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Photochemical cis-trans Isomerization of β-Styrylferrocene

Thesis by

Natalia Pisker Trifunac

In Partial Fulfillment of the Requirements

For the Degree of

Doctor of Philosophy

California Institute of Technology

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1970

(Submitted July 28, 1969)

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ABSTRACT

The effect of metal atoms on photochemical transformations has been investigated by studies of the cis-trans isomerization of β-styrylferrocene.

The photostationary state lies entirely on the side of the trans isomer in the cases of direct irradiation at 3130 Å or at 3660 Å. The quantum yield at 3130 Å is 0.00650 and does not vary with concentration. In the presence of benzophenon as sensitizer the quantum yield is 0.00540. On the other hand, the quantum yield for direct irradiation at 3660 Å decreases with increasing concentration of cis β-styrylferrocene varying from 0.00365 to 0.00198.

These results lead to the suggestion that the isomerization takes place from a triplet state of β-styrylferrocene which probably has higher energy than the lowest triplet; reaction from the third triplet seems most likely.

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INTRODUCTION

cis β-Styrylferrocene, upon direct excitation with the ultraviolet light, as well as sensitized excitation in the presence of benzophenon, undergoes photochemical isomerization to trans β-styrylferrocene. The suggested mechanism involves a chemical rearrangement from a triplet manifold. Preference is given to the reaction taking place from the third triplet state (T_3); however, the possibility that the reaction is from either the second (T_2) or the first (T_1) triplet state is also acknowledged.

Under the same conditions during which the cis $\longrightarrow$ trans isomerization was carried out, trans β-styrylferrocene does not rearrange to cis β-styrylferrocene. The photostationary state reached when pure cis β-styrylferrocene solutions are irradiated is within the experimental error, completely on the side of the trans isomer.

Most known photochemical reactions take place from the lowest excited singlet or triplet state, the reason being that the other processes such as intersystem crossing and internal conversion by which the higher electronic excited singlet or triplet states can be deactivated are faster than the chemical reactions.[3] In other words, the lifetime of the higher excited singlet or triplet state that might be involved in the reaction is too short to allow the chemical reaction to take place. However, there are cases, recently reported and

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considered as exceptions, in which the chemical reactions were suggested to involve higher electronic excited states than the first excited state. The involvement of a second triplet state was considered as a possible mechanism in the case of reactions resulting from direct excitation.[7,8] For the case of sensitized reactions, a transfer of energy of the second triplet state of the sensitizer to the substrate was postulated.[4,5,6]

The ultraviolet and visible absorption and emission spectra of ferrocene appear to have unusual characteristics due to the presence of the iron atom in the molecule. On the basis of analysis of the ultraviolet and visible absorption spectra of ferrocene[9,10,11] it has been suggested that the first (S_1) and second (S_2) singlet states in contrast to higher excited states have practically no charge-transfer character, i.e., that these excited states result from the excitation of the iron electrons with very little ring electron participation.

With this in mind it was of interest to study photochemically the nature of the electronic excited states in ferrocenes. Moreover, the unusual properties of the ferrocene excited electronic states suggested a possible unusual photochemistry of ferrocene compounds.

cis(I) and trans(II) β-Styrylferrocene (Figure 1), which contain a ferrocene substituent and which therefore allow the study of the influence of ferrocene on a photochemical behavior of the compounds of this type, were chosen as a convenient system. It is reasonable to

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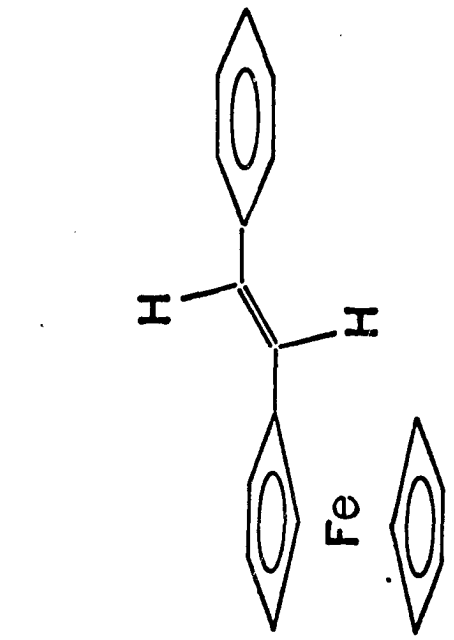
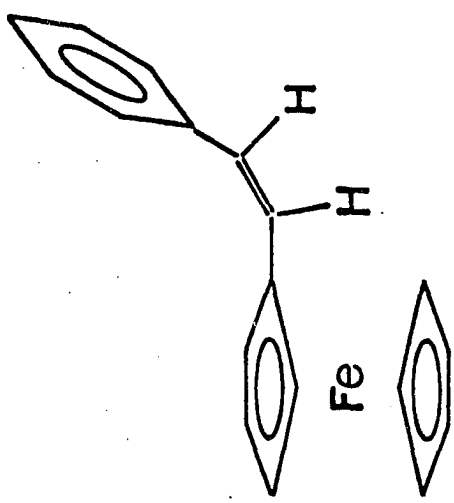


II TRANS β-STYRYLFERROCENE



I CIS β-STYRYLFERROCENE

Figure 1

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postulate that in a molecule like β-styrylferrocene only the charge-transfer portion of the excitation will lead to the efficient chemical rearrangement, i.e., that the excitation charge localized on the iron atom will not induce the isomerization of the C-C double bond. Only the excited ring electrons by virtue of being in conjugation with the double bond will be able to affect isomerization. Thus the efficiency of the isomerization of the C-C bond when the molecule is excited to a particular band in the absorption spectrum would reflect the extent of the localization versus delocalization of the excitation charge of that particular band. In other words, a comparison of the efficiency of the isomerization reaction at different wavelengths of excitation corresponding to different electronic states of the molecule studied might provide a photochemical method for distinguishing between different characteristics of the various electronic states, i.e., between the involvement of the metal electrons versus ring electrons. In addition, a chemical reaction which involves the organic part of ferrocenes, like the isomerization of the C-C double bond in β-styrylferrocene, whose efficiency depends on the extent of participation of the ring electrons, will require those electronic states which have more charge-transfer character.

In the case of β-styrylferrocene, the electronic state that is likely to be involved in the isomerization reaction is the third singlet state (S_3) or its associated triplet state (T_3). However, as mentioned

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already, S_3 (T_3) is expected to have a short lifetime compared to S_1 (T_1) and compared to S_2 (T_2). Thus the two factors, on the one hand the requirement for the charge-transfer character and therefore the requirement for the reaction from S_3 (T_3) and on the other hand the short lifetime of S_3 (T_3), oppose each other and the mechanism involved in the reaction will depend on which factor dominates.

In any case it is expected that the isomerization reaction will be inefficient but that it will become more efficient when the molecule is excited to a band with more charge-transfer character than when it is excited to a band resulting from the excitation charge localized on the iron atom.

RESULTS

cis And trans β-styrylferrocene were synthesized and characterized. cis β-Styrylferrocene, upon irradiation with ultraviolet light, was shown to isomerize photochemically to trans β-styrylferrocene, while the reverse reaction, trans → cis isomerization, was shown not to take place.

A method for determination of the composition of the cis, trans β-styrylferrocene mixture that results upon irradiation, based on monitoring the ultraviolet absorption of the irradiated solution, was developed.

The quantum yield (ϕ) for the cis → trans isomerization was measured for the reactions run under various experimental conditions.

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The photostationary state obtained upon irradiation of cis β-styrylferrocene at different wavelengths of excitation was also measured.

Synthesis of cis and trans β-stryrylferrocene

cis And trans β-styrylferrocene were successfully synthesized by the use of the Wittig Reaction.[1]

Benzyltriphenylphosphoniumbromide was synthesized according to

$$\phi_3P + \phi CH_2Br \longrightarrow [\phi_3\overset{\oplus}{P}\text{-}CH_2\phi]\overset{\ominus}{Br}$$

$$[\phi_3\overset{\oplus}{P}\text{-}CH_2\phi]\overset{\ominus}{Br} \xrightarrow{\text{base}} \phi_3\overset{\oplus}{P}\text{-}\overset{\ominus}{C}H\phi \longleftrightarrow \phi_3P{=}CH\phi$$

and subsequently reacted with ferrocenealdehyde (FcCHO)

$$\phi_3P{=}CH\phi + FcCHO \longrightarrow \begin{matrix}\phi_3\overset{\oplus}{P}\text{-}CH\phi \\ \overset{\ominus}{O}\text{—}CHFc\end{matrix} \longrightarrow \begin{matrix}\phi_3P\text{—}CH\phi \\ O\text{—}CHFc\end{matrix} \longrightarrow \phi_3PO +$$

$$\begin{matrix}\phi CH \\ \| \\ FcCH\end{matrix}$$

cis and trans β-styrylferrocene

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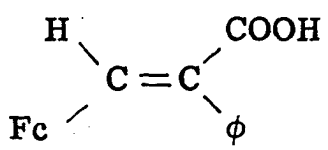
The cis-trans mixture was separated from other products by column chromatography and the pure cis and the pure trans β-stryrylferrocene were obtained by further purification with the preparative thin-layer chromatography.

The structure of the products was elucidated from the elementar analysis, nuclear magnetic resonance spectra (see Figures 2 and 3), and ultraviolet and visible absorption spectra (see Figure 4).

The synthesis of cis β-styrylferrocene through the unsaturated acid intermediate III obtained by the Perkin Reaction[2]

$$FcCHO + \phi CH_2COOH \xrightarrow[(CH_3CO)_2O]{N(C_2H_5)_3} \phi CH_2COO\text{-}COCH_3 \xrightarrow{FcCHO}$$



III

and by subsequent decarboxylation of the unsaturated acid in the presence of catalyst proved unsuccessful. The unsaturated acid III could not be obtained in a satisfactory yield. An attempt was made to improve the yield of the acid (III) by running the reaction under different experimental conditions. No such improvement was achieved. Consequently the method used for the synthesis of cis and trans β-styrylferrocene was the Wittig Reaction described above.

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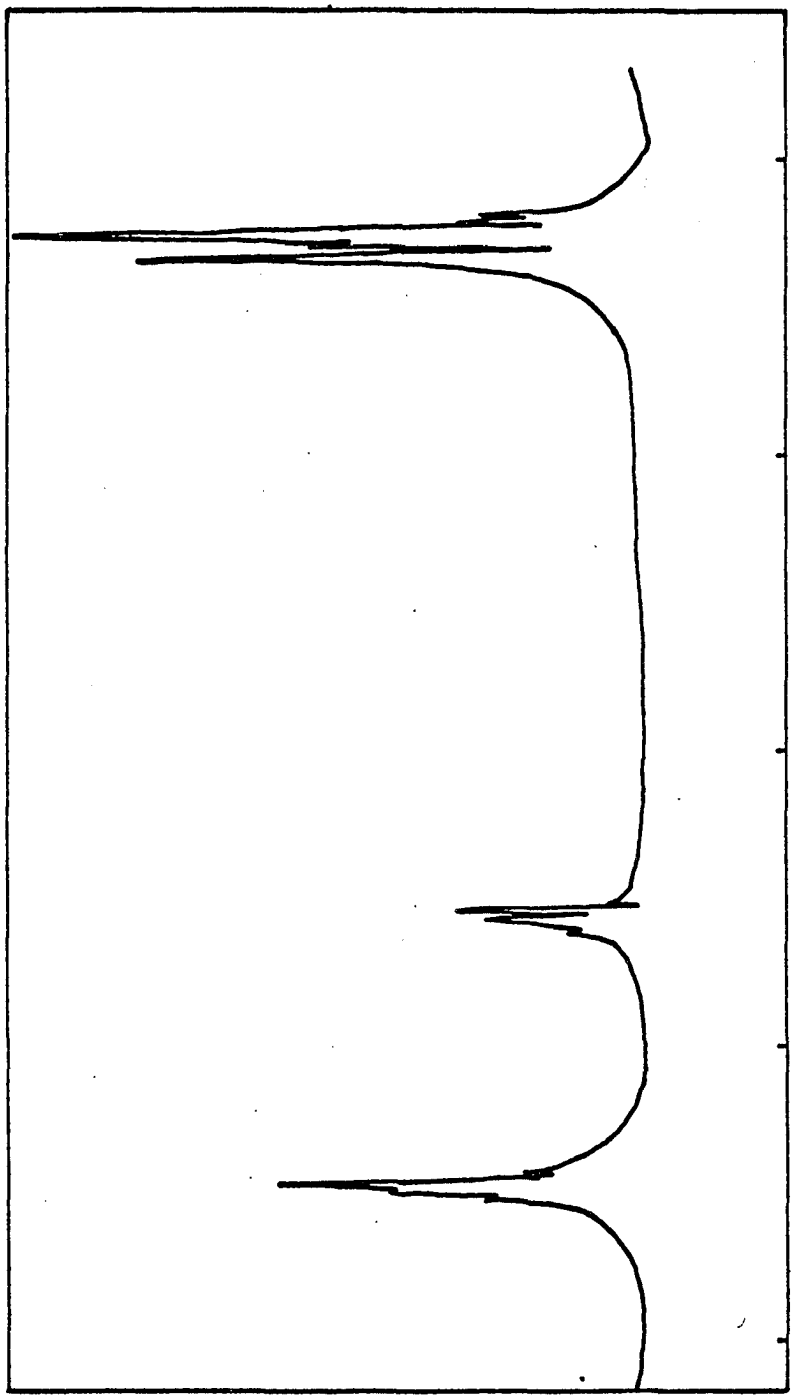

Figure 2. Nuclear magnetic resonance spectrum of cis β-styrylferrocene in carbondisulfide

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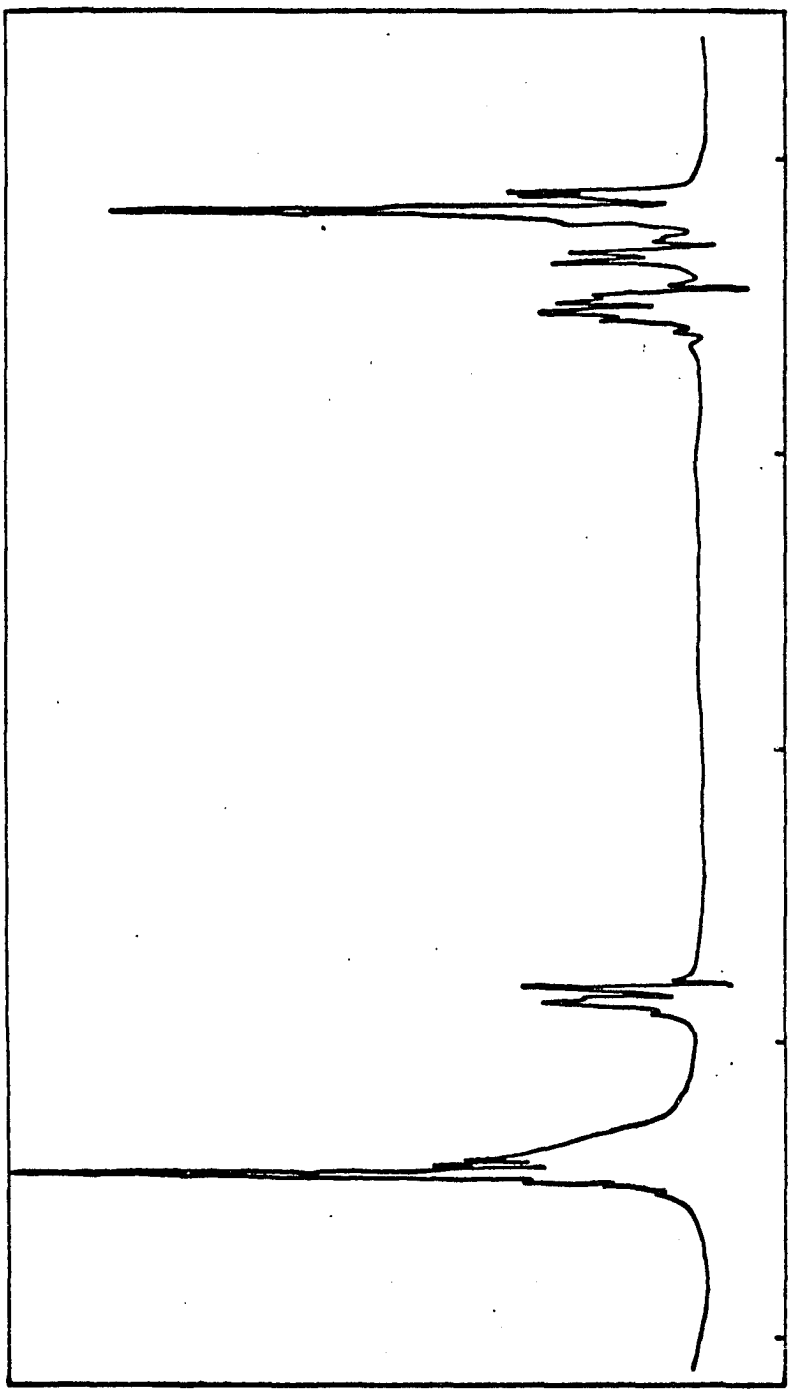

Figure 3. Nuclear magnetic resonance spectrum of trans β-styrylferrocene in carbondisulfide

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Analysis of the irradiated solutions for the content of cis and trans β-styrylferrocene

The concentration of the cis and trans β-styrylferrocene in the solutions irradiated for different time intervals was determined by monitoring the absorption of the irradiated solution in the ultraviolet from 2900 Å to 3300 Å. The values of the absorbances so obtained were used in the computer program (for IBM 7094) written for determination of the composition of the unknown mixture on the basis of the least-square fit of the data. The details of the procedure used will now be discussed.

