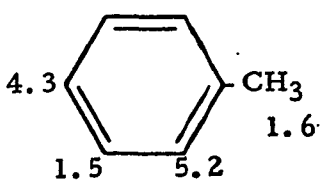
The total reactivity series for phenol formation relative to benzene is given in parenthesis following the substrates studied; this series was, mesitylene (27), p-xylene (5.2), anisole (5.1), nitrobenzene (4.4), toluene (3.2), benzene (1.00) and benzotrifluoride (0.46). This series includes substituent cleavage except for anisole and nitrobenzene as noted in Table 15.

The prf's obtained at 100°C are shown in Table 15. As expected, most prf's approach unity when the temperature is increased from 30° to 100°; the sole exception being the meta prf of anisole. Since the product distribution is essentially independent of temperature, as the relative reactivity of anisole decreases, the m-OCH_3 prf must decrease to below unity.

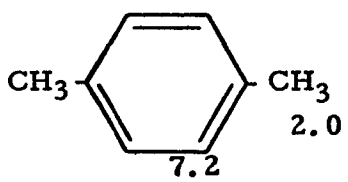
A Hammett plot analogous to that at 30° (Figure 3) can be made from the data in Table 15; this is shown in Figure 10. If the para-NO_2 point is ignored, the least squares slope is -0.72 (r = 0.88). The m-OCH_3 point is well below the best line as expected from the preceeding discussion. The p-CH_3 point is quite anomalous since it is essentially constant from 30° to 100°. This is due to the increase in the per

Table 15 Partial Rate Factors[a] from $O(^3P)$ at 100°C

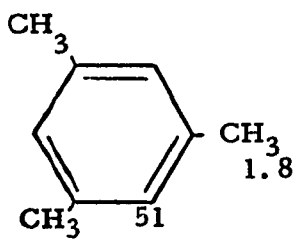
Toluene



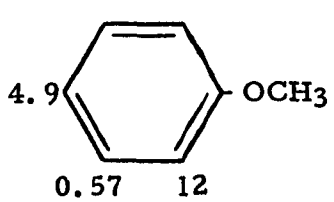
p-Xylene



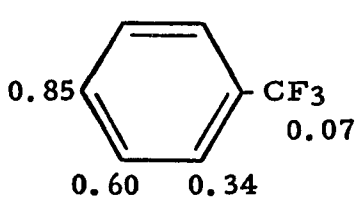
Mesitylene



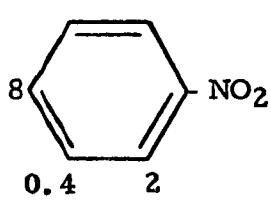
Anisole[b]



Benzotrifluoride



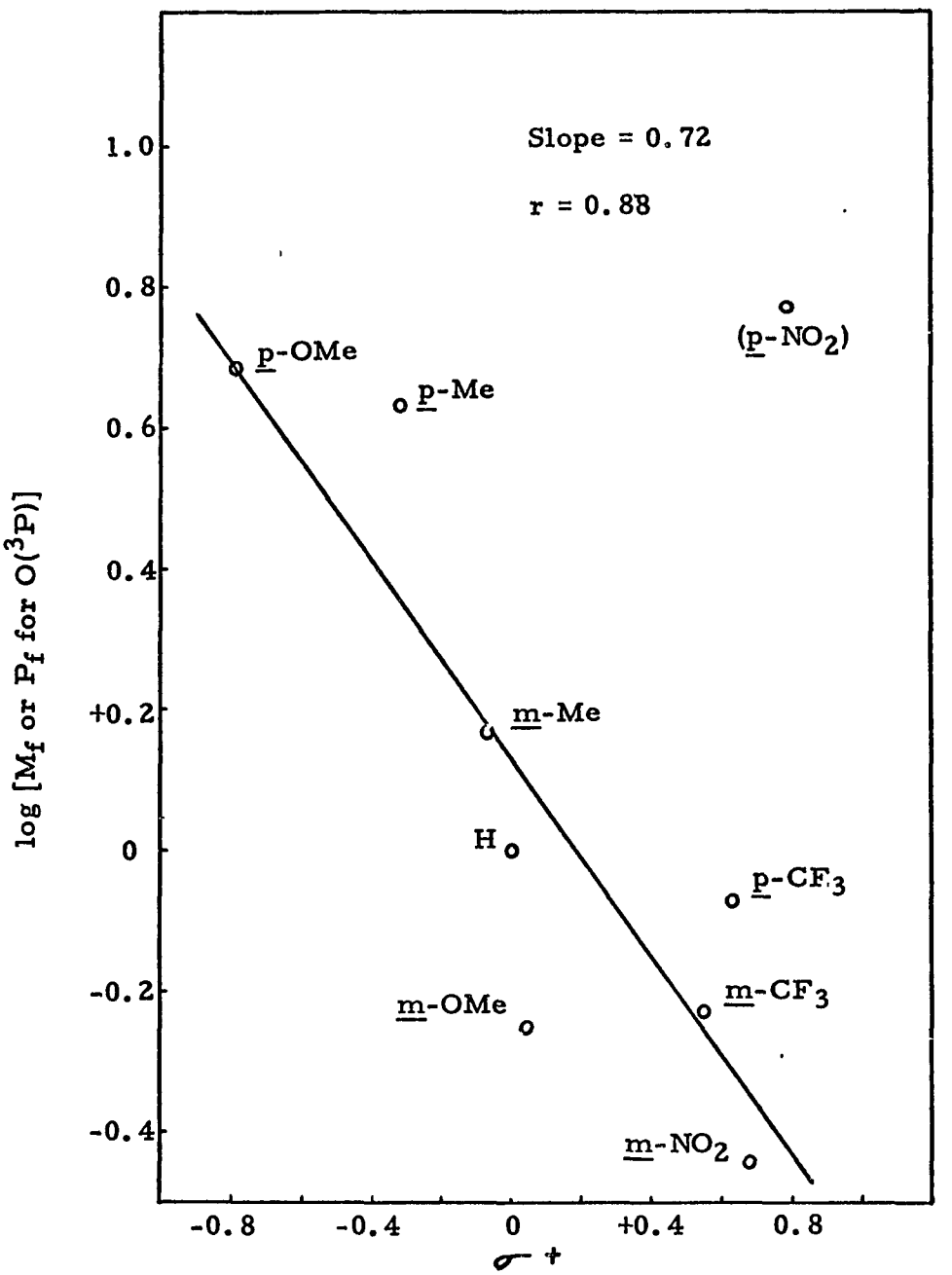
Nitrobenzene[b, c]



a Relative to Benzene (1.00).

b The partial rate factor for substituent cleavage cannot be determined because of concurrent photolysis to produce phenol.

c The values of nitrobenzene are only approximate as discussed in the text.

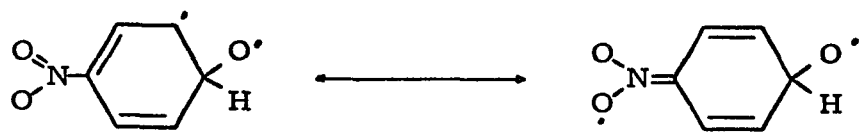


Logarithm (meta or para prf) versus σ^+ constants

Figure 10 Hammett Plot at 100°C

cent of p-cresol formed (19.3% at 30° and 24% at 100°) which offsets the decrease in the relative reactivity of toluene (4.4 at 30° and 3.2 at 100°). This discrepancy would probably be resolved upon generation of a superior column for analysis of the toluene system.

The deviation of the p-NO_2 point can easily be rationalized by resonance structures as B; this structure would be expected to be of low energy only for unsaturated substituents.



A B

In our work, only nitrobenzene can have a structure as B and only the p-NO_2 point shows a great deviation from the Hammett plot. Since an analogous structure cannot be drawn for the m-NO_2 isomer, this point agrees well with the Hammett plot. It should also be noted that both phenyl and p-nitrophenyl free radicals show the same order of prf's as $O(^3P)$ for attack on nitrobenzene[72].

The value of $k_{toluene}/k_{benzene}$ at 100° of 3.0 ± 0.2 agrees very well with that calculated from Cvetanović's data[27,28] at 120° of 2.7 ± 0.6

Nitrobenzene

Due to the problems encountered with this substrate such as low volatility, extreme difficulty in separating the phenolic products and

photodecomposition; nitrobenzene demanded and received separate treatment from the other substrates studied. The average product distributions from oxidation by the Hg^*, N_2O and direct photolysis of nitrobenzene techniques follow. Both of these techniques presumably yield $O(^3P)$ among other oxidizing species. The first set of millimole percentages in Table 16 are based upon the total identified products while the second set is for nitrophenols only and is standarized to 100%. The two product ratios given are also based on millimoles.

The total volatile products obtained by the two methods are quite different but the relative per cent of nitrophenols formed agrees well within experimental error. The direct photolysis of nitrobenzene is known to give nitrosobenzene and p-nitrophenol[91]; we have observed these products as well as phenol and the ortho- and meta-nitrophenols which would be quite difficult to determine by methods other than glc. The ratio of phenol and nitrophenols to nitrosobenzene are also quite different by the two techniques of oxidation. For the direct decomposition of nitrobenzene, the ratio of phenol to nitrosobenzene could be taken as the ratio of two decomposition paths of excited nitrobenzene; one leading to nitrosobenzene and presumably $O(^3P)$ while the other leads to phenol. The ratio of total nitrophenols to nitrosobenzene in the direct decomposition of nitrobenzene could be taken as the approximate fraction of the

91 S. H. Hastings and F. A. Matsen, J. Am. Chem. Soc., 70, 3514 (1948)

Table 16 Product Composition for Oxidation of Nitrobenzene

Technique	millimole per cent				
	C_6H_5NO	C_6H_5OH	o-$O_2NC_6H_4OH$	m-$O_2NC_6H_4OH$	p-$O_2NC_6H_4OH$
Hg^*, N_2O	0.5	19.9	15.5	3.8	60.3
$C_6H_5NO_2$ $\xrightarrow{h\nu}$	28.0	51.3	3.7	1.1	15.9

Technique	per cent			$\frac{C_6H_5OH}{C_6H_5NO}$	$\frac{\text{all } O_2NC_6H_4OH}{C_6H_5NO}$
	o-$O_2NC_6H_4OH$	m-$O_2NC_6H_4OH$	p-$O_2NC_6H_4OH$		
Hg^*, N_2O	20.6	6.0	73.4	38	170
$C_6H_5NO_2$ $\xrightarrow{h\nu}$	21.2	5.0	73.8	1.8	0.7

$O(^3P)$ generated which can be trapped as volatile products. Neither of these ratios has any similar significance for the Hg^*, N_2O technique. Equations pertaining to the photodecomposition of nitrobenzene will be given at the end of this discussion.

Once the similarity of nitrophenol composition was observed, it was obvious that photolysis of nitrobenzene apparently gave $O(^3P)$ as the intermolecular oxidizing agent. To test this hypothesis, relative reactivity runs were made using the two oxidation techniques on mixtures of p-xylene-nitrobenzene, anisole-nitrobenzene, benzotrifluoride-nitrobenzene and finally p-xylene-mesitylene-nitrobenzene. The anisole-nitrobenzene system was a failure due to inability to separate the methoxphenols well enough to obtain meaningful data. The direct photolysis of anisole to give phenol was also troublesome.

The p-xylene-mesitylene-nitrobenzene runs were able to be used to obtain semi-quantitative data only. Here the relative reactivity of nitrobenzene was not important since it was to be used only as a source of $O(^3P)$. The relative reactivity of mesitylene to p-xylene at 100^o was established to be 5.3 ± 0.5 via the Hg^*, N_2O technique. An analogous ratio of 4 ± 1 was obtained via the direct photodecomposition of nitrobenzene. These ratios provide fair evidence for reactions involving $O(^3P)$ but it is impossible to draw a definite conclusion on the identity of the oxidizing species from the direct photolysis of nitrobenzene.

The Hg^*, N_2O method gave a relative reactivity ratio of 10 ± 1

for nitrobenzene relative to benzotrifluoride; this run also gave a ratio of meta to para-trifluoromethylphenol of 1.6. When the direct photolysis of nitrobenzene was used, nitrobenzene was both the source of oxidizing agent and a primary reactant; the rate and product ratios analogous to the Hg^*, N_2O run were 90 ± 15 and 1.6. Hence the product ratio still argues for the same oxidizing agent from both techniques while the rate ratio convincingly illustrates that $O(^3P)$ cannot be the sole species capable of giving phenolic products. It is to be noted that the large change in composition of benzotrifluoride in the substrate bubbler makes the above relative rates approximate only.

