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THESIS

CHLORINATED POLLUTANT PHOTODYNAMICS

Submitted by

Gerald David Nordblom

In partial fulfillment of the requirements

for the Degree of Doctor of Philosophy

Colorado State University

Fort Collins, Colorado

April, 1973

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COLORADO STATE UNIVERSITY

April, 1973

WE HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER OUR SUPERVISION BY GERALD DAVID NORDBLOM ENTITLED CHLORINATED POLLUTANT PHOTODYNAMICS BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

Committee on Graduate Work

Adviser

Head of Department

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ABSTRACT OF THESIS

CHLORINATED POLLUTANT PHOTODYNAMICS

1, 1, 1-Trichloro-2, 2-bis(p-chlorophenyl) ethane (DDT) was photolyzed in ethanol and cyclohexane with 3100 Å light. Under nitrogen the reaction yielded 1, 1-dichloro-2, 2-bis(p-chlorophenyl) ethane and HCl. The reaction is quenched by oxygen and inhibited by n-hexyl mercaptan. A mechanism involving the 2, 2-bis(p-chlorophenyl)-1, 1-dichloroethyl radical is proposed. The photochemistry of DDT was found to evolve from a triplet excited state. Photolysis at 2537 Å produced a complex reaction mixture and was not quenched by piperylene or oxygen or inhibited by mercaptan. Oxygen quenching at 3100 Å may explain the inefficiency of DDT degradation by sunlight.

Two DDT analoges, N-(α-trichloromethyl-p-methoxybenzyl)-p-methoxyaniline and N-(α-trichloromethyl-p-methoxybenzyl)-p-methylaniline were photolyzed in diethyl ether under oxygen with 3100 Å light. Quantitative yields of p-methoxy-α, α-dichloroacetophenone and p-methoxy or p-methylanilinium hydrochloride were formed. The results are explained using an electron transfer mechanism.

Photolysis of 4, 4'-dichlorobiphenyl (DCB) in alcoholic solvents under nitrogen at 3100 Å yielded 4-chlorobiphenyl (MCB) and HCl.

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The reaction is quenched by oxygen and inhibited by n-hexyl thiol, t-butyl disulfide and to a small extent di-n-butyl sulfide. Photolysis in CH_3OD did not lead to deuterium incorporation in MCB.

Photolysis in non-alcoholic solvents yielded complex mixtures of products arising from an apparent radical reaction. In diethyl ether in the presence of CF_3CO_2H photolysis of DCB at 3100 Å yielded only MCB. Photolysis with CF_3CO_2D produced a kinetic isotope effect of 7.0. A mechanism involving an exiplex between an excited state of DCB and solvent is proposed.

Gerald David Nordblom
Chemistry Department
Colorado State University
Fort Collins, Colorado 80521
April, 1973

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Special recognition is due my wife Marilynn for her unending encouragement and devotion.

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CHAPTER I

INTRODUCTION

1, 1, 1-Trichloro-2, 2-bis(p-chlorophenyl) ethane (DDT) has been used as an insecticide for over 25 years. In recent years people have become aware of its persistence in the environment and its adverse ecological effects. In our work we have studied in detail the mechanism of direct DDT photolysis in hopes of gaining a better understanding of the pesticide's longevity. We have also attempted to produce pesticides which are photochemically labile under environmental conditions.

The main objectives of the present DDT research are (1) to determine the role of oxygen in the photodecomposition mechanism; (2) to determine the nature of the excited state responsible for the primary photochemical process; (3) to study the effect of solar light (versus ultraviolet light) on the photochemistry; and (4) to synthesize photoreactive pesticides.

Polychlorinated biphenyls (PCBs) are a class of industrial chemicals that have received much recent attention because of their adverse effects. In our research we have attempted to elucidate the photochemical products and mechanism of a PCB model, 4, 4'-dichlorobiphenyl (DCB).

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CHAPTER II

LITERATURE REVIEW

A. Photochemistry of DDT

The first reports of DDT photoreactivity were observations concerning agricultural applications. Linquist and co-workers (1) reported that DDT applied to plywood surfaces lost insecticidal activity when exposed to sunlight or G. E. 30 watt lamps for 3 days. Turell (2) found that DDT applied to plant leaves was also deactivated by sunlight.

The possibility of chemistry occurring in the early field studies led to the first laboratory experiments. Wichmann et al. (3) found that solid samples of the pesticide and several of its metabolites were photoinert, while benzene solutions, when exposed to ultraviolet light, produced yellow tars. Fleck (4, 5) observed that ethanol solutions of DDT, when photolyzed in quartz tubes by 360 watt mercury lamps, produced HCl and a compound identified as 2, 3-dichloro-1, 1, 4, 4-tetrakis(p-chlorophenyl)-2-butane. Roburn (6) photolyzed a thin film of DDT with 2537 Å lamps for several days and identified 1, 1-dichloro-2, 2-bis(p-chlorophenyl)ethylene (DDE) and 4, 4'-dichlorobenzophenone (DDCO) as photoproducts.

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When Fleck (4, 5) observed that DDT photolyzed in a γ-valerolactone solution yielded DDCO he proposed that upon photolysis DDT eliminated HCl forming DDE which was then oxidized to the ketone. The first extensive mechanistic study was done by Miller et al. (7). They found that solid DDT and hexane solutions of the pesticide were photoreactive under nitrogen. The products isolated were DDE, DDCO, 1, 1-dichloro-2, 2-bis(p-chlorophenyl) ethane (DDD), p-chlorobenzoic acid and 1, 1-bis(p-chlorophenyl) acetic acid. The radical character of the reaction was tested by using n-butyl mercaptan and iodine as scavengers. The yield of DDD increased in the presence of the thiol and decreased with I_2. This led the authors to propose the following mechanism:

$$DDT \xrightarrow{h\nu} DDT^*$$

$$DDT^* \longrightarrow (Cl\text{-}C_6H_4)_2CH\text{-}\dot{C}Cl_2 + \cdot Cl$$

I

$$I + DDT \longrightarrow DDD + (Cl\text{-}C_6H_4)_2\dot{C}\text{-}CCl_3$$

II

$$I + Cl\cdot \longrightarrow DDE + HCl$$

$$Cl\cdot + DDT \longrightarrow II + HCl$$

$$Cl\cdot + C_6H_{14} \longrightarrow \cdot C_6H_{13} + HCl$$

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$$I + II \longrightarrow DDT + DDE$$

A quantum yield of 0.16 for the disappearance of DDT was given as evidence of a short chain mechanism. Plimmer and co-workers (8) studied the 2537 Å photodecomposition of DDT in oxygenated methanol. The products included those reported by Miller. In addition, several compounds were isolated which the authors propose arose from oxygen trapping of radical I in the above scheme.

Sherman et al. (9) studied the γ-radiation of DDT in 2-propanol. The major products were DDD, HCl and acetone. A mechanism similar to Miller's (7) was hypothesized, with radical chains of twelve or more. They also reported that the 2537 Å photolysis of DDT in 2-propanol involved a chain process.

Miller and co-workers (10, 11) have shown that aromatic amines can induce the photodecomposition of DDT in the presence of oxygen. Photolysis of the insecticide with 3100 Å light in methanol containing N, N-diethylaniline (DEA) yielded DDD, DDE, DDCO, methyl-1, 1-bis-(p-chlorophenyl)acetate, α, α-bis(p-chlorophenyl)-p-diethylamino acetophenone and diethylaniline hydrochloride as major products. Small quantities of 2, 3-dichloro-1, 1, 4, 4-tetrakis(p-chlorophenyl)-2-butene, 1, 1-bis(p-chlorophenyl)-2-(p-diethylaminophenyl)-2-methoxy ethylene and 1, 1-bis(p-chlorophenyl)-2, 2-bis(p-diethylaminophenyl) ethylene were also isolated. The reaction, which is proposed to

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involve a charge transfer process, was found to be general for alkyl halides.

B. DDT Analoges

In the 26 years since DDT was introduced, extensive research has failed to produce an attractive alternative for many DDT applications. However, the very properties (12) that make DDT such an effective insecticide-its stability, low water solubility (0.002 ppm) and high lipid solubility (ca. 100,000 ppm)-cause ecological magnification (13), the accumulation and concentration of DDT in a food chain system. The growing concern about the effects of DDT on the environment has led to biodegradability studies of DDT analoges, i.e., pesticides with the same general structure. Metcalf and co-workers (12) examined the relationship of varying the ring functional groups of DDT with the ability of insects and mice to metabolize the pesticides. Alkoxy groups, especially methoxy (METHOXYCHLOR), gave compounds that were comparable to DDT in insect toxicity but more biodegradable. The authors propose enzymatic O-dealkylation as the primary detoxification process resulting in phenolic compounds which can be physically removed from the biological system. This would reduce the amount of ecological magnification in a food chain. Several of the important metabolic reactions are shown below:

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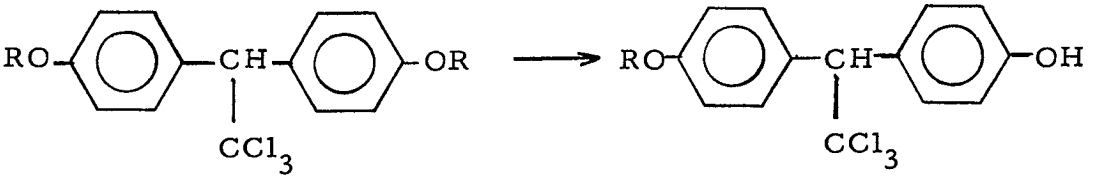
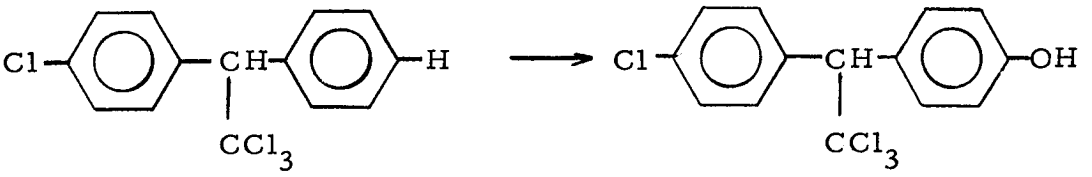
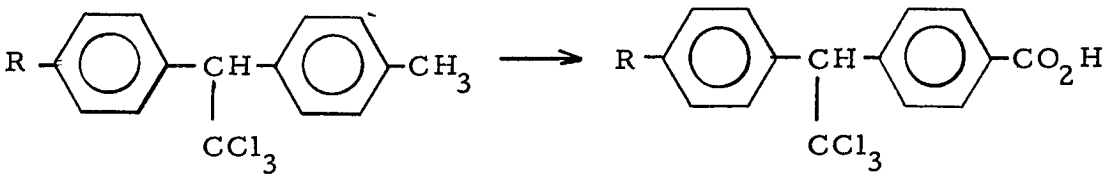
O-Dealkylation



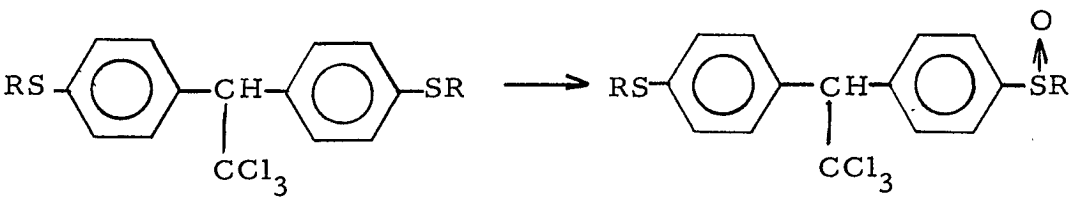
Hydroxylation



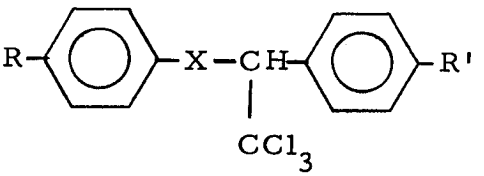
Side chain oxidation



Sulfide oxidation



In each case the resulting metabolite would be susceptible to removal from a biological system due to its increased water solubility and concomitant decreased lipid solubility. This phenomenon was noted again by Metcalf's group (14) when they studied compounds of the general class:



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When the derivative with R=R'=C_2H_5O, X=NH, ethoxyaniline, was metabolized by housefly, caterpiller or mouse liver homogenate several products were isolated including the mono- and bis-phenolic derivatives. Two minor products were p-ethoxyaniline and p-ethoxy-α,α-dichloroacetophenone.

