I. RADICAL RECOMBINATION IN SOLVENT CAGES

II. QUENCHING OF EXCITED STATES OF AROMATIC MOLECULES THROUGH EXCIPLEX FORMATION

III. MAGNETIC FIELD EFFECT ON TRIPLET-TRIPLET ENERGY TRANSFER PROCESSES

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ABSTRACT FOR PROPOSITIONS

PROPOSITION I

It is proposed that norbornadiene methyl amine (III) be tested as a quencher of aromatic ketone triplets and aromatic hydrocarbon singlets.

PROPOSITION II

It is proposed that nanosecond flash photolysis be used to study the decay of singlet exciplexes produced by quenching of aromatic singlets by dienes.

PROPOSITION III

It is proposed to use CIDNP to measure the rate of spin inversion in radical pairs and biradicals.

PROPOSITION IV

It is proposed that the mechanism of rearrangement of 3-(9′-fluorenyl)tricyclo[3.2.1 $O^{2,4}$] octene 8 (I) be investigated by studying the reaction of the title compound in acids and bases.

PROPOSITION V

It is proposed to investigate the decay modes of the excited states of $Fe(CN)_6^{4-}$.

ACKNOWLEDGMENTS

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Some of the work reported here has been collaborative. Luisa Tan and Ray Harrigan performed the emission quenching studies described in Chapter II. The magnetic field effect experiments (Chapters I and III) were conceived with the help of Dr. J. L. Charlton and Dr. T. Penner. Dr. C.-H. S. Wu is to be acknowledged for her help in setting up the radical recombination experiments. The CIDNP experiments were performed in the laboratory of Dr. J. Bargon with his assistance. The triplet exciplex quenching studies were carried out by John Robbins.

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ABSTRACT

The first section describes experiments on radical recombination rates. From the temperature and solvent dependence of quantities such as escape efficiency from primary solvent cages we deduced that the activation energy of recombination of radical pairs inside the primary cage is zero in all solvents. Some previous data on recombination rates were reinterpreted accordingly, and then we focused our attention on intersystem crossing in radical pairs. Cage efficiencies were determined in a magnetic field relative to zero field values and the significance of these results discussed.

The second section describes experiments designed to explore the mechanism of bimolecular quenching processes. Naphthalene fluorescence was quenched by trans-β-ethyl styrene and it was found that this quenching process induces intersystem crossing in naphthalene. The same quencher was used to quench naphthalene triplets and it was observed that a substantial amount of energy wastage (quenching without electronic energy transfer to the quencher) occurs in solvents other than benzene.

Energy wastage was also found in quenching of acetophenone triplets by sterically hindered olefins. We obtained kinetic evidence that olefins quench acetophenone triplets through the formation of triplet exciplexes and we estimated its lifetime for the olefin cis-2,2-dimethyl-3-hexene.

The third section relates observations that bimolecular ratios of triplet-triplet energy transfer are affected by application of a magnetic field. Efforts were made to further study this field effect using deuterated quenchers and quenchee. A hypothesis has been put forward to explain our data. Other hypotheses have been critically evaluated.

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CHAPTER I

RADICAL RECOMBINATION IN SOLVENT CAGES

Introduction

The concept of geminate recombination was first introduced by Noyes.[1] Noyes suggested that when radical pairs are formed from an initiator, some of them may recombine immediately inside the primary solvent cage, while some may recombine after they have suffered a few collisions with solvent molecules, but before they have diffused apart. The rest diffuse through the solvent and become 'free' radicals. Hammond and Waits[2] tested this model using the initiator ABN (I) and came to the conclusion that chemical methods of radical trapping cannot distinguish between primary and secondary recombinations proposed by Noyes. They noted an increase in the scavenging efficiency at a scavenger concentration sufficient to put approximately one scavenger molecule in the solvent shell of six solvent molecules surrounding the radical pair. The principal theoretical models[1-4] aim at accurately predicting the relationship between 'efficiency of cage recombination' or a related function and solvent viscosity (η). There have been essentially two kinds of relationships proposed: (1) $F \alpha 1/\eta$, (2) $F \alpha (1/\eta)^{\frac{1}{2}}$ (4). Pryor[4] has suggested that $F \alpha (1/\eta)^{\alpha}$, when $\alpha = 0.5 - 1.0$. Here $F = k_D/k_{CR}$ (see Scheme I). Presumably, this variation in α stems from the difference in shapes of the radicals and solvent molecules, since all models deal with size in terms of mass (momentum) and diffusion radius.