The rationale which appears to best correlate the difference in rates with identical product distribution is of a highly speculative nature. The identical product distribution from molecules other than nitrobenzene is easily explained as due to $O(^3P)$ from decomposition of excited nitrobenzene. The identical nitrophenol composition could be due to an intramolecular oxidation of excited nitrobenzene giving nitrosophenols in the same composition as nitrophenols from $O(^3P)$ oxidation of nitrobenzene. Air oxidation of the nitrosophenols to nitrophenols would then give the values seen in Table 16. This intramolecular oxygen transfer could also explain the enhanced reactivity of nitrobenzene in the direct photodecomposition of nitrobenzene.

The assumption that nitroso- and nitro- groups have the same directive effects is not as questionable as one might initially believe.

Analogous resonance structures can be drawn for the σ-complexes of nitrosobenzene and nitrobenzene with $O(^3P)$. Needless to say, future work would include the $O(^3P)$ oxidation of nitrosobenzene by the Hg^*, N_2O technique; this would provide evidence on both the stability of nitrosophenols and the directive effects of the nitroso group. The product distribution of nitroso- and nitrobenzene is presumed to be due to a late transition state, the detailed structure of which is close to the σ-complex shown previously. The equations pertaining to the nitrobenzene system are shown below:

$$C_6H_5NO_2 \rightarrow [C_6H_5NO_2]^* \rightarrow [C_6H_5ONO] \rightarrow NO + C_6H_5\dot{O} \xrightarrow{RH} \dot{R}. + C_6H_5OH$$

$$[C_6H_5NO_2]^* \rightarrow C_6H_5NO + O(^3P) \xrightarrow{ArH} ArOH$$

$$C_6H_5NO + O(^3P) \xrightarrow{C_6H_5NO_2} HOC_6H_4NO_2$$

$$[OC_6H_5NO] \rightarrow HOC_6H_4NO \xrightarrow{(O)} HOC_6H_4NO_2$$

In order to complete the nitrobenzene reaction sequence, the p-xylene-nitrobenzene runs should be recalled. Although p-cresol could not be separated from 2, 5-dimethylphenol when nitrobenzene was present, the total amount of p-xylene oxidation products could be determined. The direct photolysis of nitrobenzene in the presence of p-xylene gave small amounts (1.0 mg) of p-xylene oxidation products but no nitrophenols ($<$ 1.6 mg). The main product was phenol (12 mg); if the usual product

distribution of a direct photolysis of nitrobenzene run was obtained we would expect 5.5 mg of p-nitrophenol. No explanation for the large amount of phenol will be presented. The large change in composition of p-xylene in the substrate bubbler makes this system less than ideal for the study of nitrobenzene.

Free Energy Quantities

Relative Activation Energies. The Arrhenius equation can be used to calculate relative energies of activation for the substrates listed in Table 15, except nitrobenzene. Since only relative reaction rates have been determined for $O(^3P)$ oxidation, these activation energies are relative to benzene over the temperature range of 30° to 100°C. The numerical value in kcal/m follows each substrate given below; mesitylene (-3.5)[a], anisole (-3.1), p-xylene (-1.9), toluene (-1.0), benzene (0.0) and benzotrifluoride (+1.4). It is worthy of note that the data of Cvetanović[27,28] can be used to calculate an activation energy for toluene of -0.8 ± 1.1 relative to benzene over the temperature range of 120° to 220°C.

Relative Enthalpy of Activation. It can be shown that the relations between the Arrhenius energy of activation and the enthalpy of

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a The arbitrary sign convention for all free energy functions adapted here is − for less than benzene (B) and + for greater than benzene. Hence the quantities given are $\Delta E_a = E_a^X - E_a^B$, $\Delta(\Delta H^{\ddagger}) = \Delta H_X^{\ddagger} - \Delta H_B^{\ddagger}$ and $\Delta(\Delta S^{\ddagger}) = \Delta S_X^{\ddagger} - \Delta S_B^{\ddagger}$

activation and the relative activation energy and relative enthalpy of activation are:

$$E_a = H^{\ddagger} + RT \qquad \Delta E_a = \Delta(\Delta H^{\ddagger})$$

Thus the values of $\Delta(\Delta H^{\ddagger})$ are identical with those given for the ΔE_a in the preceeding paragraph.

Relative Entropy of Activation. It can be shown that the relations between the entropy of activation and reaction rate and the relative entropy of activation and relative reaction rates are:

$$\ln k = \left(\frac{kT}{h}\right) + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT}$$

$$\Delta(\Delta S^{\ddagger}) = \Delta S^{\ddagger}_X - \Delta S^{\ddagger}_B = R \ln (k_X/k_B) + \Delta\left(\frac{\Delta H^{\ddagger}}{T}\right)$$

The numerical values of $\Delta(\Delta S^{\ddagger})$ in cal/^{o}K are: mesitylene (-3.0), anisole (-5.0), p-xylene (-2.0), toluene (-0.50), benzene (0.0) and benzotrifluoride (+2.2).

Microwave Glow Discharge

Product Distributions

Benzene. The oxidation of benzene via mgd through CO_2, O_2 or N_2O gave phenol as the major product. Under the same discharge conditions, oxygen was be far the most efficient oxidizing agent toward all aromatic substrates. An example of this will be given for benzene only where the rate of phenol formation per hour was 100, 15 and 1.4 mg for

O_2, CO_2 and N_2O respectively. With N_2O, about 0.22 mg of nitrobenzene per hour was also formed; presumably this was originally present as nitrosobenzene which was air-oxidized during distillation of the excess benzene prior to glc analysis. Since the mgd and Hg^*, N_2O techniques give the same product, the only firm conclusion is that benzene reacts with whatever oxidizing agents are present to give mainly phenol.

The identities of minor products from benzene-mgd-CO_2 system were not established. The following possibilities were investigated and found to be undetectable; the estimated limit of the percent of these compounds (relative to phenol) which could have been detected is also given. Toluene, ethylbenzene, stryene, phenylacetylene, salicylaldehyde and tropone were found in less than 1%, benzaldehyde in less than 5% and benzoic acid (as methyl ester) in less than 10%.

Toluene. After having struggled with benzene in attempts to identify trace products, toluene was a pleasant substrate to work with. The products were mainly those of side chain oxidation and phenols; the product distribution of CO_2 and O_2 runs were very similar if the correct discharge condition. were chosen. This similarity was our main evidence that a species of atomic oxygen was present as the active agent in our mgd systems; selected data is given below. The reaction distance was 20 mm for each run listed; the pressure of the CO_2 run was 12 torr while that of both O_2 and N_2O was 14 torr.

Discharge Gas	Millimole Percent Relative to Known Products					
	phenol	benzyl alcohol	benzal-dehyde	o-cresol	m & p-cresols	bibenzyl
CO_2	26	10	25	16	21	2
O_2	31	13	23	11	17	5
N_2O	5	62	30	5	4	3

The lower bond energy[92] of N_2O might be expected to give rise to larger amounts of $O(^3P)$ than either O_2 or CO_2. This is not experimentally observed, N_2O giving about one-tenth the product of a CO_2 run. Apparently N_2O does not give large amounts of $O(^3P)$ since the reaction of $O(^3P)$ with N_2O is too slow[48] to compete with:

$$O(^3P) + \text{wall} \longrightarrow 1/2\ O_2$$

Hence any $O(^3P)$ would be expected to be trapped by the aromatic substrate. Since the reaction of N_2O with $O(^1D)$ is probably quite fast[48], perhaps $O(^1D)$ is the primary product of a mgd through N_2O and any $O(^3P)$ is scavenged by NO.

The lack of cresols and low overall yield argue against a high reaction temperature with $O(^3P)$ as the reason for the predominantly side chain oxidation products observed in the toluene-N_2O-mgd system. Possible reaction sequences would be either a chain reaction of benzyl

92 The bond energies of C-O, O-O and N-O in CO_2, O_2 and N_2O are 128, 119 and 39 kcal/m respectively. The CO_2 and O_2 datum is from the Handbook of Chemistry and Physics, 50 F-158 (1969) while the value for N_2O is from V. H. Dibeler, J. Chem. Phys. 47, 2191 (1967).

radicals with N_2O or $O(^1D)$ oxidation of toluene. The rationalizations relating to the N_2O-mgd are speculative only; the pertinent equations are shown below:

$$N_2O \xrightarrow{mgd} N_2 + O(^1D)$$

$$N_2O \xrightarrow{mgd} N\cdot + NO$$

$$N_2O + O(^1D) \longrightarrow N_2 + O_2 \text{ (or } 2NO)$$

$$NO + O(^3P) \longrightarrow NO_2$$

$$C_6H_5CH_3 + X\cdot \longrightarrow C_6H_5CH_2\cdot + HX$$

$$C_6H_5CH_2\cdot + N_2O \longrightarrow N_2 + C_6H_5CH_2O\cdot$$

$$C_6H_5CH_2O\cdot + C_6H_5CH_3 \longrightarrow C_6H_5CH_2OH + C_6H_5CH_2\cdot$$

$$C_6H_5CH_2O\cdot \longrightarrow C_6H_5CHO + H\cdot$$

$$C_6H_5CH_3 + O(^1D) \longrightarrow C_6H_5CH_2OH \longrightarrow C_6H_5CHO + H_2$$

X· might be N·, H·, NO, $O(^1D)$

p-Xylene. The relative product distribution observed for CO_2 and O_2 are given below; the reaction distance and pressure were 18 mm and 18 torr in both runs.

Discharge Gas	Millimole Percent Relative to Known Products			
	p-cresol	p-methylbenzyl alcohol	p-tolualdehyde	2,5-dimethyl-phenol
CO_2	15	19	44	22
O_2	25	20	39	16

Due to differences in the pressure and reaction distance from the toluene runs, no comparison between toluene and p-xylene will be attempted.

However, p-xylene is qualitatively the same as toluene with respect to the differences from the Hg^*, N_2O system.

Benzotrifluoride. The O_2 run gave 1.5 times more volatile product per hour than the CO_2 run but also gave 4 times more tar. The product distributions were not identical as expected if $O(^3P)$ was the sole source of trifluoromethylphenols. Thus O_2 gave 18% ortho-, 54% meta and 28% para-trifluoromethylphenols. CO_2 gave 29% ortho, 56% meta and 15% para-trifluoromethylphenol while the Hg^*, N_2O technique gave 25% ortho, 44% meta and 31% para-trifluoromethylphenol. The O_2-mgd run was made at a temperature of at least 50° higher than the CO_2 run; this may be part of the explanation of the difference in these runs. The higher percent of ortho isomer found in the CO_2 run was re-checked and found to be real; likewise the substantially higher meta to para ratio found for CO_2 was re-checked with a Hg^*, N_2O run and this also was quite real. The explanation is identical to that given in the following section for the cresol ratios obtained from toluene.

Variation of Products with Travel Time and Temperature

Toluene was the only substrate studied extensively with different reaction parameters. The variation in reaction parameters, travel time and product yield was given in Table 12. Table 17 below continues with the variation of product composition with travel time. The last two runs are given only for comparative purposes; T-UV 88 and 94 are Hg^*, N_2O runs made at 100°C. The hourly yield is given in milligrams of volatile

Table 17 Toluene Product Distribution at Different Travel Times and Temperatures

Travel Time (sec)	Temperature (°C)	Millimole Per Cent						Hourly Yield	o / m & p	benzaldehyde / benzyl alcohol
		phenol	benzyl alcohol	benzaldehyde	o-cresol	m & p-cresols	bibenzyl			
0.010	200	40.3	7.4	18.8	8.7	16.2	8.5	0.38	0.53	2.54
0.019	150	34.0	9.1	21.3	13.6	19.0	2.8	0.27	0.72	2.32
0.036	105	26.0	10.3	24.6	15.6	20.8	2.6	0.25	0.75	2.39
0.041	105	23.6	11.6	30.6	14.0	18.4	1.7	0.18	0.76	2.64
0.055[a]	85	10.0	14.6	36.2	21.7	17.6	< 2	0.10	1.23	2.48
0.059	85	15.2	15.9	32.6	16.5	19.2	0.6	0.13	0.86	2.05
0.074	75	9.5	15.4	37.0	19.0	19.1	< 2	0.086	1.0	2.40
0.101	75	10.0	18.9	34.7	21.6	14.7	< 2	0.076	1.47	1.84
0.155	65	5.9	22.3	25.9	31.8	14.1	< 2	0.034	2.26	1.16
Hg^*, N_2O	100	8.5	3	1	61.5	25	1	0.099	2.42	0.3
Hg^*, N_2O	100	11	2.5	1	58	26	1.5	0.154	2.19	0.4

a This run does not fit the rest of the data well; no reason for omitting the run could be found.

product per hour.