To study the effects and biodegradability of pesticides, Metcalf and co-workers (15) have developed a model ecosystem. The closed system has a terrestrial-aquatic interface and a seven-unit food chain, Sorghum (plant), Estigmene (larva), Oedogonium (algae), Physa (snail), diatoms, plankton and Gambusia (fish). The ethoxyaniline compound was applied to the sorghum and allowed to interact with the ecosystem for 33 days. The metabolites found within the different components of the ecosystem were the same as those described above plus p-ethoxybenzoic acid. An important discovery was that the ecological magnification of the ethoxyaniline from the water to the fish was found to be 0.7 compared to 1500 for DDT. Although 37 different amines, ethers and thio ethers were tested for insecticide activity, only the ethoxyaniline compound's biodegradability was studied.

Liu et al. (16) were the first to design a DDT analoge to take advantage of photodecomposition pathways. By introducing 2-chloro-5-methoxy phenyl groups for the normal p-chlorophenyl moieties in DDT a 30 nm bathochromic shift in the absorption was accomplished. The authors reasoned that this would cause the analoge (MPA) to be

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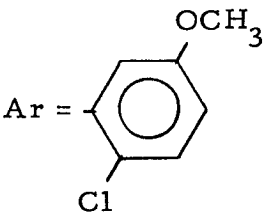
more photolabile than DDT. When MPA was photolyzed by 3000 Å light in cyclohexane or by sunlight in the solid state a photodecomposition pattern similar to that for DDT was observed, i.e.,

$$(Ar)_2CH\text{-}CCl_3 \xrightarrow{h\nu} (Ar)_2C{=}CCl_2 + (Ar)_2CHCHCl_2$$

$$(Ar)_2CHCH_2Cl + (Ar)_2CO$$



The photochemistry in solution was found to be facile (97% in 23 hr) under either nitrogen or oxygen compared to the sunlight photolysis under air (5% in 28 days).

C. Polychlorinated Biphenyl Photochemistry

Polychlorinated biphenyls (PCBs) are industrial chemicals which have received much attention over the last several years (17, 18). Once introduced into the environment PCBs are stable and accumulate in food chains in the same manner as DDT.

Very little is known about the photochemistry of PCBs. Hutzinger and Safe (19) found that when 2, 4, 6, 2', 4', 6'-hexachlorobiphenyl was irradiated with 3100 Å light in hexane, dechlorinated and isomerized products were formed as observed by glc mass

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spectroscopy. In alcohlic solutions photoproducts appeared that contained oxygen. The actual structures were never determined. The same group (20) studied the relationship of photoreactivity to the extent of chlorination. When octachlorobiphenyls were photolyzed for 24 hr in hexane under nitrogen less than 1% starting material remained. Under similar conditions tetrachloroderivatives reacted to a lesser extent, about 70%. Hutzinger and Safe also studied the photodecomposition of a commercially available biphenyl mixture, AROCHLOR 1254 (54% chlorination), in thin films and aqueous solutions. The primary processes observed were dechlorination and hydroxylation. Bills and co-workers (21) studied the photolysis of AROCHLOR 1254 in different solvents and found that decomposition (dechlorination) proceeded fastest in hexane followed by water and benzene.

Zabik et al. (22) photolyzed 3,4,3',4'-tetrachlorobiphenyl in hexane with 3000 Å light and observed a stepwise dechlorination process, i.e., the tetrachloro compound led to 3,4,4'-trichlorobiphenyl which produced 4,4'-dichlorobiphenyl and finally the very slow formation of the 4-chloro derivative (1% in 150 hr). Hustert and Korte (23) reported a similar pattern for several hexa and tetrachlorinated biphenyls.

It is obvious from the studies mentioned above that very little is known about the mechanism of PCB photodecomposition. This is

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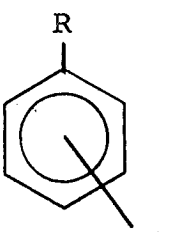
due primarily to the complexity of the compounds photolyzed and the resulting large number of products formed.

Kharasch et al. (24) photolyzed the 4-halobiphenyls in benzene with a 2537 Å radiation source and observed reductive dehalogenation and arylation. 4-chlorobiphenyl was found to photoreact 3% in 24 hr compared to 70 and 100% for the bromo and iodo compounds respectively. This difference was attributed to the order of carbon-halogen bond strengths.

Although few reports of PCBs photochemistry exist in the literature, other chloroaromatic systems have been studied. A great deal of work has centered on the general class of compounds;



1-5

where R is -OH (25), -H (26), $-CO_2H$ (27), $-NHCOC_2H_5$ (28), $-OCH_2CO_2H$ (29) and $-CH_2CO_2H$ (30, 31), because these materials are used to varying degrees as herbicides. Photolysis in aqueous solutions or as thin films generally result in replacement of the chlorines with hydroxyl groups or photoreductive dechlorination. The side group, R, may also experience photoalteration in some cases, i.e.,

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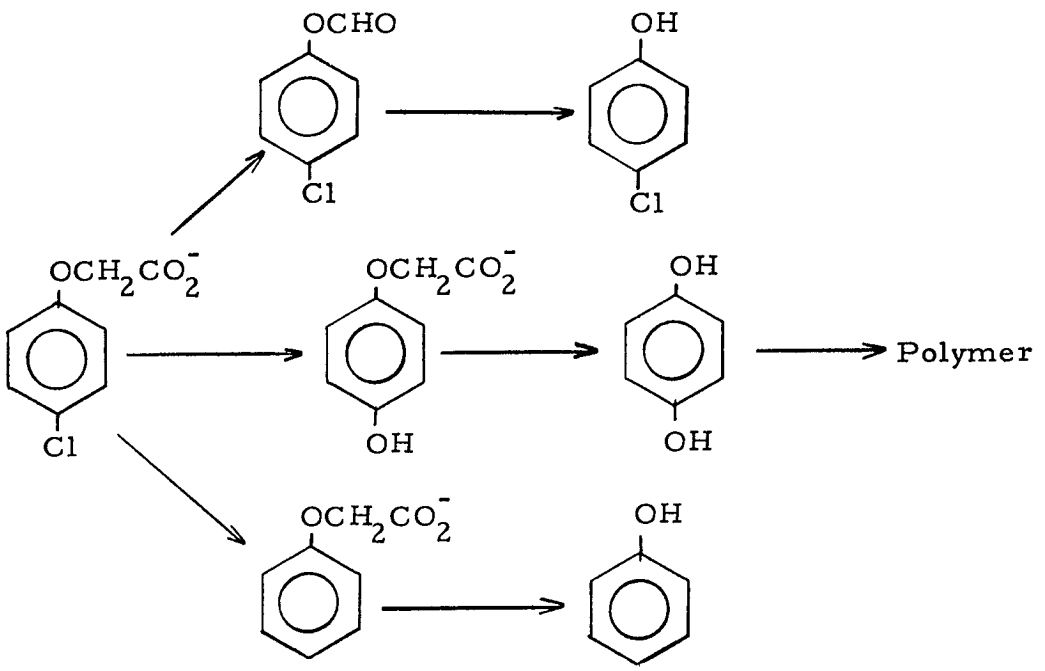
$$-NHCOC_2H_5 \longrightarrow -NH_2$$

$$-OCH_2CO_2H \longrightarrow -OH$$

$$-CH_2CO_2H \longrightarrow -CO_2H$$

An example of the above processes is the proposed (29) photodecomposition pathways of the herbicide 4-CPA, the sodium salt of 4-chlorophenoxyacetic acid.



Crosby (32) has proposed that the hydroxide ion present in water is responsible for displacement for chlorine via a photonucleophilic process, i.e., attack by a nucleophile at electron deficient sites of the photoexcited intermediates (33). Pihney and Rigby (34) found that when m-chlorophenol was irradiated by 125 w, quartz Hg lamps in 2-propanol, ethanol or dioxane the predominant products

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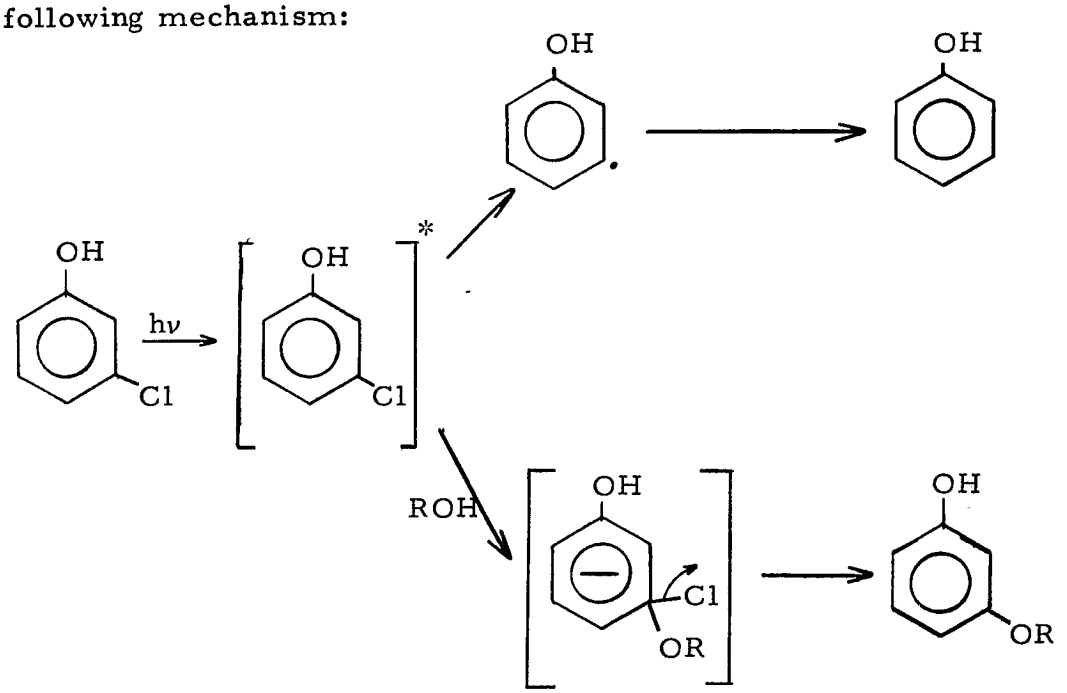
were replacement products not phenol. The authors propose the following mechanism:



A high energy light source generally must be used to induce photonucleophilic attack by neutral species (32). Indeed, the only nucleophile besides hydroxide ion (40) reported to be effective with 3100 Å light is cyanide ion (35, 36). Photolysis in non-aqueous solvents with a 3100 Å radiation source will give mainly photoreductive dechlorination products (26).

Crosby (32) has used the photonucleophilic concept to explain hydrogen replacement of chlorine in neutral methanol by proposing that the attacking nucleophile is free hydride ion. The evidence cited is the fact that the photolysis of pentachlorophenol leads primarily to 2, 3, 5, 6-tetrachlorophenol. This mechanism is highly unlikely since free hydride ions will not be present at neutral pH.

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Plimmer (37) has suggested that photoreduction occurs via a homolytic C-Cl cleavage producing a phenyl radical which abstracts hydrogen from solvent. Pihney and Rigby (30) studied the photolysis of p-chlorophenol and p-chloroacetic acid under nitrogen in ethanol and 2-propanol. They found that pinacol was formed in good yield, > 50%, and that the rate of photolysis was faster in 2-propanol than in ethanol suggesting a mechanism similar to that proposed by Plimmer (37).

Havinga and Kronenberg (38, 39) have pointed out that in photonucleophilic reactions there is a meta activation effect on the excited state of the aromatic compound. This would explain why m-chlorophenol leads to solvent displacement of chlorine (34) while the para derivative yields only phenol (30).

The photochemistry of aryliodides has been proposed to arise mainly from homolytic cleavage of the C-I bond giving an aryl radical (41).

D. Sulfur Quenching

Cohen and co-workers (42) reported in 1962 that aryl mercaptans and disulfides efficiently inhibit the photoreduction of benzophenone to benzpinacol by 2-propanol. A similar phenomena was observed in methyl-2-octylether (43). When 0.5 M degassed solutions of benzophenone were irradiated with a Hanovia high pressure lamp for 18 hr the results in the following table were observed.