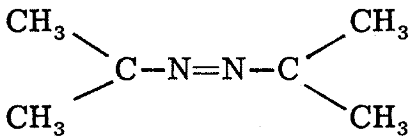
$$RN_2R \xrightarrow{k_i} \overline{2R\cdot + N_2} \xrightarrow{k_D} 2R\cdot + N_2 \xrightarrow[k_{sc}]{I\text{-}I} 2RI$$

$$\overline{2R\cdot + N_2} \xrightarrow{k_1} R - R + N_2; \qquad \overline{2R\cdot + N_2} \xrightarrow{k_2} R' + R'' + N_2$$

$$k_{CR} = k_1 + k_2$$

Scheme I

Rates of recombination inside a cage are fast, and these rates have been used as calibration points for other fast rates such as bond rotation, spin inversion and diffusion. Green[5] and Kopecky and Gillian[6] have estimated that for α-phenylethyl radical pairs and for the α-phenylethyl radical-benzyl radical system, $k_{rot} \simeq 15\ k_{comb}$, and $k_{diff} \simeq 2.5\ k_{comb}$. Here the assumption made was that loss of optical activity occurred through rotation about C–C bond in the radical, instead of tumbling. Recently Johnson and Seltzer[7] studied the thermolysis of III. They obtained much lower ratios of k_{rot}/k_{comb}. In heptane it was 0.94 while in octadecane it was 0.30, probably because there was no intervening molecule in the cage to retard recombination. However, the intervening molecule cannot be solely responsible for this discrepancy. Theory predicts that cage recombination rates should decrease about six times if there is an intervening molecule of diameter



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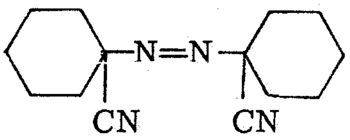

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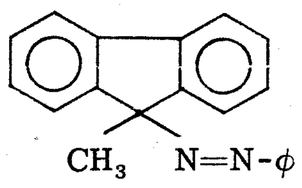


III

1.2 Å--which is approximately the diameter of N_2 molecule. Hammond and co-workers found a four-fold increase in cage recombination rate when the keteneimine from ABN was thermolysed, compared to the recombination rate during the thermolysis of ABN under similar conditions. Johnson and Seltzer[7] point out the larger radical sizes in their system, as well as their larger mass could well have reduced the rate of rotation.

The situation is more complicated when k_{cage} is compared with $k_{spin\ inv}$. Direct photolysis of N-(1-cyanocyclohexyl) pentamethylene keteneimine produces cage recombination of 24% of the radical pairs produced. This is essentially identical to that produced by thermolysis of the keteneimine. However triplet sensitization reduces the fraction of radicals recombining inside the cage to 8%. Using a simple scheme (Scheme II) we can use this data to obtain the ratio of k_{isc} to k_{cage}:

$$R - R' \xrightarrow{h\nu} \overline{R\uparrow\ \downarrow R} \xrightarrow{k_c} R - R\ (\text{etc.})$$

$$\overline{R\uparrow\ \downarrow R} \xrightarrow{k_D} 2R\cdot\ ; \qquad \overline{R\uparrow\ \downarrow R} \xrightarrow{k_{isc}} \overline{R\uparrow\ \uparrow R}$$

$$R - R' \xrightarrow{h\nu/\text{sens}} \overline{R\uparrow\ \uparrow R} \xrightarrow{k_D} 2R\cdot\ ; \qquad R\uparrow\ \uparrow R \xrightarrow{k_{isc}} \overline{R\uparrow\ \downarrow R}$$

Scheme II

If it is assumed that the intersystem crossing rates between the singlet and triplet states of the radical pair are identical, then using the data of Hammond and Fox[8] we get $k_{isc} : k_{cage} : k_{diff} = 38 : 36 : 76$. In other words, rate of spin inversion is almost equal to the rate of cage recombination. Similar results are obtained with _t_-butyl perbenzoate decomposition and benzoyl peroxide decomposition.[9] CIDNP signals reverse in sign when benzoyl peroxide is decomposed through sensitization instead of direct irradiation.[10] The behavior of azo compounds does not fall into this pattern, however. Little or no difference in cage recombination fraction was found when ABN was decomposed _via_ photosensitization. This led Bartlett[12] and Hammond[11] to suggest that in case there is an intervening molecule in between the radical pair, spin correlation is extremely weak and therefore intersystem crossing is extremely fast. Recently Bartlett and Engels[13] reexamined the data and came to the conclusion that triplet sensitization induced _cis_-_trans_ isomerization of the azo compounds. The _cis_ isomers are much more susceptible to thermal decomposition and fall apart at room temperature. These same conclusions were reached by Porter _et al._[14] who showed that decomposition on direct irradiation also takes place after _cis_-_trans_ isomerization. In other words, photolysis of azo compounds, direct or sensitized, results in the formation of the ground state _cis_-isomer which then falls apart thermally. One of our goals was to devise an experiment that would let us measure the rate of spin inversion relative to the rate of cage recombination of azo compounds.

The completion between cage recombination process and diffusive separation has been studied by many groups. The common technique is to plot log F _vs._ 1/T, when $F = k_D/k_C$. The slope is equal to the difference between E_D and E_α when E_α is the activation energy of the cage reaction (recombination and/or disproportionation).