Define $y^*(\lambda_i) \equiv y_i^* = ax_{i1} + bx_{i2}$

where $x_1(\lambda_i) \equiv x_{i1}$ - extinction coefficient of pure cis β-styrylferrocene

$x_2(\lambda_i) \equiv x_{i2}$ - extinction coefficient of pure trans β-styrylferrocene

$y^*(\lambda_i) \equiv y_i^*$ - a linear combination of extinction coefficients of pure cis and pure trans β-styrylferrocene

a, b - constants to be determined

λ_i - a chosen discrete set of n wavelengths such that i = 1, ..., n

The absorbances measured at each chosen wavelength of the unknown mixture are read into the computer and converted into extinction

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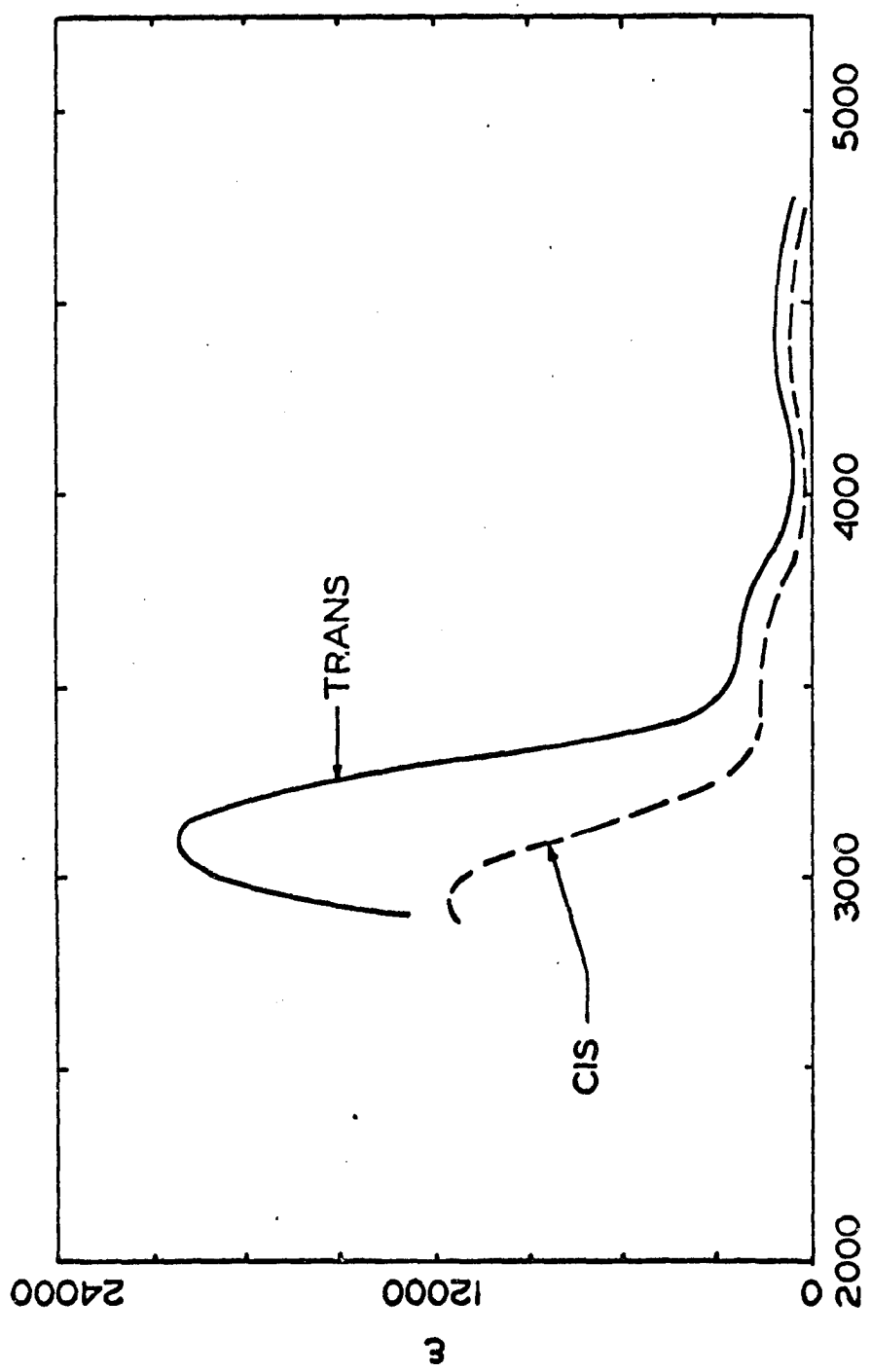

Figure 4. Absorption spectrum of cis and trans β-styrylferrocene in benzene

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coefficients y_i (i.e., $y(\lambda_i) \equiv y_i$). The values of the extinction coefficients y_i^* are fitted to those of the unknown solution (y_i), for each desired wavelength by the use of the least-square fit criterion. The values of the constants a and b are determined so that the extinction coefficient y^* is as close as possible to the extinction coefficient y so that the error given by $\sum_{i=1}^{n} (y_i - y_i^*)^2$ is minimum. This is expressed by equation (1)

$$\sum_{i=1}^{n} (y_i - y_i^*)^2 = \min. \tag{1}$$

or

$$\sum_{i=1}^{n} [\, y_i - (ax_{i1} + bx_{i2})\,]^2 = \min. \tag{1'}$$

The necessary condition for (1') to be satisfied is that

$$\frac{\partial \left[\sum_{i=1}^{n} (y_i - ax_{i1} - bx_{i2})^2 \right]}{\partial a,\ \partial b} = 0$$

In expanded form one obtains:

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$$\sum_{i=1}^{n} (y_i - ax_{i1} - bx_{i2})^2 = \sum_{i=1}^{n} (y_i^2 + a^2x_{i1}^2 + b^2x_{i2}^2 - 2y_iax_{i1} - 2y_ibx_{i2} + 2abx_{i1}x_{i2}) \equiv A$$

$$\frac{\partial A}{\partial a} = \sum_{i=1}^{n} (2ax_{i1}^2 - 2y_ix_{i1} + 2bx_{i1}x_{i2}) = 0 \qquad (2)$$

$$\frac{\partial A}{\partial b} = \sum_{i=1}^{n} (2bx_{i2}^2 - 2y_ix_{i2} + 2ax_{i1}x_{i2}) = 0 \qquad (3)$$

The set of equations (2) and (3) represent a linear system in two unknowns, a and b, and can be rewritten as follows:

$$\begin{bmatrix} 2\sum_{i=1}^{n} x_{i1}^2 & 2\sum_{i=1}^{n} x_{i1}x_{i2} \\ 2\sum_{i=1}^{n} x_{i1}x_{i2} & 2\sum_{i=1}^{n} x_{i2}^2 \end{bmatrix} \begin{Bmatrix} a \\ b \end{Bmatrix} = \begin{Bmatrix} 2\sum_{i=1}^{n} y_ix_{i1} \\ 2\sum_{i=1}^{n} y_ix_{i2} \end{Bmatrix}$$

This system can be solved by using Cramer's rule, which gives:

$$\Delta = \left(\sum_{i=1}^{n} x_{i1}^2 \right) \left(\sum_{i=1}^{n} x_{i2}^2 \right) - \left(\sum_{i=1}^{n} x_{i1}x_{i2} \right)^2$$

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$$\Delta x_1 = \left(\sum_{i=1}^{n} y_i x_{i1}\right)\left(\sum_{i=1}^{n} x_{i2}^2\right) - \left(\sum_{i=1}^{n} y_i x_{i2}\right)\left(\sum_{i=1}^{n} x_{i1} x_{i2}\right)$$

$$\Delta x_2 = \left(\sum_{i=1}^{n} x_{i1}^2\right)\left(\sum_{i=1}^{n} y_i x_{i2}\right) - \left(\sum_{i=1}^{n} x_{i1} x_{i2}\right)\left(\sum_{i=1}^{n} y_i x_{i1}\right)$$

and the unknowns a and b then become

$$a = \frac{\Delta x_1}{\Delta} \qquad b = \frac{\Delta x_2}{\Delta}$$

After a and b are determined the concentrations of cis and trans β-styrylferrocene in the unknown mixture are easily obtained as

$P_c = \frac{a}{a+b}\,100$ percent cis β-styrylferrocene

$P_t = \frac{b}{a+b}\,100$ percent trans β-styrylferrocene

$M_c = \frac{a}{a+b}\,c$ moles/liter of cis β-styrylferrocene

$M_t = \frac{b}{a+b}\,c$ moles/liter of trans β-styrylferrocene

c = total concentration of the unknown mixture given in moles/liter

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If the sensitizer is present in the mixture, the values of the absorbances that correspond to it (calculated from its concentration and extinction coefficient) are substracted from the absorbance of the total mixture (for each wavelength) before the least-square fit is applied.

The computer plots y, y^* and the difference $y - y^*$ against wavelength (λ). The typical plot is given in Figure 5 for the solution with cis and trans β-styrylferrocene only and in Figure 6 for the solution of cis, trans β-styrylferrocene and benzophenon (the sensitizer used).

The difference $y - y^*$ should be small (within experimental error) as long as there is no other compound besides cis and trans β-styrylferrocene (and benzophenon in the case of the sensitized reaction) that absorbs in the wavelength region studied. The deviation of the determined values of extinction coefficients (ϵ) for cis, trans styrylferrocene and benzophenon from the absolutely correct ones is not reflected in the relative difference between y and y^*. However, the accuracy of the final result, i.e., of the concentrations of cis and trans β-styrylferrocene in the unknown mixture will depend on the correctness of the determined values of ϵ.

If a new compound that absorbs in the wavelength region studied is forming during the irradiation, one should be able to detect

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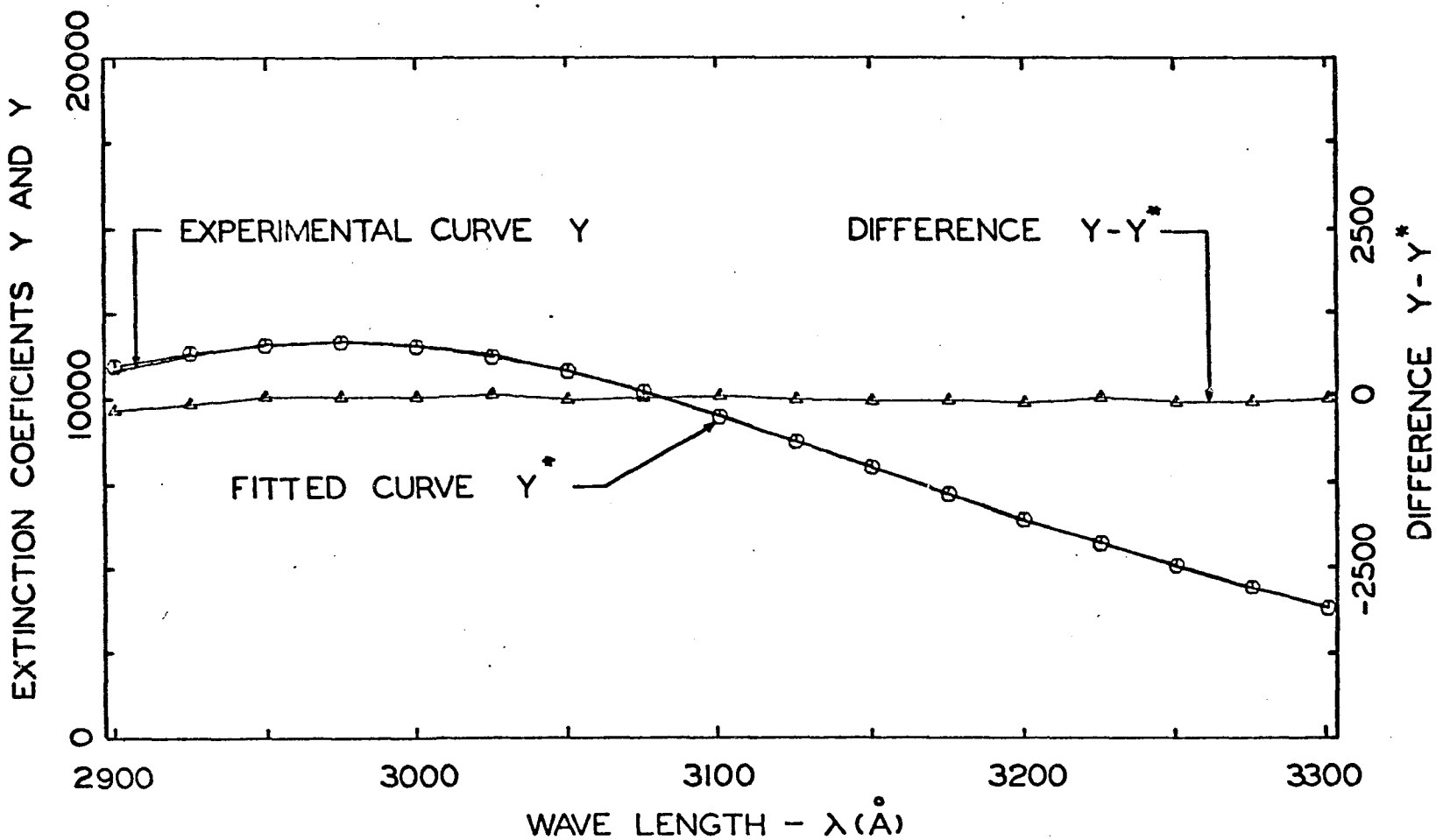

Figure 5. Typical computer output of the least-square fit program for a mixture of cis and trans β-styrylferrocene

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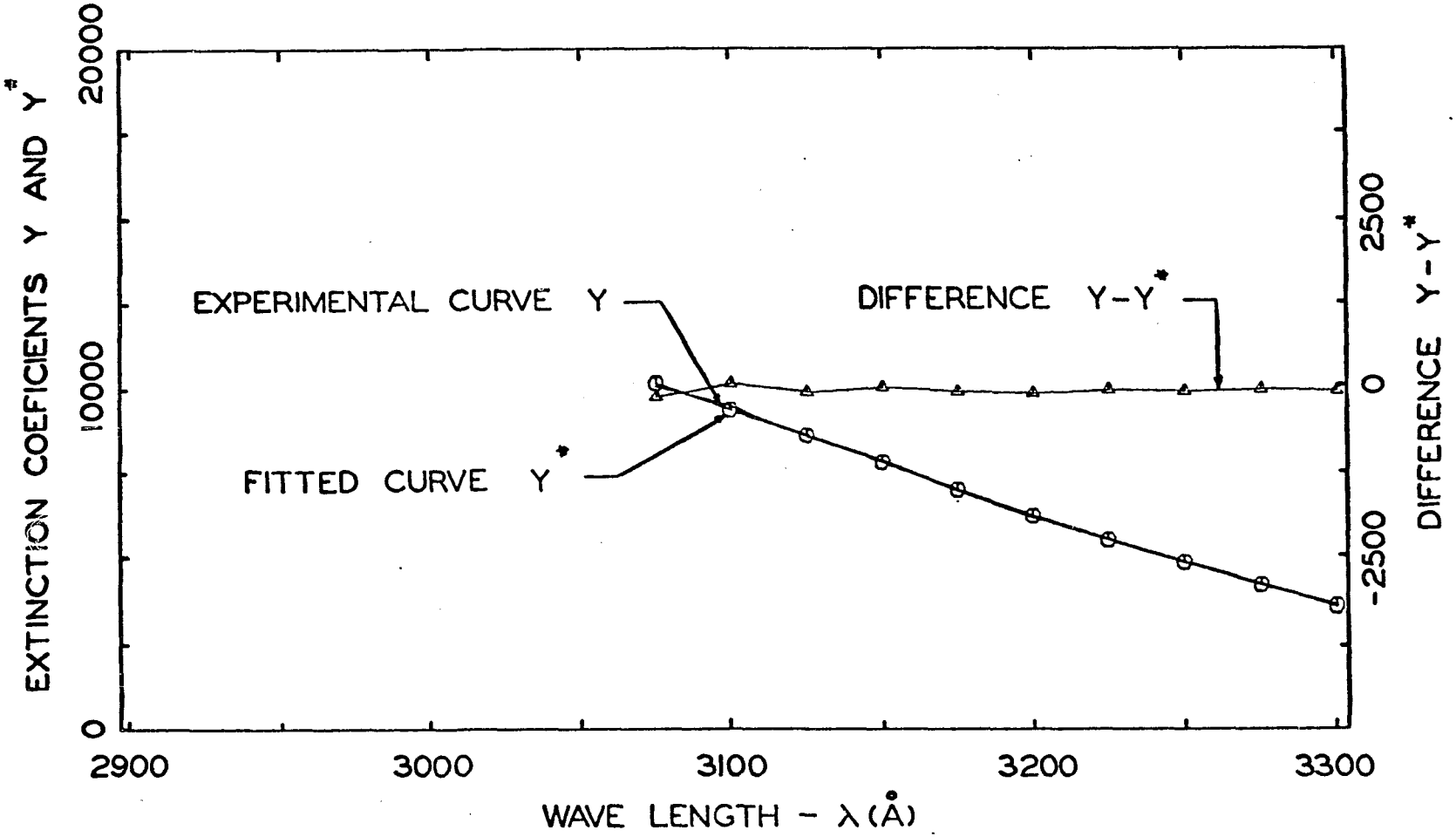

Figure 6. Typical computer output of the least-square fit program for the mixture of cis and trans β-styrylferrocene for the case of benzophenon-sensitized reaction ($y(\lambda)$ corresponding to benzophenon has been substracted from $y(\lambda)$ of the total mixture).

its presence by observing the change in the shape of the plotted error curve, i.e., of the difference $y - y^*$. For illustration, a case is given in Figure 7 in which the presence of a side product that is interfering with the analysis can be detected from the irregular shape of the error curve. This is even more apparent when different plots of error curves for different times of irradiation of the same solution are compared and when a systematic deviation of the error curve $y - y^*$ as the irradiation time increases is observed. In contrast to this situation, a case is presented in Figure 6 where the error curve is practically on the λ axis indicating that $y - y^*$ is insignificant, i.e., that there are no side products interfering with the analysis and that the experimental errors are very small.

The chosen wavelength range in the ultraviolet absorption spectrum for the analysis of the cis-trans β-styrylferrocene mixtures is between 2900 Å and 3300 Å (Figure 5). In this region cis and trans β-styrylferrocene have significantly different values of extinction coefficients (Table 1, Figure 4). Moreover, the maxima are reasonably separated, the maximum of cis β-styrylferrocene is at 2950 Å in benzene solution (Figure 4) and of trans β-styrylferrocene, also in benzene solution, is at 3100 Å (Figure 4).

The range of the analysis of the ultraviolet absorption spectrum

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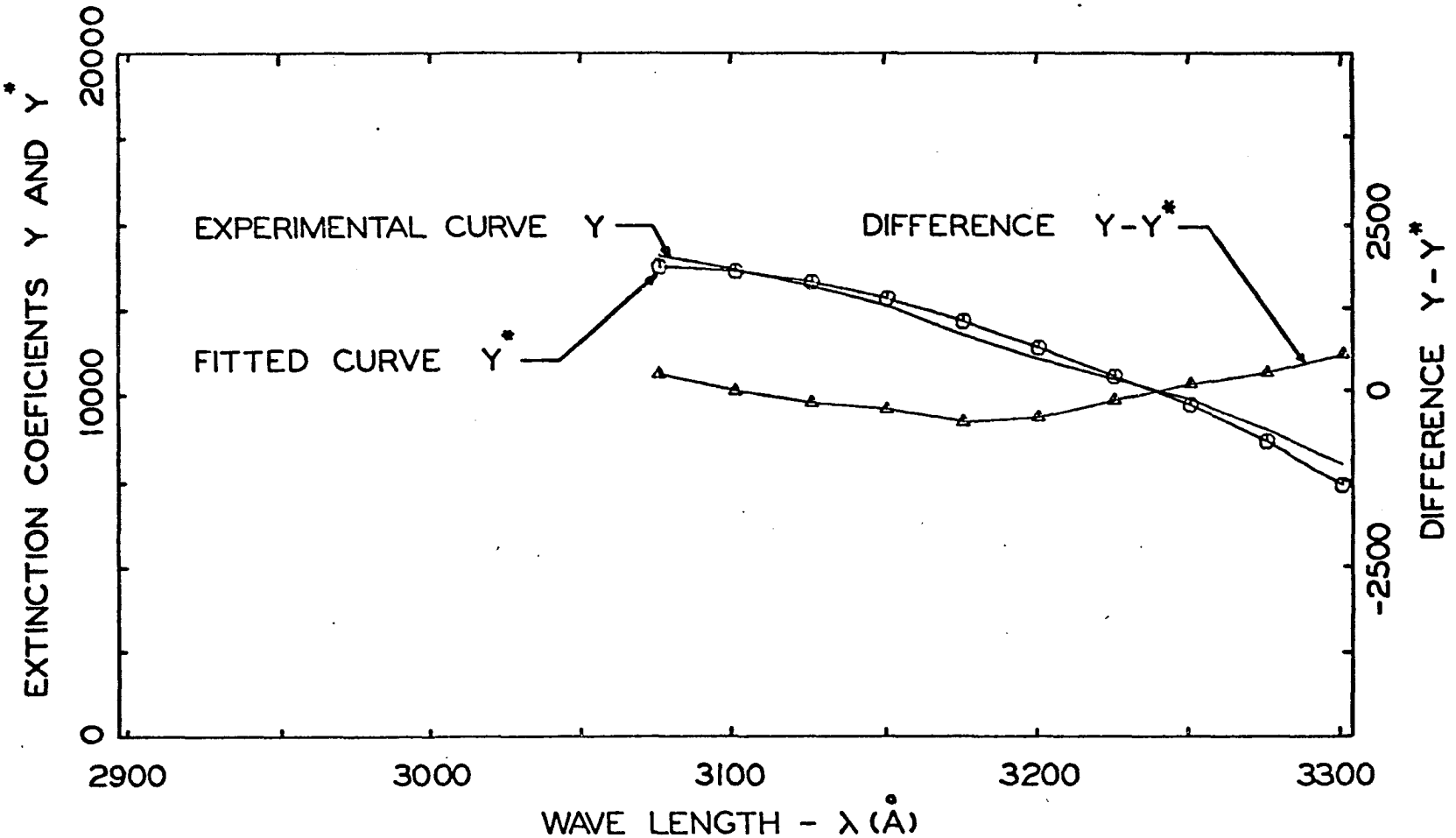

Figure 7. Computer output of the least-square fit program for the mixture of cis and trans β-styryl-ferrocene for the case of benzophenon-sensitized reaction (y(λ) corresponding to benzophenon has been substracted from y(λ) of the total mixture). The presence of the side products is indicated by the shape of the error curve ($y - y^*$).