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Inhibition of Benzophenone Photoreduction

Inhibitor		(PhCOH) Formed
Compound	mol/l	%[2]
------	------	100
PhSSPh	0.0060	4
PhSSPh	0.0136	0
PhSH	0.0090	7
PhSH	0.0214	0
PhSPh	0.0220	100

Efficiency versus time studies showed that the inhibitor was not consumed. A plot of % inhibition vs. concentration of sulfur compound was linear to about 80% inhibition then remained constant. The data for ArSH and ArSSAr (Ar = mesityl) lie on the same line when the disulfide concentrations were doubled which implied that the inhibition was a function of RS·. For this to be true there must be a labile equilibration of ArSSAr and ArSH. 0.375 mol Ph_2CO was irradiated in the presence of 0.00437 mol ArSSAr for 2 hours resulting in a mixture of 72% ArSH and 28% ArSSAr. When 0.00872 mol ArSH was used as inhibitor the same 72:28 ratio was obtained. The photolysis of the disulfide alone in the alcohol produced only 8% ArSH indicating that benzophenone is vital in the sulfur equilibration.

To determine if 2-propanol enters into the inhibitory process the ketone and the sulfur compounds were irradiated alone in optically active 2-octanol resulting in no racemization. However, the

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photolysis of benzophenone in the presence of either inhibitor led to the loss of optical activity.

To explain the data Cohen proposed the following mechanism:

$$Ph_2CO \xrightarrow{h\nu} Ph_2CO^*$$

$$(CH_3)_2CHOH + Ph_2CO^* \longrightarrow \underset{1}{Ph_2\dot{C}OH} + \underset{2}{(CH_3)_2\dot{C}OH}$$

$$1 + ArSSAr \longrightarrow Ph_2CO + ArSH + ArS\cdot$$

$$1 + ArS\cdot \longrightarrow Ph_2CO + ArSH$$

$$2 + ArSH \longrightarrow (CH_3)_2CHOH + ArS\cdot$$

The authors refer to the process as a "chain inhibition of a non-chain reaction." The sulfur compounds provide a pathway to complete the following process;

$$Ph_2\dot{C}OH + (CH_3)_2\dot{C}OH \longrightarrow Ph_2CO + (CH_3)_2CHOH$$

which is very favorable thermodynamically but unfavorable kinetically.

Cohen's group (44) found the photoreduction of acetophenone to also be retarded by disulfides and mercaptans but not sulfides. The observation that the inhibition rate decreased as the reducing agent was changed from 2-propanol to α-methylbenzyl alcohol to benzhydrol substantiates the original mechanism.

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Cohen and Sherman (45) found the same retardation effect when bezophenone was irradiated with ^{60}Co γ-rays. This study and one in which the same authors (46) examined the flash photolysis of Ph_2CO in 2-propanol showed that the sulfur compounds were not affecting the ketone triplet state or its initial abstraction of a hydrogen atom.

Wagner and Zepp (47) found that in benzene solutions n-butyl mercaptan quenched the excited triplet states of acetophenone. By measuring the phosphorescence of the ketone the following data was obtained:

Quencher	$k_q T (M^{-1})$
C_4H_9SH	78
C_4H_9SD	74
2,5-dimethyl hexa-2,4-diene	26,000

From the $k_q T$ (quenching efficiency) values two things are apparent, the quenching process does not involve abstraction of hydrogen from the mercaptyl group and the thiols are very poor quenchers compared to the diene which deactivates the ketone at a diffusion controlled rate (48).

Cohen and Guttenplan (49) observed that di-n-butyl sulfide acted as a benzophenone excited state quencher and a weak photoreducing agent. The quenching efficiency was approximately 50 times that

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reported for n-butyl mercaptan (47). The authors proposed the following mechanism:

$$Ph_2CO^* + RSCH_2R' \longrightarrow {}^3(Ph_2\dot{C}\bar{O}\cdot\ R\overset{+}{\dot{S}}CH_2R')$$

$$^3 \longrightarrow Ph_2CO + RSCH_2R'$$

$$^3 \longrightarrow Ph_2\dot{C}OH + RS\dot{C}HR'$$

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CHAPTER III

EXPERIMENTAL

A. Instrumentation

Gas Chromatography--A Bendix model 2110 gas chromatograph equipped with electron capture detector was used with a 6 ft x $\frac{1}{2}$ in Teflon-lined aluminum column packed with 5% OV-1 on 60/80 mesh Chromosorb W. Operating conditions were: injection port 170-180°, column oven 180° and flow rate 35 ml/min. Preparative collection was performed on a F and M Hewlett-Packard model 5750 gas chromatograph equipped with thermal conductivity detector and splitter. The column employed was a 6 ft x $\frac{1}{2}$ in aluminum column packed with 5% SE 30 on 60/80 mesh Chromosorb W. Conditions were: flow rate 30 ml/min, injection port 220° and column oven 250°.

Ultraviolet Spectra--All ultraviolet spectra were obtained with a Cary 17 spectrometer.

Nuclear Magnetic Resonance Spectra--All spectra were obtained on a Varian T-60 spectrometer with chemical shifts reported in δ. Deuterochloroform with 1% TMS was used as solvent.

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Infrared Spectra--Measurements were made on a Perkin-Elmer model 457 grating spectrometer. Spectra of solids were obtained from KBr pellets and liquids as smears between salt plates.

Mass Spectra--Mass spectral data was measured with an A. E. I. model MS-12 spectrometer using a direct probe.

Fluorescence Emission Spectra--Spectra were obtained on a Hitachi model MPF-2A Fluorescence Spectrometer.

Melting Points--A Laboratory Devices Mel-Temp melting point apparatus was used. Temperatures are uncorrected.

Photolyses--A Rayonet photochemical reactor, equipped with merry-go-round and sixteen 2537, 3100 or 3500 Å lamps was used. Samples were photolyzed in Pyrex tubes at 3100 and 3500 Å while quartz tubes were used for 2537 Å irradiation. Degassing was accomplished by 5 min nitrogen flush at 0° or six freeze-thaw cycles at 0.005 mm Hg followed by sealing in vacuo.

B. Synthesis

Synthesis of N-(α-trichloromethyl-p-methoxybenzyl)-p-methoxyaniline (DMA) and N-(α-trichloromethyl-p-methoxybenzyl)-p-methylaniline (MMA)--The two amines were prepared by Metcalf's method (14). Mp DMA 110-111°, mp lit. (14) 112°. Mp MMA 85-85°, mp lit. (14) 86°. The nmr spectrum of DMA displayed singlets at 4.96 (1H), 4.22 (1H), 3.68 (3H), 3.75 (3H), a doublet at 6.67 (4H) and an

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AA'XX' system (4H), A 6.85, X 7.52 (J_{AX} = 4.5 cps). The nmr spectrum of MMA had singlets at 5.08 (1H), 4.59 (1H), 3.84 (3H) and 2.22 (3H), a multiplet at about 6.95 (4H) and an AA'XX' system (4H), A 6.83, X 7.60 (J_{AX} = 4.5 cps).

Synthesis of p-methoxy-β,β-dichlorostyrene--The compound was prepared using Speziale and Ratts' method (50) yielding a clear liquid, bp 70-73° at 0.05 mm Hg. The uv spectrum showed two bands, λ_{max} 2760 Å, ϵ = 13,300 and λ_{max} 2260 Å, ϵ = 7550. Absorptions in the nmr spectrum were singlets at 6.90 (1H) and 3.85 (3H) and an AA'XX' system (4H), A 6.90, X 7.54 (J_{AX} = 4.2 cps). The ir spectrum displayed peaks at 2992, 1608 and 1510 cm^{-1}. The mass spectrum showed a parent peak with m/e equal to 202 with P, P+2 and P+4 in the ratio 1.00:0.70:0.11 indicating two chlorine atoms. Other prominent peaks were 187 (48.5%), 159 (41.5%), 123 (26.2%) and 89 (33.6%). Anal. Calculated for $C_9H_8OCl_2$: C, 53.23; H, 3.97; Cl, 34.92. Found: C, 53.48; H, 3.92; Cl, 34.82.

C. Photolyses

Photolysis of DDT--DDT (17.7 mg, 0.5 mmol) was dissolved in 50 ml of distilled 95% ethanol or spectral grade cyclohexane. 5 ml samples were placed in 15 x 160 mm culture tubes. The atmosphere, oxygen or nitrogen, was accomplished by a five min flush at 0° with the appropriate gas. The HCl was identified by precipitation of AgCl

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with a $AgNO_3$ solution and by measuring pH with a pH meter. DDD was identified by comparing retention times of authentic samples and by co-injection. In sensitized reactions, the concentration of the sensitizers (Baker Sensitizer Kit) was adjusted so as to absorb at least 95% of the radiation. Further purification of DDT was accomplished by four recrystallizations from 95% ethanol (10 gm/75 ml) followed by zone refining on a Fisher Zone Refiner. L-(-)-tryptophan, t-butyl disulfide, n-hexyl mercaptan, di-n-butyl sulfide and folic acid were reagent grade and used without further purification. DEA and piperylene were distilled under nitrogen.

Photolysis of DDE--DDE (15.9 mg, 0.5 mmol) was dissolved in 50 ml of 95% ethanol. Sensitizer's (Baker Sensitizer Kit) concentrations was set so that they absorbed at least 95% of the radiation. 5 ml samples were placed in 15 x 160 mm culture tubes, degassed with a five min nitrogen flush at 0° and capped with serum caps. The reaction mixture was analyzed with the Bendix glc.

Photolysis of DMA and MMA--DMA (0.907 gm, 2.5 mmol) or MMA (0.867 gm, 2.5 mmol) was dissolved in 100 ml of reagent grade ether. When dry ether was used a sealed container of Fisher anhydrous ether was opened and used immediately. Degassing was accomplished by both nitrogen flush and six freeze-thaw cycles at 0.005 mm Hg followed by sealing in vacuo. Photolysis of five ml samples under air produced a yellow solution and light brown

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precipitate. The solid material was filtered, washed with 5% $NaHCO_3$ solution and extracted with ether. The ether was removed under reduced pressure. The resulting residues were analyzed by comparing their nmr spectrum with the spectrum of authentic p-anisidine (DMA photolysis) and p-toluidine (MMA photolysis). This was reconfirmed by co-injection analysis on the F and M glc.

In DMA photolysis the filtrate was concentrated under reduced pressure yielding a yellow oil which was purified by kügelrohr distillation yielding a white solid that was identified as p-methoxy-α,α-dichloroacetophenone. Mp 74-75°, mp lit. (51) 75-76°. The nmr spectrum gave singlets at 6.72 (1H) and 3.96 (3H) and an AA'XX' system (4H), A 7.03, X 8.18 (J_{AX} = 4.2 cps). The mass spectrum showed a parent peak with m/e equal to 218 with P, P+2 and P+4 in the ratio 1.00:0.68:0.15 indicating two chlorine atoms. Other prominent peaks were 184 (2.4%), 155 (7.4%), 135 (100%), 107 (8.5%), and 77 (28.5%). The nmr spectrum and mass spectral fragmentation pattern correspond very well with data found for p-ethoxy-α,α-dichloroacetophenone (14). In MMA photolysis, filtration of the p-toluidine yielded a yellow oil. Analysis by nmr gave a spectrum that was a combination of the spectrum for starting material and p-methoxy-α,α-dichloroacetophenone. The relative amounts as determined by integration were found to be 68% MMA and 32% acetophenone which corresponds with 35% recovery of p-toluidine.

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Photolysis of p-methoxy-β,β-dichlorostyrene--The styrene (131 mg, 0.65 mmol) was dissolved in 50 ml diethyl ether. 5 ml samples were placed in 15 x 160 mm culture tubes without degassing and capped with serum caps. The samples were photolyzed for four hours and analyzed by glc. About 90% starting material remained and no acetophenone was formed.

The styrene (26 mg, 0.13 mmol) and DMA (125 mg, 0.15 mmol) were dissolved in 50 ml of diethyl ether. DMA (125 mg, 0.15 mmol) was dissolved in 50 ml diethyl ether for a control sample. 5 ml samples were photolyzed for 30 min without degassing. In the control experiment about 25% p-methoxy-α,α-dichloroacetophenone was formed while only 15% was formed in the presence of the styrene.