Sometimes F is defined in a somewhat different manner, so that $E_\eta - E_\alpha$ is obtained, when E_η is the activation energy of viscous flow. These measurements are rather ambiguous in our opinion, for they do not take into account solvation of the radicals and they measure quantities that cannot be called activation energies in the usual sense of the term, particularly if the radical is small. I am unaware of any theoretical treatment that explains the relationship between E_α of methyl radicals, for example, and the C—H vibrational modes.[33] Sometimes the stabilization produced by solvation becomes the major quantity among all 'activation energies' operating in the cage, and E_α may become negative. Usually attempts are made to keep solvation constant in a series of experiments by using a series of saturated hydrocarbons as solvents. It is known, however, that attempts to obtain a continuously varying viscosity scale by adding small amounts of high polymers to fluid hydrocarbon solvents result in apparent anomalous relationship of F _vs._ η. Therefore we decided to investigate if the shape of solvent molecules would affect the F _vs._ η relationship at all. Solvation is perhaps also responsible for the fact that little correlation can be drawn between cage recombination percentages and bimolecular termination rates of radicals. Thus Weiner and Hammond[15] obtained 9.4×10^8 lt mole^{-1}sec^{-1} as the rate constant of recombination by 2-cyano-2-propyl radicals in benzene, and compared it with k_D which is known to be 6×10^9 lt mole^{-1}sec^{-1}.[15] The cage fraction then comes out as 0.16, compared to values close to 0.6-0.7 obtained by Walling and Kurkov[16] who used conventional scavenging methods. This would imply that solvation reduces the recombination rate, since Weiner and

Hammond measured the recombination rate of two fully solvated 'free radicals' encountering each other at a rate assumed to be equal to k_D. This recombination would perhaps involve an additional activation energy equal to the energy of stabilization due to solvation. Scavenging techniques measure the fraction of radicals that recombine in the solvent cage in which they are generated, and perhaps recombination is competitive with solvation; it is also possible that solvation tends to hold the two radicals together in the solvent cage longer, thus actually increasing the fraction that recombines in the cage. We therefore considered it essential to investigate the extent of solvation of radicals by aromatic solvents. There is a report that nitroxide radicals are solvated by aromatics,[17] and the energy of stabilization is estimated to be ~ 1 kcal/mole in benzene.

Results and Discussion

There is some controversy on the mode of decomposition of ABN (I) and ACC (II). Concerted fission was first proposed for a symmetric azo compound by Ramsberger.[27] However, Rafikov et al. presented evidence of a diazenyl radical from photolytic decomposition of ABN at 77 °K.[18] This does not necessarily prove that decomposition of ABN is non-concerted in a fluid solvent at 60 °-70 °C. Crawford and Takagi[26] have presented thermochemical arguments as well as arguments based on rate data to support their conclusion that symmetric as well as asymmetric azo compounds undergo non-concerted decomposition in the gas phase. Recently vibrational relaxation of a diazenyl radical has been directly observed in fluid solution using picosecond flash photolysis techniques.[19] This experiment also indicates that in fluid solution, at room temperature the diazenyl radical from ABN is exceedingly short-lived, and breaks up after 2-3 vibrations of the C—N bond. We are interested in the diazenyl radical only if it acts as a chemical intermediate, capable of being quenched either inside the cage by the other radical or by a suitably reactive solvent molecule.

$$\overline{RN_2R'} \underset{k\text{-}1}{\overset{k_1}{\rightleftharpoons}} \overline{R\cdot + \cdot N_2 - R'} \xrightarrow{k_D} R\cdot + \cdot N_2R \longrightarrow P + N_2$$

$$\overline{R\cdot + \cdot N_2 - R'} \xrightarrow{k_2} \overline{R\cdot + R'\cdot + N_2} \xrightarrow{k_C} R - R' + N_2$$

$$\overline{R\cdot + R'\cdot + N_2} \xrightarrow{k_D} R\cdot + R'\cdot + N_2 \longrightarrow P + N_2 \quad .$$

Scheme III

It is quite possible that the transition state of decomposition of ABN resembles an asymmetric radical pair, and the diazenyl radical decomposes to give N_2 and an alkyl radical during vibrational relaxation.[33] If this is the case then the diazenyl radical does not have a chemically significant lifetime, in that it cannot be quenched or made to decay in any mode other than splitting off a N_2 molecule. Pryor and Smith have devised an elegant scheme for testing whether a given precursor undergoes nonconcerted fission (Scheme III). If the observed rate of decomposition of the azo compound varies with solvent viscosity for a series of similar solvents (so that the solvation of the azo compound does not change), the mode of decomposition is non-concerted. k_2 and k_D must be competitive with k_{-1}, for this test to successfully discriminate between concerted and nonconcerted bond scission. For asymmetric azo compounds, competition between k_D and k_2 can be investigated by monitoring the racemization of an optically active azo compound. Experiments of this nature provide ample evidence that asymmetric azo compounds undergo non-concerted fission.[4,7,22] We applied the viscosity test to ABN and ACC. Their decomposition in presence and absence of the scavenger was followed spectrophotometrically. It was found that the first order rate of decomposition of ABN is $2.40 \pm 0.02 \times 10^{-5}$ sec^{-1} in isooctane and 2,3-dimethylbutane at 72 °C. This indicates that either $k_2, k_D \gg k_{-1}$ or that the decomposition is concerted. Similar results were obtained for ACC. We conclude that bond breaking in ABN and ACC is concerted, at least in a chemical sense.