It must be remembered that the temperature quoted in Table 17 is that found for the discharged gas at different reaction distances (travel times) when no organic substrate is being oxidized. As shown in Figure 2, oxidation by the mgd is characterized by a blue luminescence located where the discharged gas and organic substrate are initially mixed. This "flame" is quite localized, having a width of one to two millimeters. Oxidation is presumably essentially complete within the boundaries of this flame; the temperature of this flame is referred to as the actual temperature of the reaction. The actual temperature of the reaction is most probably much higher than that given in Table 17. Also, the difference between the actual temperature and the given temperature at short travel times is expected to be much larger than at long travel times.

Numerous qualitative conclusions can be drawn from Table 17. The most striking example is the decrease in phenol yield as the travel time increases. As the travel time increases from 0.010 sec to 0.155 sec, the phenol yield falls from 40 to 6%. The yield of bibenzyl also decreases rapidly with an increase in travel time; part or all of this effect may be due to back-diffusion of toluene into the discharge at short travel times (this implies short reaction distances). An analogous explanation for phenol is ruled out by the fact that cleavage of toluene to benzyl free radical would be expected to be much more favorable than cleavage to phenyl radicals which were then oxidized to phenol. Also, no biphenyl

is found in toluene runs. Table 17 appears to suggest that both phenol and bibenzyl could arise from the same active species of atomic oxygen.

Inspection of the ratio of ortho to meta and para-cresols shows that there is a definite correlation with both travel time and temperature. This could be explained as a change in the ratio of two oxidizing agents as the travel time changes. Alternatively, an increase in selectivity of one species of atomic oxygen, presumably $O(^3P)$, as the temperature decreases could also explain the observed trend in the above ratio. The most important observation is that at long travel times this ratio indeed appears to approach that found for $O(^3P)$ as defined by the Hg^*, N_2O runs.

Another ratio of interest is that of benzaldehyde to benzyl alcohol. The formation of excited benzyl alcohol from $O(^3P)$ at a high reaction temperature might be expected to form benzaldehyde by loss of a molecule of hydrogen. As the travel time increases, the reaction temperature would decrease making the formation of benzaldehyde less important relative to stabilization of the benzyl alcohol precursor. Table 17 shows that the ratio of aldehyde to alcohol falls from 2.5 to 1.2 as the travel time is increased fifteen-fold. The low ratio found in Hg^*, N_2O runs is due to the high pressure stabilizing the initially formed alcohol.

To summarize the above arguments, the decrease in temperature of the discharged gas with increasing travel time provides two explanations for the variation of product distribution noted in Table 17. The travel time alone might imply the existence of three oxidizing agents;

the one of shortest lifetime giving phenol and bibenzyl, the one of intermediate lifetime giving cresols and side chain oxidation products and the one of longest lifetime, $O(^3P)$, giving mainly cresols. Since both O_2 and CO_2 exhibit analogous product variation with travel time, these agents would possibly be different electronic states of atomic oxygen. Emphasis on the temperature effects would imply $O(^3P)$ reacting at different temperatures was responsible for the product variations. As pointed out in Chapter 1, $O(^3P)$ is considered to be the most important, and sometimes only, species in discharge systems; hence $O(^3P)$ which reacts at a lower temperature as the travel time increases, is most probably the best explanation.

It should be noted that Avramenko[39] also found a flame where the discharged oxygen collided with the organic substrate. This flame was thought to be due to a free radical chain process (combustion) involving OH radicals; Avramenko eliminated the flame in his experiments. Perhaps side chain oxidation is due to free radical processes while cresol formation is due to $O(^3P)$ addition.

A corollary to our explanation would indicate that at sufficiently long travel times only cresols, in a distribution identical with Hg^*, N_2O runs, would be formed since only $O(^3P)$ would be reacting at a temperature of 100°C or less. This has not been completely tested due to the analytical techniques used in mgd runs but it appears that this behavior is found. At long travel times, the yield of volatile products approaches

zero; a careful investigation of the product distribution from long travel times is in order.

Attempts to determine the relative reactivity of various substrates by a mgd through CO_2 were largely unsuccessful. The relative rates were difficult to reproduce and gave only very poor internal agreement. For example, the relative rates of reaction of benzene and toluene to cyclohexane were found to be 0.34 and 0.24 respectively. This would give a rate ratio of toluene to benzene of 0.70. The relative rates of benzene and toluene to benzotrifluoride were found to be 3.6 and 4.45 respectively. This would give a rate ratio of toluene to benzene of 1.25. A competitive run between toluene and benzene gave toluene as 1.03 times more relative than benzene; thus the deviation between these three values is 30%.

The reasons for this discrepancy are believed to be inadequate trapping techniques and temperature effects which provide a leveling effect on relative reaction rates. Although development of a trap capable of quantitative recovery of the unreacted hydrocarbons would erase one problem, the high temperature[a] of the reaction flame would appear to make mgd a poor candidate for the determination of relative reactivities.

Lifetimes of Atomic Oxygen

The data of Table 12 can be used to determine the collisional

a An approximate value for the temperature of the reaction flame can be obtained by plotting the logarithm of the relative reactivity (Hg^*, N_2O) of toluene to benzene versus 1/T. At k_T/k_B of 1.03, a temperature of 800°C is obtained.

lifetime of the atomic oxygen resulting from a mgd through CO_2. If the kinetic scheme is assumed to be pseudo first-order in oxygen atoms, the resulting equation is:

$$-\frac{d\,[\text{oxygen}]}{dt} = \frac{d\,[\text{products}]}{dt} = k\,[\text{oxygen}]$$

$$\text{hence } \log\,[\text{products}] = \frac{-k}{2.303}\,t$$

If our initial assumption is correct, a plot of the logarithm of the total millimoles of product versus the travel time will define a straight line with a slope equal to -k/2.303. This plot is shown in Figure 11. Toluene was the substrate used to trap the atomic oxygen. A good straight line is found, the slope of which is -7.0_6 ($r = 0.96$); thus the pseudo-first order rate constant for decay of our active species is $-16.3\ \text{sec}^{-1}$. The lifetime of a species which obeys first order kinetics is defined to be the reciprocal of the rate constant while the half life is 0.69 times the lifetime. Hence Figure 11 provides a lifetime of 0.061 sec and a half life of 0.042 sec under our experimental conditions.

The plot described above utilized only nine of the many toluene-CO_2 runs done. Due to the fact that the amount of product would be expected to be dependent upon the efficiency of the microwave generator, any correlation would be restricted to the time interval in which this efficiency remains constant. The data used in the above calculation were obtained over a six week period using the same microwave generator.

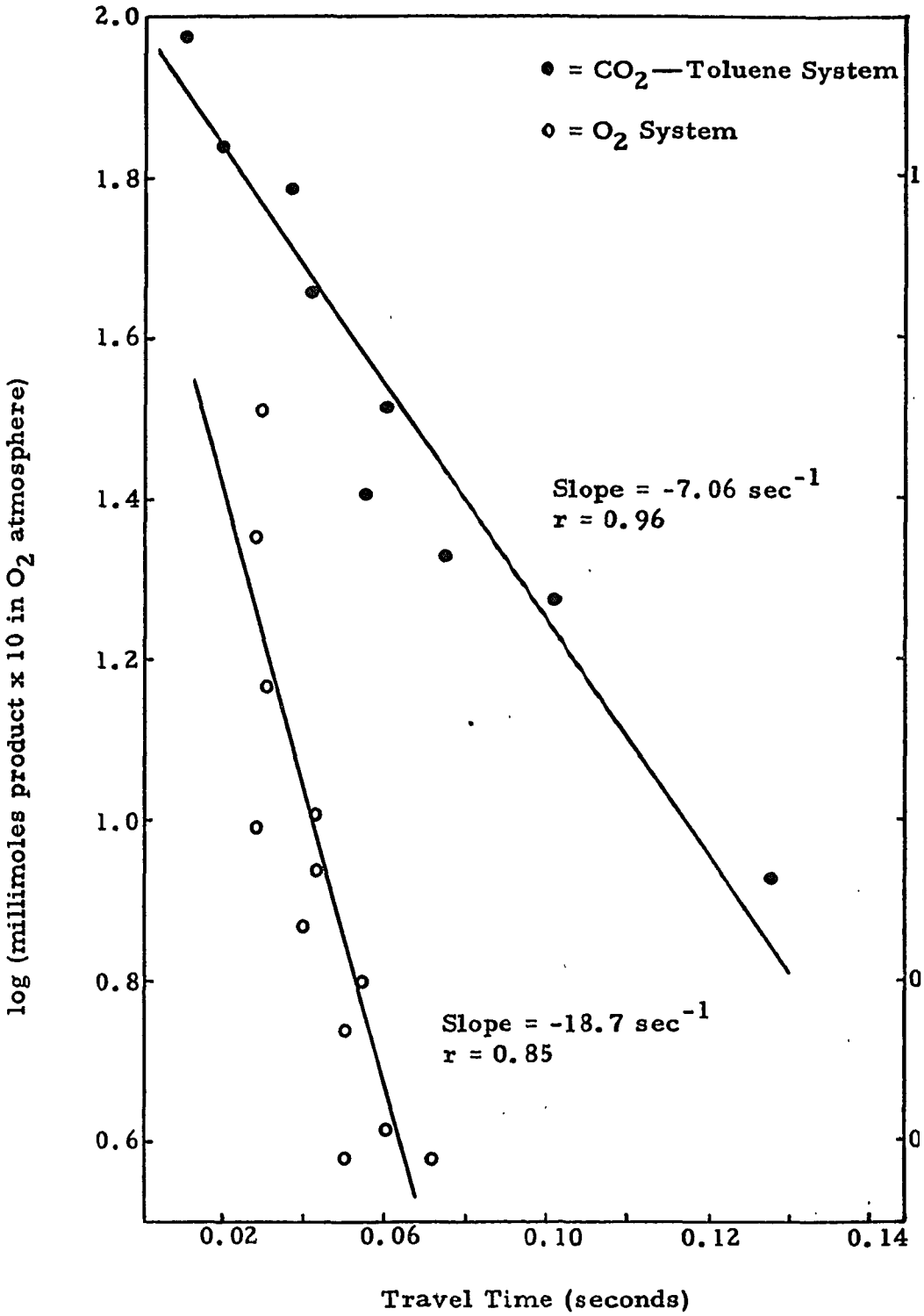

Figure 11 Lifetimes of Atomic Oxygen

Upon failure of the klystron oscillator, subsequent data were obtained using an essentially new generator and did not correlate well with the old data.

An analogous plot can be made for O_2-mgd runs with various substrates. This plot assumes that the active species will react to the same extent no matter what the organic substrate may be and is shown in Figure 11. A fair straight line is gotten with a slope of -18.7 sec^{-1} ($r = 0.85$); the decay constant, lifetime and half life are 43.1 sec^{-1}, 0.023 sec and 0.016 sec respectively. The lifetime of our active species in either a CO_2 or O_2 atmosphere is much larger than expected from the kinetic work of other investigators on the deactivation of $O(^1D)$ to $O(^3P)$. From the data of Sauer[93] and Hunten and McElroy[94], the lifetime of $O(^1D)$ at our pressures would be expected to be 1.6×10^{-5} sec in CO_2 and 8×10^{-4} sec in O_2.

The data for $O(^3P)$ disappearance is limited to ozone formation; the data of Kaufman[95] give a lifetime of 0.013 sec for $O(^3P)$ in an O_2 atmosphere under our reaction conditions. Quite obviously, $O(^3P)$ appears to be the active species in our discharge work with O_2. Until the rate constant for $O(^3P)$ recombination in a CO_2 atmosphere is found, it

93 M. C. Sauer, Jr., J. Phy. Chem., 71, 3311 (1967)
94 D. M. Hunten and M. B. McElroy, Reviews of Geophysics, 4, 303 (1966)
95 F. Kaufman's data as listed by M. C. Sauer, Jr. and L. M. Dorfman, J. Am. Chem. Soc., 87, 3801 (1965).

would seem reasonable that $O(^3P)$ be considered to be the active species in the CO_2 system also.

It should be noted that our kinetic equation assumes that only one oxidizing agent is present in the mgd system. A good test of this is constant product distribution versus travel time. Table 18 illustrates that either we have two or more oxidizing agents or the change in temperature with reaction distance is sufficient to allow one species to account for the change in distribution of the toluene oxidation products. Since benzyl alcohol and benzaldehyde could be attributed to a combustion process, the apparent lifetime for phenols is also tablulated in Table 18. Elimination of the side chain oxidation products does not change the lifetime appreciably.