4,4'-Dichlorobiphenyl Photolysis--DCB (111.6 mg, 0.5 mmol) was dissolved in 2-propanol or cyclohexane (500 ml) to prepare a stock solution. Aliquots (5 ml) were placed in 15 x 160 cm pyrex test tubes, at which time either nitrogen or oxygen was bubbled through the sample for 5 min at 0°. In sensitized reactions, the concentration of the sensitizer was adjusted so as to absorb >95% of the radiation. Following photolysis, product analysis was carried out by glc, where retention times were compared to authentic samples. HCl was identified by following the pH with a pH meter and by the precipitation of AgCl when a $AgNO_3$ solution was added to the sample. The stability of 4-chlorobiphenyl was checked by dissolving (9.4 mg,

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0.05 mmol) in 2-propanol (50 ml) from which 5 ml samples were irradiated as above.

Azoisobutyronitrile (AIBN) Initiation--DCB (11.2 mg, 0.05 mmol) and AIBN (0.8 mg, 0.005 mmol) were dissolved in 2-propanol (50 ml). Aliquots (5 ml) were placed in Pyrex tubes degassed by six freeze-thaw cycles at 0.005 mm Hg and sealed in vacuo. The samples were placed in a Brinkman Lauda K-2/R constant temperature bath at 90° for 60 and 90 min and analyzed by glc.

Quantum Yield--Benzophenone (0.91 g, 5.0 mmol) and benzhydrol (0.92 g, 5.0 mmol) were dissolved in benzene (50 ml) and used as an actinometer. DCB (11.2 mg, 0.05 mmol) was taken up to 50 ml with 2-propanol. Two 5 ml samples of each solution were placed in long-stemmed Pyrex tubes and degass by six freeze-thaw cycles at 0.005 Hg and sealed in vacuo. The samples were irradiated for 1 hr. The amount of DCB reacted, determined by glc, was found to be 7%. Using uv spectroscopy the amount of benzophenone reacted was found to be 65%. The quantum yield was calculated to be 0.002.

Sulfur Quenching Studies--Samples of 5 ml were degassed by 5 min nitrogen flush or freeze-thaw and photolyzed. Product analysis was by glc.

Fluorescence Quenching--5.0×10^{-4} M DCB samples were made up with quencher concentrations varying from 5.0×10^{-4} to 1.0×10^{-2}. Quenchers used were n-hexyl mercaptan, di-n-butyl

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sulfide, and tert-butyl disulfide. Emission spectra were obtained on a Hitachi MPF-2A Fluorescence Spectrometer. The samples were run at room temperature without degassing.

DCB Solvent Study--DCB (11.2 mg, 0.05 mmol) was dissolved in the appropriate reagent grade solvent (50 ml). 5 ml samples were degassed by the previously described freeze-thaw process. The samples were analyzed by glc.

Kinetic Isotope Effect in CD_3OD--DCB (1.2 mg, 0.005 mmol) was dissolved in 2 ml of CD_3OD (99.5%, Aldrich). An identical solution was prepared using CH_3OH. 1 ml samples were placed in 7 x 160 mm tubes and degassed by freeze-thaw. Photolysis for 23 hours yielded 25% MCB in both solvents ($k_H/k_D = 1.0$) while photolysis for 43 hours yielded 36% MCB in CD_3OD and 35% in CH_3OH ($k_H/k_D = 0.97$).

Kinetic Isotope Effect in Diethyl Ether-CF_3CO_2D--The deuterated acid was synthesized by adding D_2O (4.0 gms, 0.2 mol) to $(CF_3CO)_2O$ (21.0 gms, 0.1 mol). The resulting mixture was distilled and the 68-70° fraction kept. Analysis by nmr showed the acid to have 96% deuterium incorporation.

DCB (56 mg, 0.25 mmol) was dissolved in 49 ml diethyl ether and 1 ml CF_3CO_2D. An identical solution was made up using CF_3CO_2H. The absorption spectrum is identical in both solutions.

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Photolysis for 48 hr yielded 35% MCB in the presence of the CF_3CO_2H and 5% in the presence of CF_3CO_2D (k_H/k_D = 7.0).

Photolysis of DCB in CH_3OD--DCB (25 mg, 0.22 mmol) was dissolved in 50 ml CH_3OD (99.5%, Stohler Isotope Chemicals). 5 ml samples were degassed by freeze-thaw process and photolyzed for 48 hr. The MCB was collected from the F and M glc. The mass spectrum was identical to the mass spectrum of an authentic sample of MCB, indicating no deuterium incorporation.

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CHAPTER IV

RESULTS AND DISCUSSION

A. DDT Photochemistry

Although the mechanism of DDT photolysis has been studied (4, 5, 7, 8), several important aspects remain unelucidated. We report here on the role of oxygen, the effect of irradiation wavelength and the nature of the excited state responsible for the primary photophysical process.

Direct Photolysis

The extent of DDT photodecomposition at 3100 Å under varying conditions is summarized in Table I.

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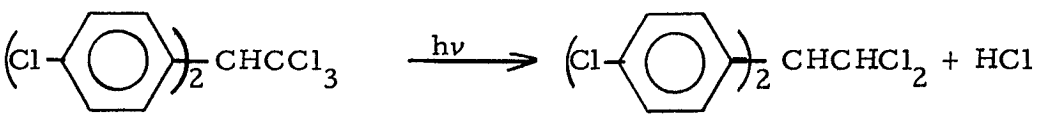
TABLE I

Direct DDT Photolysis[a]

Solvent	Radiation Time (min)	Atmosphere	Additive	%DDT[b]
Ethanol	180	O_2	-	100
	30	N_2	-	77
	60	N_2	-	63
	90	N_2	-	44
	180	N_2	-	17
	180	N_2	piperylene[c]	100
	180	N_2	n-hexyl thiol[d]	91
	180	N_2	di-n-butyl sulfide[e]	60
Methanol	180	O_2	-	100
	180	N_2	-	80
Cyclohexane	180	O_2	-	100
	180	N_2	-	58

[a] 1.0×10^{-3} mol/l DDT
[b] DDD and HCl only products
[c] 5.0×10^{-2} mol/l
[d] 5.0×10^{-3} mol/l
[e] 5.0×10^{-3} mol/l

The reaction produces only DDD and HCl.



DDT DDD

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No reaction was observed in the presence of oxygen. Under nitrogen there was a slight difference in photolysis rates in the various solvents. The relative rates in ethanol, cyclohexane and methanol was about 5:2.5:1. The difference is probably not due to changes in the absorption spectrum of DDT as the extinction coefficient at 3100 Å varies less than 2% from solvent to solvent. A more plausible explanation would be that the reaction is a radical chain process that involves hydrogen abstraction from the solvent. The trend, at least, of the reaction rates follows a similar trend in ease of hydrogen abstraction, i.e., ethanol > cyclohexane > methanol (52, 53). There appears to be no dependence on solvent polarity.

The photolysis rate is slowed by a factor of about ten in the presence of n-hexyl thiol and about two with di-n-butyl sulfide. Thiol quenching has traditionally been cited as evidence for a radical chain mechanism (9) while both sulfides and thiols have been shown to quench excited triplet states (47, 49). We believe that the greater inhibition efficiency of n-hexyl thiol is evidence for both radical trapping and excited state quenching.

Sherman and co-workers (9) found that γ-irradiation of DDT in degassed alcohol solutions produced only DDD and HCl. Inhibition in this non-photolytic system by mercaptan strongly supports a radical chain mechanism. Sherman proposed the following scheme:

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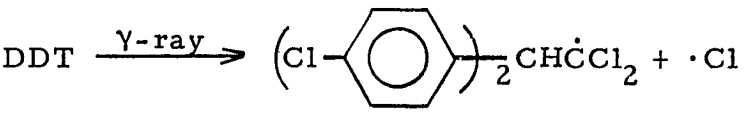

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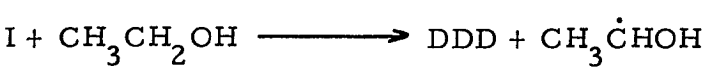
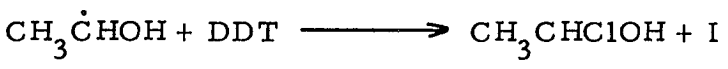
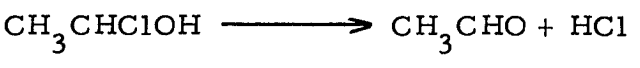
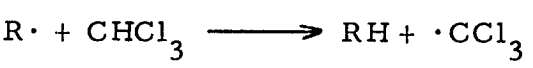
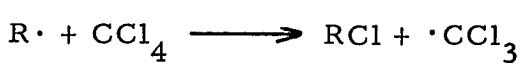






The stability of DDD in the reaction is in itself evidence that our data fits Sherman's mechanism. Reaction of a solvent radical with either DDD or DDT will produce the same intermediate, I, in analogy to chloroform (55).





Sensitization

Piperylene, a known triplet state quencher (54), very effectively quenched the photolysis of DDT. This would suggest the intermediacy of a triplet state in our system. Care was taken to keep the quencher concentration lower than 1.0×10^{-2} mol/l as high levels of piperylene can quench singlet states (56). The action of oxygen could also be attributed to triplet quenching (54).

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The mechanism can now be expanded to include the photoreactive states:

$$DDT\,(S_0) \xrightarrow{h\nu} DDT\,(S_1)$$

$$DDT\,(S_1) \longrightarrow DDT\,(T_1)$$

$$DDT\,(T_1) \longrightarrow I + \cdot Cl$$

To obtain additional evidence supporting a triplet mechanism a series of triplet sensitizers was used. The reactions were run with 1.0×10^{-3} mol/l DDT in degassed ethanol at either 3100 or 3500 Å. The sensitizer concentration was adjusted so as to absorb at least 95% of the radiation to preclude any direct photolysis. The results of this study are summarized in Table II.

The data in Table II seem straight forward, indicating that the photolysis proceeds through a triplet state that lies between 59 and 53 Kcal/mol above the ground state. Sensitization in cyclohexane gives the same results. A problem with this interpretation is that DDT should not have a triplet state with such a low energy and if it did it should not decompose to give radical I since the C-Cl bond energy is about 70 Kcal/mol for trichloro methyl groups (52). If only about 56 Kcal/mol are available, C-Cl cleavage could proceed only with additional energy either from a thermal source or another photon of light. Neither, however, is highly probable due to the short life-time of the triplet state. Phosphorescence spectroscopy (57, 58) has

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TABLE II

Triplet Sensitization of DDT Photolysis

Sensitizer	E_t[a] (Kcal/mol)	Reaction[b]
Diethylaniline	77	+
Benzophenone	69	+
Biphenyl	65	+
Phenanthrene	62	+
2-Acetonaphthone	59	+
9-Fluorenone	53	-
Pyrene	49	-
Benz(d, e)anthracen-7-one	47	-

[a] Reference 54
[b] + DDD and HCl formed, - no reaction

shown the lowest lying triplet of DDT to be about 70 Kcal/mol above the singlet ground state. This is as expected when the relative triplet energies of chlorobenzene, p-chlorotoluene and carbon tetrachloride are considered. From phosphorescence spectra (58) the triplet energy level of chlorobenzene has been placed at 72 Kcal/mol and p-chlorotoluene at 71 Kcal/mol. To verify these energies we studied the photoreduction of benzophenone (E_t = 69 Kcal/mol) in degassed ethanol at 3500 Å in the presence of 1% piperylene, p-chlorotoluene and chlorobenzene. By following the disappearance of benzophenone

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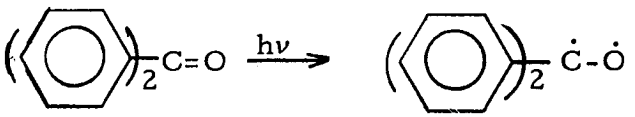
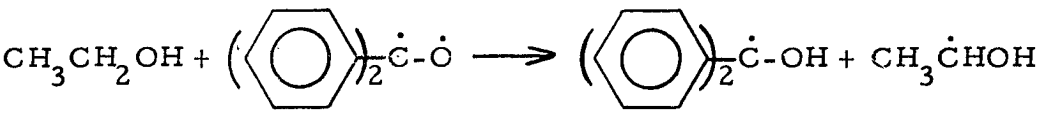
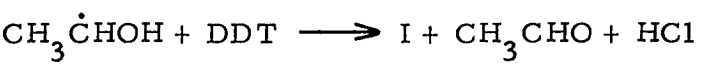
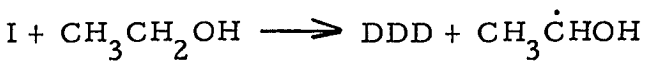
via ultraviolet spectroscopy we found that piperylene quenched the photoreduction while the chloro aromatic compounds did not, placing their triplet level higher than 69 Kcal/mol. The triplet state of the trichloromethyl moiety is also higher than that of benzophenone since the photochemistry of the ketone is not quenched by carbon tetrachloride (59).