The cage escape efficiency (defined as $a = k_D/[k_c + k_D]$) of ABN and ACC have been measured using a variety of scavengers. Hammond et al. found I_2 an excellent choice.[20] Bartlett and Funahashi[21] compared the scavenging efficiencies of galvinoxyl, di-t-butylnitroxide and iodine and found that the scavenging ability of galvinoxyl was 1.15 times that of iodine. Three scavengers were tried in our work: iodine, di t-butylnitroxide, and t-butylstyryl nitroxide. It was found that the cage efficiencies obtained by using these three scavengers agreed to within 2% with each other, and thereafter iodine was used exclusively, for it is much easier to handle. The loss of iodine was followed spectrophotometrically. The following equation was used: $-dI_2/dt = a k_i [ABN]_0$.[20] This holds if the destruction of ABN (or ACC) is not carried to more than 4% of the initial concentration. Tables I and II give the "a" values found for ABN and ACC.

Plots of F′ Against $(1/\eta)^{\alpha}$

A roughly linear correlation is found when cage escape fractions are plotted against solvent viscosities (Figure 1). Significant deviations are seen for the chlorinated solvents, chlorobenzene and carbon tetrachloride. The escape fraction is smaller for these solvents, an indication perhaps of the heavier masses of these solvent molecules and larger values of E_{η}. A better estimate of the solvation effects can be made from $F'(= 1/a - 1)$ plots vs. $\eta^{\frac{1}{2}}$. Here $F' = 1/F$. If we write, following Pryor,[4] $k_D = A_D \exp(-E_D/RT) = A_D(A_V/\eta)^{\alpha}$, since $E_D = \alpha E_V$, and $\eta = A_V \exp(E_V/RT)$. Then $F' = 1/a - 1 = k_c/k_D = k_c \eta^{\alpha}/A_D A_V{}^{\alpha}$.

TABLE I

Escape Fractions Measured for ABN

Solvent	62.25 °C	72.25
2-Methylpentane	0.84	
Isooctane	0.82	
2,3-Dimethylbutane	0.84	
_n_-Nonane	0.78	
_n_-Octane	0.81	
_n_-Heptane	0.818	
Benzene	0.66	0.714[2]
Chlorobenzene	0.60[20]	
Carbon Tetrachloride	0.45[20]	
Toluene	0.65	

TABLE II

Cage Escape Fractions for the Initiator ACC

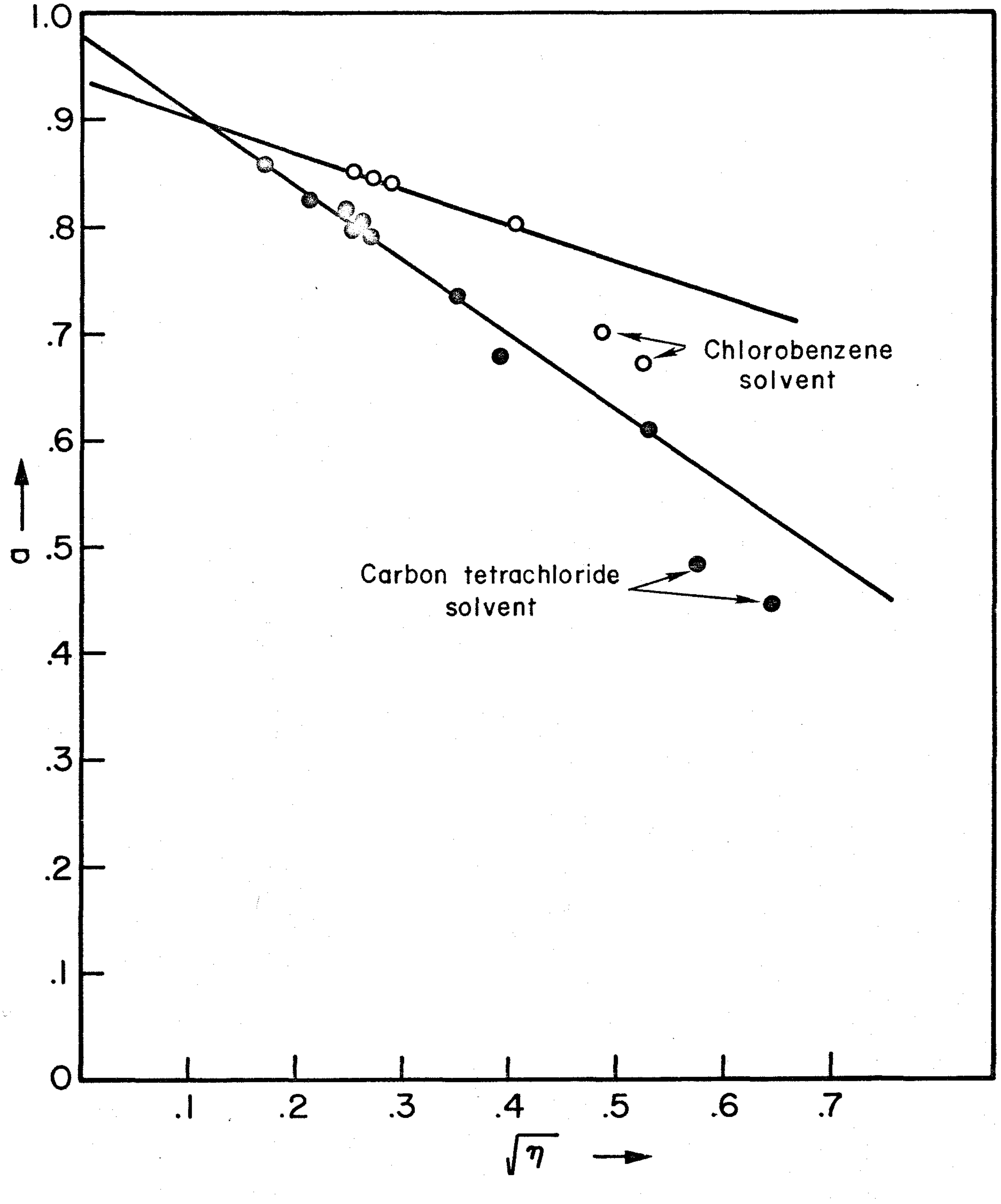
Solvent	72.25 °C	79.97 °C	100.12 °C
Isooctane	0.83		
2,4-Dimethylpentane	0.84		
Benzene	0.79		
Chlorobenzene		0.673[20]	0.697[20]
Carbon Tetrachloride	0.48		