TABLE 1

Extinction coefficients (ϵ) in benzene
The values were obtained by least-square fit
(Figures 9, 10, 11)

Wavelength in Å (λ)	trans β-styryl-ferrocene	cis β-styryl-ferrocene	benzophenon
2900	12774	11463	1621
2925	14133	11657	1244
2950	15520	11644	843
2975	16920	11469	440
3000	18013	11070	234
3025	18999	10463	128
3050	19706	9796	80
3075	20052	8976	65
3100	20103	8015	63
3125	19821	7149	67
3150	19270	6270	73
3175	18427	5415	81
3200	17379	4655	89
3225	16181	3990	96
3250	14943	3416	103
3275	13342	2897	111
3300	11374	2478	118
3500	2180*	1505*	
3660	2077*	1208	1208
3130	19700*	7085	
4500	1038*	494*	

*These numbers were obtained by simple averaging over the available number of experimental data points.

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is shorter from 3075 Å to 3300 Å (Figure 6) when benzophenon is present. This is because benzophenon has considerably higher absorption at shorter wavelength (Table 1, Figure 8) and in addition because it is present in relatively high concentrations in order to absorb most of the incident light.

It has already been mentioned that it is important that the values of the extinction coefficients for cis and trans β-styrylferrocene and for benzophenon be known with a high degree of accuracy. The extinction coefficients were evaluated in the following way: several solutions of various concentrations of the compound whose extinction coefficients were to be determined have been prepared and their ultraviolet absorption spectra measured. The absorbances at desired wavelengths in the ultraviolet spectrum measured were read with the data reducer (0.99 D, Benson, Lehner Corp.). The data reducer works on the following principle: a mobile cross hair is placed on the point that is to be read and by pressing the controller, the corresponding value is recorded by the typewriter. The absorbances of the solution studied so obtained were converted into extinction coefficients which have been statistically analyzed according to the criterion given by R.B. Fischer.[12] Some values of extinction coefficients were rejected on the basis of 95% probability and some others on the basis of more than 95% and less than 99% probability. The remaining extinction coefficients were converted into absorbances

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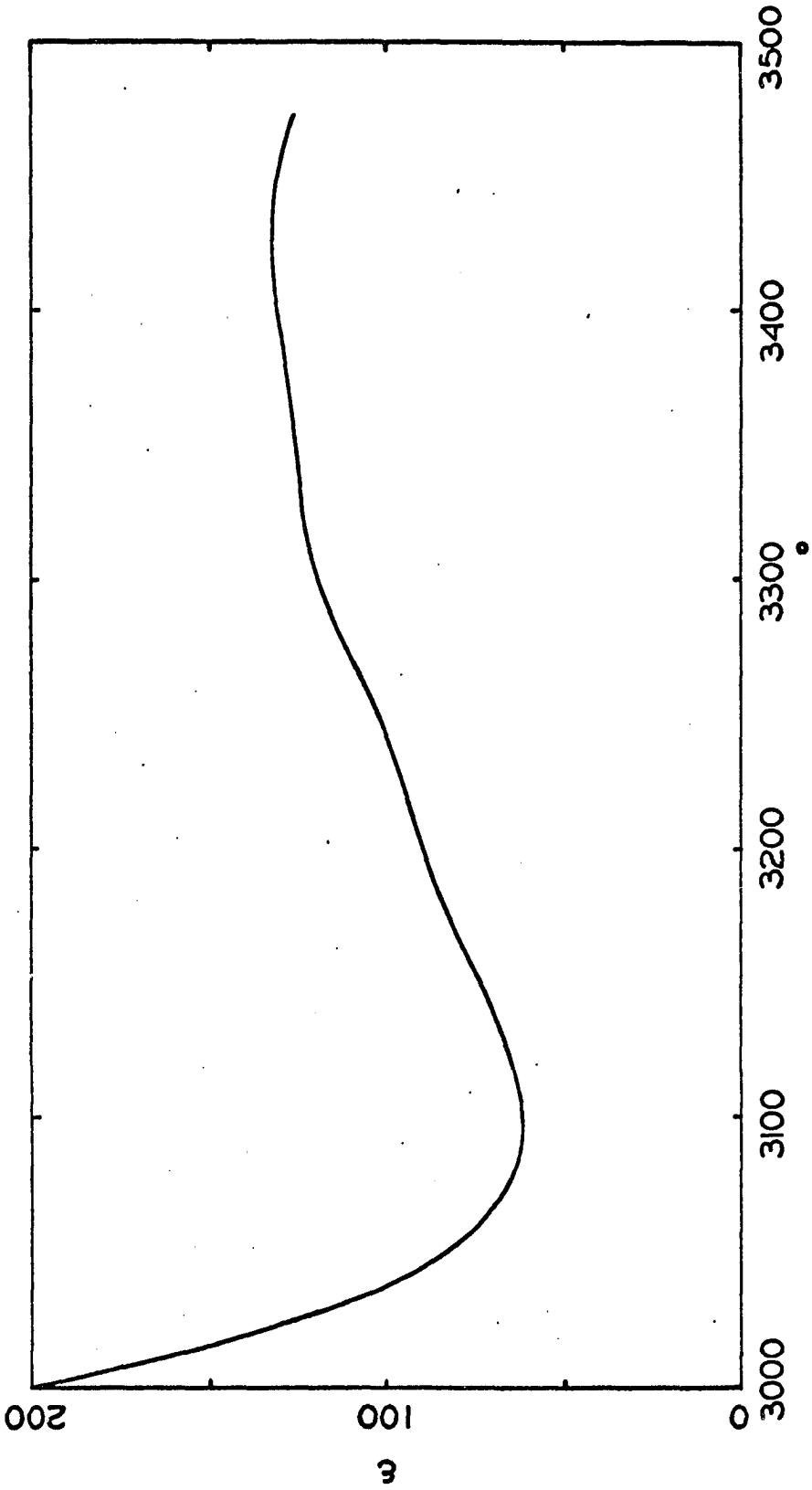

Figure 8. Absorption spectrum of benzophenon in benzene

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which were plotted against corresponding concentrations and a best least-square fitted line was drawn through the points. All the computations and plottings were done with the computer (IBM 7094). The extinction coefficients were evaluated from the slope of the least-square fitted line. The described procedure was used for determining extinction coefficients at each desired wavelength for cis and trans β-styrylferrocene and benzophenon (Table 1). Plots of absorbances at 3100 Å against concentrations and the least-square fitted line are given in Figures 9, 10, 11 for cis, trans β-styryl-ferrocene and benzophenon, respectively.

Quantum yields for the cis → trans photochemical isomerization of β-styrylferrocene

The quantum yields for the cis → trans photochemical isomerization of β-styrylferrocene have been measured. Degassed benzene solutions of various concentrations were irradiated at different wavelengths of excitation. The reaction was also carried out in the presence of benzophenon, which was used as a sensitizer.

The obtained values of the quantum yields for the direct isomerization reaction at 3130 Å and 3660 Å as well as for the sensitized reaction are given in Table 6. The quantum yields in all three cases are very low. The reaction was monitored by analyzing the composition of the solution for different times of irradiation, i.e.,

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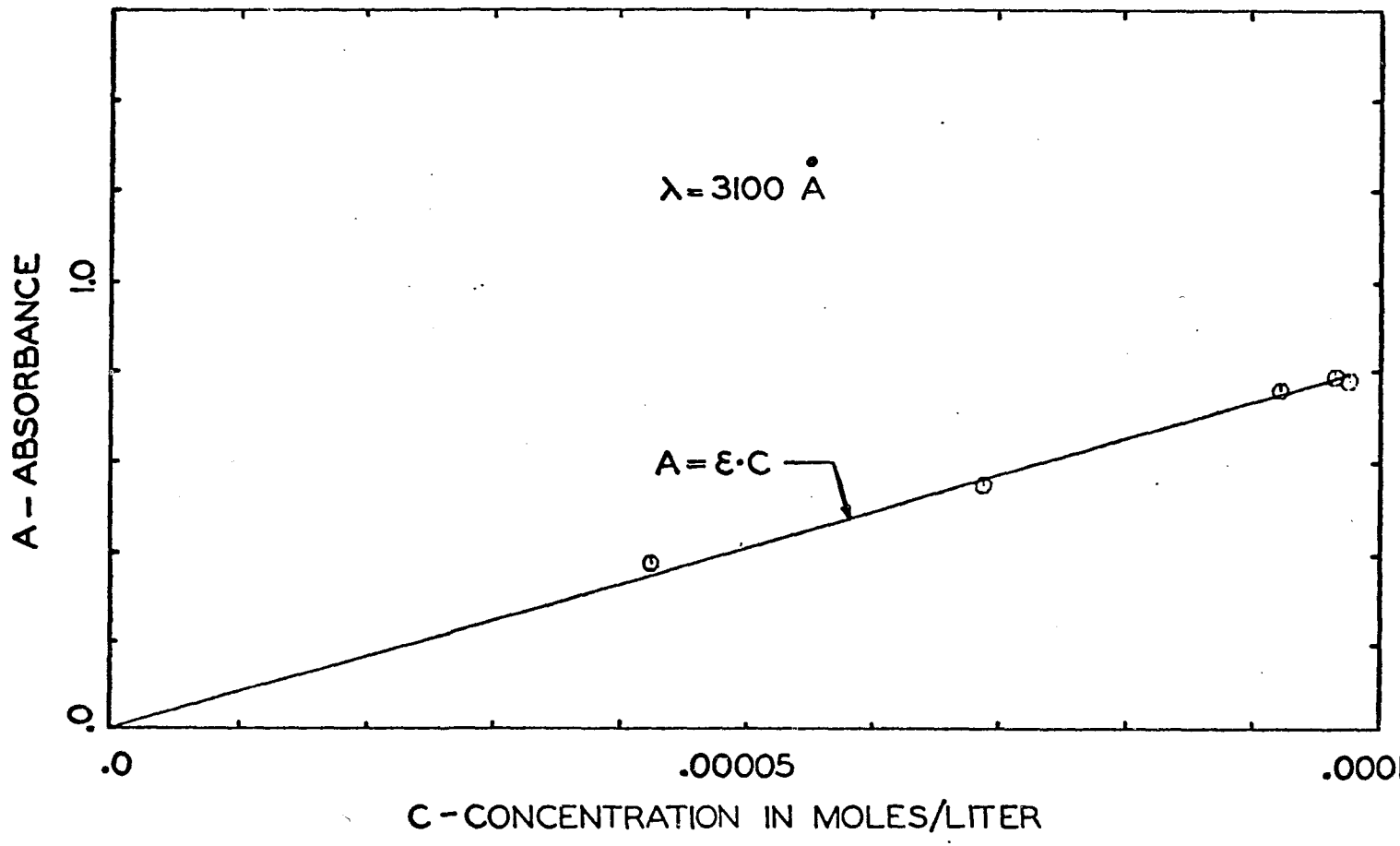

Figure 9. Determination of extinction coefficient of cis β-styrylferrocene for 3100 Å by a least-square fit through experimental points.

at different percentages of conversion to trans β-styrylferrocene. Usually several samples irradiated to the same percent of conversion were analyzed, in order to improve the accuracy of the measurements.

The intensity of the excitation light was measured with the ferrioxalate actinometry.[17b] The quantum yields (ϕ) were calculated from the following definition:

$$\phi = \frac{\text{moles of product}}{\text{number of Einsteins absorbed}} = \frac{\text{moles of trans } \beta\text{-styrylferrocene}}{\text{light intensity x irradiation time}}$$

The number of moles of trans β-styrylferrocene formed at various times of irradiation have been determined by analyzing the ultraviolet spectra of the unknown mixture with the computer program already described. The following corrections (if necessary) of the initially obtained quantum yields have been made:

a) correction for only partial absorption of the incident light by cis β-styrylferrocene.

b) correction for some absorption of the incident light by trans β-styrylferrocene formed.

c) correction for partial absorption of the incident light by the cis β-styrylferrocene in the benzophenon-sensitized reactions.

No correction was made for the competition between the cis and trans β-styrylferrocene for the energy transfer from benzophenon, i.e.,

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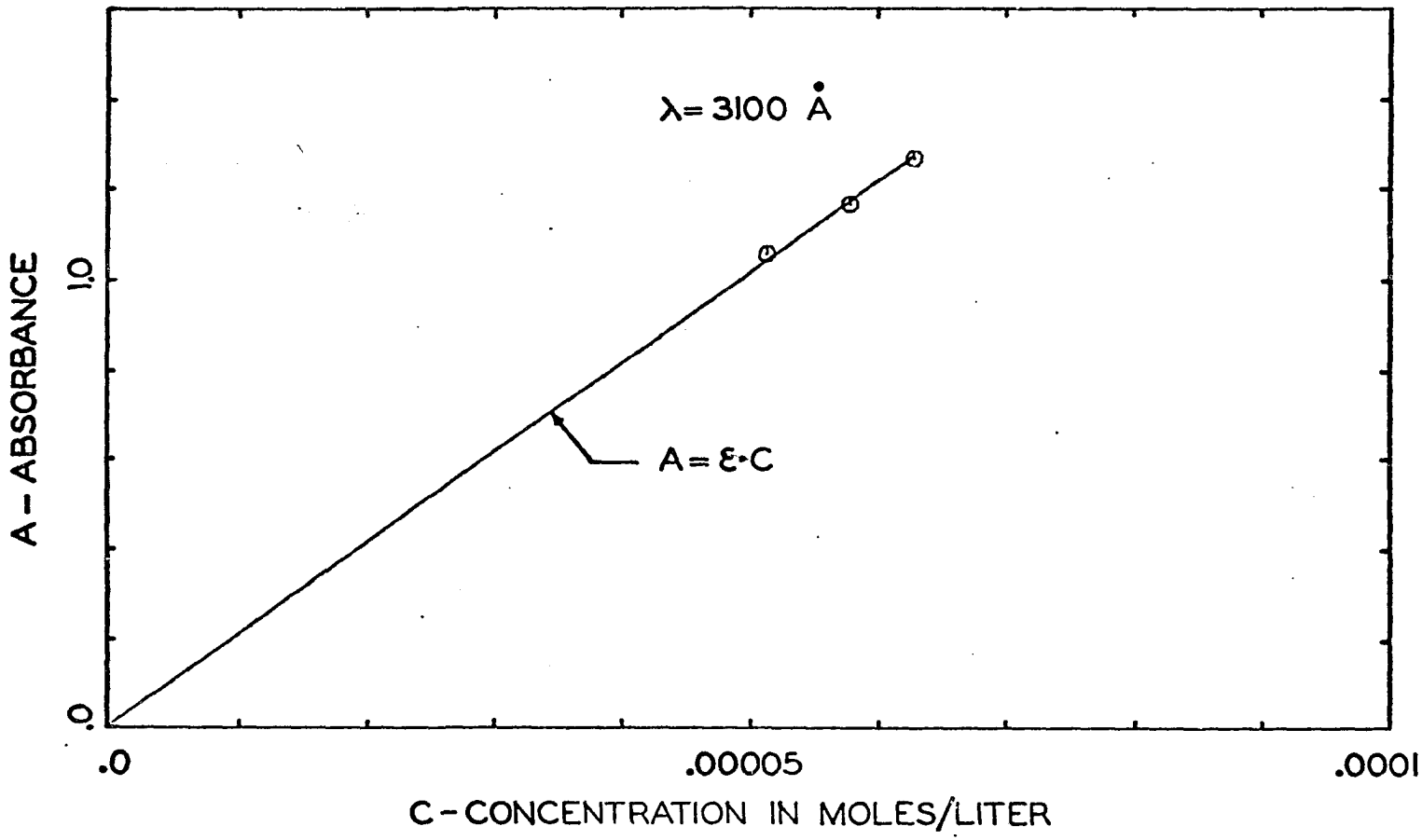

Figure 10. Determination of extinction coefficient of trans β-styrylferrocene for 3100 Å by a least-square fit through experimental points.

for some energy transfer from benzophenon to trans β-styrylferrocene formed.