Table 18 Apparent Lifetimes of Atomic Oxygen in a CO_2 Atmosphere

Toluene Oxidation Product	Slope (sec^{-1})	Decay Constant (sec^{-1})	Apparent Lifetime (sec)
Phenol	-13.6	31.3	0.032
Bibenzyl	-31.4	72.2	0.014
Benzaldehyde	-6.33	14.6	0.068
Benzyl alcohol	-3.75	8.62	0.12
o-Cresol	-3.42	7.86	0.13
m & p-Cresols	-7.78	17.9	0.056
Cresols & phenol	-8.04	18.5	0.054
Total Products	-7.06	16.3	0.061

Miscellaneous Oxidations of Toluene

Photolysis of NO_2

Attempts to use NO_2 to generate $O(^3P)$ proved fruitless when toluene was the substrate. The known products of the photolytic run[a] were 10% benzaldehyde and 2% benzyl alcohol while the dark reaction gave 15% of the aldehyde and 4% of the alcohol. Neither of these products are expected to be formed in large quantities in the $O(^3P)$ oxidation of toluene; hence the identity of the oxidizing agent would best be postulated as NO_2. The unidentified products are probably assorted nitro and nitrosotoluenes.

Since the reaction of $O(^3P)$ with NO_2 to give NO and O_2 is close to diffusion controlled ($k_{NO_2} = 3.4 \times 10^9$ $\underline{M}^{-1}$ sec^{-1})[96], perhaps toluene could not compete with the NO_2 for the $O(^3P)$ presumably formed. The rate constant for toluene reacting with $O(^3P)$ would be about 5.4×10^7 M^{-1} sec^{-1} as estimated from the data of Cvetanović[1] and our relative reactivity work. The data given in Chapter 6 can be used to calculate a rate ratio of NO_2 to toluene for reaction with $O(^3P)$ in our system of 25; hence perhaps the toluene-NO_2 runs were not conducted in the proper manner to observe $O(^3P)$ oxidation of toluene. It would appear that a ratio of toluene to NO_2 of 500 - 1000 would be required in future toluene-

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a Recall Chapter 6 where the identity of the dark and photolytic runs are in doubt.

96 I. W. M. Smith, Trans. Faraday Soc., 64, 378 (1968)

NO_2 photolytic runs in order to have the majority of $O(^3P)$ react with toluene rather than NO_2.

Photolysis of O_3

Attempts to generate $O(^1D)$ via photolysis of O_3 at 2537 Å met the same fate as the $O(^3P)$ work discussed above. The blank run between toluene and O_3 gave benzaldehyde and benzyl alcohol as expected for $O(^1D)$. The photolytic run also gave side chain oxidation but gave twice as much unidentified material as the dark run; less than 5% of cresols were present in either run. Since the increase in total volatile products upon irradiation was only five fold, the O_3 system does not lend itself to convenient study of $O(^1D)$ oxidation of toluene at 30°C. The reaction products may be ascribed to O_3 only, excited O_3 or O_3 and $O(^1D)$ giving the same products; we have no preference for any of these possibilities.

Toluene Blank Runs

A number of photolytic runs with toluene were done with carrier gases not expected to produce oxidation. Thus toluene was photolyzed with O_2, CO_2, N_2O, N_2, air and He with a mercury lamp and small amounts of products, predominately side chain oxidation, were obtained. The products and yields of these runs are listed below in Table 19. The yield is given in mg/hr for all volatile products.

It is of interest to note that as steps were taken to remove O_2, longer degassing, more pure gas, and discontinued use of rubber tubing, the amount of bibenzyl increased at the expense of the other oxidation

Table 19 Toluene Blank Runs

Gas Used	Lamp Used	Yield	Millimole Per Cent						
			Benzaldehyde	Benzyl Alcohol	o-Cresol	Phenol	m & p Cresols	Bibenzyl	Unidentified
O_2	450	0.15	60.5	9	17.5		10.5	< 10	2.5
Air	7[a]	1.3	52.	14.5	23	< 2	11	< 1	< 10
N_2O	450	1.0	8.1	49.2	18.5	3.1	14.6	6.5	< 10
N_2O	7	1.0	14.	60.	12	< 2	8	4	< 10
CO_2	7	3.1	29.0	61.5	6.8	< 1	2.7	< 5	< 10
N_2	7	2.0	10	56	32		< 2	< 2	< 10
He	7	0.6	3	56	1.5		1	31.	7.5
He	Supracil	1.2	< 3	36	< 3	< 3	< 3	64.	< 3

a The Hanau low-pressure mercury lamp is abbreviated 7 for 7 watts.

products. It is believed that these oxidations are due to excited toluene dissociating to benzyl radicals which either dimerize or scavenge any O_2 in the system.

An approximate value of the quantum yield of bibenzyl for the Supracil-Helium run listed in Table 19 can be made; this value is about 8.5×10^{-5}. The first assumption used to calculate the quantum yield of bibenzyl was that the Hanovia specifications for the Supracil lamp are correct; the intensity of the lamp is 10 watts at 2537 Å. The second assumption was that toluene absorbs the entire 10 watts (7.6×10^{-2} Einsteins per hour); calculations using the extinction coefficient of toluene as 200 show that toluene absorbs 97% of the light under our reaction conditions. The final assumption was that benzyl alcohol was due to benzyl radicals, hence the benzyl alcohol yield was divided by two and added to the yield of bibenzyl to obtain a corrected yield of bibenzyl. An approximate value[a] for the quantum yield of hydrogen in photolysis of liquid toluene at 2537 Å is 1×10^{-4}. The agreement of the quantum yields of bibenzyl and hydrogen imply that a primary reaction in photolysis of toluene is dissociation of toluene to benzyl free radicals as given below:

$$C_6H_5CH_3 \xrightarrow{h\nu} C_6H_5CH_2\cdot + H\cdot$$

$$2C_6H_5CH_2\cdot \longrightarrow C_6H_5(CH_2)_2C_6H_5$$

$$2H\cdot \longrightarrow H_2$$

a See reference 68, page 518.

Oxidation of Non-Aromatic Compounds

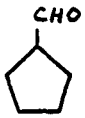
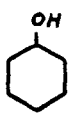
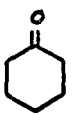
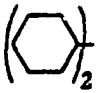
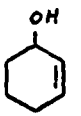
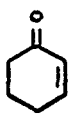
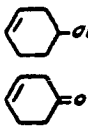
Cyclohexene

Oxidation of this substrate was accomplished via direct photolysis of N_2O (450 watt lamp in the quartz cell), mgd and Hg^*, N_2O techniques. Table 20 gives the yield and per cent composition obtained from each method; the yield is given in mg/hr for total identified volatile products.

The products of $O(^3P)$ oxidation found by Cvetanović[27] were verified in our work with the Hg^*, N_2O technique. In addition, 5% of unsaturated alcohols and ketones were found. These were not reported by Cvetanović. It is uncertain whether the unsaturated products are due to $O(^3P)$ or another species. An analogous situation exists for toluene where small quantities of side chain oxidation may be due to excited toluene, benzyl free radicals or another species of atomic oxygen.

Direct photolysis of N_2O presumably generates $O(^1D)$. This run gave 72% of the unsaturated alcohols and ketones. Only 24% of $O(^3P)$ type products were formed. This run apparently shows that $O(^1D)$ undergoes allylic C-H insertion faster than addition to the double bond; this was not reported by previous investigators[27]. Perhaps excited cyclohexene or cyclohexenyl free radicals are the active species in this run. This interpretation is strengthened by the observation that $O(^1D)$ does not discriminate between the secondary and primary C-H bonds of propane[19]; hence the observed affinity for allylic hydrogens would be

Table 20 Oxidation Products of Aliphatic Compounds

Substrate	Method	Yield	Millimole Per Cent								
											Uniden-tified Products
c-C_6H_{10}	Hg*, N_2O	100.	16.6	10	14.6	45.0	-	1.8		2.0	20
"	$N_2O \xrightarrow{hv}$	6.5	3.8	4.2	9.8	10.0	-	50.6		19.2	2.4
"	mgd-CO_2	55	25.2	9.9	22.1	25.2	-	5.7	8.4	3.3	0.2
"	mgd-O_2	55	24.0	3.6	7.3	14.5	-	12.5	28.8	1.6	7.7
c-C_6H_{12}	Hg*, N_2O	144.	-	18.2	7.3	15.8	57.5	-	-	-	1.2
"	Hg*, N_2	53.	-	7.1	3.7	0.6	83.2	-	-	-	5.4
"	$N_2O \xrightarrow{hv}$	3.0	-	100	5	1	2	-	-	-	5
"	$NO_2 \xrightarrow{hv}$	4.7	-	6	5	10	10	-	-	-	89
"	$O_3 \xrightarrow{hv}$	67.	-	28.9	69.8	5	5	-	-	-	1.3
"	mgd-CO_2	30.	-	43.8	42.2	3.3	0.2	3.5	1.4	0.3	5.5
"	mgd-O_2	40.	-	20.4	20.3	9.4	0.2	1.3	1.9	0.5	46.2
"	mgd-N_2O	8.0	-	24.2	7.8	2	5	10	10	10	68.

surprising.

The mgd runs gave a product distribution intermediate to the $O(^3P)$ and $O(^1D)$ type products mentioned above. It is unfortunate that runs at different travel times were not made in order to determine if a shift toward $O(^3P)$ products would be observed. This will be further discussed in Chapter 9.

Cyclohexane

As illustrated in Chapter 7, cyclohexane could not be studied by the Hg^*, N_2O technique. A mercury photosensitized decomposition of the substrate to cyclohexyl free radicals was observed through the identification of bicyclohexyl. The presence of cyclohexyl radicals was further confirmed by the increase in bicyclohexyl which occurred when less O_2 was present (N_2 replaced N_2O). The 450 watt lamp showed that excited mercury was responsible for the formation of cyclohexyl free radicals since the change from the low-pressure Hanau lamp to the 450 watt lamp (reversed Hg line) gave a decrease in bicyclohexyl from 83% to less than 10%.

The direct photodecomposition of N_2O with the 450 watt lamp and quartz filter in the presence of cyclohexane apparently gave a clean reaction of $O(^1D)$ with the substrate. The expected C-H insertion products were found; thus two runs gave 91% cyclohexanol with 9% cyclohexanone and 100% cyclohexanol and less than 5% cyclohexanone. The absence of bicyclohexyl removes cyclohexyl radicals as a possible intermediate.

The $O(^1D)$ work cited in Chapter 1 agrees well with our results.

The NO_2 system proved equally as disappointing with cyclohexane as it did with toluene. A photolytic run gave essentially the same products as the dark reaction, but contained slightly more unidentified products than the dark run. The expected product of C-H abstraction, bicyclohexyl, was present in less than 10% in both runs. Presumably the oxidizing agent in both runs is NO_2. Assorted nitrates, nitrites, nitro and nitroso compounds are probably the major products.

Ozonolysis of cyclohexane was found to be sufficiently slow to allow a photolytic decomposition of O_3 to $O(^1D)$. Thus the photolytic run gave 40 times more volatile product than an analogous dark reaction. The composition of products was found to be fairly similar in these two runs; cyclohexanol and cyclohexanone accounted for more than 90% of the volatile products. If only $O(^1D)$ was reacting with the substrate, the ratio of alcohol to ketone would be greater than ten based on the observations above with N_2O. The observed ratios for the O_3 system were 2 and 0.5 for the dark and photolytic runs respectively. This discrepancy can be easily accounted for by oxidation of the initially formed alcohol to the ketone by O_3[97].

Discharge runs with either CO_2 or O_2 gave 70 to 80% of cyclohexanol and cyclohexanone. Small amounts of cyclohexene type products

97 G. A. Hamilton, B. S. Ribner and T. M. Hellman, Advan. Chem. Ser., 77, 15 (1968)

were also observed. Passage of N_2O through the mgd gave 68% unidentified products and 32% of $O(^1D)$ type oxidation products. The products of the mgd technique are not particularly revealing in the quest for the identity of the oxidizing agents present in the discharge. The absence of bicyclohexyl is surprising since $O(^3P)$ is presumably a major active species in the discharges. No explanation of this fact is offered. Table 20 lists the product distribution of cyclohexane products obtained by the various techniques of oxidation. The total yield is for all volatile products in mg/hour.