FIGURE 1

Escape fraction vs. η.

● - ABN

○ - ACC


1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
a
.1
.2
.3
.4
.5
.6
.7
√η
Chlorobenzene solvent
Carbon tetrachloride solvent

If $\alpha = \frac{1}{2}$, then a plot of k_c/k_D vs. $(\eta)^{\frac{1}{2}}$ should have a slope equal to $k_c/A_D A_V^{\frac{1}{2}}$. The product $A_D A_V^{\alpha}$ is expected to remain constant, since $8\,RT/3000\,\eta = k_{diff} = (k_D)^{1/\alpha}$, according to Osborne and Porter.[28] It is seen that this slope is the smallest for aliphatic hydrocarbons and increases as we go from saturated hydrocarbons to benzene, to chlorobenzene, and finally to carbon tetrachloride (Figures 2a and b). This variation of the slope can be explained by postulating that k_c increases in the same direction, an unattractive hypothesis for solvation would reduce k_c rather than increasing it. Another possibility is that solvation reduces the rate of diffusion by adding a certain energy of stabilization to E_D. If this was the case, then different solvents would need different values of α for a good fit. This was not found necessary. Therefore the only interpretation that would fit the data is that changes were taking place in the values of A_D and A_V. This is to be expected for solvents with dissimilar structures. The main conclusion is that cage effects studies give no indication of an additional energy barrier existing due to solvation. This same conclusion was reached in a more qualitative manner by Koenig and Fischer.[22] They rationalized these observations by arguing that solvation should equally affect both cage recombination and diffusive separation processes. Additional comments are made on this matter in the next subsection.

Activation Energy of Recombination of Radicals Inside Cage

Another interesting aspect of the plots is that F′ values determined at two different temperatures in benzene lie in the same line

FIGURE 2a

Plot of F′ vs. $\sqrt{\eta}$ for ABN.