A plot of the quantum yield at 3130 Å against concentration is shown in Figure 19 and the same plot for the case of irradiation at 3660 Å is presented in Figure 20. The lines shown in Figures 19 and 20 were obtained by a least-square fit of the data points. The computations were made with IBM 7094 computer and the drawings by the Calcomp plotter. The line in Figure 19 can be considered to be nearly parallel to the concentration axis. In other words, the quantum yield at 3130 Å, for all practical purposes, does not change with concentration. On the other hand, the line in Figure 20 has a considerable negative slope indicating that the quantum yield at 3660 Å decreases with increasing concentration. The quantum yield at 3660 Å is significantly lower than the quantum yield at 3130 Å. This can be readily seen from Figure 21 in which the quantum yield against concentration, both for irradiation at 3130 Å and for irradiation at 3660 Å has been plotted. The quantum yield for the benzophenon-sensitized reaction (also given in Figure 21) appears to be somewhat lower than the quantum yield for irradiation at 3130 Å. However, it should be remembered that no correction was made for some energy transfer from benzophenon to trans β-styrylferrocene, i.e., for some benzophenon energy waste. If this correction is estimated and introduced, the quantum yield for the benzophenon-sensitized reaction would match the quantum yield at 3130 Å. Thus we conclude that the quantum yield for the benzophenon-sensitized reaction is the same as the quantum yield obtained for

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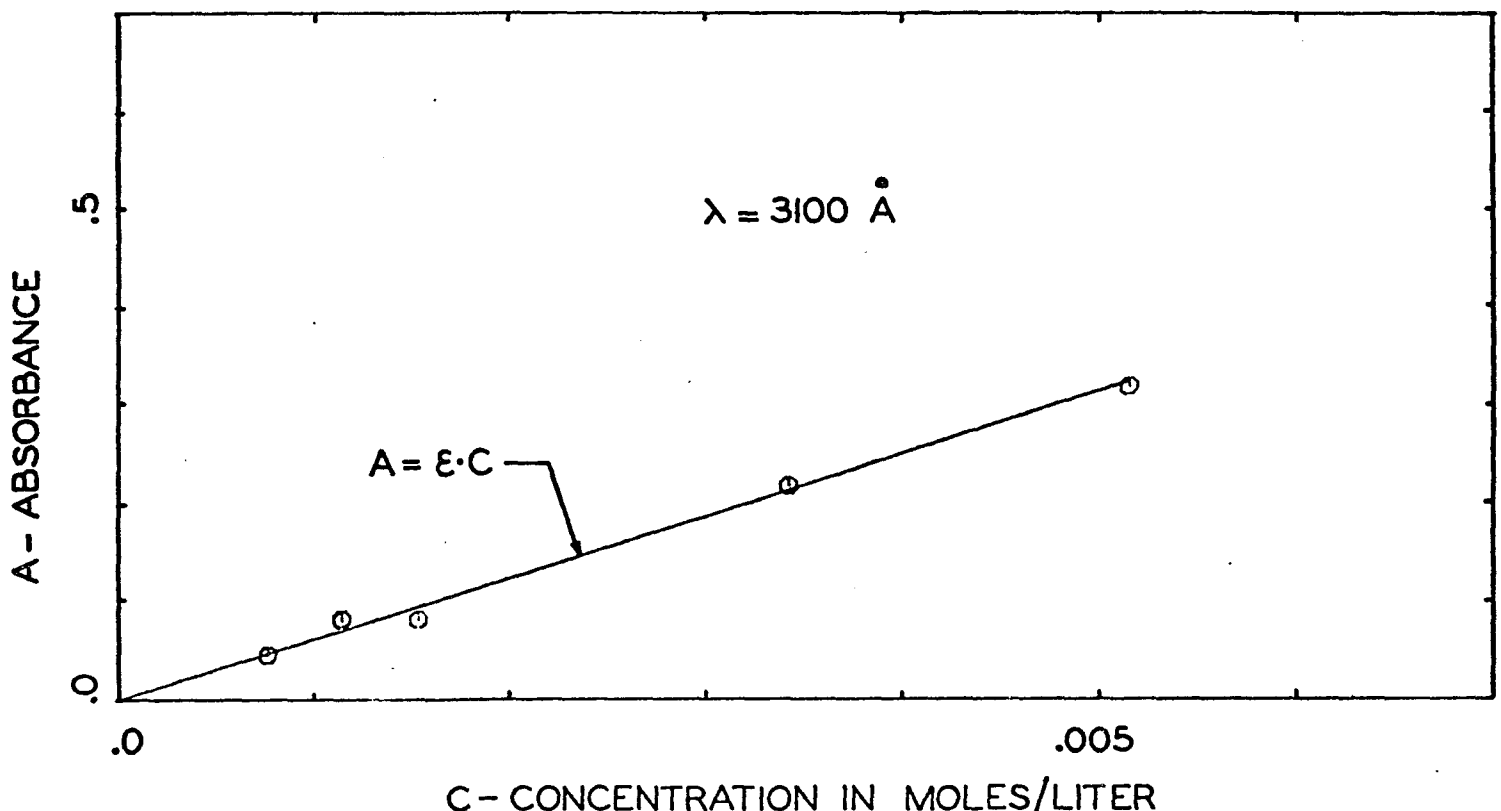

Figure 11. Determination of extinction coefficient of benzophenon for 3100 Å by a least-square fit through experimental points.

irradiation at 3130 Å.

For the direct reaction no side products for the extent to which the reaction was carried out in the quantum yield measurements (usually between 10-20% conversion) were observed. The side products could not be detected either during the analysis of the composition of the irradiated solution with the computer program described or with the thin-layer chromatography. The same was true for the sensitized reactions if the concentration of benzophenon was about 5×10^{-2} moles/liter and if the concentration of cis β-styrylferrocene was about 5×10^{-4} moles/liter (Figure 6); however, for a less concentrated solution, about 5×10^{-3} moles/liter benzophenon and about 5×10^{-5} moles/liter cis β-styrylferrocene, a systematic change upon irradiation could be observed in the plotted error curve (Figure 7).

Photostationary state

The photostationary state starting with cis β-styrylferrocene in benzene solution was measured at 3130 Å (Table 8, Figure 22) and at 3660 Å (Table 9, Figure 23). The side products formed in a small amount after a long period of irradiation (before all cis β-styrylferrocene was converted to the trans isomer). The presence of the side products was noticed on a thin-layer chromatogram while they did not seem to have significantly interfered with the analysis of the composition of the irradiated solutions with the described computer program. For the benzophenon-sensitized reaction, the photostationary state

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could not be reached without the formation of the side products in a considerable amount.

Solutions of trans β-styrylferrocene of different concentrations ranging from 5×10^{-4} moles/liter to 5×10^{-5} moles/liter in benzene were irradiated both in the presence and absence of benzophenon; the direct reaction was carried out at 3130 Å and at 3660 Å. In no case could the presence of cis β-styrylferrocene be detected (the analysis was done with the computer program described and qualitatively with the thin-layer chromatography).

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DISCUSSION

Quantum yields for the photochemical isomerization of the cis β-styrylferrocene to trans β-styrylferrocene

In order to discuss the implications of the results presented, it is necessary to know, or at least to have an estimate, of the energy levels that might be involved in the photochemical reactions of the molecule studied.

For β-styrylferrocene no direct knowledge of this kind, aside from the information that can be obtained from the ultraviolet and visible absorption spectra, is available. However, there are experimental and theoretical results concerning the values of energy levels in ferrocene. These data will be used to estimate the energy levels of interest in β-styrylferrocene.

The ultraviolet and visible spectrum of ferrocene is given in Figure 12 and the same spectra of cis and trans β-styrylferrocene are given in Figure 4. The band in the visible region of the room temperature spectrum of ferrocene at 4400 Å and of cis and trans β-styrylferrocene at 4500 Å can be resolved into two bands at liquid nitrogen temperature.[14] The visible absorption spectra of the cis β-styrylferrocene at room temperature and at low temperature are given in Figure 13. Upon the Gaussian resolution of the bands in the visible region of the low temperature spectrum of cis β-styrylferrocene the

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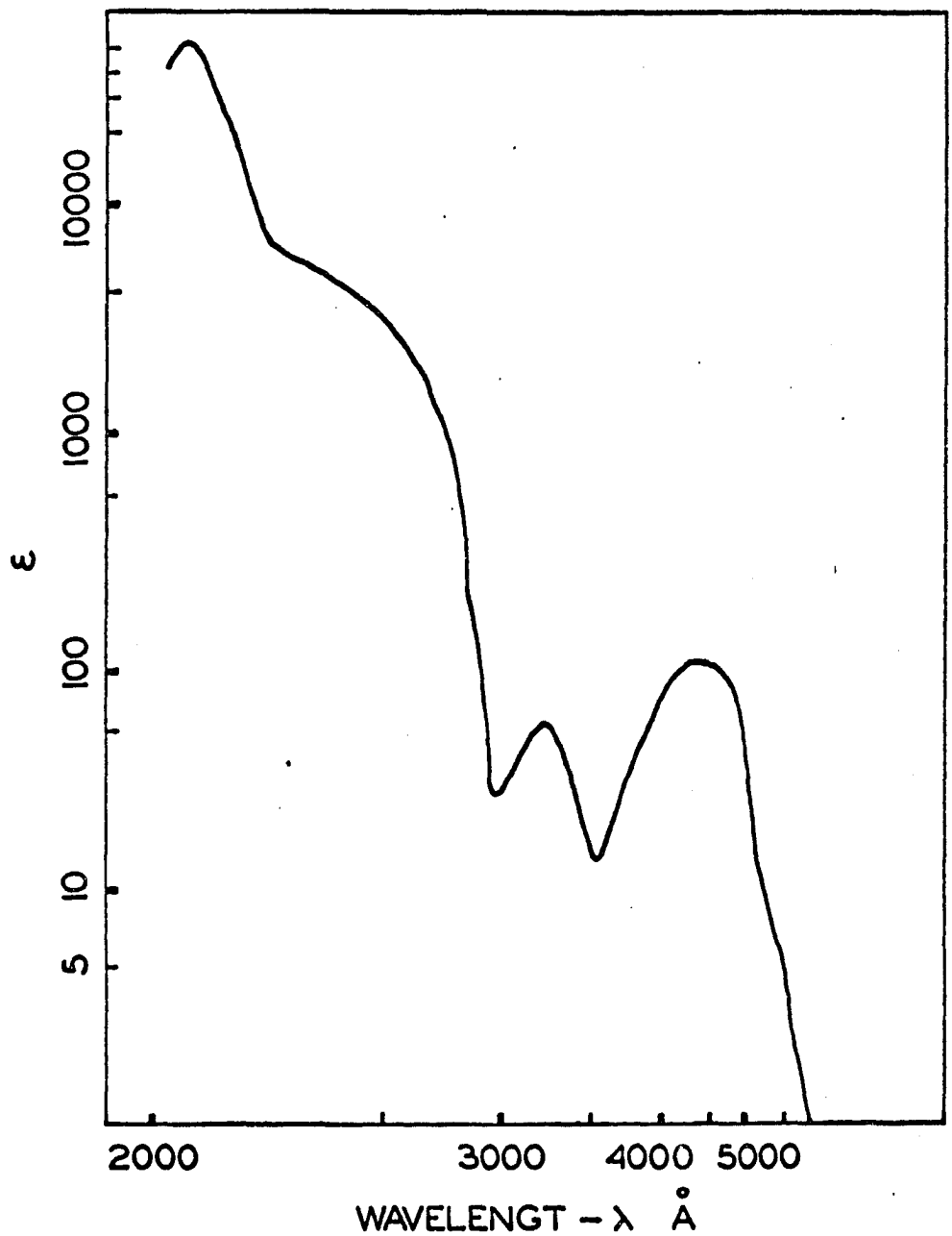

Figure 12. Absorption spectrum of ferrocene in isopentane at 24° C (reproduced from the paper by Scott and Becker[9]).

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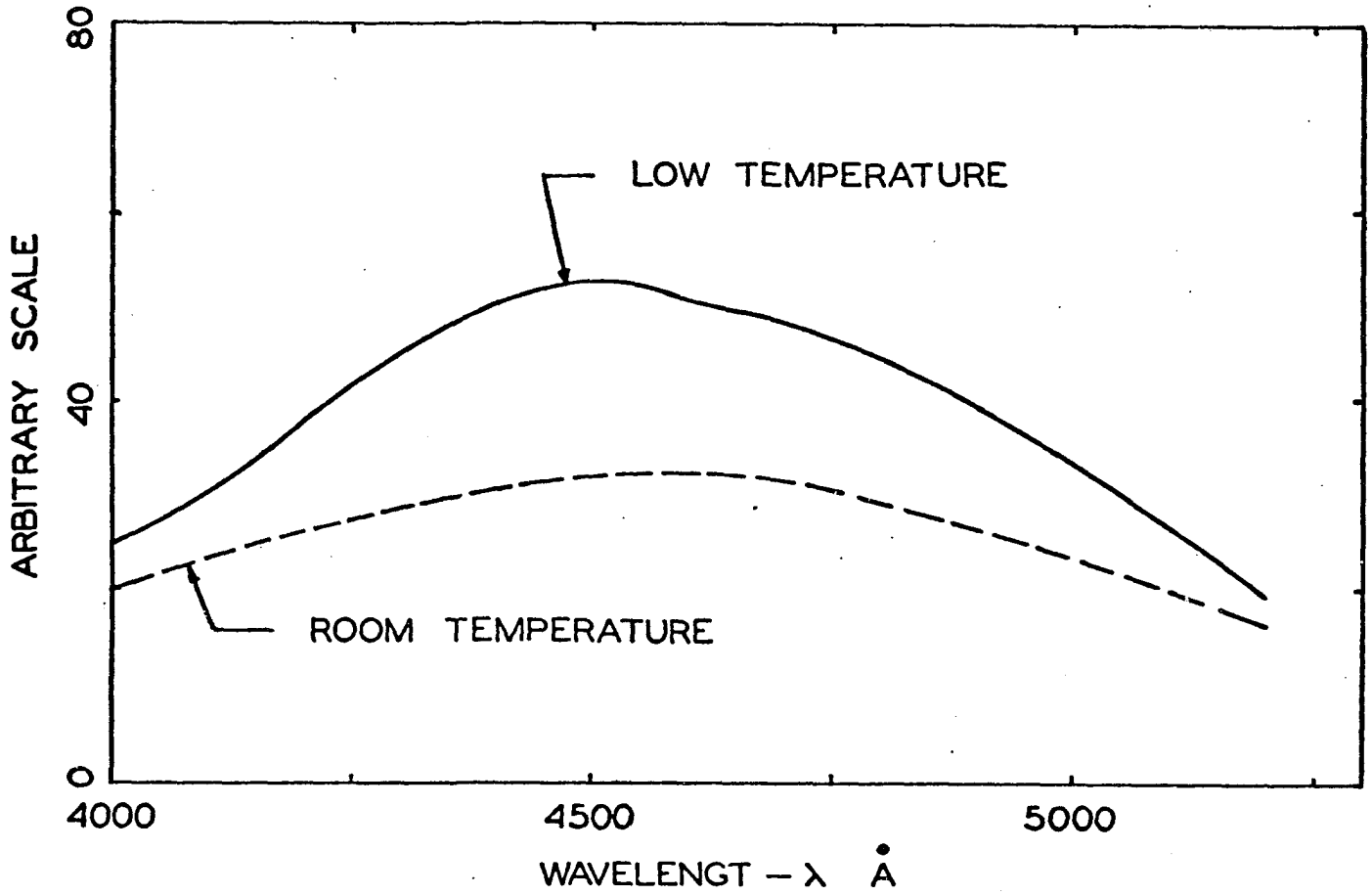

Figure 13. Visible absorption spectrum of cis β-styrylferrocene in EPA at room temperature and at liquid nitrogen temperature (the spectra were taken by Mr. Y.S. Sohn).

new maxima corresponding to the maximum at 4500 Å in the room temperature spectrum are at 4500 Å and at 4940 Å (Figure 14). The Gaussian resolution of the corresponding bands in the ferrocene spectrum gives the new maxima at 4610 Å and at 4150 Å.

In spite of the fact that as early as 1960 it was observed[13] that the 4400 Å band in the absorption spectrum of ferrocene at room temperature can be resolved into two bands at low temperature, only recently was this confirmed in the work mentioned above.[14] In the meantime some authors reported contrary results;[10] they observed no splitting of the band at 4400 Å at low temperature. Moreover, the room temperature asymmetry of that band, according to the same authors, disappeared at low temperature.

If the longest wavelength band in the low temperature spectrum is assigned to the first singlet excited state and the shorter wavelength bands to the second and third singlet states, respectively, then the energies of the three lowest singlet excited states for ferrocene and cis β-styrylferrocene are as given in Table 2.

There is evidence that 4400 Å, 3240 Å, and 2600 Å bands in the absorption spectrum of ferrocene (Figure 12) differ in their assigned characteristics. It will be assumed that the bands at 4500 Å, 3500 Å, and 2900 Å (in n-hexane), or 2950 Å (in benzene) of the cis β-styrylferrocene (Figure 4) have similar characteristics as the corresponding bands of the ferrocene molecule.

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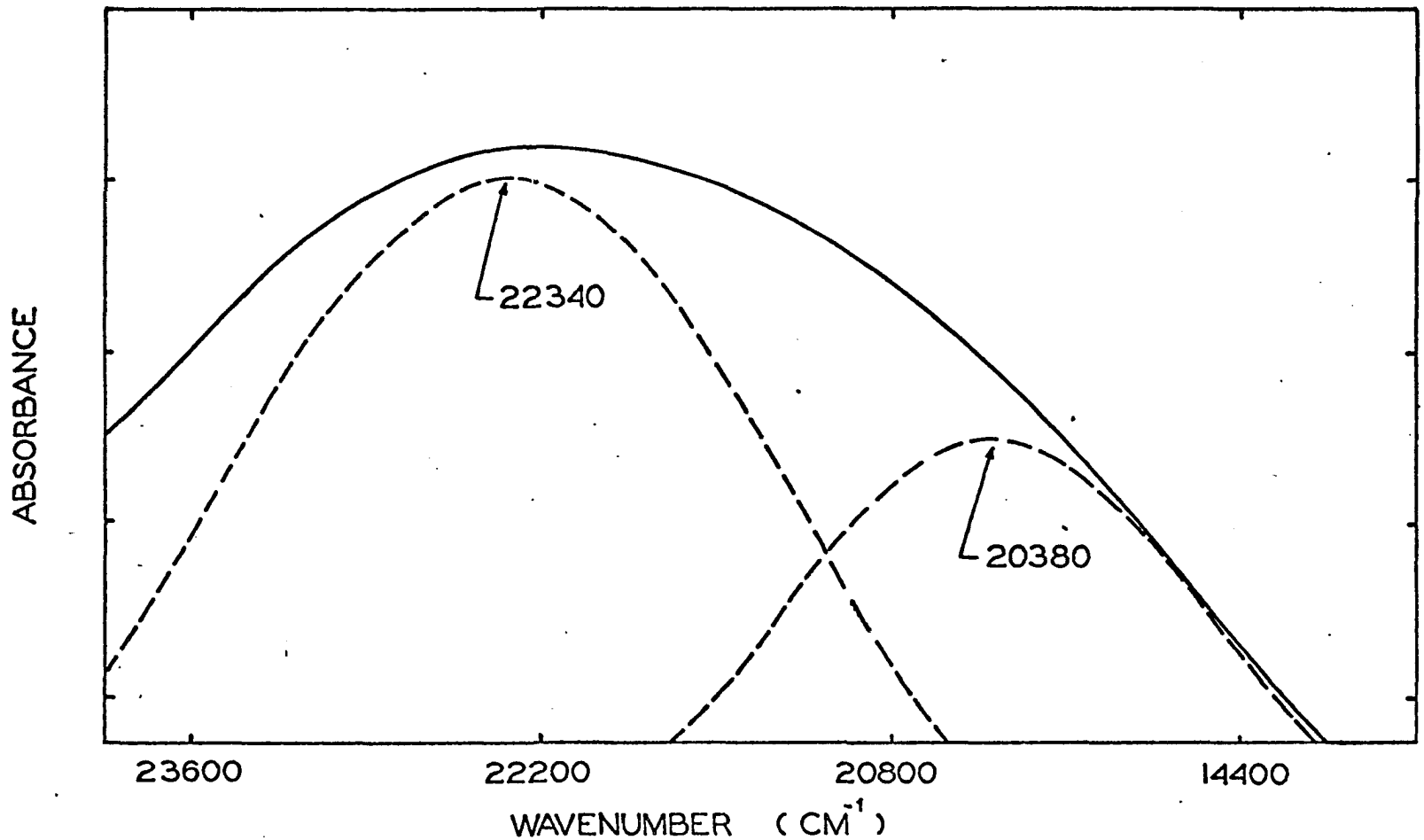

Figure 14. Gaussian resolution of the low temperature spectrum of cis β-styrylferrocene, showing the maxima at 20380 cm^{-1} (58.1 kcal/mole, 4940 Å) and at 22340 cm^{-1} (63.8 kcal/mole, 4500 Å). The absorbances are given in arbitrary scale. The resolved spectrum was obtained from Mr. Y.S. Sohn.