Propane and Butane

Both substrates suffered extensive fragmentation when oxidized by the mgd technique. The principal products were the corresponding alcohols and ketones; lower molecular weight alcohols and ketones were also formed. The product distribution of butane is reminescent of Avramenko's[39] work on ethane and would imply that Avramenko is actually using two or more oxidizing agents (as $O(^1D)$ or O_3) in his work or his reaction temperature is much higher than he believes. Either of these could be the explanation for the lack of agreement between him and most other investigators.

CHAPTER IX

RECOMMENDATIONS FOR FUTURE WORK

Kinetic Isotope Effects

One of the more interesting questions raised by our work is the possibility of an intramolecular isotope effect. The oxidation of benzene-d by the Hg^*, N_2O technique would appear to provide an answer to this question. The mass spectrometer would be used to determine the amount of phenol and monodeuterophenol. Since there would be sizable contributions to the intensities of masses 93, 94 and 95 from both phenols, a careful analysis and disection of the observed mass spectral intensities would be required to obtain a meaningful value of the isotope effect. In connection with the above problem, if the orientation effects of a proton and deuteron are the same, the use of di- and tri-deuterobenzene would give mass spectra which would be much easier to analyze and give an identical isotope effect as monodeuterobenzene.

The mechanism postulated for $O(^3P)$ oxidation of aromatic hydrocarbons might be expected to show different isotope effects for different compounds depending on how early the rate determining transition state is. If one assumes that the more reactive compounds have an earlier transition state, the magnitude of k_H/k_D would be expected to be less than that of benzene for all compounds with relative reactivities greater

than benzene. Conversely, fluorobenzene and benzotrifluoride might have k_H/k_D values greater than that observed for benzene. Obviously, compounds on opposite ends of the reactivity spectrum would be best to study since the effects in k_H/k_D would be maximized. Mesitylene-d_3 and benzotrifluoride-d_5 would be good choices on this basis. Both compounds have the added experimental advantage of being less volatile than phenol and consequently easier to handle in the mass spectrometer, Mesitylene-d_3 has even more good points, being easily available and giving virtually one product.

Yet another example of an interesting kinetic isotope effect would be the study of neopentane-d_{12} by both Hg^*, N_2O and direct photodecomposition of N_2O. This would give an isotope effect for two different species of atomic oxygen under essentially identical experimental conditions and allow a close comparison of the amount of C-H cleavage in the transition state for abstraction and insertion reactions. It can be visualized that molecular orbital calculations might be used to provide an interesting insight into these reactions. Mass spectral analysis of the highly volatile products might prove to be an experimental stumbling block but at least the deuterated starting material is commercially available.

Nitrobenzene System

There are several obvious areas which need work in the nitrobenzene system. Among these are repetition of the relative reactivity of nitrobenzene to benzotrifluoride by both the Hg^*, N_2O and direct photode-

composition of nitrobenzene techniques; these are the only $O(^3P)$ runs which have not yet been duplicated. The difference in volatility between benzotrifluoride and nitrobenzene necessitates independent volatilization of these compounds; of course, a "mixing chamber" would be required prior to the introduction of the mixture into the reaction cell. In order to preserve the experimental setup used in this thesis, compounds of volatility similar to nitrobenzene (benzonitrile, benzaldehyde, ethyl benzoate or biphenyl) could be co-oxidized with nitrobenzene in future relative reactivity runs. Either of these changes would eliminate the large concentuation changes that plagued the present work. The use of nitrobenzene as a source of $O(^3P)$ in relativity runs should also be extended to substrates which could give a relative rate ratio of higher precision than that of the mesitylene+p-xylene system. This could show if nitrobenzene gives $O(^3P)$ as the only intermolecular oxidizing agent.

As mentioned in Chapter 8, the oxidation of nitrosobenzene by $O(^3P)$ is a "must" reaction since we have postulated that nitrosobenzene gives the same phenol ratio as nitrobenzene. The stability of nitrosophenols with respect to air oxidation to nitrophenols could also be investigated at this time. Unofrtunately the separation of both nitroso- and nitrophenols would most probably be a major analytical problem. Since the large excess of nitrobenzene would be absent, (unless nitrosobenzene with $O(^3P)$ gave nitrobenzene as a major reaction), the identification of phenol, o-nitrosophenol and o-nitrophenol would probably be the easiest

analytical task.

Interesting oxidations by Hg^*, N_2O and direct photodecomposition of nitrobenzene techniques could be done on nitrobenzene and perdeuteronitrobenzene mixtures. This substrate has the advantages of being commercially available, possessing mainly one product and giving relatively non-volatile product phenols. If our postulated scheme of nitrobenzene oxidation is correct, the k_H/k_D values from both techniques could be very similar since late transition states would be expected for both nitroso- and nitrobenzene σ-complexes with $O(^3P)$. If an excited state nitrobenzene molecule is either being oxidized or acts as the oxidizing agent, the value of k_H/k_D might be less than one due to the known ability of deuterium to enhance the radiative lifetime of excited molecules.[98]

Identification of Possible Products

The production of oxepin from Hg^*, N_2O or direct photodecomposition[a] of N_2O oxidation methods on benzene should be investigated. The identification of this product would probably be limited to glc analysis since uv and nmr would suffer from the large excess of benzene present as well as the known product phenol. Even glc identification might prove difficult due to the benzene present; low temperatures (less than 60°C),

a If this method did give oxepin, one of the first questions would be whether the reaction was $O(^1D)$ oxidation of benzene or $O(^3P)$ oxidation of Dewar benzene.

98 N. J. Turro, "Molecular Photochemistry". W. A. Benjamin, Inc. New York, 1967, p 69

a long column (20' x 1/8") and high nitrogen flows (100 ml/min) would be necessary. The synthesis and identification of oxepin has been accomplished[99], thus half of this problem can be considered solved.

The $O(^3P)$ oxidation of t-butylbenzene gave t-butyl alcohol as a tentative product. Since iso-butylene could be easily visualized as a product of substituent cleavage, it would be of interest to determine if iso-butylene or its products of $O(^3P)$ oxidation are present in a t-butylbenzene run. At the same time, a more concrete identification of t-butyl alcohol and the possible presence of dimethylphenylacetaldehyde and biphenyl would be of interest. The analysis of all these products would be useful in determining the complete $O(^3P)$ oxidation scheme of t-butylbenzene. This knowledge could then be extended to the other alkylbenzenes. The choice of t-butylbenzene for extended study is based primarily on the facts that side chain oxidation is a very minor process and cleavage products would be of higher molecular weight (more convenient glc analysis) than those of other alkylbenzenes. Due to similarity in glc techniques involved, a search for methanol from toluene and ethanol from ethylbenzene oxidations by $O(^3P)$ would also be of interest and conveniently done at this time.

Identity of Oxygen Atoms from mgd

The generation of $O(^3P)$ from NO_2 and $O(^1D)$ from O_3 for reaction

99 E. E. van Tamelan and D. Carty, J. Am. Chem. Soc. 89, 3922 (1967)

with toluene was stymied by dark reactions with oxygen precusor. It would be of great interest to photolize NO_2 and O_3 in the presence of fluorobenzene, benzotrifluoride or t-butylbenzene. The absence of benzyl hydrogens in these compounds would presumably be quite helpful in eliminating the side chain oxidation products which were important for toluene. It must be remembered that the ratio of organic substrate to NO_2 or O_3 should be at least 1000. If the above techniques, or the direct photodecomposition of N_2O, were successful, a comparison of product distribution could be made with that obtained from the mgd technique. This appears to be one of the best methods of confirming the identity of the oxidizing agents present in a mgd. Benzotrifluoride would be one of the best choices for initial study since the glc separation of the isomeric phenol products is excellent.

The change in product distribution with travel time could also be of great significance in establishing the identity of the oxidizing species from a mgd. Thus, benzotrifluoride, cyclohexene and toluene would conceivably show a shift to $O(^3P)$ type products as the travel time is increased. In this regard, a new glc column should be prepared for the separation of cresols obtained from oxidation of toluene. A two part column (in series) would appear to be a good first choice; the first column being a 2' x 1/4" column of 5% Phos on a Chromosorb W while the second column was a 6' by 1/4" 15% ApH on Chromosorb W. Another possibility would be a 6' by 1/8" 0.2% Phos on glass beads column with a 20' by 1/8" 0.2% ApH on

glass beads column.

Finally, work on the actual reaction temperatures in the mgd is needed. The temperature of the flame with CO_2, O_2 and N_2O would be quite interesting since the variation in product distribution with O_2 and CO_2 may well be due mainly to temperature differences. The low product yield of N_2O oxidations would imply that the preponderance of side chain oxidation observed is not solely due to temperature.

$O(^3P)$ Oxidations at 100°C

Due to residual uncertainty in the meaningfulness of the prf's determined for $O(^3P)$ at 100°C, extension of work at this temperature would seem advisable. The large amount of scatter in the Hammett plot (Figure 10) is disconcerting since analytical difficulties does not appear to be the entire explanation. Difficulty in keeping the temperature at a constant 100°C could be responsible for this scatter since the relative reactivities are temperature dependent. The relative reactivities provide a major contribution to the prf's, hence any small change in these reactivities would be magnified in the prf's. In this regard, a jacketed reaction cell could be very useful; circulation of steam in this jacket would appear to be capable of providing a constant 100°C.

As stated in Chapter 8, unsaturated substituents would be expected to give anomalous ortho and para prf's as observed for nitrobenzene. Due to their volatility, a study of benzaldehyde, ethyl benzoate, acetophenone, benzonitrile, styrene and phenylacetylene would be best

accomplished at 100°C. Due to availability and stability of products, the first three substrates listed above would be the best choices for study. Benzaldehyde could prove especially interesting in that the ortho and para prf's would be larger than expected from σ^+ constants and hydrogen abstraction to give benzil or overall carbon-hydrogen insertion to benzoic acid might be observed.

APPENDIX 1

KINETIC ISOTOPE EFFECT

Hydrocarbon Ratio

The relative reactivity equation used for the kinetic isotope effect is identical to that used for the toluene run in Appendix 3. The standard abbreviations used in mass spectroscopy of amu for atomic mass unit and M for the parent ion will be used here. All sample calculations are for the reaction solution of run B-UV5. The ration of deuterobenzene to benzene was calculated from the ratio of the mass spectral peak heights of each compound.

Corrections for the pressure drop while sweeping the region 76 to 86 amu and the ^{13}C contributions of the M-1 peaks had to be made to obtain this ratio. If the hydrocarbon pressure inside the mass spectrometer was constant, successive sweeps of the spectrum would have identical intensities. It is experimentally observed that the intensities decrease slightly in successive sweeps; hence a correction for this pressure drop must be made.

The time scale used in these analysis was 60 seconds to sweep the 10 amu spectrum and 30 seconds to bring the pen to its starting point. Hence the time for three complete sweeps is 180 seconds while the time to sweep one amu is 6 seconds. The intensity of the C_6D_6 peak fell 0.6

squares over three sweeps, hence the decrease in intensity would be 0.02 squares per amu. The average intensity of C_6D_6 was, 105.6 squares giving a fraction decrease of 0.0002 per amu. Analogous treatment of the C_6H_6 peak and averaging of the two fractions gives an average fraction decrease of 0.0001 per amu.

In order to place all peaks on the same pressure scale, a pressure correction is subtracted from each peak in the spectrum. The spectrum is swept from 86 to 76 amu, hence the fraction decrease is multiplied by the number of amu's from the lowest measurable peak then multiplied by the observed intensity of the peak to be corrected. The resulting figure is subtracted from the observed intensity. In run B-UV5, the pressure correction was made from amu 77, thus the observed intensity of the C_6D_6 peak was decreased by 0.1 square as shown below.

pressure correction for C_6D_6 = fraction decrease per amu x amu's from 77 x observed intensity

$$= 0.0001 \times 7 \times 105.6 = 0.1$$

Analogous calculations for all other peaks show the correction to be insignificant; hence the corrected intensities of the spectrum are as given in Table 21.

The natural isotopic abundance of ^{13}C is 1.08 per cent[100]; thus the fraction of ^{13}C present in benzene is 6 atoms times 1.08% ^{13}C per atom. The M-1 peaks of C_6H_6, C_6HD_5 and C_6D_6 were of intensity 17.3, 9.9 and 4.1 respectively. These intensities are multiplied by 0.0648 to

100 F.W. McLafferty, "Interpretation of Mass Spectra". W.A. Benjamin, Inc., New York 1966, p. 210

obtain the ^{13}C contributions to the parent compounds. The calculated ^{13}C contributions are 1.1, 0.6 and 0.2 for C_6H_6, C_6HD_5 and C_6D_6 respectively; the corrected intensity of the parent compound is shown in the last column of Table 21.