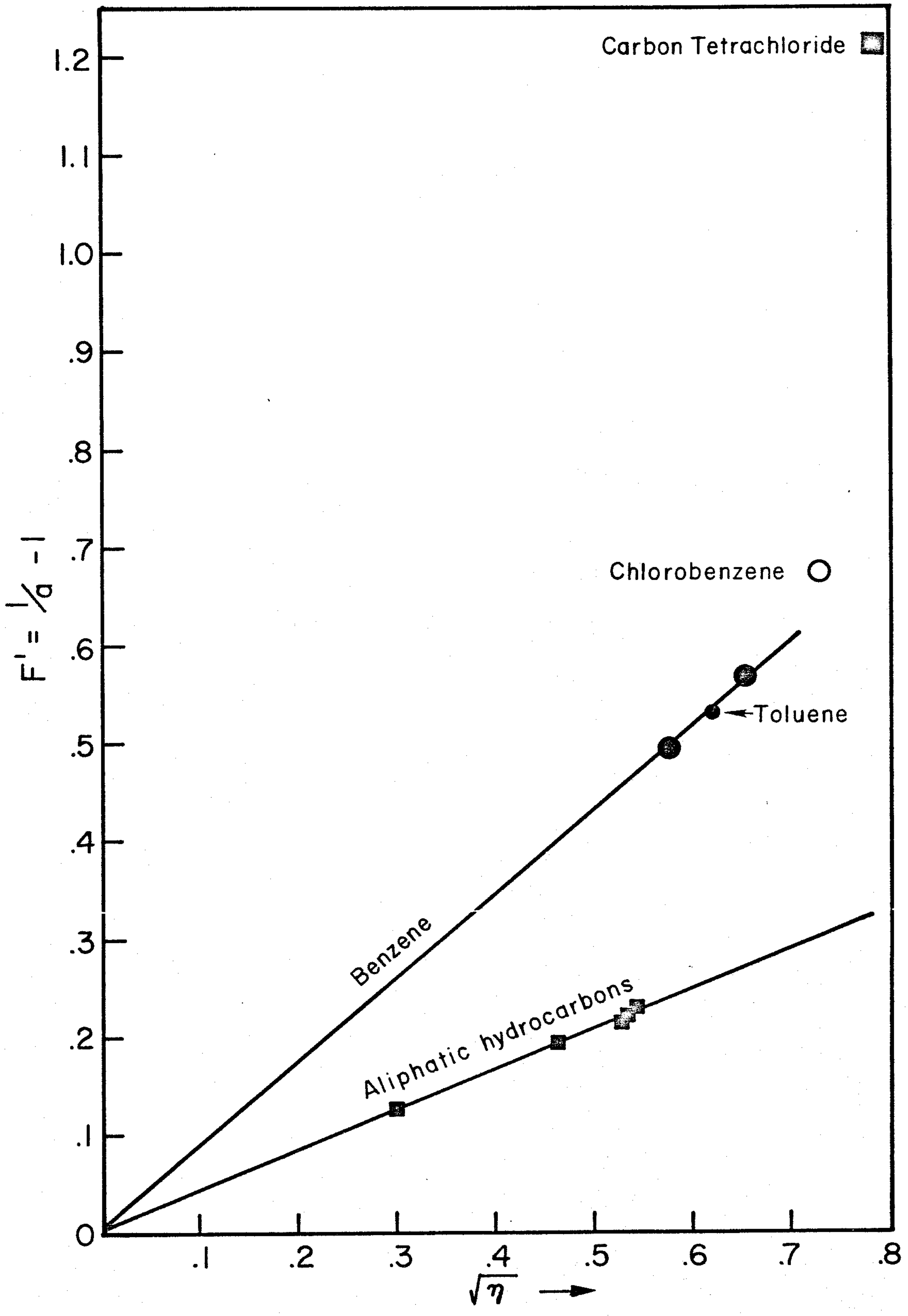
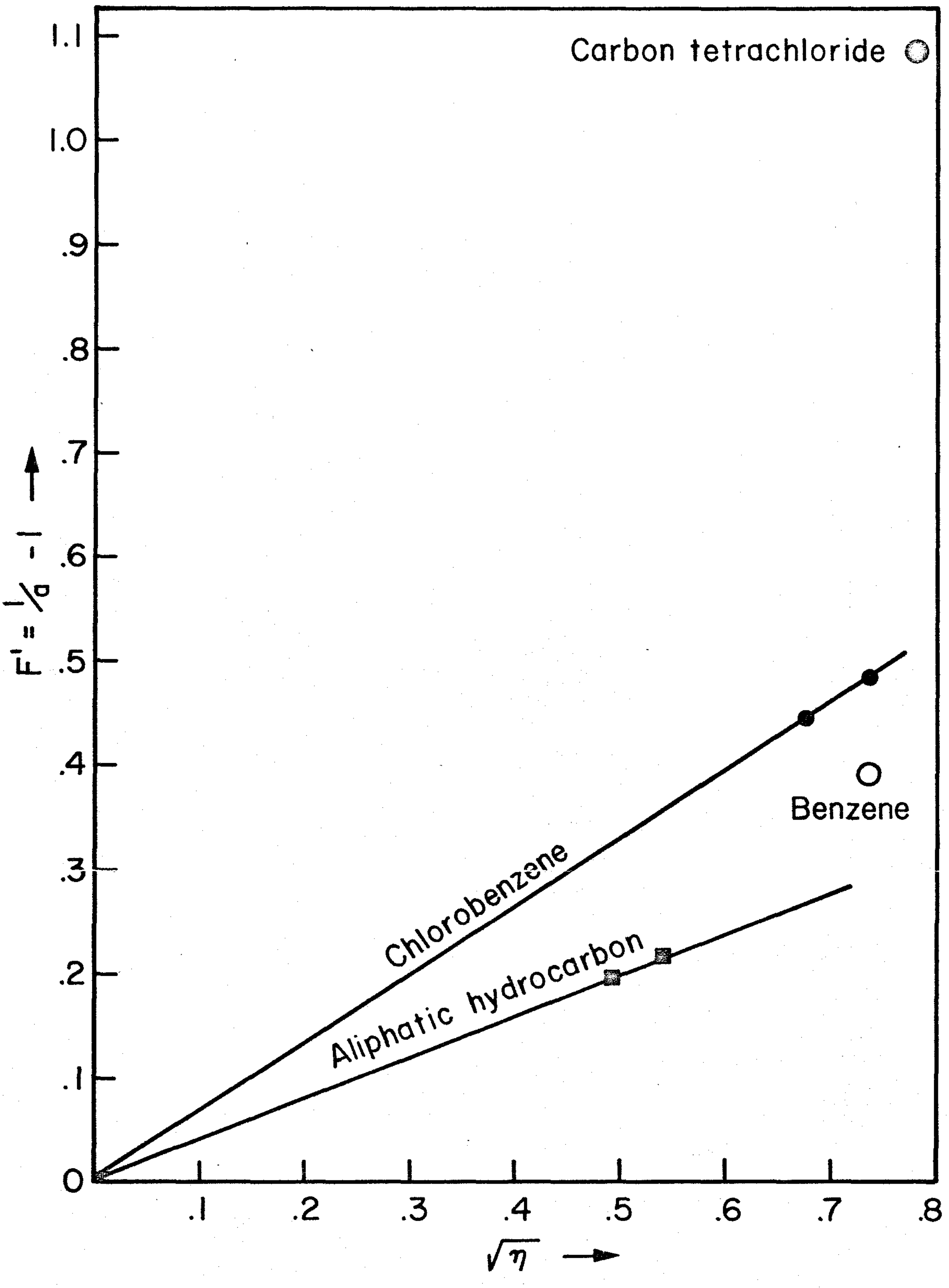

Carbon Tetrachloride
Chlorobenzene
Toluene
Benzene
Aliphatic hydrocarbons
$F' = 1/a - 1$
$\sqrt{\eta}$
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
1.1
1.2

FIGURE 2b

Plot of F′ vs. $\sqrt{\eta}$.