TABLE 2

Correlation between the maxima in the low-temperature spectra in EPA, ethanol, and the singlet states

Ferrocene

maximum in Å	maximum in kcal/mole	assigned singlet state
4110	62	S_1
4150	68.9	S_2
3250*	88*	S_3

cis β-Styrylferrocene

maximum in Å	maximum in kcal/mole	assigned singlet state
4940	58.1	S_1
4500	63.8	S_2
3500	81.7	S_3

* room temperature

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Scott and Becker[9] reported that the 4400 Å band in the ferrocene absorption spectrum shows the following characteristics: the band is blue shifted with decrease in temperature, which they interpret as suggesting a relatively pure symmetry-forbidden d-d transition (d refers to the 3d orbitals in the iron atom), which occurs because of the vibrational distortion of molecular symmetry; the position of the band is not affected by substitution on the ring, suggesting that it corresponds to a transition highly localized on the iron atom.

On the basis of these results, Scott and Becker assigned the 4400 Å band to a forbidden d-d transition localized on the iron atom.

Armstrong et al.[10] also reported that the 4400 Å band is insensitive to substitution on the ring and in addition that it does not show vibrational structure. No vibrational structure of the spectrum is expected if the transitions that result in a particular absorption band are perturbed by rotation of the rings, one relative to the other.[10] Iron 3d electrons are more likely to be perturbed by the relative position of the rings than the ring electrons. Consequently the 4400 Å band was assigned to a relatively pure 3d-3d transition largely, but by no means completely, localized on the iron atom. This assignment is somewhat more flexible but in good agreement with the one made by Scott and Becker.

Russian authors,[11] from their studies of the influence of the

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substitution on the spectral characteristics of ferrocene, came to conclusions which are consistent with those made by Scott and Becker[9] and by Armstrong et al.[10] The substitution effect was found to be additive in the case of the 4400 Å band, while there was no additivity for 3240 Å and for the higher energy bands. This result supports the conclusions mentioned earlier that the 4400 Å band involves the iron electrons and that the higher energy bands involve ring electrons which are delocalized over the whole system.

The ferrocene band at 4400 Å (Figure 12) is shifted to 4500 Å in cis β-styrylferrocene (Figure 4 shows the spectrum in benzene; the position of the maxima at 4500 Å and at 3500 Å in β-styrylferrocene does not considerably shift on change of solvent.). This indicates that the substitution with the styrene portion on the ferrocene ring results in a small shift of the band at 4400 Å in ferrocene to 4500 Å in cis β-styrylferrocene. This observation, in conjunction with the above discussion, suggests that the 4500 Å transition of β-styrylferrocene is mostly localized on the iron atom, although it appears to involve the ring electrons to a small extent, i.e., to have some charge-transfer character as well.

Scott and Becker reported[9] that the band at 3240 Å in ferrocene, in contrast to the band at 4400 Å, did not show any change with variation in temperature and moreover that it was shifted with substitution on the ring. The conclusion based on these

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results was that the 3240 Å band must involve molecular orbitals of the ring.

Similarly, Armstrong et al.[10] assigned the band at 3240 Å to a forbidden electronic transition containing much 3d character, and having an intramolecular charge-transfer character as well. This assignment was made on the basis that the 3240 Å band in ferrocene is not sensitive to temperature changes, that it has no vibrational structure, and that it does shift on substitution on the ring.

In light of the preceding discussion and the fact that the 3240 Å band in ferrocene (Figure 12) is shifted to 3500 Å in cis β-styryl-ferrocene (Figure 4), the latter transition appears to involve more ring electrons than the transition resulting in the band at 4500 Å.

In summary, it seems that the bands at 4400 Å and at 3240 Å in the absorption spectrum of ferrocene (at 4500 Å and at 3500 Å in cis β-styrylferrocene) do not involve the iron d electrons and the ring electrons to the same extent. The 4400 Å band in ferrocene (the 4500 Å band in cis β-styrylferrocene) has less charge-transfer character than the band at 3240 Å (at 3500 Å in cis β-styrylferrocene).

The next maximum below the 3240 Å band in the absorption spectrum of ferrocene is at 2600 Å (Figure 12) (the corresponding band in cis β-styrylferrocene in n-hexane is at 2900 Å and in benzene is at 2950 Å, Figure 15). The band at 2600 Å in ferrocene was

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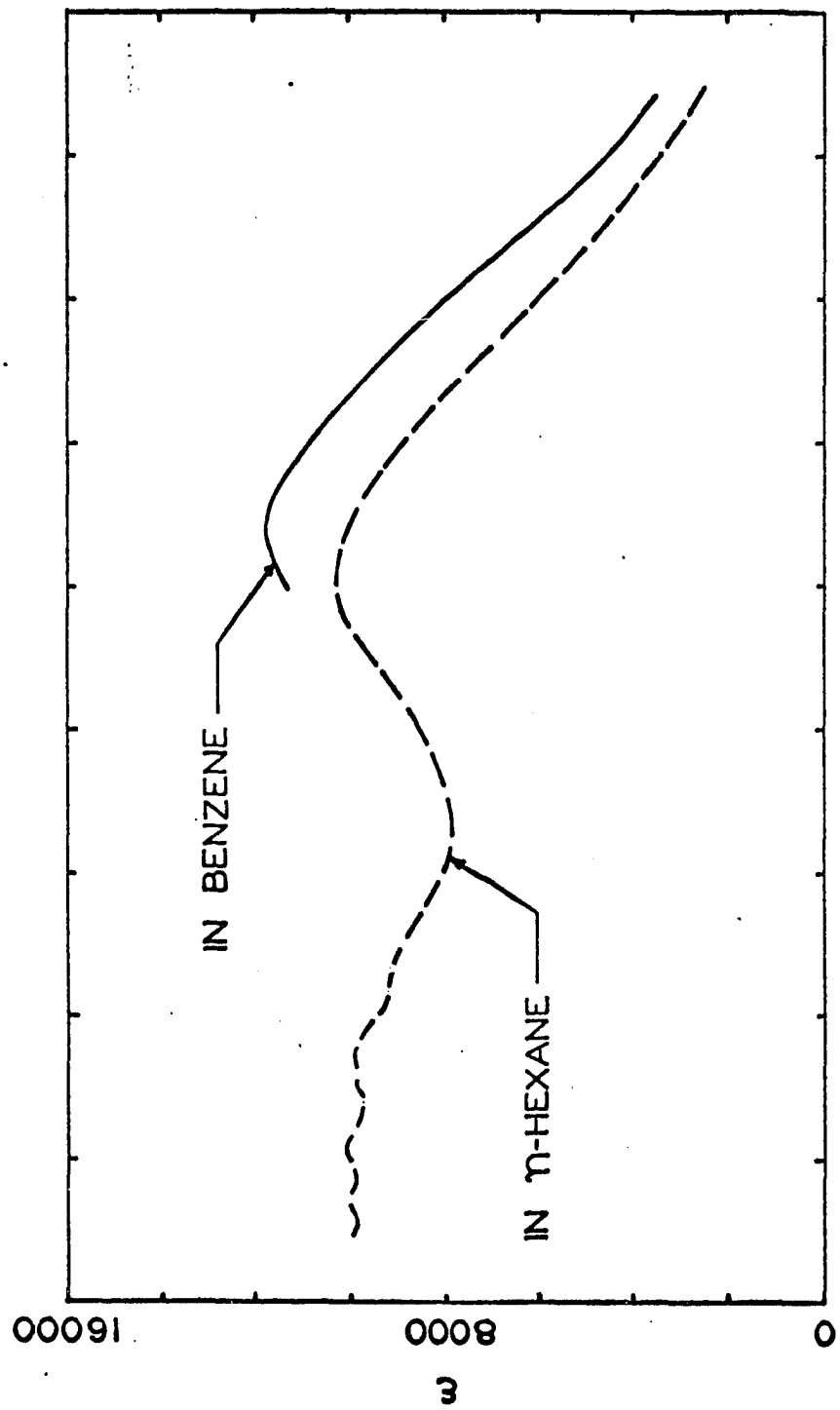

Figure 15. Absorption spectrum of cis β-styrylferrocene in benzene and in n-hexane.

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assigned by Scott and Becker[9] to an allowed transition with forbidden character. This assignment was made on the basis that the band at 2600 Å on substitution undergoes a red shift and intensification. Armstrong et al.[10] reported that the 2600 Å band in ferrocene has no vibrational structure and that it is more sensitive towards substitution than the maximum at 3240 Å. Consequently, they assigned the band at 2600 Å to a charge-transfer intramolecular electronic transition of the 3d-MO type, which involves more ring electrons than the 3240 Å band. It can be concluded that the band at 2600 Å in ferrocene (at 2900 Å in n-hexane, or at 2950 Å in benzene solution in cis β-styrylferrocene) has mostly a charge-transfer character.

In view of the above conclusions, the different amount of the charge-transfer character of the bands at 4400 Å and at 3240 Å in ferrocene can be explained in the following way: the 3240 Å band gains some charge-transfer character from the tail of the band at 2600 Å, while the same kind of mixing between the 2600 Å and the 4400 Å band is much smaller because the 4400 Å and 2600 Å bands are further separated.[15]

If the analogous explanation is assumed to hold for cis β-styrylferrocene, then the greater involvement of the ring electrons in the band at 3500 Å than in the band at 4500 Å can be explained by assuming better mixing between the tail of the maximum at 2900 Å

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and the 3500 Å band than between the more distant bands at 2900 Å and at 4500 Å.

The energies of the three lowest triplet states in ferrocene assigned by Armstrong et al.[10] are given in Table 3. These values correspond to the three shoulders on a tail on the longest wavelength side of the band at 4400 Å in the absorption spectrum of ferrocene.

Scott and Becker[9] observed only one shoulder at 5280 Å in the long wavelength region of the ferrocene absorption spectrum. On the basis of its low intensity and its sensitivity to heavy atom solvents, they assigned the shoulder at 5280 Å to a forbidden singlet $\longrightarrow$ triplet absorption corresponding to the forbidden singlet $\longrightarrow$ singlet absorption at 3240 Å. In addition, the same authors reported emission corresponding to the absorption at 5280 Å. The emission was found to depend on the excitation frequency. It could be seen only when the 3240 Å band was excited and not when the 4400 Å band was excited.

Armstrong et al.[10] were not able to see any emission. Moreover, they pointed out that, according to their triplet energy scheme (Table 3), the emission observed by Scott and Becker[9] would correspond to the emission from the higher excited triplet state than the lowest excited triplet. In terms of the known fast rates of competing processes, that seemed to them very unlikely.

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TABLE 3

Ferrocene triplet energies assignment

Armstrong et al.[10]

The energy values were obtained from the solution absorption spectrum

triplet state	energy in Å	energy in kcal/mole
T_1	7150	40
T_2	6060	47.1
T_3	5410	52.8

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Gray and Sohn[14,15] on the basis of their experimental and theoretical results, suggest a triplet energy assignment for the ferrocene molecule different from the one made by Armstrong et al.[10] (Table 4). The energy of T_1 was estimated from the singlet $\longrightarrow$ triplet absorption spectrum to be 54 kcal/mole (5300 Å) and from the ligand field calculation to be 53 kcal/mole (5390 Å). The values of T_2 (59.7 kcal/mole, 4790 Å) and of T_3 (64 kcal/mole, 4470 Å) were obtained from the ligand field calculations.

If the emission data by Scott and Becker[9] are explained in terms of the triplet energy assignment made by Gray and Sohn (Table 4) it follows that the observed emission in ferrocene is from T_1 and therefore could be real. The emission as already mentioned was observed only when ferrocene was excited to the 3240 Å band and not when it was excited to the 4400 Å band. This suggests that the intersystem crossing from S_2 to either T_3, T_2, T_1 does not take place or that it is inefficient as compared to the intersystem crossing from S_3 to either T_3, T_2, T_1, i.e., that the production of either T_3, T_2, T_1 is more efficient via S_3 than via S_2. This point will be useful in later discussion.

The data concerning the photochemical isomerization of the cis β-styrylferrocene will be discussed in light of the energy scheme given in Figure 16. The values of triplet energies of ferrocene obtained by Gray and Sohn (Table 4) are taken as an upper limit

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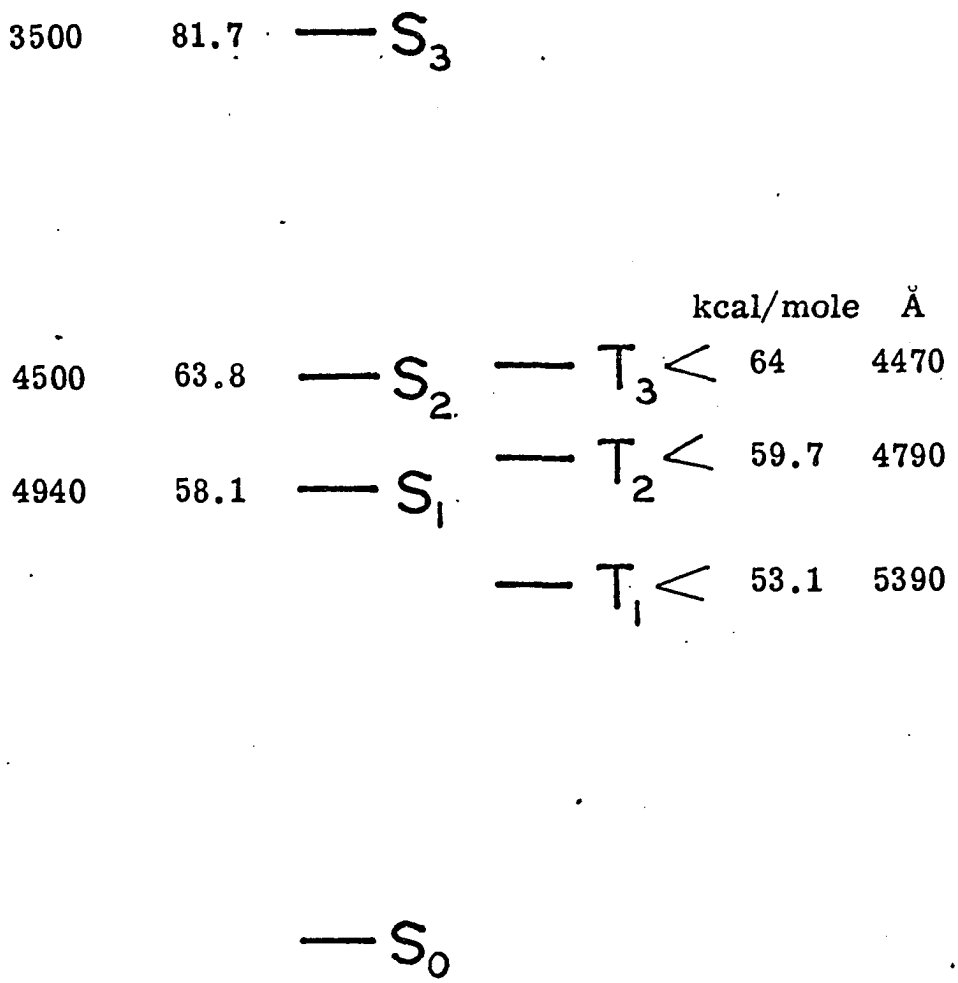

Figure 16. Estimated energy levels of cis β-styrylferrocene. The ferrocene triplet energies by Gray and Sohn are used as an upper limit estimate of the triplet energies of β-styrylferrocene.

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TABLE 4

Ferrocene triplet energies assignment

Gray and Sohn

The energy values were obtained from the Ligand Field calculations

triplet state	energy in Å	energy in kcal/mole
T_1	5390	53.1
T_1*	5300	54
T_2	4790	59.7
T_3	4470	64

*This value was obtained from the singlet-to-triplet absorption spectrum.

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estimate of the triplet energies in cis β-styrylferrocene. It is expected that the triplet energies in cis β-styrylferrocene will have lower values than those in the ferrocene molecule due to a greater electron delocalization.

The quantum yield for the photochemical cis ⟶ trans isomerization of β-styrylferrocene depends on the wavelength of irradiation. The quantum yield is higher at 3130 Å than at 3660 Å (Table 6, Figure 21). The quantum yield for the benzophenon-sensitized reaction is the same as for the direct reaction at 3130 Å (Table 6, Figure 21, see remarks on page 27). Essentially no concentration dependence of the quantum yield is observed at 3130 Å (Table 6, Figure 19), while at 3660 Å the quantum yield decreases with increasing concentration (Table 6, Figure 20).

In the case of excitation with 3130 Å S_3 is efficiently excited (see Figure 17 for the filter characteristics and Table 5 for the output of the lamp used), while in the case of excitation with 3660 Å only S_2 (S_1) is efficiently excited (see Experimental part, page 77 for isolation of 3660 Å). The isomerization can also be induced by irradiation at 4360 Å in which case S_2 (S_1) is excited (Figure 18 shows the transmission characteristics of the 3-73 Corning glass color filter).

There are several possible paths by which the molecule can isomerize once excited to the S_3 or S_2 (S_1) state. The reaction can take place from S_3 in the case of 3130 Å excitation, but only from

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TABLE 5

Spectral energy distribution of radiated mercury lines in Hanovia medium pressure quartz mercury vapor lamp[21]

mercury lines (Å)	radiation energy (watts)
5780	20.0
5461	24.5
4358	20.2
4045	11.0
3660	25.6
3341	2.4
3130	13.6
3025	7.2
2967	4.3
2894	1.6

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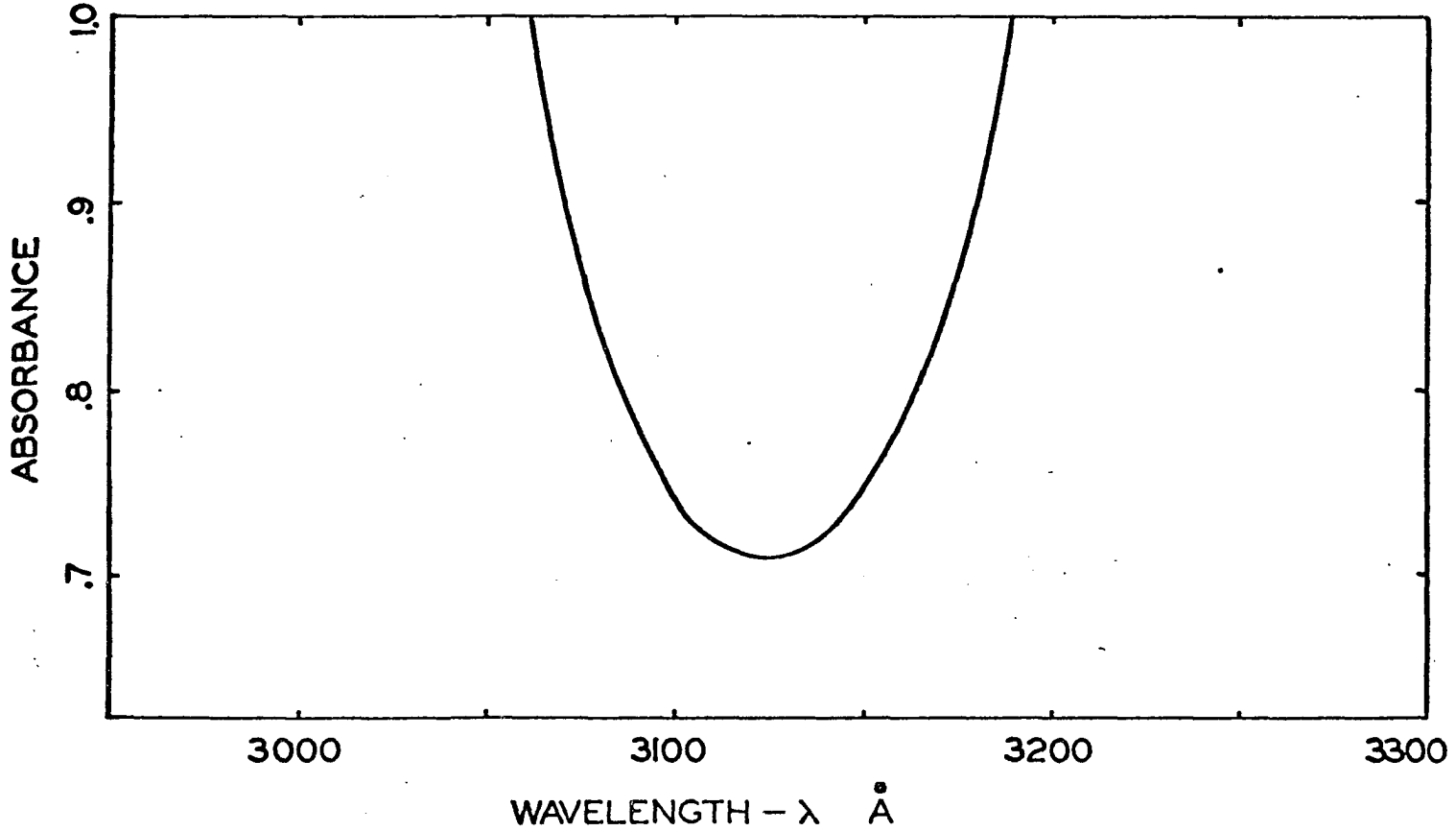

Figure 17. The absorbtion characteristics of the filter solution used for isolation of 3130 Å mercury line.