Table 21 Mass Spectral Intensities of Hydrocarbons in B-UV5

Compound	amu	Observed Intensity	Total Fraction Decrease due to Pressure	Pressure Corrected Intensity	^{13}C Corrected Intensity
	77	17.3	0.0	17.3	
C_6H_6	78	105.6	0.0001	105.6	104.5
	79	6.7	0.0002	6.7	
	80	2.4	0.0003	2.4	
	81	0.3	0.0004	0.3	
	82	9.9	0.0005	9.9	
C_6D_5H	83	4.1	0.0006	4.1	3.5
C_6D_6	84	105.6	0.0007	105.5	105.3
	85	6.3	0.0008	6.3	

From the mass spectra of a neat deuterobenzene sample, the intensity ratio of amu 78 to the parent amu 84 was found to be 0.0075. Thus the 105.7 peak height of C_6D_6 is expected to have an amu 78 height of 0.8 squares. This number must also be substracted from the observed height of amu 78 to obtain the true intensity of C_6H_6 of 103.7. This amu 78 peak in neat deuterobenzene is not believed to be benzene itself due to

the high purity (99.5%) of the deuterobenzene used. Neat benzene does exhibit an M-3 peak[a] which would correspond to the M-6 peak observed in our work. Now the mole ratio of deuterium to hydrogen is as shown below:

$$\text{mole ration } \frac{D}{H} = \frac{6(\text{intensity of } C_6D_6) + 5 (\text{intensity of } C_6HD_5)}{6(\text{intensity of } C_6H_6) + \text{intensity of } C_6HD_5}$$

$$= \frac{6(105.3) + (3.5)}{6(103.7) + 3.5} = 1.04$$

The initial and final substrates remaining in the bubbler gave analogous D/H ratios of 1.02 and 1.01 respectively. The average of these three determinations is 1.02 ± 0.01; this value is used to calculate the relative reactivity of benzene to deuterobenzene as shown in the following section.

Phenol Ratio

The product ratio was calculated in an analogous manner as the hydrocarbon ratio. The corrections for pressure drop and ^{13}C contributions were calculated exactly as in the preceding section; the results of which are shown in Table 22.

The amu 98 peak can be divided into the C_6D_5O cation from C_6D_5OH and C_6D_4HOH parent compound by assuming that C_6D_5OH and C_6H_5OH will have the same intensity ratio of M-1 to M peaks. For C_6H_5OH and C_6H_5O cation, this ratio is 0.0175; thus C_6D_5O cation

a See reference 100, page 44.

should have an intensity of 1.4 (from 0.0175 x 82.4). The intensity of C_6D_4HOH is then found, by the difference between the total intensity of amu 98 and the calculated intensity of C_6D_5O cation, to be 2.9 (from 4.3 - 1.4). An analogous calculation for C_6D_5O cation from C_6D_5OD gives an intensity of 0.03, hence this process can be assumed to be negligible.

Table 22 Mass Spectral Intensities of Phenols in B-UV5

Compound	amu	Observed Intensity	Pressure Corrected Intensity	Calculated ^{13}C Intensity of M-1 peak	^{13}C Corrected Intensity
	93	1.7	1.7	.0648x1.7 = 0.1	-
C_6H_5OH	94	96.8	96.7	" x96.6 = 6.3	96.6
	95	9.4	9.4	" x3.1 = 0.2	3.1
	96	1.1	1.1	" x0.9 = 0.06	0.9
	97	0.8	0.8	" x0.7 = 0.04	0.7
C_6D_4HOH + C_6D_5O	98	4.3	4.3	" x4.3 = 0.3	4.3
C_6D_5OH	99	82.9	82.4	" x82.1 = 5.3	82.1
C_6D_5OD	100	6.8	6.8	" x1.5 = 0.09	1.5
	101	0.5	0.5		0.4

The intensity of the C_6D_5OD peak is found by the difference between the observed intensity of amu 100 and the calculated intensity of this peak due to ^{13}C contributions from amu 99. The observed intensity was 6.8 while the ^{13}C intensity was 5.3; hence the intensity of C_6D_5OD

is 1.5

A small fraction of the C_6D_5OH peak is due to overall C-H insertion into C_6D_5H. If one assumes there is no intramolecular kinetic isotope effect, the intensity of this peak would be one-fifth that of C_6D_4HOH (which arises from overall C-D insertion into C_6D_5H). Appropriate calculations follow:

Intensity of C_6D_5OH from C_6D_5H = 1/5 (Intensity of C_6D_4HOH)

= 1/5 (2.9) = 0.6

Intensity of C_6D_5OH from C_6D_6 = Total intensity of C_6D_5OH minus Intensity of C_6D_5OH from C_6D_5H

= 82.1 - 0.6 = 81.5

The phenol ratio in B-UV5 is calculated as shown below:

$$\frac{\text{phenol from } C_6H_6}{\text{phenol from } C_6D_6 \text{ and } C_6D_5H} = \frac{C_6H_5OH + C_6D_5OH \text{ from } C_6D_5H}{C_6D_5OD + C_6D_5OH \text{ from } C_6D_6 + C_6D_4HOH \text{ from } C_6D_5H}$$

$$= \frac{96.6 + 0.6}{1.5 + 81.5 + 2.9} = 1.13$$

The relative reactivity of benzene to deuterobenzene is then calculated as shown below.

$$\frac{k_H}{k_D} = \frac{C_6H_5OH}{C_6D_5OD + C_6D_5OH + C_6D_4HOH} \times \frac{\text{benzene-d}}{\text{benzene-h}}$$

$$= 1.13 \times 1.02 = 1.15$$

Run B-UV3 gave a value k_H/k_D of 1.13; thus the average is 1.14. Although the precision of these values is 0.01, the estimated error is 0.04; thus the kinetic isotope effect is given as 1.14 ± 0.04.

APPENDIX 2

PRODUCT YIELD OF TOLUENE-O(^{3}P) RUN

This sample calculation is for run T-UV99 using the 1-Phos column at 142°C with a nitrogen flow of 44 ml/minute. The other glc parameters were as given in Chapter 3. Meta and para-cresols were analyzed on the ApH column, while the 1-Phos column was used for benzaldehyde, benzyl alcohol, phenol, o-cresol, two unidentified products and the sum of m- and p-cresol. All averaged figures in this appendix are quoted together with the largest difference of an individual value from the average value.

Standard solutions of phenol, o-cresol and m-cresol in toluene and phenol, o-cresol and p-cresol in toluene were prepared and two injections of each standard made at an attenuation of 800. The first standard solution utilized 39.7 mg phenol, 48.0 mg o-cresol, 22.7 mg m-cresol and 25.2521 g toluene; of this, 2.872 and 5.380 mg were injected into the glc. The second injection gave 1.495, 1.92 and 0.865 square inch peaks for phenol, o-cresol and m-cresol respectively. From the weight fraction of the standard, the amount of standard actually injected in the second analysis can be calculated as shown for phenol:

$$\text{weight fraction phenol} = \frac{0.0397}{0.0397+0.0480+0.0227+25.2521} = 1.565\times10^{-3}$$

weight phenol injected = $1.565 \times 10^{-3} \times 5.38$ mg = 8.42×10^{-6} g

Since this weight gave rise to a peak area of 1.495 square inches, the weight of phenol required to produce one square inch of area is:

$$\frac{8.44 \times 10^{-6} \text{ g}}{1.495 \text{ in}^2} = 5.63 \times 10^{-6} \text{ g/in}^2$$

The same calculation is done for all standards in each injection, the average of these calculations is: phenol ($5.66 \pm 0.12 \times 10^{-6}$ g/in^2, o-cresol ($5.17 \pm 0.20 \times 10^{-6}$ g/in^2), m-cresol (5.57×10^{-6} g/in^2), and p-cresol ($5.47 \pm 0.20 \times 10^{-6}$ g/in^2). The average of the m- and p-cresols is then $5.52 \pm 0.20 \times 10^{-6}$ g/in^2. For benzaldehyde, benzyl alcohol and the two unidentified products, the average of the four standards ($5.45 \pm 0.20 \times 10^{-6}$ g/in^2) is used to calculate the amount of these products formed. Previous analysis have shown this to be an excellent assumption for non-overlapping peaks as these minor products are.

The reaction solution of T-UV99 weighed 6.0362 g; three injections of 6, 4 and 4 ul were made from this solution. The second injection weighed 3.555 mg; the weight of compound responsible for each peak was calculated as shown below for phenol.

area of phenol peak = 0.307 in^2

weight of phenol injected = 0.307 in^2 x 5.66×10^{-6} g/in^2 = 1.74×10^{-6} g

$$\text{weight of phenol in reaction solution} = 1.74 \times 10^{-6} \text{ g} \times \frac{6.0362 \times 10^{3} \text{ mg}}{3.555 \text{ mg}} = 2.95 \text{ mg}$$

The same calculation is done for each peak found in the reaction solution. The results from the second injection and the average from all three injections are given in Table 23; all units in the table are as given in the first row of data.

The relative amounts of m- and p-cresol are calculated in a manner entirely analogous to that for the other products. The data is then tabulated as given in Table 24 for T-UV99. In all runs, the molecular weight of unknown products is assumed to be that of the parent hydrocarbon plus oxygen; thus for U-1 and U-2 in Table 24, the molecular weight is 108.

An important ratio to be used in the following appendix is that of phenol to the total cresols; for T-UV99, this ratio is:

$$\frac{0.0313}{0.3563} = 0.08785$$

Table 23 Sample Data of Toluene Yield

Compound	Retention time	glc area	Weight per in^2 area of standard	Weight compound in second injection	Average weight of all analyses
Benzaldehyde	2.4 min	0.05 in^2	5.45×10^{-6} g/in^2	0.46 mg	0.50 $\pm$ 0.04 mg
U-1	3.2	0.05	5.45 "	0.46	0.40 $\pm$ 0.06
U-2	4.0	0.05	5.45 "	0.46	0.30 $\pm$ 0.16
Benzyl Alcohol	5.0	0.11	5.45 "	1.02	0.98 $\pm$ 0.04
Phenol	8.9	0.307	5.66 "	2.95	2.93 $\pm$ 0.07
o-Cresol	10.4	3.005	5.17 "	26.38	26.13 $\pm$ 0.25
m- and p-Cresol	14.	1.36	5.52 "	12.75	12.34 $\pm$ 0.41

Table 24 Summation of Data for T-UV99

Compound	Weight (mg)	Millimoles	Millimole Per Cent total products	phenols	cresols
Benzaldehyde	0.50	0.0042	1.0		
U-1	0.40	0.0037	0.9		
U-2	0.30	0.0028	0.7		
Benzyl Alcohol	0.98	0.0091	2.2		
Phenol	2.93	0.0313	7.7	8.1	
o-Cresol	26.13	0.2420	59.4	62.4	67.9
p-Cresol	6.53	0.0605	14.9	15.6	17.0
m-Cresol	5.81	0.0538	13.2	13.9	15.1
Total	43.5	0.4074	100.0	100.0	100.0

APPENDIX 3

RELATIVE REACTION RATES TOWARD $O(^3P)$

Derivation of Rate Equation

The rate equation is assumed to be first order in both $O(^3P)$ and aromatic substrate. The concentration of $O(^3P)$ is assumed to be constant giving pseudo first order equations shown below:

let the concentration of benzene be [HArH]

let the concentration of phenol be [HArOH]

let the concentration of other aromatic be [XArH]

let the concentration of substituted phenols be [XArOH]

$$\text{then } \frac{d[HArOH]}{dt} = k_1' \, O(^3P)[HArH] = k_1 \, [HArH] \tag{1}$$

$$\frac{d[XArOH]}{dt} = k_2' \, O(^3P)[XArH] = k_2 \, [XArH] \tag{2}$$

In order to integrate the above equations easily, it is assumed that the variation in aromatic is linear with time. For benzene, the following integration can be made:

$$[HArH] = At + B \tag{3}$$

$$\text{then} \quad d[HArOH] = k_1 \, (At + B) \, dt \tag{4}$$

$$[HArOH] = k_1 \, (\frac{At^2}{2} + Bt + C) \tag{5}$$

$$\text{at } t = 0,\ [HArOH] = C = 0$$

$$\text{therefore,} \qquad [HArOH] = k_1 \left(\frac{At^2}{2} + Bt\right) \tag{6}$$

In an analogous manner, the other substrate yields:

$$[XArOH] = k_2 \left(\frac{A't^2}{2} + B' t\right) \tag{7}$$

The ratio of product phenols is then given by equation 8 from which t can be cancelled to give equation 9.

$$\frac{[XArOH]}{[HArOH]} = \frac{k_2 \left(\frac{A't^2}{2} + B' t\right)}{k_1 \left(\frac{At^2}{2} + Bt\right)} \tag{8}$$

$$\frac{[XArOH]}{[HArOH]} = \frac{k_2 \left(\frac{A't}{2} + B'\right)}{k_1 \left(\frac{At}{2} + B\right)} \tag{9}$$

The above terms for the concentration of each substrate can be taken as the average concentrations during the run. The molar ratio of substrates found in the trap is set equal to the concentration terms of equation 9 in order to obtain equation 10. This step is permissible since the geometry of the reaction cell and length of run are the same for both substrates. Rearrangement of equation 10 gives equation 11.

$$\frac{[XArOH]}{[HArOH]} = \frac{k_2 [XArH]\,\text{ave}}{k_1 [HArH]\,\text{ave}} \tag{10}$$

$$\frac{k_2}{k_1} = \frac{[XArOH]}{[HArOH]} \frac{[HArH]\,\text{ave}}{[XArH]\,\text{ave}} \tag{11}$$

Equation 11 is the equation for the relative reactivity of XArH with respect

to HArH. Here, the average concentration is taken to be that substrate recovered in the reaction solution plus that substrate oxidized. It is assumed that tar formation from each substrate is in the same ratio as the oxidation products from each substrate. It should be pointed out that the assumption of equation 3 will be true only if the relative concentration of substrates in the liquid bubler is nearly constant. Hence the change in mole fraction of the bubbler must be kept small. Likewise, the average concentration used in deriving equation 10 demands that the amount of substrate oxidized be much smaller than the amount of substrate found in the reaction solution. Thus both the per cent change in the liquid bubbler and per cent oxidation were kept below 5% whenever possible; these quantities are tabulated in Table 6. It should be noted that the derivation of equation 11 used no assumptions of ideality or equilibrium for the aromatic substrates; hence equation 11 is quite flexible as long as the substitution noted between equations 9 and 10 is justified.