The possibility of singlet sensitization by the compounds in Table II can be ruled out because the process would be endothermic for every sensitizer except biphenyl. The direct interaction of sensitizer with solvent giving the ethanol radical which could initiate the chain reaction is a possibility, e.g., with benzophenone:









However, phenanthrene induces the formation of DDT and is not known to photoreduce like aryl ketones.

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Involvement of a DDE impurity as a possible chain initiator was suspected. To test this hypothesis we attempted to sensitize the photolysis of DDE with the results shown in Table III.

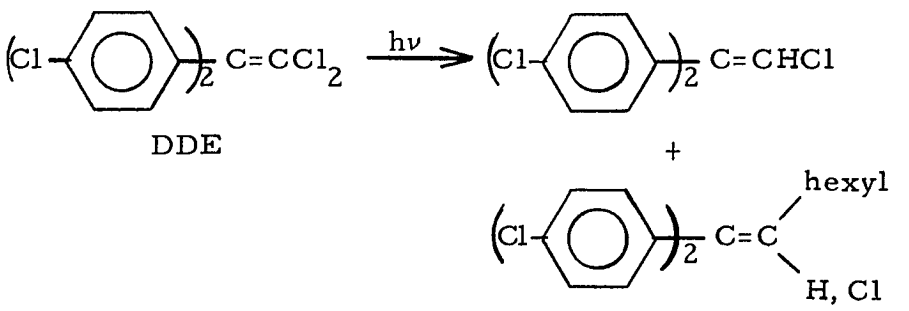
TABLE III

Triplet Sensitization of DDE Photolysis

Sensitizer	E_t[a] (Kcal/mol)	% Reaction[b c]
Benzophenone	69	12
Phenanthrene	62	0
2-Acetonaphthone	59	0
9-Fluorenone	53	0
Pyrene	49	0

[a] Reference 54
[b] 2 hour photolysis at 3500 Å
[c] 1.0×10^{-4} mol/l DDE in degassed ethanol

The photoproducts of the benzophenone sensitization were not identified although they were undoubtedly analogous to products isolated by Korte and co-workers (60) when they photolyzed DDE in hexane.



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Since the sensitization by benzophenone was slow (12% in 2 hours compared to 86% in 1 hour for DDT) the triplet energy of DDE is probably equal to or slightly lower than 69 Kcal/mol (61). This estimate was verified by emission phosphorescence spectroscopy (58).

The DDE impurity theory was further disproven by spiking a sample of DDT with 1% DDE and photolyzing the mixture. The rate of DDD formation was not affected.

The possibility of a non-DDE impurity causing the unusual photochemistry was tested by comparing photolysis rates of the DDT normally used (Aldrich Gold Label, 99+%) with a sample which had been rigorously purified (Gold Label, recrystallized four times and zone refined). There was no difference in the rate casting doubt on the impurity idea.

The nature of the initiation by triplet sensitizers, therefore, remains obscure. Since the reaction involves a radical chain it appears that there is some low energy route to radicals which could initiate DDD formation.

Aromatic Amine Photosensitization

Miller and co-workers (10, 11) observed complex reaction mixtures when DDT was photolyzed in the presence of N, N-diethylaniline (DEA) under oxygen in methanol. To account for this the authors proposed that a charge transfer complex between the first excited singlet state of DEA and the ground state of DDT was formed which

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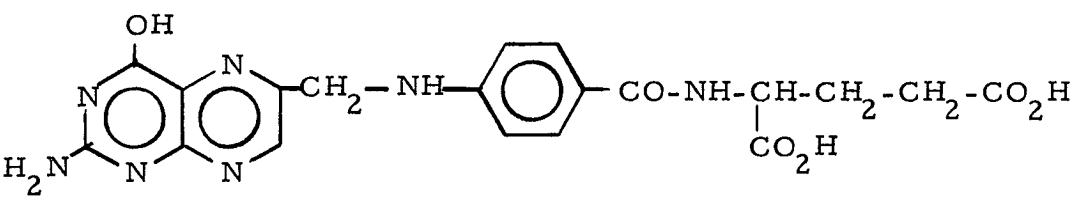
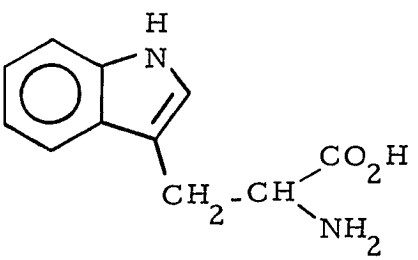
subsequently decomposed to products. In the present study sensitization of DDT photodecomposition by DEA under nitrogen produced only DDD and HCl (Table II). It appears that under oxygen the radical chain is inhibited. This inhibition may arise from several effects including radical trapping and triplet state quenching.

The fact that DEA induced DDT photodecomposition under oxygen prompted us to explore other compounds containing the aniline moiety. Of special interest were two naturally occurring compounds, L-(-)-tryptophan and folic acid.



Folic Acid



Tryptophan

The amino acid tryptophan has been the subject of much photochemical study (62), since the indole group absorbs solar radiation. Indeed, much of the photochemistry of proteins arises from the initial absorption by the tryptophan residue. The amino acid has been shown to be an efficient triplet sensitizer, E_T = 71 Kcal/mol (63).

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This was substantiated when tryptophan was found to induce the conversion of DDT to DDD and HCl under nitrogen (70% in 4 hr). In a manner analogous to DEA, tryptophan induced the photodecomposition of DDT in the presence of oxygen (30% in 4 hr).

Folic acid, a mammalian vitamin found in green plants, behaved in a similar way. Degradation of DDT was accomplished under both oxygen (20% in 5 hr) and nitrogen (56% in 4 hr).

The results of the "natural" sensitizer studies are not direct evidence that tryptophan and folic acid induced DDT photodecomposition are environmentally important degradative pathways. The results show only that such interactions are possible.

Wavelength Dependence Study

The photolysis of DDT in ethanol at 2537 Å produces a very complex reaction mixture (7, 8). To summarize our results, at 2537 Å the photolysis of DDT was not quenched or inhibited by oxygen, piperylene or n-hexyl thiol. In contrast at 3100 Å only DDD and HCl are produced (Table I) and the reaction is quenched or retarded by piperylene, oxygen and thiol. The diverse chemistry at 2537 and 3100 Å may be explained by the following energy diagram.

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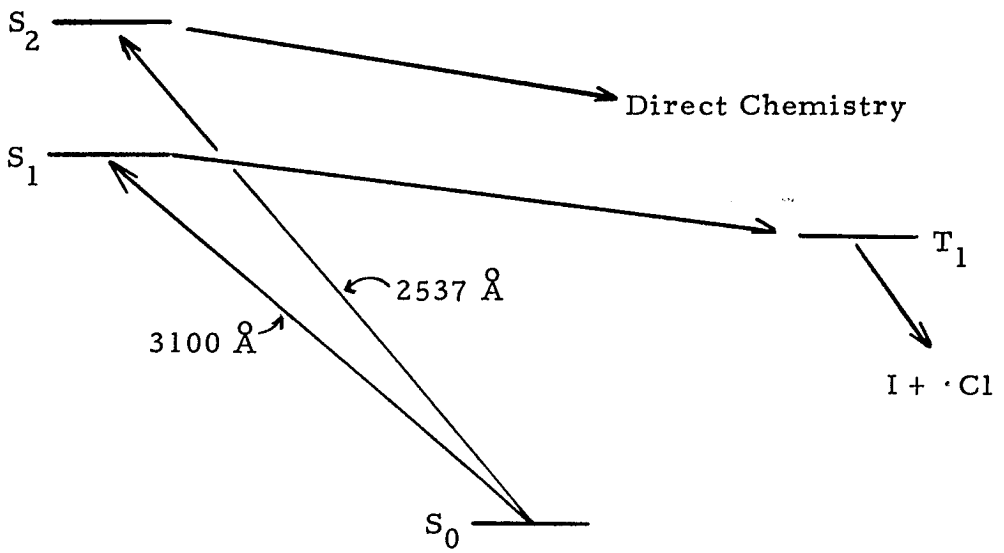

Energy Diagram for DDT

The absorption spectrum of DDT shows a weak band (ϵ=410) at about 3060 Å and an extremely intense band (ϵ=24, 300) at 2360 Å. Therefore, photolysis at 2537 Å populates a high energy singlet state, (S_2), from which direct, non-chain processes could lead to products yet not be quenched by oxygen and piperylene or inhibited by thiol. Irradiation at 3100 Å, however, would populate S_1 from which inter-system crossing to T_1 is competitive with direct chemistry and produces the simple, quenchable chemistry summarized in Table I.

The single, most important discovery evolving from this study is the quenching of solar wavelength (λ > 2900 Å) photochemistry by oxygen. This may explain the long lifetime of DDT in the environment. DDT absorbs light and is photoreactive but the reaction is quenched by atmospheric oxygen.

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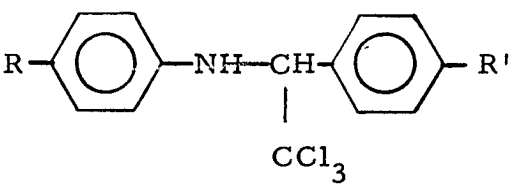
B. DDT Analoge Photochemistry

Having observed the ability of DEA to photoinitiate the decomposition of DDT in the presence of oxygen it seemed important to design a biodegradable pesticide by incorporation of the aniline moiety into the DDT structure. As noted in the literature review Metcalf and co-workers (14) prepared a series of compounds of the general structure,



but did not knowingly investigate their photoproperties.

We prepared two derivatives, N-(α-trichloromethyl-p-methoxybenzyl)-p-methoxyaniline, R = R' = OCH_3 (DMA) and N-(α-trichloromethyl-p-methoxybenzyl)-p-methylaniline, R = CH_3, R' = OCH_3, (MMA) using Metcalf's method. The ultraviolet spectral data as obtained with a Cary 17 spectrometer are compared with the spectral data of DDT in Table IV.

DMA and MMA were photolyzed with 3100 Å light in aerated diethyl ether for four hours. The photoproducts isolated were the insoluble anilinium hydrochlorides and p-methoxy-α,α-dichloroacetophenone. Yields are summarized in Table V. The accidental

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exposure of a 5.0×10^{-2} molar ether solution of DMA to the fluorescent light in the laboratory for 24 hr also afforded a quantitative yield of p-anisidine hydrochloride and the acetophenone.

TABLE IV

Ultraviolet Spectral Data for DMA, MMA and DDT

Compound	λ_{max} Å	ϵ	$\epsilon_{3100\ Å}$ [a]
DMA[b]	3055	1690	1610
	2800	2040	
	2330	18,800	
MMA[b]	2978	2220	1020
	2440	14,900	
	2145	10,000	
DDT[c]	3062	410	400
	2660 (sh)[d]	890	
	2360	24,300	

[a] Extinction coefficient at 3100 Å

[b] Diethyl ether

[c] Absolute ethanol

[d] Shoulder

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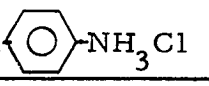
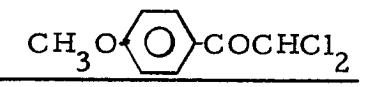
TABLE V

Photolysis of DMA and MMA

Starting material	% Reaction	Product %[a]	
			
DMA[b]	100	92	95
MMA[c]	32[d]	35	32[d]

[a] Relative to starting material

[b] 5.0×10^{-2} mol/l

[c] 5.0×10^{-2} mol/l

[d] Determined by nmr

The photolysis of DDT for four hours in aerated 95% ethanol at 3100 Å yielded no reaction.

The data in Table V is evidence for a tremendous photoactivation of the DDT analoges DMA and MMA by the incorporation of an aniline group into the pesticide structure. This may be partially due to the increased $\epsilon_{3100\ \text{Å}}$ as shown in Table IV, but the main factor is undoubtedly the non-quenchable singlet chemistry of the aniline moiety.