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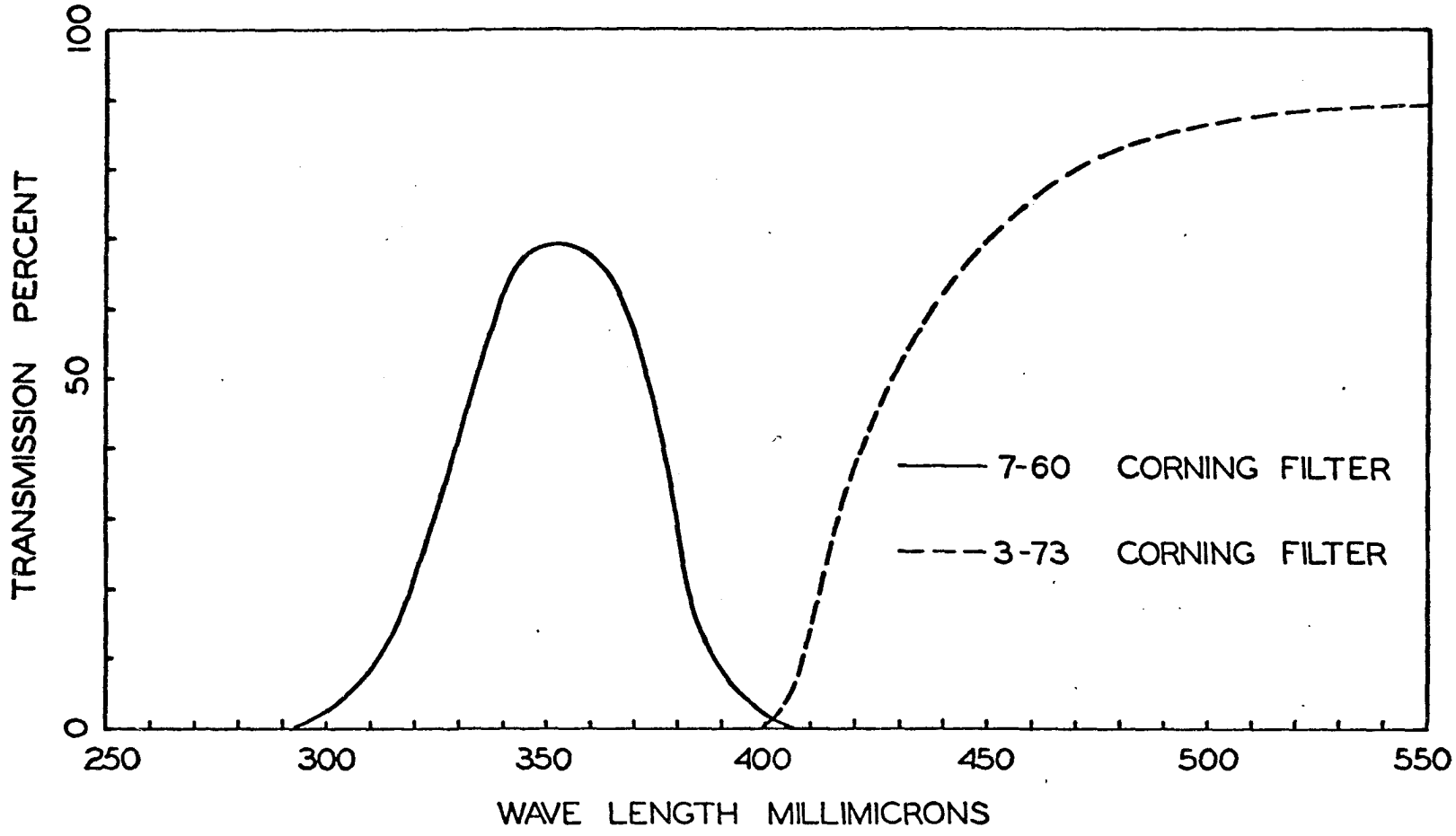

Figure 18. Transmission characteristics of the 7-60 and 3-73 Corning glass color filters (reproduced from Corning catalogue[23]).

TABLE 6

Quantum yields for the cis → trans photochemical isomerization of β-styrylferrocene in benzene solution*

Quantum yields for direct irradiation at 3130 Å

starting concentration of cis β-styrylferrocene (moles/liter)	light intensity (Einstein/min.) x 10^{-8}	quantum yield
1.11×10^{-3}	2.39	0.00696
6.27×10^{-4}	2.56	0.00632
5.60×10^{-4}	3.09	0.00662
5.55×10^{-4}	2.39	0.00642
7.85×10^{-5}	3.16	0.00608
5.02×10^{-5}	2.56	0.00672

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TABLE 6 continued

Quantum yields for direct irradiation at 3660 Å

starting concentration of cis β-styrylferrocene (moles/liter)	light intensity (Einstein/min.) x 10^{-8}	quantum yield
7.4×10^{-4}	3.23	0.00198
5.6×10^{-4}	5.37	0.00214
5.52×10^{-4}	3.15	0.00202
3.7×10^{-4}	3.23	0.00279
7.4×10^{-5}	3.23	0.00310
5.55×10^{-5}	3.23	0.00321
5.52×10^{-5}	3.15	0.00365

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TABLE 6 continued

Quantum yields for the benzophenon-sensitized reaction

starting concentration (moles/liter)		light intensity (Einstein/min.)	quantum yield
cis β-styrylferrocene	benzophenon	x 10^{-8}	
5.6×10^{-4}	4.87×10^{-2}	5.37	0.00542
5.78×10^{-4}	5.53×10^{-2}	3.23	0.00539

*The given values of quantum yields are averages of two or more measurements. The accuracy of the quantum yield is estimated to be of the order of 5 - 10%.

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S_2 (S_1) in the case of 3660 Å excitation. Thus chemical rearrangement from S_3 is not possible when light of 3660 Å is used. Since the same chemical rearrangement occurs when cis β-styrylferrocene is irradiated at either 3130 Å or at 3660 Å the obligatory involvement of S_3 in the chemical rearrangement seems unnecessary. If the reaction were only from S_2 (S_1) there would not be any difference in the quantum yield at 3130 Å and at 3660 Å. Thus we conclude that the chemical rearrangement probably does not occur from either the S_3 or S_2 (S_1) state. The wavelength effect on the quantum yield would not be observed either if the reaction were from the vibrationally excited ground state (S_0^{ν}). Therefore chemical rearrangement from S_0^{ν} is unlikely. Moreover the quantum yield at 3130 Å is the same as the quantum yield for the benzophenon-sensitized reaction, which suggests the same mechanism in the two cases. It is well established[16] that in the benzophenon-sensitized reactions the triplet energy of benzophenon (T_1 = 69 kcal/mole)[17a] is transferred to the substrate--in our case to cis β-styrylferrocene. Since the quantum yield at 3130 Å is the same as the quantum yield for the benzophenon-sensitized reaction, the involvement of the triplet of benzophenon (T_1) and therefore of a triplet of cis β-styrylferrocene, is suggested. In addition, one can postulate that probably all chemical rearrangement of cis β-styrylferrocene occurs from some triplet state. Thus we conclude that the isomerization appears to take place from the triplet manifold,

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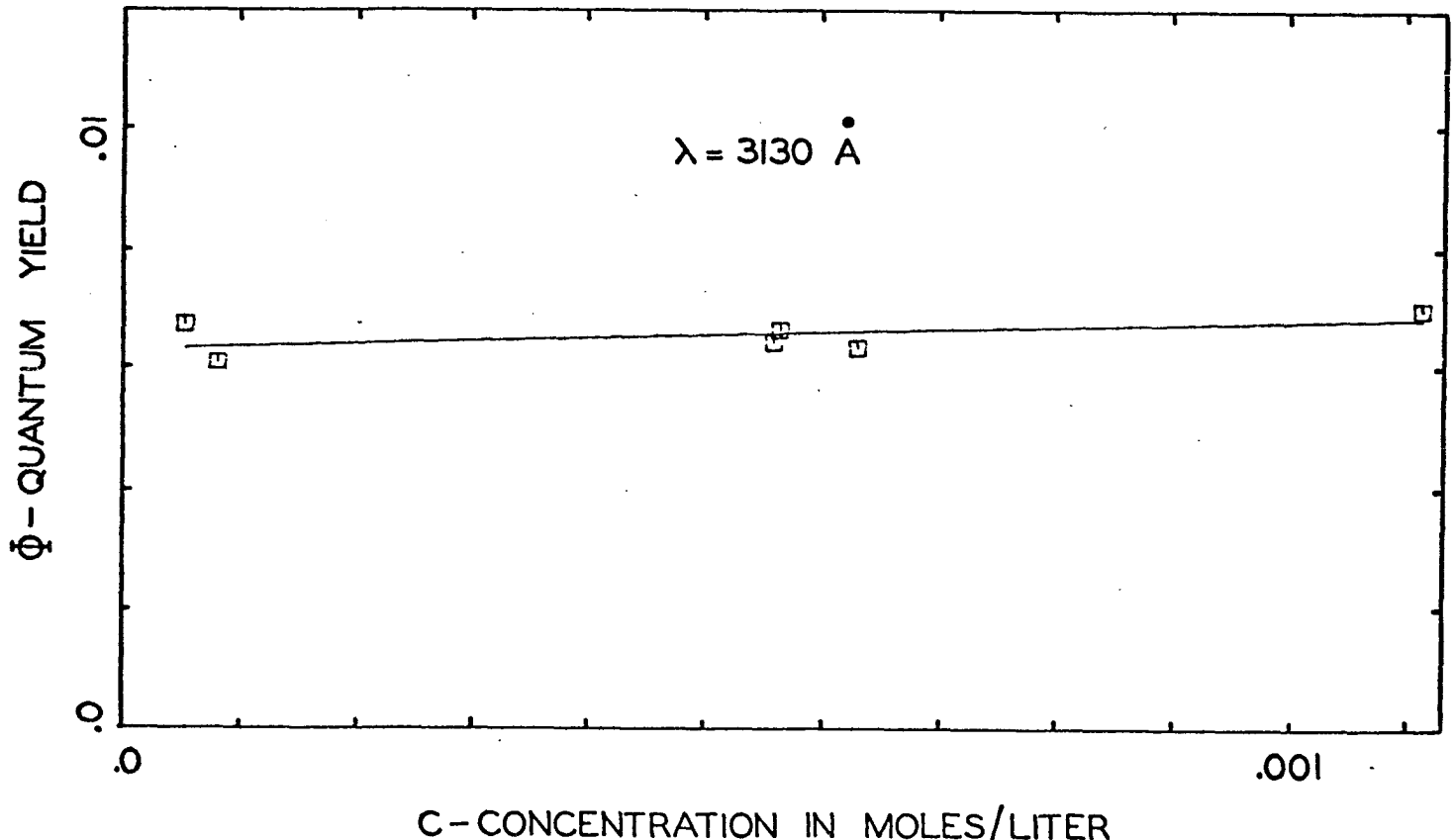

Figure 19. Quantum yield for the cis ⟶ trans isomerization of β-styrylferrocene in benzene at 3130 Å as a function of concentration of cis β-styrylferrocene.

the question being which triplet is the one involved in the reaction.

The difference in the extent of the charge-transfer character of the bands at 4500 Å and 3500 Å in the absorption spectrum of β-styrylferrocene have already been mentioned. If we postulate that only the charge-transfer portion of the excitation leads to the efficient chemical rearrangement the following situation, depending on the wavelength of excitation light, is observed: when cis β-styrylferrocene is excited to the 4500 Å band with 3660 Å (and 4360 Å), most of the excitation charge is localized on the iron atom, since this band has very little (if any) charge-transfer character and the carbon-carbon double bond involved in the isomerization is not affected much (if at all); on the other hand, since the excitation of the band at 3500 Å with light of 3130 Å appears to involve mostly the ring electrons, i.e., to have more charge-transfer character, the carbon-carbon double bond will be excited to an appreciable extent, which would allow isomerization to occur.

In view of what has been said, the cis $\longrightarrow$ trans isomerization of β-styrylferrocene seems more likely to take place from a triplet state corresponding to the singlet at 3500 Å, i.e., from T_3 rather than from a triplet state corresponding to the singlets in the visible region, i.e., from T_2 or T_1 (Figure 16). T_3, in the case of irradiation at 3130 Å can be formed by intersystem crossing from S_3. In the case of irradiation at 3660 Å , T_3 can be formed by intersystem crossing from S_2 (S_1).

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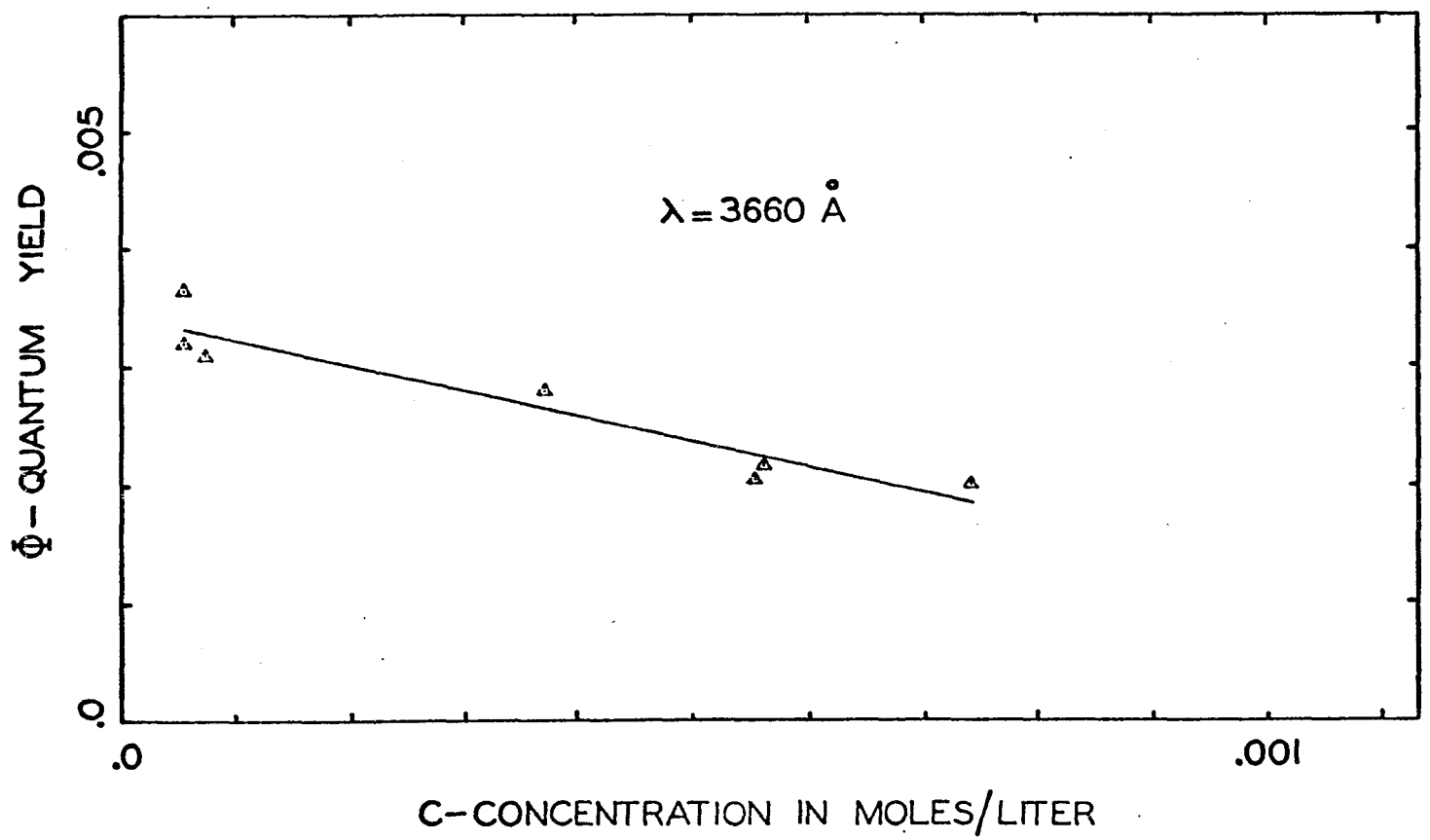

Figure 20. Quantum yield for the cis → trans isomerization of β-styrylferrocene in benzene at 3660 Å as a function of concentration of cis β-styrylferrocene.

From the studies of the emission spectra of ferrocene, it has already been seen that the intersystem crossing from S_3 to either T_3, T_2, T_1 is more efficient than the intersystem crossing from S_2 to either T_3, T_2, T_1. In the present study this point is reflected in the higher quantum yield at 3130 Å compared to the quantum yield at 3660 Å (Figure 21). The reaction at 3130 Å is more efficient because of the more efficient production of T_3 via S_3 than via S_2 (in the case of irradiation at 3660 Å). Furthermore, since the intersystem crossing from S_3 to T_3 is more efficient than the intersystem crossing from S_2 to T_3, the deactivation of S_3, by collisions with the cis β-styrylferrocene molecules in their ground state, cannot compete efficiently in the case of 3130 Å excitation as can collisional deactivation of the S_2 state in the case of 3660 Å excitation. Consequently, no concentration effect is observed when excitation is induced with 3130 Å, while the quantum yield decreases with increasing concentration when excitation is induced with 3660 Å.

The following scheme summarizes the mechanism for the direct reaction if preference is given to the reaction from T_3.