Sample Calculation of Relative Reactivity

The oxidation products of run RR-UV74 were calculated exactly as those shown in the preceding appendix. From the total cresols of 0.1404 millimoles, the amount of phenol arising from toluene is calculated assuming identical product distributions in the neat toluene and relative reactivity runs. Then the amount of phenol from oxidation of benzene is calculated by difference from the total phenol as shown below.

phenol from toluene = total cresols x $\frac{\text{phenol}}{\text{cresols}}$ in neat run

= 0.1404 x 0.08785 = 0.0123 millimoles

phenol from benzene = total phenol - phenol from toluene

= 0.1213 - 0.0123 = 0.1090 millimoles

Thus the ratio of phenols from toluene to phenol from benzene is 1.401 as given below:

$$\frac{CH_3C_6H_4OH + C_6H_5OH}{C_6H_5OH} = \frac{0.1404 + 0.0123}{0.1090} = 1.401$$

The analysis of the reactants is done exactly as that for the products. For RR-UV74, the weight of benzene found was 3.099 g while that of toluene was 1.171 g. The weights of oxidation products are converted to the weight of the parent hydrocarbon they represent by multiplication by the ratio of the molecular weight of the parent to that of the product. For toluene, the amount of toluene consumed is:

$$\text{toluene consumed} = \text{weight phenol} \times \frac{\text{M Wt}^a \text{ toluene}}{\text{M Wt phenol}} + \text{weight cresols} \times \frac{\text{M Wt toluene}}{\text{M Wt cresol}}$$

$$= 1.55 \times \frac{92}{94} + 15.16 \times \frac{92}{108} = 15 \text{ mg}$$

For benzene, a total of 8.5 mg was oxidized. The total weights of toluene and benzene passed through the reaction cell were 1.186 and

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a M Wt is the abbreviation for molecular weight.

3.108 g respectively. Division of these weights by the appropriate molecular weight gives 12.89 and 39.85 millimoles of toluene and benzene respectively; thus the ratio of benzene to toluene in RR-UV74 is 3.091.

As given previously, the relative reactivity is simply the product of the phenol ratio and the hydrocarbon ratio. For RR-UV74,

Relative reactivity of toluene to benzene = k_T/k_B

$$k_T/k_B = \frac{\text{phenols from toluene}}{\text{phenol from benzene}} \times \frac{\text{benzene}}{\text{toluene}}$$

$$= 1.401 \times 3.091 = 4.33$$

The duplicate run RR-UV75 gives a value k_T/k_B of 4.43; thus the average value as shown in Table 7 of Chapter 4 is 4.38 ± 0.05.

Sample Calculation of Partial Rate Factors

Derivation of PRF Equation

The rate of reaction of a particular position of a compound is given by the relative amount of product from that position times the total reaction rate of the compound. This is shown below for the positions of toluene (Z = CH_3). The rate of one ortho- position of toluene is thus:

$$k_o = \frac{\%\ o}{100} \quad \frac{k_T}{2} \tag{12}$$

Likewise, the remaining positional rates are given by

$$k_m = \frac{\%\ m}{100} \quad \frac{k_T}{2} \tag{13}$$

$$k_{\underline{p}} = \frac{\%\underline{p}}{100} k_T \tag{14}$$

$$k_z = \frac{\%\ z}{100} k_T \tag{15}$$

Equation 12 can be divided by the expression for the rate of one position of benzene to give equation 17.

$$\text{k/each position in benzene} = k_B/6 \tag{16}$$

$$\frac{\text{k/each } \underline{o}\text{-position}}{\text{k/each position in benzene}} = \frac{k_{\underline{o}}}{k_B/6} = \frac{(\%\underline{o}/100)k_T/2}{k_B/6} \tag{17}$$

By definition, a prf[a] is the reactivity of one position of a compound relative to one position of another compound. The notation used in this thesis is O_f for the statistically corrected rate ($k_{\underline{o}}$) of formation of an ortho-substituted phenol (e.g. o-cresol from toluene) relative to the statistically corrected rate ($k_B/6$) of formation of phenol from benzene. M_f, P_f and Z_f have analogous connotations.

$$\text{Thus} \quad O_f = \frac{k_{\underline{o}}}{k_B/6} = 3\left(\frac{\%\ \underline{o}}{100}\right)\frac{k_T}{k_B} \tag{18}$$

$$M_f = 3\left(\frac{\%\ \underline{m}}{100}\right)\frac{k_T}{k_B} \tag{19}$$

$$P_f = 6\left(\frac{\%\underline{p}}{100}\right)\frac{k_T}{k_B} \tag{20}$$

$$Z_f = 6\left(\frac{\%\ z}{100}\right)\frac{k_T}{k_B} \tag{21}$$

The total rate of reaction of toluene (k_T) is given by the summation of rates of individual positions (equation 22). From this equation and the def-

a Abbreviation used for partial rate factor is prf.

inition of prf's, it can be shown that equation 23 must hold. Equation 23 is convenient for checking the internal consistency of prf's calculated from equations 18 through 21.

$$k_T = 2\,k_{\underline{o}} + 2\,k_{\underline{m}} + k_{\underline{p}} + k_z \qquad (22)$$

$$k_T/k_B = \frac{2\,O_f + 2\,M_f + P_f + Z_f}{6} \qquad (23)$$

Sample Calculation

The calculations below refer to toluene relative to benzene in run RR-UU74. The tabular summary of these calculations is given in Table 7.

The use of equation 23 verifies the consistency of these prf's.

$$O_f = 3\left(\frac{58}{100}\right) 4.33 = 7.5$$

$$M_f = 3\left(\frac{15.8}{100}\right) 4.33 = 2.05$$

$$P_f = 6\left(\frac{18.2}{100}\right) 4.33 = 4.7$$

$$Z_f = 6\left(\frac{8.0}{100}\right) 4.33 = 2.09$$

Derivation of Alternate Rate Equation

It is instructive to consider the derivation of another equation for the calculation of relative reaction rates[a]. Starting with equations 1 and 2, equations 24 and 25 can be easily derived as shown below:

a J. McKelvey is primarily responsible for this derivation. Dr. R. A. Pierotti was quite helpful in making clear the subleties of equations 11 and 35.

let the partial pressure be P

let the mole fraction in the substrate bubbler be X

let the vapor pressure of the pure hydrocarbon be P^o

let the moles in the substrate bubbler at any time be N

from the division of equation 2 by equation 1 we find

$$\frac{d[XArOH]}{d[HArOH]} = \frac{k_2}{k_1} \frac{[XArH]}{[HArH]} \tag{24}$$

but $[XArH] = P_{XArH} = P^o_{XArH} X_{XArH}$

hence $$\frac{d[XArOH]}{d[HArOH]} = \frac{k_2}{k_1} \frac{P^o_{XArH} X_{XArH}}{P^o_{HArH} X_{HArH}} = \frac{k_2}{k_1} \frac{P^o_{XArH} N_{XArH}}{P^o_{HArH} N_{HArH}} \tag{25}$$

By assuming Raoult's Law holds to obtain equation 25, we also assume that equilibrium is always established between the liquid and gas phases in the substrate bubbler. To obtain equation 28, it is assumed that the mass transfer constants (Q) are equal since HArH and XArH are miscible, at the same temperature, and are being swept out of the bubbler by the same gas at the same flow rate. Use of Raoult's Law gives equation 32.

$$-\frac{dN_{XArH}}{dt} = Q_{XArH} P_{XArH} \tag{26}$$

$$-\frac{dN_{HArH}}{dt} = Q_{HArH} P_{HArH} \tag{27}$$

$$\frac{dN_{XArH}}{dN_{HArH}} = \frac{Q_{XArH} P_{XArH}}{Q_{HArH} P_{HArH}} = \frac{P_{XArH}}{P_{HArH}} \tag{28}$$

$$\frac{dN_{XArH}}{dN_{HArH}} = \frac{P^o_{XArH} X_{XArH}}{P^o_{HArH} X_{HArH}} = \frac{P^o_{XArH} N_{XArH}}{P^o_{HArH} N_{HArH}} \tag{29}$$

$$\frac{dN_{XArH}}{N_{XArH}} = \frac{P^{o}_{XArH}}{P^{o}_{HArH}} \frac{dN_{HArH}}{N_{HArH}} \tag{30}$$

$$\ln\left(\frac{N^{o}_{XArH}}{N_{XArH}}\right) = \frac{P^{o}_{XArH}}{P^{o}_{HArH}} \ln\left(\frac{N^{o}_{HArH}}{N_{HArH}}\right) \tag{31}$$

$$N_{XArH} = N^{o}_{XArH} \left(\frac{N_{HArH}}{N^{o}_{HArH}}\right)^{P^{o}_{XArH}/P^{o}_{HArH}} \tag{32}$$

From substitution of equation 32 into equation 25, we arrive at:

$$\frac{d[XArOH]}{d[HArOH]} = \frac{k_2}{k_1} \frac{P^{o}_{XArH}}{P^{o}_{HArH}} \frac{N^{o}_{XArH}}{N_{HArH}} \left(\frac{N_{HArH}}{N^{o}_{HArH}}\right)^{P^{o}_{XArH}/P^{o}_{HArH}} \tag{33}$$

Equation 33 is integrated by assuming that the change in N_{HArH} is very small from actual conversion to HArOH (that is the per cent oxidation is negligible). After applying the boundary condition of zero time, the following equations are obtained:

$$\text{at } t = 0, \; [XArOH] = [HArOH] = 0$$

$$\frac{[XArOH]}{[HArOH]} = \frac{k_2}{k_1} \frac{P^{o}_{XArH}}{P^{o}_{HArH}} \frac{N^{o}_{XArH}}{N_{HArH}} \left(\frac{N_{HArH}}{N^{o}_{HArH}}\right)^{P^{o}_{XArH}/P^{o}_{HArH}} \tag{34}$$

$$\frac{k_2}{k_1} = \frac{[XArOH]}{[HArOH]} \frac{P^{o}_{HArH}}{P^{o}_{XArH}} \frac{N^{o}_{HArH}}{N^{o}_{XArH}} \left(\frac{N^{o}_{HArH}}{N_{HArH}}\right)^{P^{o}_{XArH}/P^{o}_{HArH}} \tag{35}$$

It is seen that under the limiting conditions of no change in N_{HArH}, equation 35 reduces to equation 36. Comparison of equations

36 and 11 leads to equation 37. Equation 37 can also be derived by including Raoult's Law in the method used to derive equation 11. For hydrocarbon mixtures which behave ideally (p-xylene + benzene), the agreement was shown to be good (within 1%) for equation 37.

$$\frac{k_2}{k_1} = \frac{[XArOH]}{[HArOH]} \frac{P^o_{HArH}}{P^o_{XArH}} \frac{N^o_{HArH}}{N^o_{XArH}} \tag{36}$$

$$\frac{P^o_{HArH}}{P^o_{XArH}} \frac{N^o_{HArH}}{N^o_{XArH}} = \frac{[XArH]^{trap}_{ave.}}{[HArH]^{trap}_{ave.}} \tag{37}$$

All relative rates reported in this thesis were calculated via equation 11. Since equation 35 assumes that Raoult's Law holds, equilibrium between the liquid and gas phase is achieved, the mass transport constants (Q) cancel, and the activity coefficients of HArH and XArH cancel, it is much less flexible than equation 11. However, the relative rates via equation 35 usually agreed with those from equation 11 to within 10%. A comparison between the relative reaction rates (Hg^*, N_2O) from the two equations follows:

Substrate	relative to Substrate	(Equation 11) k_2/k_1	(Equation 35) k_2/k_1	% Difference[a]
Toluene	Benzene	4.33	4.14	4.3
p-Xylene	Benzene	10.15	9.53	6.1
Benzotrifluoride	Benzene	0.280	0.253	9.7
Anisole	p-Xylene	1.47	1.33	9.5
Nitrobenzene	Benzotrifluoride	9.7	1.85	81.

a Difference between rates from equation 35 and 11, divided by rate from equation 11 and multiplied by 100.