The mode of decomposition is unique in that it leads to the fragmentation of the carbon skeleton. Previous compounds studied have, upon degradation, only been changed functionally. Liu et al. (16) found that photolysis of 1, 1, 1-trichloro-2, 2-bis(2-methoxy-5-chlorophenyl) ethane (MPA) only altered the trichloromethyl group and Metcalf and co-workers (12) observed that when DDT analoges

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were metabolized the major changes were only found in the functional groups on the ring. However, when Metcalf et al. (14) placed tritium labeled N-(α-trichloromethyl-p-ethoxybenzyl)-p-ethoxyaniline (II) in a model ecosystem, some p-ethoxyaniline (III), p-ethoxy-α,α-dichloroacetophenone (VI) and p-ethoxy benzoic acid (V) were produced. Although the authors attribute these products to metabolism, our results suggest that they could arise from photolysis. This becomes more evident when the data from Metcalf's paper is scrutinized in detail. When the different elements of the food chain were assayed the amount of C-N cleavage products, III, IV and V, relative to the total tritium activity was as follows; water 57%, algae 36%, snail 22% and mosquito 7%. It appears that the elements in which the pesticide would absorb the most sunlight have the largest amounts of photoproducts.

From the photoproducts formed it is clear that cleavage of the molecule is between the aniline and benzyl moieties. Although the temperature of the photoreactor was only 40°, it seemed prudent to test if a dark reaction could account for this cleavage. An aerated, 5×10^{-2} mol/l ether solution of DMA was heated in a sealed, opaque system at 55 ± 1° for six hours. 100% starting material was recovered.

When considering possible modes of C-N bond rupture, two diverse types of chemistry are found. Ogata and Takagi (64) studied

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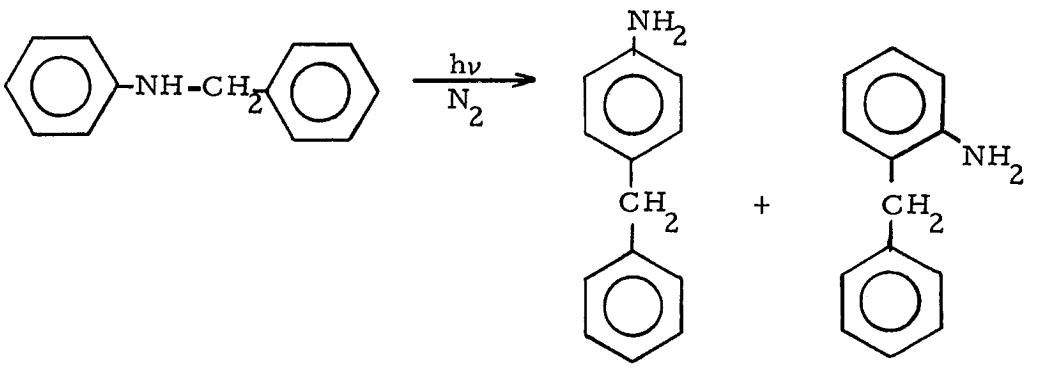
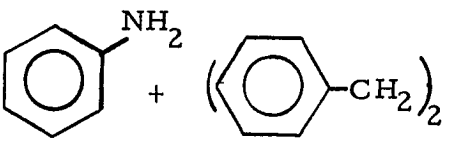
the 2537 Å photolysis of N-benzyl anilines in isopropyl alcohol-t-butyl alcohol systems. In a typical reaction the following products were formed:



Major Products



Minor Products

The mechanism proposed by the authors involves homolytic C-N bond cleavage to give anilinium and benzyl radicals in a solvent cage. Coupling in the solvent cage leads to the major products, while the minor products are produced after the intermediate radicals escape the solvent enclosure. In another analogous system Kochi and Ratcliff (65) studied the photolysis of dibenzylamine in various solvents at 2537 Å. The authors propose the intermediacy of benzyl and benzylamine radicals in the following reaction:

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$$(PhCH_2)_2NH \xrightarrow{h\nu} PhCH_3 + PhCH_2NH_2 +$$

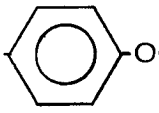
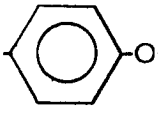
$$PhCH = NCH_2Ph + (PhCH_2)_3N +$$

$$(PhCH_2)_2$$

A series of radical reactions can be proposed for our system which start with benzyl and aniline radicals and eventually lead to the observed products, e.g., scheme I.

Scheme I

$$ArNHCHAr' \xrightarrow{h\nu} Ar\dot{N}H + Ar'\dot{C}HCCl_3 \quad (1)$$

$$Ar = \text{  } -OCH_3, -CH_3, \quad Ar' = \text{  } -OCH_3$$

$$Ar\dot{N}H + SH\,(\text{solvent}) \longrightarrow ArNH_2 + S\cdot \quad (2)$$

$$Ar'\dot{C}HCCl_3 + O_2 \longrightarrow Ar'CH(O_2\cdot)CCl_3 \quad (3)$$

$$2\,Ar'CH(O_2\cdot)CCl_3 + 2\,SH \longrightarrow 2\,Ar'CH(OH)\text{-}CCl_3 + O_2 + S\text{-}S \quad (4)$$

$$Ar'CH(OH)CCl_3 \longrightarrow \left[Ar'\text{-}C(OH)=CCl_2\right] + HCl \quad (5)$$

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$$\left[\begin{array}{c} OH \\ | \\ Ar'C = CCl_2 \end{array}\right] \longrightarrow \begin{array}{c} O \\ \| \\ Ar'C\text{-}CHCl_2 \\ VI \end{array} \qquad (6)$$

$$ArNH_2 + HCl \longrightarrow Ar\overset{+}{N}H_3\overset{-}{C}l \qquad (7)$$

The trapping of the benzyl radical to form the alcohol (steps 3 and 4) is a well established reaction (66, 67, 68).

Another possible intermediate which could lead to compound VI is p-methoxy-β, β-dichlorostyrene as shown in scheme II.

Scheme II

$$Ar'CH{=}CCl_2 + O_2 \longrightarrow \begin{array}{c} OH \\ | \\ Ar'CHCHCl_2 \end{array} \qquad (8)$$

$$Ar'CH{=}CCl_2 + H_2O \xrightarrow{H^+} \begin{array}{c} OH \\ | \\ Ar'CHCHCl_2 \end{array} \qquad (9)$$

$$\begin{array}{c} OH \\ | \\ Ar'CHCHCl_2 \end{array} + R\cdot \longrightarrow \begin{array}{c} OH \\ | \\ Ar'\dot{C}CHCl_2 \end{array} \qquad (10)$$

$$\begin{array}{c} OH \\ | \\ Ar'\dot{C}CHCl_2 \end{array} + R\cdot \longrightarrow VI \qquad (11)$$

The autooxidation of styrene with oxygen (69) would involve a peroxy radical as in step 3.

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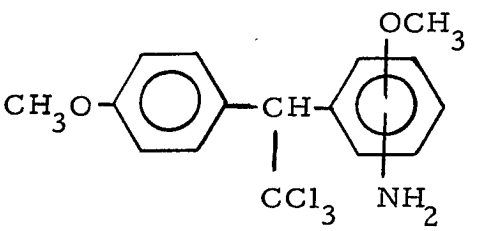
Schemes I and II provide reactions that could possibly lead to products but cannot totally explain our results. Scheme I should produce coupled products similar to those found by Ogata (64), i.e.,



If the α-trichloromethyl benzyl radical were much more stable than benzyl radical, one might expect escape from the solvent cage and no products such as those above. However, once in the bulk of the solvent the following reaction should be competitive with step 3:

$$Ar'\dot{C}HCCl_3 + SH \longrightarrow Ar'CH_2CCl_3 + S\cdot$$

Since no β,β,β-trichloroethyl anisole was found scheme I probably does not contribute significantly in our system. This was substantiated when two samples of DMA were photolyzed under identical conditions except one was under nitrogen and the other under oxygen. In both cases α,α-dichloro-p-methoxyacetophenone (VI) was formed suggesting that dissolved oxygen is not the source of carbonyl oxygen. The samples were analyzed by glc and compared to the authentic sample of VI by co-injection. To preclude the possibility of oxidation of some intermediate to the observed products following photolysis,

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the samples were tested before they were exposed to the atmosphere. To test the highly improbable possibility that the carbonyl oxygen was derived from the solvent, i.e., from the ether oxygen, the photolysis was carried out in acetonitrile with the same results. VI was formed under both nitrogen and oxygen.

The intermediacy of p-methoxy-β,β-dichlorostyrene, as in scheme II, in the formation of VI was disproved by photolyzing it under conditions similar to those in which DMA was studied. Product VI was not formed. Photolysis of a mixture of DMA and the styrene gave lower yields of VI.

The only source of carbonyl oxygen remaining is from water in the solvent. Indeed, we found that when DMA was photolyzed under nitrogen in anhydrous ether for 30 minutes no reaction took place, while photolysis under nitrogen for 30 minutes in ether saturated with distilled water afforded 20-25% formation of VI and p-anisidine hydrochloride. This result can be explained by considering the second type of unusual chemistry possible for our system.

Several groups (70, 71, 72, 73) have studied the photolytically induced interactions of amines with carbontetrachloride. For aromatic amines the proposed initial process is complexation of an excited singlet state of the amine with CCL_4 followed by electron transfer.

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$$ArNH_2 \xrightarrow{h\nu} ArNH_2^*$$

$$Ar\overset{*}{N}H_2 + CCl_4 \longrightarrow \left[ArNH_2 \cdot CCl_4\right]^*$$

$$\left[ArNH_2 \cdot CCl_4\right]^* \longrightarrow Ar\overset{+\cdot}{N}H_2 + Cl^- + \dot{C}Cl_3$$

$$Ar\overset{+\cdot}{N}H_2 + Cl^- + \dot{C}Cl_3 + RH \longrightarrow Ar\overset{+}{N}H_3\bar{C}l + \dot{C}Cl_3 + R\cdot$$

When alkyl groups are attached to the amine nitrogen, iminium ions will result from α-hydrogen abstraction disproportionation.

$$2\ Ar\overset{+\cdot}{N}HCH_3 \longrightarrow Ar\overset{+}{N}H_2CH_3 + Ar\overset{+}{N}H{=}CH_2$$

In our system the electron transfer would be intramolecular as illustrated in scheme III.

Scheme III

$$ArNHCHAr' \xrightarrow{h\nu} ArNHCHAr'^* \quad (12)$$
$$\quad\ CCl_3 \qquad\qquad\quad CCl_3$$

$$ArNHCHAr'^* \longrightarrow Ar\overset{+\cdot}{N}HCHAr' \quad (13)$$
$$\quad\ CCl_3 \qquad\qquad\ Cl^-\ \cdot CCl_2$$

$$Ar\overset{+\cdot}{N}HCHAr' + SH \longrightarrow Ar\overset{+\cdot}{N}HCHAr' + S\cdot \quad (14)$$
$$Cl^-\ \cdot CCl_2 \qquad\qquad\ Cl^-\ CHCl_2$$

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$$\mathrm{ArNHCHAr' + ArNHCHAr' \longrightarrow ArNH{=}CAr' + ArNHCHAr'} \quad (15)$$
$$\mathrm{Cl^-\ CHCl_2 \qquad Cl^-\ \cdot CCl_2 \qquad\qquad Cl^-\ CHCl_2 \qquad Cl^-\ CHCl_2}$$

$$\mathrm{ArNH{=}CAr' + H_2O \longrightarrow ArNH_3Cl + Ar'CCHCl_2} \quad (16)$$
$$\mathrm{Cl^-\ CHCl_2 \qquad\qquad\qquad\qquad\qquad\qquad O}$$

In analogy to step 16 Hauser and Lednicer (74) found that benzophenone iminium salts were readily hydrolyzed by neutral water at room temperature.

$$\mathrm{Ph_2C{=}NR_2Cl + H_2O \longrightarrow Ph_2CO + R_2NH_2Cl}$$

$$\mathrm{R = H,\ CH_3}$$

Other N-dealkylations have been reported in studies in which electron transfer from amines to C-Cl bonds are proposed (10, 11, 75, 76).

An alternate to step 15 could be

$$\mathrm{2\ ArNHCHAr' \longrightarrow ArNH_2CHAr' \qquad ArNH{=}CHAr'} \quad (17)$$
$$\mathrm{Cl^-\ CHCl_2 \qquad\qquad Cl^-\ CHCl_2 \qquad Cl^-\ CHCl_2}$$
$$\text{VII}$$

However, since p-methoxy-α-chloroacetophenone was not detected, compound VII was probably not present in very high concentrations, indicating that step 17 is not important.