1) $\text{cis}^{S_0} \xrightarrow{h\nu} \text{cis}^{S_3(S_2)}$

2) $\text{cis}^{S_3(S_2)} \longrightarrow \text{cis}^{T_3}$

3) $\text{cis}^{T_3} \longrightarrow \text{trans}^{S_0}$

4) $\text{cis}^{S_2(S_3)} + \text{cis}^{S_0} \longrightarrow 2\ \text{cis}^{S_0}$

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1) the excitation of cis β-styrylferrocene to the S_3 state with 3130 Å or to the S_2 state with 3660 Å.
2) the intersystem crossing from either the S_3 or S_2 state to T_3.
3) the photochemical isomerization from T_3 of cis β-styrylferrocene
4) deactivation of either the S_3 or S_2 state by collisions with the ground state cis β-styrylferrocene molecules, important for the case of 3660 Å excitation, i.e., for the collisional deactivation of S_2, relatively unimportant for the case of 3130 Å excitation, i.e., for the collisional deactivation of S_3.

Similarly, the scheme for the benzophenon-sensitized reaction, again if preference is given to the reaction from T_3, is the following:

$$1)\ \phi_2CO^{S_0} \xrightarrow{h\nu} \phi_2CO^{S_1}$$

$$2)\ \phi_2CO^{S_1} \longrightarrow \phi_2CO^{T_1}$$

$$3)\ \phi_2CO^{T_1} + cis^{S_0} \longrightarrow cis^{T_3} + \phi_2CO^{S_0}$$

$$4)\ cis^{T_3} \longrightarrow trans^{S_0}$$

1) excitation of the sensitizer (benzophenon) to S_1.
2) intersystem crossing from S_1 to T_1 (of benzophenon).
3) triplet energy transfer from the sensitizer to the substrate (cis β-styrylferrocene).
4) cis → trans isomerization from T_3 of cis β-styrylferrocene.

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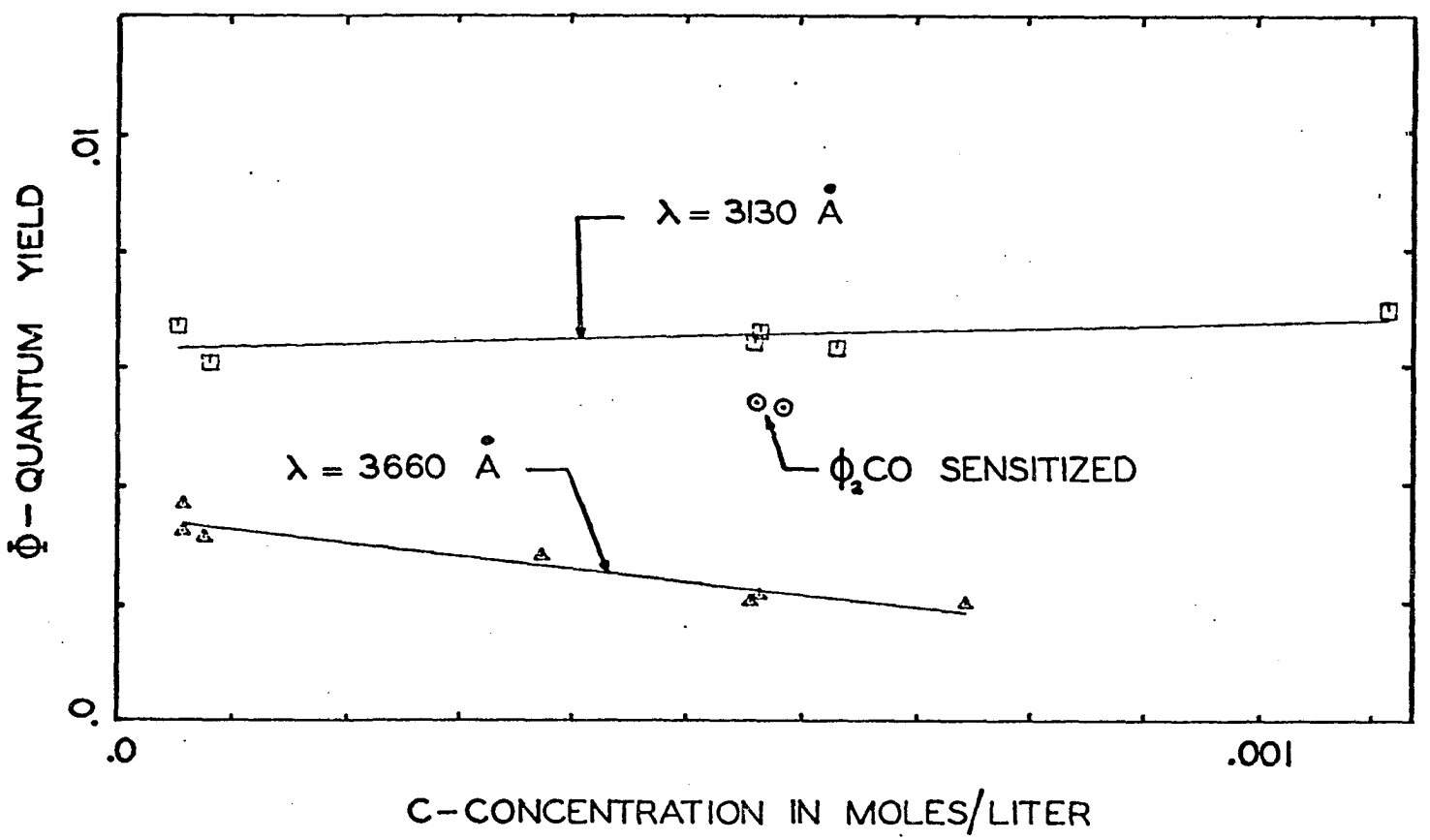

Figure 21. Comparison of the quantum yields for the cis ⟶ trans isomerization of β-styrylferrocene in benzene at 3130 Å, at 3660 Å, and of the quantum yield for the benzophenone-sensitized reaction (see the remark on page 27 concerning the latter values).

Although the preference is given to the photochemical rearrangement taking place from the T_3 state (on the basis that T_3 has more charge-transfer character than T_2 or T_1), the involvement of the T_2 or T_1 excited states, alone or in conjunction with the T_3 state, cannot be completely excluded. Upon excitation to S_2 (3660 Å) the T_2 (T_1) state can be formed in one or in a combination of several following ways:

$$
\begin{array}{l}
\ulcorner\!\longrightarrow T_3 \longrightarrow T_2 \longrightarrow T_1 \\
S_2 \longrightarrow T_2 \longrightarrow T_1 \\
\llcorner\!\longrightarrow T_1
\end{array}
$$

$$
\begin{array}{l}
S_1 \longrightarrow T_2 \longrightarrow T_1 \\
\llcorner\!\longrightarrow T_1
\end{array}
$$

and similarly in the case of excitation to S_3 (3130 Å):

$$
\begin{array}{l}
\ulcorner\!\longrightarrow T_3 \longrightarrow T_2 \longrightarrow T_1 \\
S_3 \longrightarrow T_2 \longrightarrow T_1 \\
\llcorner\!\longrightarrow T_1
\end{array}
$$

$$
\begin{array}{l}
\ulcorner\!\longrightarrow T_3 \longrightarrow T_2 \longrightarrow T_1 \\
S_2 \longrightarrow T_2 \longrightarrow T_1 \\
\llcorner\!\longrightarrow T_1
\end{array}
$$

$$
\begin{array}{l}
S_1 \longrightarrow T_2 \longrightarrow T_1 \\
\llcorner\!\longrightarrow T_1
\end{array}
$$

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It should be noted that the kinetic analysis of the data, assuming that the quenching of the singlet excited state (S_2) by cis-β-styrylferrocene molecules in the ground state (S_0) is diffusion-controlled ($k_q = 10^{10}$ l/mole sec) reveals that the lifetime (τ) of the excited state that is being quenched is 7.5×10^{-6} sec.

$$\frac{d(S_2)}{dt} = k(S_2) + k_q(S_2)(S_0)$$

$$\frac{\phi_1}{\phi_2} = \frac{\dfrac{k(S_2)}{k(S_2) + k_q(S_2)(S_0)_1}}{\dfrac{k(S_2)}{k(S_2) + k_q(S_2)(S_0)_2}}$$

ϕ_1 = quantum yield at concentration $(S_0)_1$

ϕ_2 = quantum yield at concentration $(S_0)_2$

$$\frac{\phi_1}{\phi_2} = \frac{k + k_q(S_0)_2}{k + k_q(S_0)_1}$$

$$\frac{0.00198}{0.00365} = \frac{k + 10^{10} \times 5.52 \times 10^{-5}}{k + 10^{10} \times 7.4 \times 10^{-4}}$$

$k = 7.5 \times 10^6$ sec^{-1}

$\tau = 7.5 \times 10^{-6}$ sec

A lifetime of 7.5×10^{-6} sec appears to be too long for a higher excited singlet state unless the molecule shows marked fluorescence.

The following explanation could also account for ϕ decrease with increase in concentration for irradiation at 3660 Å and for the absence of such concentration dependence for irradiation at 3130 Å.

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The 3660 Å line was not isolated with a monochromator, but with a set of filters which could pass other Hg lines lying close to the line at 3660 Å. The 3660 Å line is on the tail of the absorption band at 3500 Å in cis-β-styrylferrocene. This band at 3500 Å might be composed of two absorptions; one that has characteristics similar to a ferrocene absorption (at 3240 Å) and the other one being similar to a stilbene absorption (around 3200 Å). For that reason, even though two different Hg lines are close, they can activate different transitions of the cis-β-styrylferrocene molecule. Possibly only activation of the stilbene-like transition leads to efficient reaction. (The triplet state associated with this transition is possibly the one that is responsible for the reaction.) Consequently, of the two Hg lines, absorption of only one may lead to reaction. If the Hg line that causes the reaction is completely absorbed (or nearly so), even at low concentration, while the other line that does not cause the reaction is only partially absorbed, the increase in concentration would result in an appreciable increase only of the absorption of the line that has partially been absorbed at lower concentration. Since that line does not cause reaction the net result would be that the amount of reaction would remain constant in spite of an increase in the total amount of the incident light that is absorbed. Thus a larger fraction of the incident light will appear to have been absorbed, while the amount of reaction remains constant leading to an apparent decrease in ϕ as the concentration of cis-β-styrylferrocene is increased.

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If the chemical rearrangement were from T_2 (T_1) the higher quantum yield at 3130 Å could again be due to a more efficient production of T_2 (T_1) via S_3 than via S_2. For the reasons analogous to those given for the case of T_3 involvement, the quantum yield decrease with increasing concentration at 3660 Å would be observed and no such concentration dependence would exist in the case of excitation at 3130 Å.

The absolute values of the quantum yield for the direct reaction of the cis β-styrylferrocene at all wavelengths of excitation used and of the sensitized reaction in the presence of benzophenon are very low when compared to the efficiency of the cis → trans isomerization reactions of other similar systems. For instance from Table 7 it can be seen that the quantum yield for the direct, as well as for the benzophenon-sensitized isomerization reaction of stilbene is much higher than the quantum yield for the corresponding reaction of cis β-styrylferrocene. The fact that the quantum yield for the direct cis → trans isomerization reaction of β-styrylferrocene at 3130 Å is the same as the quantum yield for the benzophenon-sensitized isomerization suggests it is unlikely that the inefficiency of the sensitized reaction is due to the inefficient triplet energy transfer from benzophenon to the substrate (the intersystem crossing efficiency of benzophenon is almost 1)[18] while in the direct

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TABLE 7

Quantum yield for the cis ⟶ trans isomerization of stilbene

	concentration (moles/liter)		quantum yield	
	stilbene	benzophenon	$\phi_{c \to t}$	$\phi_{t \to e}$
direct irradiation at 3130 Å in n-hexane at 25° C[22]	8×10^{-6}		0.32	0.59
benzophenon-sensitized reaction[16]	5×10^{-2}	5×10^{-2}	0.38	0.45

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reaction that it is due to the inefficient intersystem crossing. Rather it seems that the loss of energy takes place after the triplet state has been formed.

We suggest that the low efficiency of the cis → trans isomerization of β-styrylferrocene is probably due to the fact that the reaction takes place from a triplet state higher than the lowest excited triplet, i.e., from the third triplet state. The lifetime of the higher triplet states is generally very short and the isomerization reaction might not be able to compete efficiently with other fast deactivation processes. In addition, as it has already been mentioned, even the T_3 state is not of a pure charge-transfer character; thus some inefficiency might come from the partial localization of the excitation charge on the iron atom as well.

Again, the low efficiency of the isomerization reaction could also be explained if the reaction were postulated to be from T_2 or T_1. If the isomerization were from the T_2 state both arguments used in the case of the reaction from the T_3 state would be applicable, but the one concerning the charge-transfer requirements would be more important in this case. If the reaction were from T_1 the latter argument would be the only possible one.

Besides the already mentioned reasons for our preference for postulating that the isomerization is from the T_3 state, we favor the same mechanism because of analogy with ferrocene-olefin complexes which react from a higher electronic state than the lowest triplet state.[19] In the reactions of the ferrocene-olefin complexes mentioned, ferrocene catalyzes the cis-trans isomerization of pyperylene and dimerization of

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isoprene. The reactions of these dienes can be induced only when excitation energy is at least as high as the electronic transition corresponding to the band at 3240 Å in the absorption spectrum of ferrocene. Several mechanistic possibilities that could account for the results obtained were considered. The most likely one was the excitation of the ferrocene-diene complex to a singlet state higher than the first excited singlet, which crosses over to a higher triplet state and consequently dissociates into a triplet state diene and a ground state ferrocene*. The dissociation of the ferrocene-diene complex from a higher triplet state into a ground state ferrocene and triplet state diene is more likely to take place than the dissociation of the complex from the first excited triplet state into the same products, which is an endothermic process. The triplet state diene thus produced undergoes isomerization or dimerization.

It appears that ferrocene both intramolecularly (in the cis → trans isomerization of β-styrylferrocene) and intermolecularly (in the ferrocene-catalyzed isomerization of the dienes) is capable of reacting from a triplet state higher than the lowest triplet. In spite of the fact that most photochemical reactions take place from the lowest excited singlet or triplet state, a few reports have recently appeared in which the involvement of the second triplet state was considered as a possible mechanism.[4-8] This suggests that the lifetime of the higher excited states of some systems is not as short as hitherto believed. Ferrocene and cis β-styrylferrocene seem to be an additional example.

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*The data were interpreted in terms of different energy assignments for ferrocene than the ones used in the present work.

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Photostationary states

The photostationary state obtained on irradiation of the pure cis β-styrylferrocene solutions, both at 3130 Å (Table 8, Figure 22) and at 3660 Å (Table 9, Figure 23) lie, within the experimental error, completely on the side of the trans isomer. Furthermore, when solutions of trans β-styrylferrocene are irradiated under the same conditions under which the cis ⟶ trans reaction was carried out, no isomerization takes place. It seems reasonable to make the following assumptions:

a) trans β-styrylferrocene absorbs light and is excited to a singlet state corresponding to the one involved in the rearrangement of cis β-styrylferrocene.

b) trans β-styrylferrocene excited singlet state undergoes intersystem crossing to the corresponding triplet state with the same or nearly the same efficiency as the cis β-styrylferrocene does.

c) the lifetime of the trans β-styrylferrocene triplet state is the same as the lifetime of the cis β-styrylferrocene triplet state.

On the basis of these assumptions and of the results obtained, we conclude that the intermediate(s) that results upon excitation of either isomer decays always to trans β-styrylferrocene. One possibility is that since trans β-styrylferrocene is more stable than cis β-styrylferrocene, the activation energy necessary for the transition from

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TABLE 8

Photostationary state for the cis → trans isomerization of β-styrylferrocene in benzene at 3130 Å

irradiation time hours		minutes	% cis/% trans
4	and	40	89 / 11
8	and	20	80 / 20
12	and	40	73 / 27
23	and	20	59 / 41
32	and	50	50 / 50
75	and	35	30 / 70
286	and	55	100 / 0

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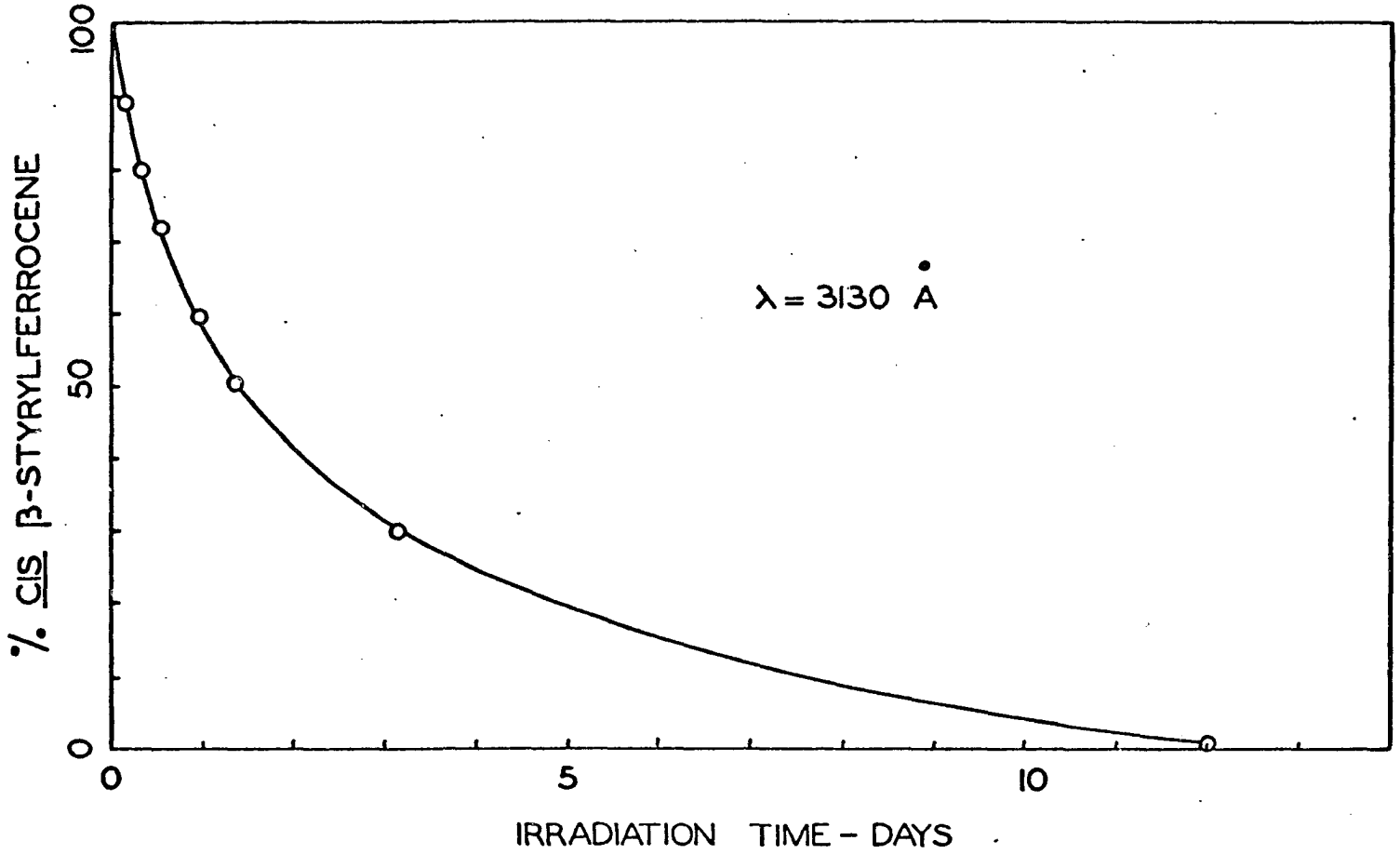

Figure 22. Photostationary state obtained when 7.8×10^{-5} moles/liter cis β-styryl-ferrocene was irradiated in benzene solution at 3130 Å.