It is believed that equation 11 is more applicable to our system. This is true since equilibrium between the liquid and vapor phases may not be established with our rapid (100-200 ml/min) flows of N_2O through the substrate bubbler. Also, ideality is a more tenuous assumption for aromatic compounds with hetero-atoms. For aromatic mixtures which differ greatly in volatility, equation 35 may be a better method of describing the system, since equation 35 is independent of change in mole fraction of the substrate bubbler. At the present time, insufficient data exists to test the variation in relative reactivity with change in bubbler composition.

BIBLIOGRAPHY[a]

1 R. J. Cvetanović, Advan. Photochem., 1, 115 (1963)

2 R. J. Cvetanović, Can. J. Chem., 36, 623 (1958)

3 R. J. Cvetanović, J. Chem. Phys., 23, 1375 (1955)

4 J. T. Herron and R. D. Penzhorn, J. Phys. Chem., 73, 191 (1969)

5 M. D. Sheer and R. Klein, ibid., 73, 597 (1969)

6 R. Klein and M. D. Sheer, ibid., 73, 1398 (1969)

7 A. N. Hughes, M. D. Sheer and R. Klein, ibid., 70, 798 (1966)

8 R. Klein and M. D. Sheer, ibid., 72, 616 (1968)

9 D. Saunders and J. Heicklen, ibid., 70, 1950 (1966)

10 D. Saunders and J. Heicklen, J. Am. Chem. Soc., 87, 2088 (1965)

11 R. C. Mitchell and J. P. Simons, J. Chem. Soc., Sect. B, 1005 (1968)

12 W. J. R. Tyerman, Trans. Faraday Soc., 65, 163 (1969)

13 S. J. Moss and K. R. Jennings, Trans. Faraday Soc., 64, 686 (1968)

14 A. Y-M. Ung and H. I. Schiff, Can. J. Chem., 40, 486 (1962)

15 F. J. Wright, J. Chem. Phys., 38, 950 (1963)

16 F. J. Wright, Tenth Symposium (International) on Combustion, 387 (1965)

17 W. K. Stuckey and J. Heicklen, J. Chem. Phys., 46, 4843 (1967)

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a The more common periodicals are abbreviated; the abbreviations used are those employed by Chemical Abstracts in their annual guide to the chemical literature, Access 1 (1969).

18 J. T. Herron and R. E. Huie, J. Phys, Chem., 73, 1326 (1969)

19 H. Yamazaki and R. J. Cvetanović, J. Chem. Phys., 41, 3703 (1964)

20 I. Haller and G. C. Pimentel, J. Am. Chem. Soc., 84, 2855 (1962)

21 D. G. Williamson and K. D. Bayes, J. Phys. Chem., 73, 1232 (1969)

22 C. A. Arrington et al., J. Chem. Phys. 43, 525 (1965)

23 R. J. Cvetanović, Can. J. Chem., 34, 775 (1956)

24 H. E. Avery and R. J. Cvetanović, J. Chem. Phys., 43, 3727 (1965)

25 A. Kato and R. J. Cvetanović, Can. J. Chem., 46, 235 (1968)

26 H. Kawasaki and Y. Takezaki, Bulletin of the Institute of Chemical Research; Kyoto University, 42, 378 (1964)

27 G. Boocock and R. J. Cvetanović, Can. J. Chem., 39, 2436 (1961)

28 G. R. H. Jones and R. J. Cvetanović, Can. J. Chem., 39, 2444 (1961)

29 S. L. Kopczynski, International Journal of Air and Water Pollution 8, 107 (1964)

30 P. L. Hanst, E. R. Stephens and W. E. Scott, Journal of the Air Pollution Control Association, 5, (Feb.), 219 (1956)

31 S. Sato and R. J. Cvetanović, Can. J. Chem., 36, 1668 (1958)

32 W. B. DeMore, J. Phys. Chem., 73, 391 (1969)

33 G. A. Castellion and W. A. Noyes, Jr., J. Am. Chem. Soc., 79, 290 (1957)

34 E. Murad and W. A. Noyes, Jr., J. Am. Chem. Soc., 81, 6405 (1959)

35 G. Paraskevapoulos and R. J. Cvetanović, J. Chem. Phys., 50 590 (1969)

36 W. B. DeMore and O. F. Raper, J. Chem. Phys., 46, 2500 (1967)

37 W. B. DeMore and O. F. Raper, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Florida, April (1967) No. R 028

38 L. I. Avramenko, I. I. Ioffe and R. V. Lorentso, Doklady Akad, Nauk SSSR, 66, 1111 (1949); Chem. Abstr., 43, 7922g (1949)

39 L. I. Avramenko and R. V. Kolesnikova, Advan. Photochem., 2, 25 (1964)

40 L. I. Avramenko, R. V. Kolesnikova and G. I. Savinova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, No. 1, 36 (1963); Chem. Abstr., 58, 10770e (1963)

41 L. I. Avramenko, R. V. Kolesnikova and G. I. Savinova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 253 (1967); Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 2, 247 (1967)

42 L. I. Avramenko, R. V. Kolesnikova and G. I. Savinova, Izv. Akad. Nauk SSSR, Ser. Khim. No. 1, 22 (1967); Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 1, 19 (1967)

43 R. P. Wayne, Advan. Photochem. 7, 311 (1969)

44 E. J. Corey and W. C. Taylor, J. Am. Chem. Soc., 86 3881 (1964)

45 R. L. Brown, J. Phys. Chem., 71 2492 (1967)

46 F. J. LeBlanc, O. Oldenberg and N. P. Carlton, J. Chem. Phys., 45, 2200(1966)

47 C. W. Nutt and A. J. Biddlestone, Trans. Faraday Soc., 58, 1368 (1962)

48 W. D. McGrath and J. J. McGarvey, Planetary and Space Science 15, 427 (1967)

49 G. Kvifte and L. Vegard, Geofysiske Publikasjoner, Utgitt av det Norske Videnskaps Akademi i Oslo, 17, 3 (1947)

50 G. O. Brink, J. Chem. Phys., 46, 4531 (1967)

51 L. Elias, E. A. Ogryzlo and H. I. Schiff, Can. J. Chem., 37, 1680 (1959); L. Elias and H. I. Schiff, ibid, 38, 1657 (1960)

52 E. A. Ogryzlo and H. I. Schiff, J. Chem. Phys., 32, 628 (1960)

53 J. M. S. Jarvie and R. J. Cvetanović, Can. J. Chem., 37, 529 (1959)

54 F. Kaufman, Proc. Roy. Soc. London, A247, 123 (1958).

55 L. Elias, J. Chem. Phys. 38, 989 (1963)

56 A. Fontijn and R. Ellison, J. Phys. Chem., 72, 3701 (1968)

57 K. Sugino and E. Inoue, Bull. Chem. Soc., Japan, 24, 93 (1951)

58 E. Inoue and K. Sugino, Advan. Chem. Ser. 21, 313 (1959)

59 N. Sonoda et al., Advan. Chem. Ser. 76, 352 (1968)

60 H. Gilman and W. E. Catlin, Org. Syn., Coll. Vol. 1, 188 (1948)

61 J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentic-Hall, Inc., Englewood Cliffs, N.J., 1965,p 36

62 O. Grummitt, J. Liska and G. Greull, Org. Syn., 44, 26 (1964)

63 C. J. Gogek, R. Y. Moir and C. B. Purves, Can. J. Chem., 29, 946 (1951)

64 J. R. Lindsay Smith, R. O. C. Norman and C. K. Radda, Journal of Gas Chromatography, 3, 146 (1964)

65 D. A. Gordon, Ph. D. Thesis, Georgia Institute of Technology; Atlanta, Ga. p 143 (1953)

66 L. M. Stock and H. C. Brown, Advan. Phy. Org. Chem. 1, 35 (1963)

67 H. E. Gunning and O. P. Strausz, Advan. Photochem. 1, 209 (1963)

68 J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", John Wiley and Sons, Inc., New York, 1966,p 106

69 N Kharash, R. K. Sharma and H. B. Lewis, Chem. Commun., 418 (1966)

70 G. H. Williams, "Homolytic Aromatic Substitution", Pergamon Press, Oxford, 1960

71 D. H. Hey, M. J. Perkins and G. H. Williams, Chem. Inc., London 83 (1963); R. T. Morrison, J. Cazes, N. Samkoff and C. A. Howes, J. Am. Chem. Soc., 84 4152 (1962)

72 R. Itô, T. Migita, N. Morikawa and O. Simamura, Tetrahedron, 21 955 (1965)

73 J. Hine, "Physical Organic Chemistry", 2nd ed. McGraw-Hill, New York, 1962,p 471

74 K. Bowden, Can. J. Chem. 41, 2781 (1963)

75 C. L. Liotta and D. F. Smith, Jr., Chem. Commun. 416 (1968); also private communication

76 H. H. Jaffé, Chem. Rev., 53, 191 (1953)

77 C. L. Liotta, Chem. Commun., 388 (1968); also private communication.

78 M. Charton, J. Org. Chem., 34, 278 (1969)

79 E. Baciocchi and G. Illumimati, Prog. Phy. Org. Chem. 5, 1 (1967)

80 E. Berliner, Prog. Phy. Org. Chem., 2, 253 (1964)

81 J. McKelvey, private communication

82 P. B. D. De la Mare and J. H. Ridd, "Aromatic Substitution, Nitration and Chlorination", Academic Press, Inc., New York, 1959

83 G. A. Olah, S. J. Kuhn and B. A. Hardie, J. Am. Chem. Soc., 86, 1055 (1964)

84 H. C. Brown and J. D. Brady, J. Am. Chem. Soc., 74, 3570 (1952)

85 J. S. Hogg, D. H. Lohmann and K. E. Russell, Can. J. Chem. 39, 1588 (1961)

86 C. Gardner Swain, W. H. Stockmayer and J. T. Clarke, J. Am. Chem. Soc., 72, 5426 (1950)

87 J. A. Howard and K. U. Ingold, Can. J. Chem. 41, 1744 (1963)

88 E. S. Huyser, J. Am. Chem. Soc. 82, 394 (1960)

89 G. A. Russell and R. C. Williamson, Jr., ibid, 86, 2357 (1964)

90 G. A. Olah, S. J. Kuhn and S. H. Flood, ibid, 84, 1688 (1962)

91 S. H. Hastings and F. A. Matsen, ibid, 70, 3514 (1948)

92 Handbook of Chemistry and Physics , 50, F-158 (1969); W. H. Dibeler, J. Chem. Phys. 47, 219 (1967)

93 M. C. Sauer, J. Phy. Chem. 71, 3311 (1967)

94 D. M. Hunten and M. B. McElroy, Reviews of Geophysics 4, 303 (1966)

95 M. C. Sauer, Jr. and L. M. Dorfman, J. Am. Chem. Soc. 87, 3801 (1965)

96 I. W. M. Smith, Trans. Faraday Soc. 64, 378 (1968)

97 G. A. Hamilton, B. S. Ribner and T. M. Hellman, Advan. Chem. Ser., 77, 15 (1968)

98 N. J. Turro, "Molecular Photochemistry", W. A. Benjamin, Inc., New York, 1967, p 69

99 E. E. van Tamelan and D. Carty, J. Am. Chem. Soc. 89, 3922 (1967)

100 F. W. McLafferty, "Interpretation of Mass Spectra", W. A. Benjamin, Inc., New York, 1966, p 210.

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