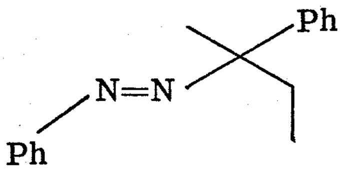

Carbon tetrachloride
Chlorobenzene
Aliphatic hydrocarbon
Benzene
F' = 1/a - 1
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
.1
.2
.3
.4
.5
.6
.7
.8
√η

for ABN, and the same effect is observed for ACC also in chlorobenzene. Our previous equation: $\eta = A_V \exp(E_V/RT)$. We find that

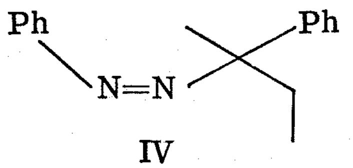
$$(k_c/k_D)_{T_1}/(k_c/k_D)_{T_2} = M(\eta_{T_1}/\eta_{T_2})^{\frac{1}{2}}$$

$$= M' \exp \tfrac{1}{2}(E_V/RT_2 - E_V/RT_1) = -M' \exp[(E_c - E_D)/R(1/T_1 - 1/T_2)]$$

when $T_2 > T_1$. This reduces to $E_D - E_c = \frac{1}{2}E_V$; since E_D has been assumed to be $\frac{1}{2}E_V$, $E_c \simeq 0$. It is interesting to note that Bartlett[12] plotted $\log(k_{diff}/k_{comb})$ vs. $1000/T$ and obtained $E_D - E_c = 1.3$ kcal/mole, for cumyl radicals produced from azo cumene in toluene. He assumed $E_D = E_\eta$ (or E_V) = 2.6 kcal/mole. If we assume, in line with more recent phenomenological theory, that $E_D = \frac{1}{2}E_\eta$, then $E_c \simeq 0$ for cumyl radicals. This again does not really go against one's intuition, for then the whole of the discrepancy between observed bimolecular termination rates of radicals and diffusion controlled encounter rate in a solvent can be attributed to solvation and intersystem crossing. The same conclusion was reached by Hamilton[37] who measured bimolecular termination rates of substituted ketyl radicals in alkane solvents. This also explains readily why Johnson and Seltzer[7] reported such high rates of recombination inside the cage (1-3 times the rate of rotation about C—C single bonds). Porter and Marnett[27] reported that IV isomerized to V with high retention on photolysis.



V



IV

The authors suggest that the *trans*-isomer is probably being formed as a recombination product of the radical pair generated through photolytic decomposition of IV, which probably has a dissociative excited state with an exceedingly short lifetime. This hypothesis can be confirmed by thermally decomposing IV and looking for V and analyzing its optical activity.

This hypothesis ($E_c \simeq 0$) enables us to rationalize Weiner's cage effect data obtained from bimolecular termination rates of radicals. We start with our estimate of the relative values of k_{diff}, k_{comb}, and k_{isc} (defined in the scheme below) as 38 : 36 : 76.

$$\overline{R\uparrow\ \uparrow R} \underset{k_{isc}}{\overset{k_{isc}}{\rightleftharpoons}} \overline{R\uparrow\ \downarrow R} \xrightarrow{k_c} R - R + \text{etc.}$$

$$\overline{R\uparrow\ \uparrow R} \xrightarrow{k_D} 2R\cdot\ ; \qquad \overline{R\uparrow\ \downarrow R} \xrightarrow{k_D} 2R\cdot$$

We then multiply k_{comb} by 4, since there is no inert molecule separating this radical pair (*vide supra*). A simple calculation thereafter indicates that the fraction of radicals combining in the cage in this case ought to be greater than or equal to 0.3. The lower value is obtained from straightforward extrapolation of the ABN-keteneimine photolysis data. The higher value could not be much more than 0.4, since the keteneimine thermolysis and photolysis data yield essentially the same fraction of in-cage recombination. This indicates that this quantity is not very sensitive to the amount of kinetic energy the radicals possess.

Weiner's data indicate that the rate of bimolecular termination of the cyanopropyl radicals in benzene is 9.4×10^{8} lt $\text{mole}^{-1}\text{sec}^{-1}$. To obtain the correct cage fraction we ought to compare it with the actual diffusion rate in benzene,[28] i.e., 1.1×10^{10} It $\text{mole}^{-1}\text{sec}^{-1}$, not the highest bimolecular triplet quenching rate observed in that solvent, since the latter rate is attenuated by factors such as solvation of the excited states, inefficiency during energy transfer, and so on. The correct cage fraction from Weiner's data is thus 0.085. This four-fold decrease from the expected cage fraction is attributed to solvation of the radicals by benzene, the resulting stabilization being equal to 1.0 kcal/mole^{-1} approximately. As has been pointed out above, the energy of solvation of the nitroxide radical by benzene has been estimated to be 0.9 kcal/mole^{-1} larger than the solvation of the corresponding hydroxylamine in the same solvent.