TABLE 9

Photostationary states for the cis ⟶ trans isomerization of β-styrylferrocene in benzene at 3660 Å

Irradiation time			% cis / % trans
days		hours	
2	and	7	82 / 18
3	and	5	77 / 23
3	and	22	69 / 31
5	and	23	58 / 42
6	and	22	54 / 46
12	and	8	39 / 61
18			23 / 77
24			14 / 86
32			10 / 90
37	and	18	4 / 96
42	and	19	1 / 99

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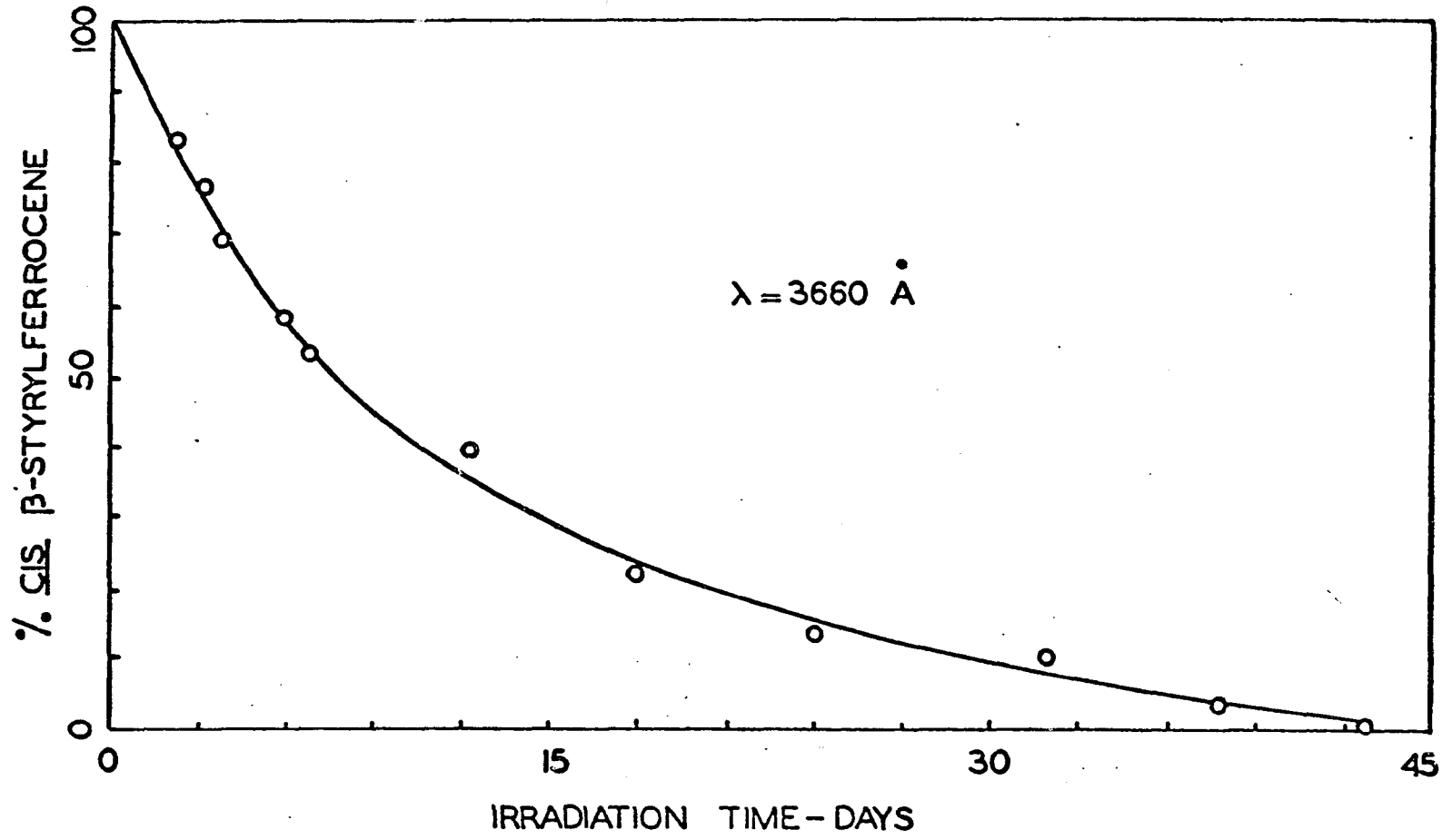

Figure 23. Photostationary state obtained when 8.4×10^{-5} moles/liter cis β-styryl-ferrocene was irradiated in benzene solution at 3660 Å.

the intermediate to trans β-styrylferrocene ground state is less than the activation energy necessary for the transition from the corresponding intermediate to cis β-styrylferrocene ground state.

Summary

cis β-Styrylferrocene was shown to isomerize photochemically to trans β-styrylferrocene. The suggested mechanism for this chemical rearrangement induced both by direct excitation and by benzophenon-sensitized excitation involves a triplet state of cis β-styrylferrocene. The preference was given to the reaction taking place from the T_3 state rather than from the T_2 or T_1 states. The possibility that the isomerization is from T_3 was favored on the following basis: S_2 and S_1 (as well as their associated triplet states) in cis β-styrylferrocene were assumed to have the same characteristics as the ones described for the corresponding states in the ferrocene molecule. They were taken to result mostly from the excitation of the metal 3d electrons in contrast to the S_3 state (and its corresponding triplet) which was assumed to have considerably more charge-transfer character. Consequently the carbon-carbon double bond was thought to have more excitation energy, i.e., more chance to isomerize when the molecule is in the T_3 state than when it is in the T_2 or T_1 state . In addition the involvement of the T_3 state did not seem improbable on the basis that it has already been suggested that

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a state higher than the first excited triplet of the ferrocene-diene complex is involved in the reaction in which ferrocene catalyzes the photochemical isomerization of pyperylene and dimerization of isoprene. Moreover, the involvement of the T_2 state in a few other systems has recently been reported as well. However, the possibility that the chemical rearrangement of the cis β-styrylferrocene takes place from either T_2 or T_1 has also been acknowledged.

The higher quantum yield at 3130 Å was explained in terms of the observation that the production of T_3 is more efficient via S_3 (3130 Å) than via S_2 (3660 Å). The concentration effect at 3660 Å and the absence of such an effect at 3130 Å was considered to be also a consequence of a more efficient intersystem crossing to T_3 from S_3 (3130 Å) than from S_2 (3660 Å). The deactivation of the S_2 state (3660 Å) by the collisions with the ground state cis β-styrylferrocene molecules was considered to be more efficient (and even more so as the concentration increases) than the deactivation of the S_3 state. The observation that the quantum yield at 3660 Å decreases with increasing concentration, while the quantum yield at 3130 Å does not depend significantly on the concentration of the cis β-styrylferrocene was so explained.

The low absolute values of the quantum yield were attributed to the short lifetime of the T_3 state and in addition to a possible energy waste due to the excitation charge being partially localized on the iron atom even in the T_3 state.

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The observation that ϕ for the reaction at 3130 Å and ϕ for the benzophenon-sensitized reaction are the same implies that the low efficiency of the direct reaction is not due to the inefficient singlet → triplet intersystem crossing and that the inefficiency of the sensitized reaction is not due to inefficient energy transfer from benzophenon to cis-β-styrylferrocene.

The photostationary state obtained when cis-β-styrylferrocene was irradiated has been shown to be completely on the side of the trans isomer (within experimental error); trans-β-styrylferrocene was shown not to rearrange to cis-β-styrylferrocene under the experimental conditions used.

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EXPERIMENTAL

Synthesis of cis and trans β-styrylferrocene by the Wittig Reaction

Benzyltriphenylphosphoniumbromide

Triphenylphosphine (126 mmoles) and benzylbromide (120 mmoles) were dissolved in 300 ml of xylene (reagent grade) and the mixture was refluxed for twenty-six hours with stirring. The white crystals formed were filtered, washed with xylene, and dried over the vacuum. The yield was high.

cis and trans β-Styrylferrocene

Ferrocenealdehyde (4.7 mmoles, Research Org. Chem. Co., grade P, recrystallized from n-hexane) and benzyltriphenylphosphoniumbromide (2.55 mmoles) were dissolved in 10 ml absolute ethanol (reagent, pure grade). Sodiumethoxide, prepared by dissolving sodium (44 mmoles) in 20 ml ethanol, was added slowly from the dropping funnel to the reaction mixture stirred with the magnetic bar. The reaction was carried out under nitrogen. The mixture was stirred at room temperature for two days. Subsequently the solvent was evaporated and the residue chromatographed on a column (silica gel, Davison Chemical, Grace). Ligroin (60-70°) was used as eluent.

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Further purification and separation of the cis and the trans β-styrylferrocene was done by the use of preparative thin-layer chromatography (silica gel, Merck, A.G.). Ligroin (60-70° C) was used to develop the plates. Since both cis and trans β styryl-ferrocene are colored, they can easily be distinguished on the thin-layer chromatogram; trans β-styrylferrocene is the slower travelling one.

trans β-Styrylferrocene crystallizes from n-hexane; the crystals have a deep orange color, melt at 119° C, and are soluble in common organic solvents. The nuclear magnetic resonance spectrum of trans β-styrylferrocene in carbondisulfide is given in Figure 3. The ultraviolet and visible spectra in benzene and in n-hexane are given in Figures 4 and 24. Analysis calculated for carbon and hydrogen: C 75.02%; H 5.58%; Found (Spang, Microanalytic Lab.): C 74.76%; H 5.58%.

cis β-Styrylferrocene was isolated as a yellowish oil; it is soluble in common organic solvents. The nuclear magnetic resonance spectrum in carbondisulfide is shown in Figure 2. The ultraviolet and visible spectra in benzene and in n-hexane are shown in Figures 4 and 15. Analysis calculated for carbon and hydrogen: C 75.02%; H 5.58%; Found (Spang, Microanalytic Lab.): C 73.6%; H 5.38%.

Preparation of the thin-layer plates

Silica gel (50g, $PF_{254+366}$, Merck A.G., without $CaSO_4$) was

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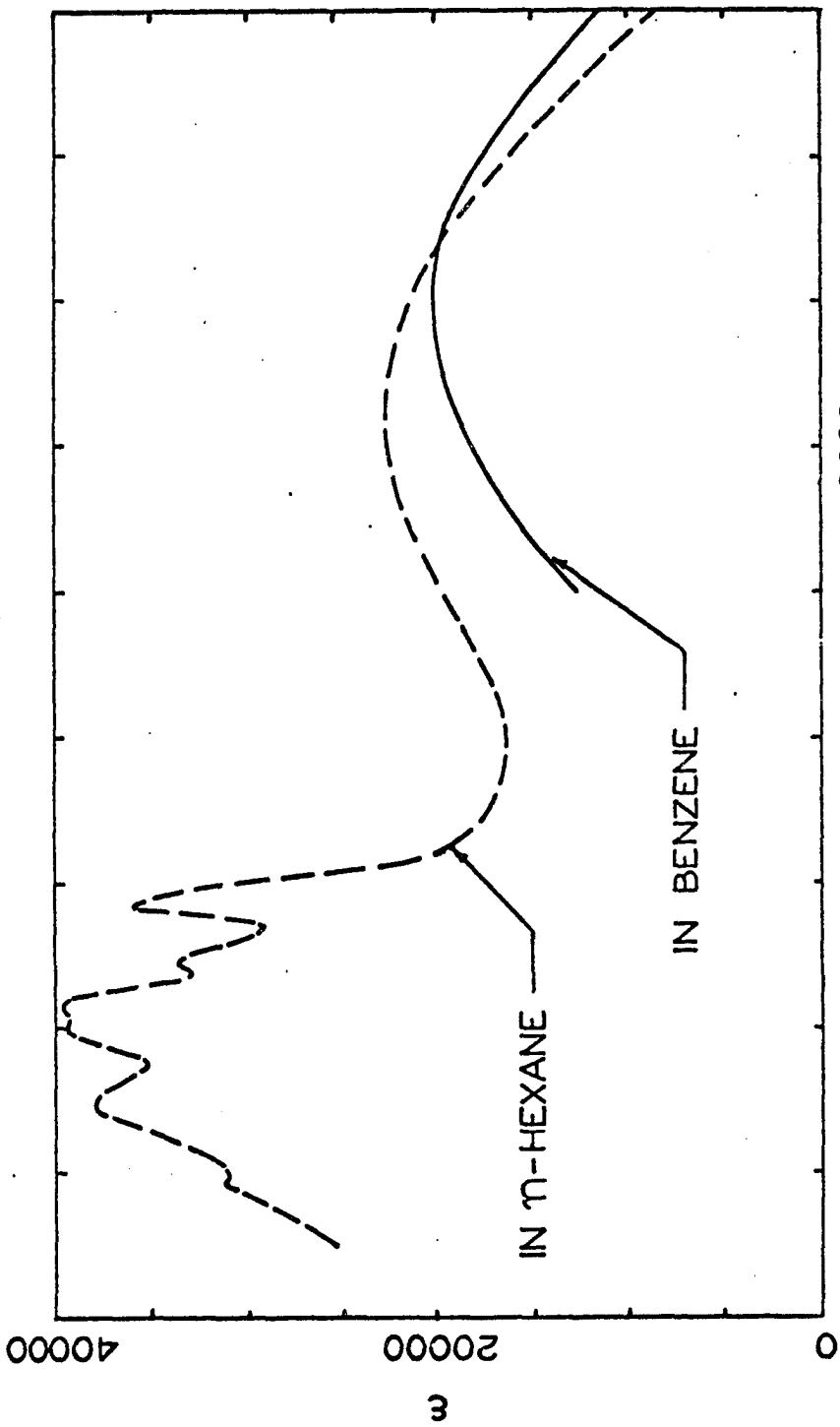

Figure 24. Absorption spectrum of trans β-styrylferrocene in benzene and in n-hexane.

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shaken for a few seconds with 125 ml distilled water in a round-bottom flask provided with a glass stopper. From the prepared silica gel mixture 2mm thick plates were made. The plates were dried over night on the air, then left in the oven for half an hour at 110° C and stored in a container with calcium chloride.

Eastman Chromagram Sheets, type K 301 R (silica gel) were used also, but not for preparative purposes.

Materials

1,10-Phenanthrolenemonohydrate, Matheson, Coleman and Bell, reagent grade was recrystallized from distilled water, M.P. 99° C.

Ferricamoniumsulphate, $Fe_2(SO_4)(NH_4)_2 \times 24H_2O$, Baker Chemical, reagent grade.

Potassiumoxalate, $K_2C_2O_4 \times H_2O$, Baker analyzed, reagent.

Benzene, T.A. Hinton, 99.99% was used without further purification.

n-Hexane, Phillips, pure grade, used for the ultraviolet spectra.

Benzophenon, Matheson, Coleman and Bell, reagent grade, recrystallized five times from warm ethanol.

Filters and lamps used in the irradiation experiments

The lamp used for irradiation was a medium pressure 450 w

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mercury vapor resonance Hanovia lamp. The spectral energy distribution of radiated mercury lines in the lamp are given in Table 5.

Filters used for isolation of 3660 Å mercury line

The uranium glass filter which absorbs part of the 3341 Å mercury line and all of the lines with the wavelength less than 3341 Å[20a] was placed nearer to the lamp and 7-60 Corning glass color filter was placed further from the lamp. The transmission characteristics of the latter filter are given in Figure 18.

Filter used for isolation of 3130 Å mercury line

The line at 3130 Å was isolated with a 1 cm thick solution filter which was prepared by dissolving 10 g Na_2CO_3 and 0.5 g $Na_2Cr_2O_7$ x $2H_2O$ (Matheson, Coleman and Bell, reagent) in distilled water and diluting to one liter with distilled water.[20b] The absorption characteristics of the prepared solution are shown in Figure 17.

Filter used for isolation of 4360 Å and higher wavelength mercury lines

The line at 4360 Å and the higher wavelength lines were isolated with the 3-73 Corning glass color filter. The transmission characteristics of this filter are shown in Figure 18.

Preparation of the samples for irradiation

Exactly three milliliters (a 3 ml pipet was used) of the solution to be irradiated were placed in the test tube. Pyrex test tubes were used for the experiments performed at 3660 Å (4360 Å) and

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quartz tubes were used when the excitation light was 3130 Å. The test tubes had a glass joint (with a grease trap) by which they were attached to the vacuum line on which they were evacuated by three freeze-pump-thaw cycles, with cooling in liquid nitrogen, at a pressure of about 5×10^{-4} mm Hg. After evacuation the test tubes were sealed.

Spectra

Ultraviolet and visible spectra were measured with a Carey 14 spectrophotometer. Since the determination of the composition of the irradiated solution was based on the analysis of the ultraviolet spectra those had to be accurately measured. Each time, before the spectra were taken, the base-line was carefully zeroed. Often the base-line was checked both at the beginning and at the end of a series of measurements. All the solutions of the appropriate concentration needed for the measurements of the spectra were prepared by transferring with a pipet a desired amount of the irradiated solution to a volumetric flask and by subsequent dilution.

The nuclear magnetic resonance spectra were taken on the NMR Varian Model A-60A.

Irradiation of the samples

The same set-up for irradiation described in reference 20[b] was used. The lamp for irradiation was placed in a quartz well through

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which the distilled water for cooling was circulated. The well had two concentric reservoirs (each 1 cm thich) for solution filters. The glass filters were mounted around the outside of the quartz well except for the uranium filter which was cylindrical and could be placed between the lamp and the well.

Actinometry

The light intensity of each isolated wavelength was measured with theferrioxalate actinometry.[17b] Potassiumferrioxalate solution was prepared by adding 3 ml of 0.2 M ferricamoniumsulphate solution in 0.1 N sulfuric acid to 3 ml of 0.6 M potassiumoxalate solution in 0.1 N sulfuric acid. Potassiumferrioxalate solution (3 ml) was placed in pyrex or quartz test tubes. One test tube was saved for a blanck and the others were irradiated for a measured time period. The irradiated solution (2 ml) was transferred into a 10 ml volumetric flask. One milliliter of phenanthrolene solution in water (0.1%) and one milliliter of acetic acetate buffer were added and diluted to 10 ml with water. The optical density at 5100 Å of the prepared solution was measured using the non-irradiated solution as a reference. The light intensity was calculated from the following equation:

$$I = \frac{ODFV}{\phi At} \quad \text{Einstein/min.}$$

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V - volume of the irradiated solution in ml

OD - optical density at 5100 Å

ϕ - quantum yield at the wavelength of irradiation

t - irradiation time

A - fraction of the light absorbed at wavelength of irradiation

$\phi_{3130} = 1.24$ $\quad A_{3130} = 1$

$\phi_{3660} = 1.21$ $\quad A_{3660} = 1$ $\quad \epsilon_{5100} = 11010$

$\phi_{4360} = 1.11$ $\quad A_{4360} = 0.615$

$$F = \frac{V_{FLASK(10\ ml)}}{V_{ALIQUOT(2\ ml)}} \cdot \frac{1}{\epsilon_{5100}} \times 10^{-3} = 4.53 \times 10^{-7}$$

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