Scheme III requires at least 0.05 mol/l water in the ether to afford total hydrolysis of the iminium salt in step 17. Rowley and

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Reed (77) found that water is soluble in ether to the extent of 1.47%, which is equivalent to 0.6 mol/l. We found that, because of its hygroscopic nature, extreme care must be taken to keep the ether dry enough to prevent the formation of the aniline hydrochlorides and V.

Scheme III does not explain all aspects of our observations. For instance, we do not know why, in anhydrous solvent under nitrogen, we see no disappearance of starting material. The importance, however, of this study lies in the fact that compounds which have insecticidal properties were shown to be very photoreactive under 3100 Å light and oxygen. Unlike DDT, photolysis may be the principle degradation process of these compounds in the environment.

C. 4,4'-Dichlorobiphenyl Photochemistry

4,4'-dichlorobiphenyl (DCB) was chosen for study as a simple model of chlorinated biphenyls. We hoped to obtain information pertaining to the photolysis mechanism on a molecular basis. Such information is lacking in studies reported to date.

Photolysis in Alcohols

The photolysis of 1.0×10^{-3} M DCB in degassed alcohol solvents (2-propanol and methanol) by 3100 Å light led to the formation of 4-chlorobiphenyl (MCB) and HCl. In typical reactions 36% MCB was formed after 22 hr in 2-propanol and 25% MCB was formed in methanol. Photolysis of DCB in CH_3OD afforded no incorporation of

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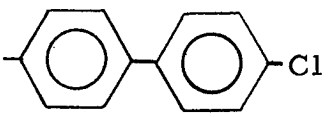
deuterium in MCB. This would suggest the intermediacy of an aryl radical similar to one proposed by Kharasch and Sharma (41) for the photoreductive deiodination of aryl iodides.

$$ArCl \xrightarrow{h\nu} ArCl^{*} \qquad Ar = \text{  }$$

$$ArCl^{*} \longrightarrow Ar\cdot + \cdot Cl$$

$$Ar\cdot + R_2CHOH \longrightarrow ArH + R_2\dot{C}OH$$

$$R_2\dot{C}OH + \cdot Cl \longrightarrow R_2CO + HCl$$

Attempts to detect the photooxidized products failed because a sufficiently sensitive method, glc or colorimetric (79) was not found. The formation of acetone in 2-propanol or formaldehyde in methanol was, therefore, never proven. A small amount of pinacol (about 10% relative to solvent), however, was identified when the reaction was carried out in 2-propanol substantiating the intermediacy of the 2-propanol radical.

$$2(CH_3)_2\dot{C}OH \longrightarrow (CH_3)_2COHCOH(CH_3)_2$$

MCB was found to be stable for up to 50 hr at 3100 Å due to an extinction coefficient of less than ten at this wavelength. In contrast, DCB has an extinction coefficient at 3100 Å of 289 in 2-propanol and 316 in methanol.

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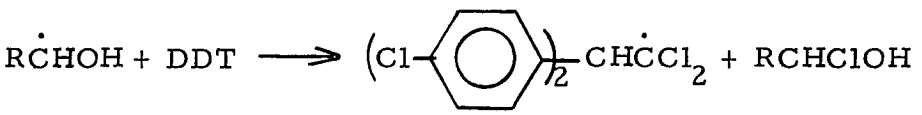
We have postulated a radical chain mechanism for the photolytic decomposition of DDT to DDD, with abstraction of chlorine atoms by alcohol radicals as a propagation step.



$$\dot{R}CHOH + DDT \longrightarrow (Cl\text{-}C_6H_4)_2\dot{C}HCCl_2 + RCHClOH$$

$$RCHClOH \longrightarrow RCHO + HCl$$

Chlorine abstraction from DCB by a solvent radical would, however, be highly unlikely due to the high C-Cl bond energy. Indeed, the stability of MCB points to a non-chain process. One would not expect radicals to be able to differentiate between DCB and MCB and both species should disappear in a chain mechanism.

AIBN has been shown to be an effective radical source, which should initiate the reaction of DCB if a chain mechanism holds. We found, however, that 10^{-4} mol/l AIBN did not cause 10^{-3} mol/l DCB in 2-propanol to form MCB. The non-chain character of the reaction is also indicated by the low quantum yield of 0.002 found at 3100 Å.

The nature of ArCl* in our mechanism was elucidated by doing a sensitization study. The decomposition of DCB, which has a triplet energy (E_t) of 62.5 Kcal/mol (61), to MCB was sensitized by benzophenone (E_t 69.0 Kcal/mol), acetone (E_t 84.0 Kcal/mol) and triphenylene (E_t 67.0 Kcal/mol), indicating that the primary photochemical process could involve a triplet electronic state. This was

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substantiated by the fact that under oxygen, an efficient triplet quencher, in 2-propanol the reaction was slowed (5% reaction in 24 hr). Prolonged irradiation under oxygen produced a multiplicity of products in addition to MCB.

In spite of the apparent existence of alcohol radicals, the Kharasch mechanism cannot be in effect for several reasons. Photolysis in CD_3OD gave a kinetic isotope effect on the quantum yield of DCB disappearance of 1.0. If hydrogen abstraction was involved in a rate determining step, k_H/k_D would be greater than 1.0. The isotope effect on abstraction by phenyl radicals is 4.5 for toluene and 4.2 for acetone (53). Kharasch et al. (80) found that aryl radicals from the photodeiodination of aryl iodides abstracted hydrogen 5-7 times more rapidly from methanol than deuterium from methanol-$\underline{d}_4$. Additional evidence against the Kharasch mechanism comes from a consideration of bond energies. A C-Cl bond of about 80 Kcal/mol (32) would have to be broken with 62.5 Kcal/mol available to the excited triplet state of DCB.

We need to postulate a mechanism in which alcohol radicals are formed, and the removal of hydrogen is not involved in the rate determining step. Furthermore, direct cleavage of the C-Cl bond does not seem reasonable. Such a scheme is shown below.

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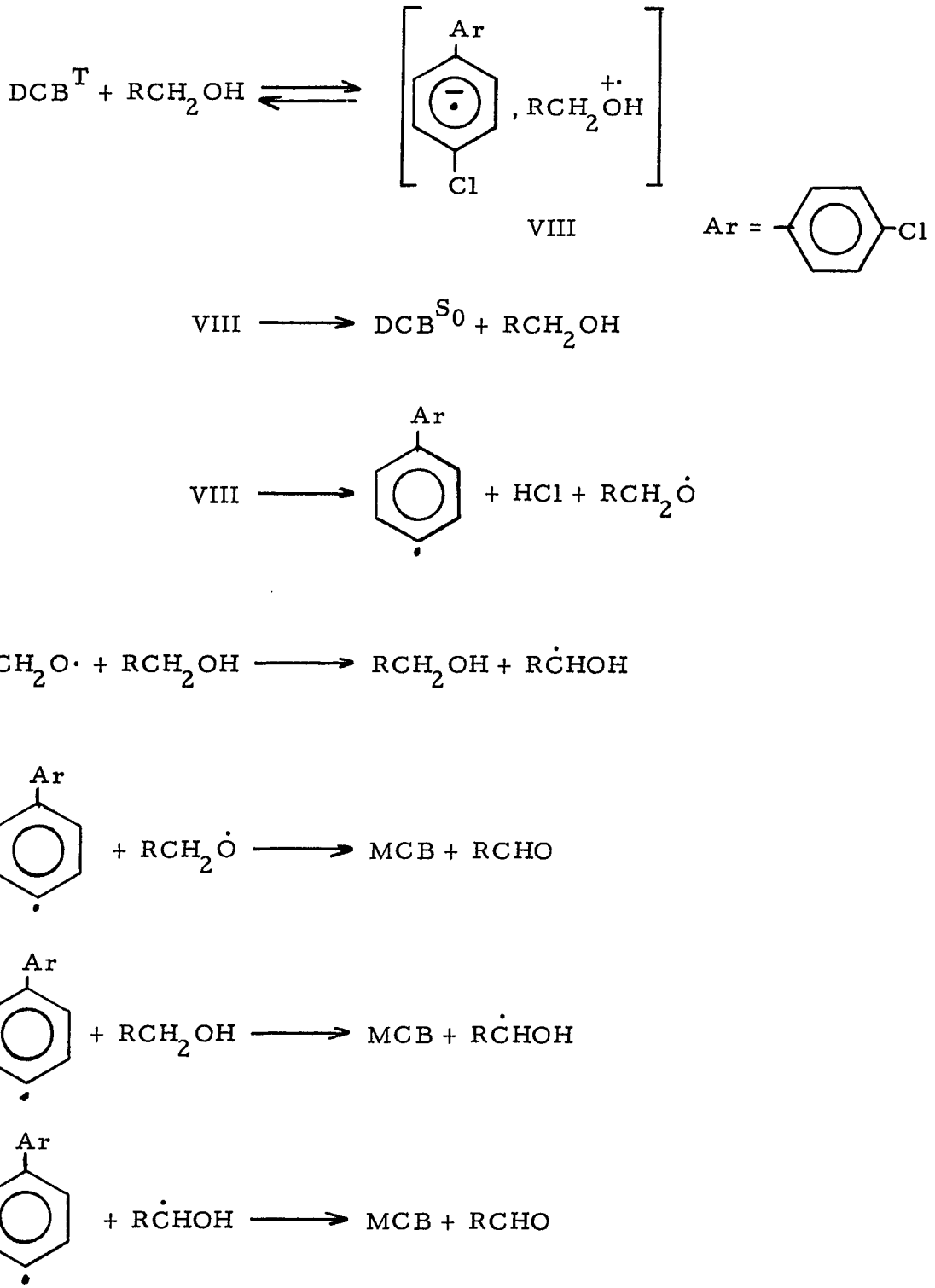

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The nature of the photolysis in 2-propanol is not changed by the addition of CF_3CO_2H. In contrast, the nature of the photolysis in diethyl ether, which will be discussed later, is very dependent on added acid.

The above type of exiplex process is not without precedent. Ledwith and co-workers (81, 82) studied the photochemical oxidation of primary and secondary alcohols by 1, 1'-dimethyl-4, 4'-bipyridylium dichloride (paraquat dichloride, PQ^{+2}) and proposed the following mechanism:

$$PQ^{+2} \xrightarrow{h\nu} (PQ^{+2})^*$$

$$RCH_2OH + (PQ^{+2})^* \longrightarrow \underset{\text{IX}}{\left[PQ^{+\cdot},\ RCH_2\overset{+\cdot}{O}H\right]}$$

$$\text{IX} \rightleftharpoons \underset{\text{X}}{\left[PQ^{+\cdot},\ RCH_2\dot{O},\ H^+\right]}$$

$$\text{X} \xrightarrow{PQ^{+2}} 2\ PQ^{+\cdot} + RCHO + 2H^+$$

The existence of species IX was demonstrated by using phenolic compounds as electron donors (83), yielding stable, colored crystalline complexes.

Ledwith et al. (82) found kinetic isotope effects of 1.4 or less when paraquat dichloride was photolyzed in CD_3OD. The authors

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attributed this to the fact that the rate limiting step was formation of exiplex IX. This result is similar to the k_H/k_D value of 1.0 we obtained, indicating that formation of exiplex VIII is the rate limiting process.

Sulfur Quenching

The photolysis of DCB in 2-propanol at 3100 Å in the presence of various sulfur compounds gave the results summarized in Tables VI-VIII. MCB is formed in essentially quantitative yield.

TABLE VI

Efficiency of DCB Quenching by t-Butyl Disulfide[a]

Quencher Concentration mol/l	ϕ/ϕ_o [b]
5.0×10^{-6}	0.95
1.0×10^{-5}	0.93
2.0×10^{-5}	0.85
4.0×10^{-5}	0.72
8.0×10^{-5}	0.50
1.0×10^{-4}	0.34
2.0×10^{-4}	0.14
5.0×10^{-4}	0.16
7.5×10^{-4}	0.15

[a] 48 hr photolysis, 1.0×10^{-3} mol/l DCB

[b] % MCB formed with quencher/% MCB formed in absence of quencher

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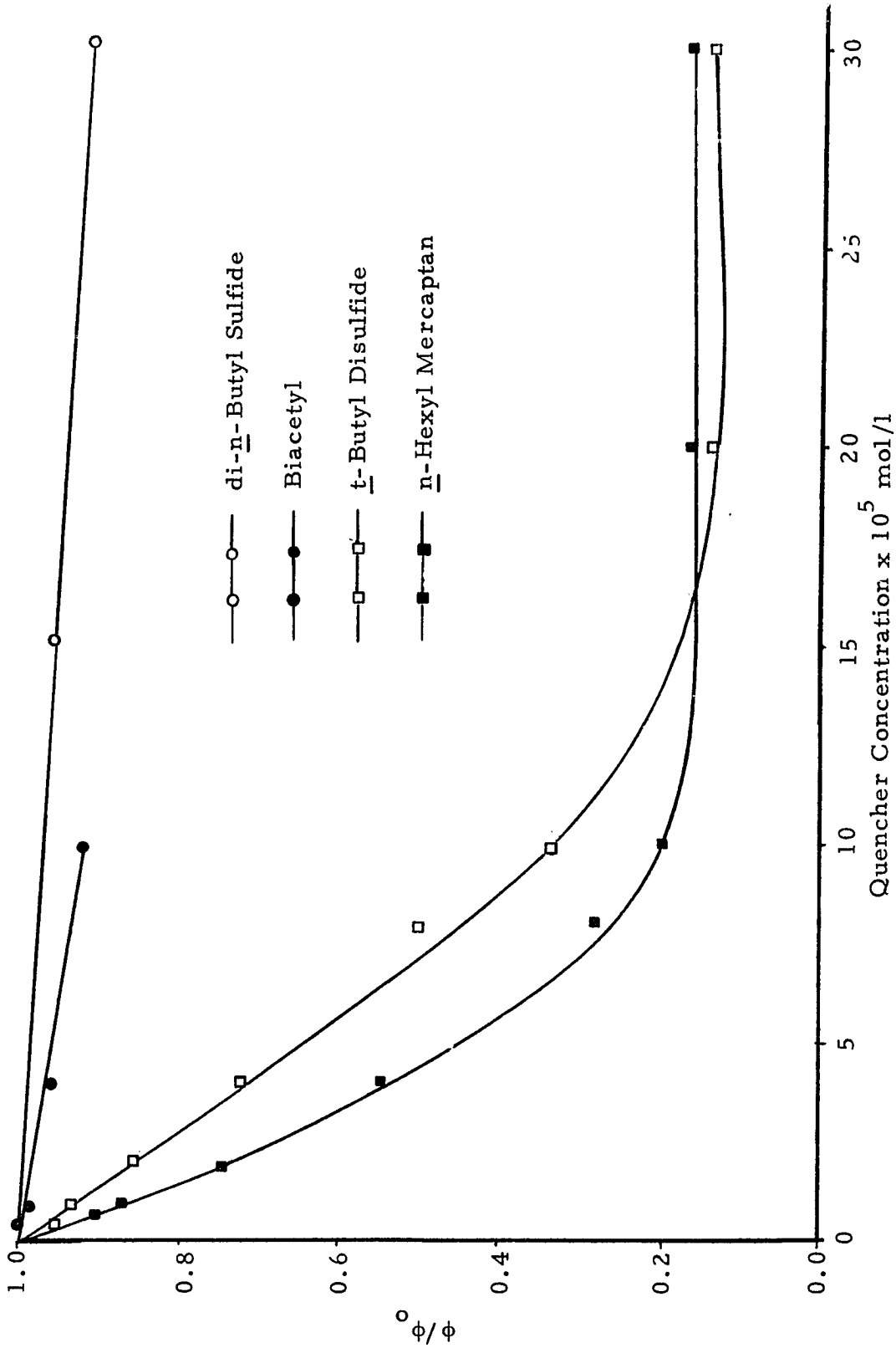

Fig. 1. DCB Quenching Efficiencies of Sulfur Compounds

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The data, as shown in Figure I, depict a tremendous inhibition by the thiol and disulfide and a lesser amount of inhibition by the sulfide. This and the fact that the quenching efficiency of the thiol and disulfide levels out at about 0.15 is analogous to observations made by Cohen and co-workers (42, 43, 44) for the inhibition of benzophenone photoreduction. The authors postulated the following steps for the inhibition of the ketyl radical.

$$Ph_2\dot{C}OH + RSSR \longrightarrow Ph_2CO + RSH + RS\cdot$$

TABLE VII

Efficiency of DCB Quenching by n-Hexyl Mercaptan[a]

Quencher Concentration mol/l	ϕ/ϕ_o
5.0×10^{-6}	0.96
8.0×10^{-6}	0.90
1.0×10^{-5}	0.87
2.0×10^{-5}	0.74
4.0×10^{-5}	0.54
8.0×10^{-5}	0.28
1.0×10^{-4}	0.18
2.0×10^{-4}	0.16
3.0×10^{-4}	0.16
4.0×10^{-4}	0.16
5.0×10^{-4}	0.15
6.0×10^{-4}	0.16
7.0×10^{-4}	0.16

[a] 48 hr photolysis, 1.0×10^{-3} mol/l DCB

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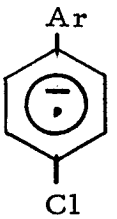
$$Ph_2\dot{C}OH + RS\cdot \longrightarrow Ph_2CO + RSH$$

The sulfide, due to its structure, is incapable of such a reaction.

In our system inhibition by disulfide is probably due to electron transfer to the sulfur compound.



$$+ RSSR \longrightarrow DCB + RS\cdot + RS^-$$

TABLE VIII

Efficiency of DCB Quenching by di-n-Butyl Sulfide[a]

Quencher Concentration mol/l	ϕ/ϕ_o
9.7×10^{-4}	0.91
1.1×10^{-3}	0.90
2.6×10^{-3}	0.84
3.9×10^{-3}	0.68
7.0×10^{-3}	0.53
9.7×10^{-3}	0.36

[a] 48 hr photolysis, 1.0×10^{-3} mol/l DCB

This type of reaction will not explain the inhibition by thiol since thiols and sulfides have similar electron affinities (48).

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However, the radical initiated formation of disulfide from thiol is very facile (84).

$$R'_2\dot{C}OH + RSH \longrightarrow R'_2CHOH + RS\cdot$$

$$2RS\cdot \longrightarrow RSSR$$

Therefore, the inhibition by mercaptan is caused by electron transfer to disulfide which arises from the thiol. The sulfide is incapable of such a process.

Emission quenching experiments were carried out to test if the sulfur compounds were interacting with excited states of DCB. Varying concentrations of thiol, disulfide or sulfide did not diminish the intensity of the DCB fluorescence indicating that the sulfur compounds are not quenching the excited singlet state of DCB. We were unable to detect the room temperature phosphorescence of DCB and consequently could not study the triplet quenching. However, biacetyl, a classical triplet quencher (54), gave results summarized in Table IX and Figure I.

TABLE IX

Efficiency of DCB Quenching by Biacetyl[a]

Quencher Concentration mol/l	ϕ/ϕ_o
8.0×10^{-6}	0.98
1.0×10^{-5}	0.96
4.0×10^{-5}	0.94
1.0×10^{-4}	0.92

[a]48 hr photolysis, 1.0×10^{-3} mol/l DCB

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Higher concentrations of biacetyl were not used because the quencher would have absorbed more than 5% of the radiation. The results show that the sulfide may be quenching the triplet state of DCB but the thiol and disulfide are interacting with some intermediate more long lived than an excited state. We propose that this intermediate is the exiplex VIII.

Solvent Study

The photolysis of DCB was also studied in a variety of other solvents. In several systems complex mixtures of products other than MCB were formed which were different for each solvent. The result of these studies are shown in Table X.

In the case of cyclohexane, bicyclohexyl and chlorocyclohexane were identified as products indicating the presence of cyclohexyl radicals. Indeed, AIBN thermolysis in cyclohexane, diisopropyl ether and diethyl ether yielded mixtures of compounds several of which corresponded by glc co-injection, to products formed in DCB photolysis. This is indicative of free radical processes being responsible for the complex reaction mixtures.

Only in diethyl ether in the presence of CF_3CO_2H is the photochemistry similar to that found in alcoholic solvents. To explain this the following scheme is proposed.

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TABLE X

DCB Photolysis Solvent Study[a]

Solvent	Additive	% DCB Reaction	Products
2-Propanol	--	36	MCB
	2% CF_3CO_2H	36	MCB
Methanol	--	25	MCB
Diisopropyl ether	--	15	complex[b]
Diethyl ether	--	4	complex
	2% CF_3CO_2H	25	MCB
	2% CF_3CO_2H[c]	35	MCB
	2% CF_3CO_2D[c]	5	MCB
	2% CF_3CO_2H + t-butyl disulfide[d]	5	MCB
Cyclohexane	--	9	complex
	2% CF_3CO_2H	11	complex
Hexane	--	16	complex
Acetonitrile	--	30	complex

[a] 22 hr photolysis, 1.0×10^{-3} mol/l DCB

[b] Trace amounts of MCB detected by glc

[c] 48 hr photolysis, 5.0×10^{-3} mol/l DCB

[d] 1.0×10^{-4} mol/l t-butyl disulfide

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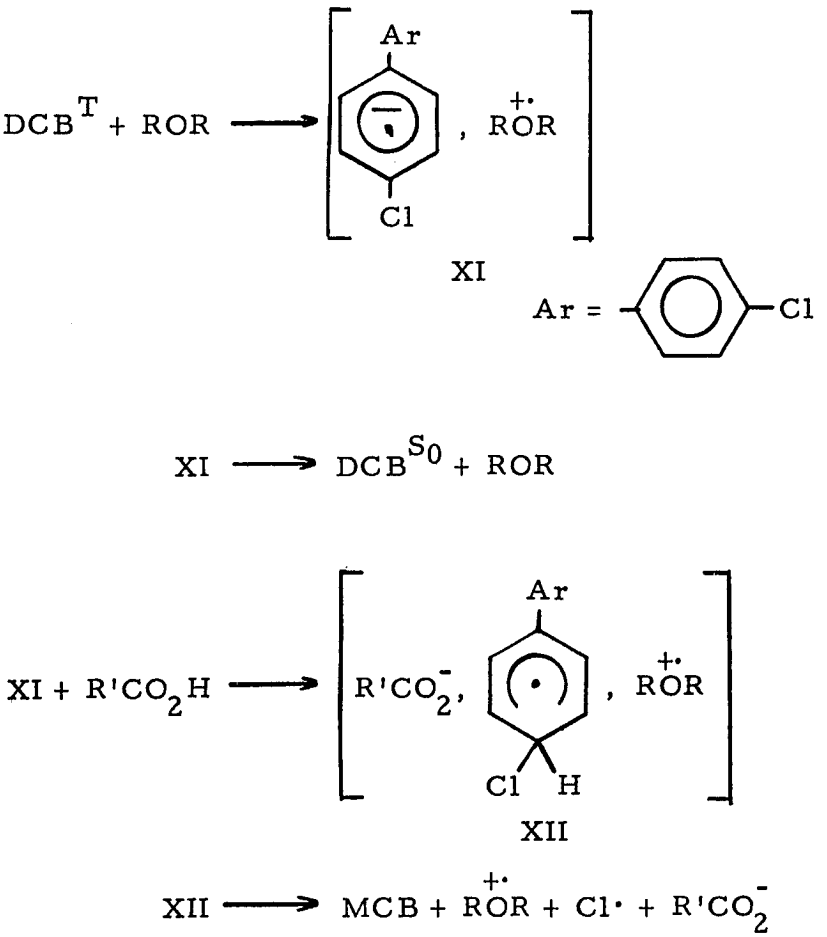

In this mechanism one would expect to see a kinetic isotope effect on the quantum yield of MCB formation arising from the protonation step. Indeed, photolysis of DCB in diethyl ether in the presence of CF_3CO_2D produced a k_H/k_D value of 7.0. In the absence of acid exiplex XI decays to give ground state DCB and solvent. The inhibition of MCB formation by t-butyl disulfide suggests that an intermediate similar to the exiplex proposed for alcoholic photolysis is present in the photolysis of DCB in acidic diethyl ether.

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The importance of a heteroatom in the solvent is demonstrated by the fact that the addition of acid to cyclohexane did not lead to the formation of MCB. The basic mechanistic difference between alcohol and ether is that the exiplex formed in alcohol, VIII, has a direct route to products, whereas, in ether formation of DCB requires an external proton source.

From the literature review it is apparent that the generally accepted mechanism for the photolysis of aryl chlorides at wavelengths above 3000 Å involves direct C-Cl cleavage to form aryl radicals and chlorine atoms. This thesis is the first real mechanistic study of aryl chloride photolysis and demonstrates that other pathways are more reasonable.

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