Effect of the Shape of Solvent Molecules on F'

The data show that a single straight line gives excellent fit for all aliphatic hydrocarbon solvents. There is no real difference in the cage effect values between solvents octane and isooctane. This eliminates the shape of solvent molecules as a variable, unless of course we go to extreme cases such as very large polymeric chains added to fluid hydrocarbons in order to increase kinematic viscosity.

Study of Spin Inversion in Caged Radical Pairs

Our discovery that $E_c \simeq 0$ raises an important question: Why the fraction of radicals recombining in the cage is not much more than what it is. Part of this inefficiency in the case of azo compounds is perhaps the presence of an intervening N_2 molecule. However, even in compounds such as the keteneimine there is significant escape of radicals from the cage. Part of this inefficiency may be due to the fact that the radical fragments may possess substantial kinetic energy and translational momenta away from each other. The probable primary step in diffusive separation is perhaps some kind of interaction with the solvent which produces some stabilization and sets up approximately equal activation barriers in the path of recombination as well as diffusive processes. One of the major reasons for this inefficiency perhaps is that intersystem crossing in a singlet radical pair may compete with cage recombination. Schematically,

$$\mathrm{I} \xrightarrow{k_1} \overline{\mathrm{R}\!\uparrow\ \downarrow\!\mathrm{R}} \underset{k_{isc}}{\overset{k_{isc}}{\rightleftharpoons}} \overline{\mathrm{R}\!\uparrow\ \downarrow\!\mathrm{R}} \longrightarrow 2\mathrm{R}\cdot$$

$$\overline{\mathrm{R}\!\uparrow\ \downarrow\!\mathrm{R}} \xrightarrow{k_c} \mathrm{R-R}\,; \qquad \overline{\mathrm{R}\!\uparrow\ \downarrow\!\mathrm{R}} \xrightarrow{k_D} 2\mathrm{R}\cdot$$

Scheme IVa

$$d[\mathrm{R-R}]/dt = k_c\{k_1[\mathrm{I}] + 1/[k_D/k_{isc}^2 + 1/k_{isc}]\}/k_{isc} + k_D + k_c \quad .$$

Precisely the opposite conditions hold when a triplet radical pair is generated, for example, on sensitized decomposition of peroxides or the keteneimine mentioned earlier. We can use the following scheme:

$$I \xrightarrow{k_1} \overline{R\uparrow\uparrow R} \underset{k_{isc}}{\overset{k_{isc}}{\rightleftharpoons}} \overline{R\uparrow\downarrow R} \xrightarrow{k_D} 2R\cdot$$

$$\overline{R\uparrow\uparrow R} \xrightarrow{k_D} 2R\cdot \; ; \quad \overline{R\uparrow\downarrow R} \xrightarrow{k_c} R-R$$

Scheme IVb

In that case the rate of cage recombination is directly proportional to k_{isc}:

$$d[R-R]/dt = k_1 k_c k_{isc}[I]/(2k_D k_{isc} + k_D^2 + k_c k_{isc} + k_c k_D) \; .$$

Recent CIDNP Studies on Biradicals and Radical Pairs

Information on the rate of intersystem crossing can be obtained from CIDNP studies on these systems. The first indication that the singlet-triplet split is not insignificant came from the observation of Garst *et al*.[29] They found that the intersystem crossing process between radical system (alkyl-$Np^{\ominus}$) is at a maximum at a field strength of ~ 0.10 kG. The CIDNP emission is induced by $T_{-1} \rightarrow S$ mixing and this mixing is optimal when $J = \frac{1}{2}g\beta Ho$, Ho being the applied field. Berson and others observed CIDNP in the dimerization of cyclopentadiene radical,[30] and Closs[31] interpreted this observation on the basis of the postulate of Garst *et al*. Later Closs[32, 23] reported CIDNP from aldehydes produced on photolysis of cyclic ketones. The emission intensity was a function of the intensity of the magnetic field in which the photolysis was performed. The maximum emission intensity corresponded with magnetic field Ho, in accordance with the above equation. Ho varied from 1-10 kG for cyclic ketones, $(CH_2)_n\,C=0$, n = 7-13. The distance between the radical centers in such ketones is expected to be similar to the distance separating the cyanopropyl radical pair in the primary cage. CIDNP has been looked for in ABN photolysis but not in the signals of tetracyanobutane, the cage recombination product. Closs points out that in case of a biradical, net intersystem crossing can be observed only if the biradical is produced in the triplet state, since there is no competitive diffusive pathway. This is not a limitation for the radical pairs we are interested in. It is a matter of satisfaction that this modified CIDNP theory predicts a magnitude of the rate of spin inversion, that is in keeping with rates estimated from kinetic observations. Closs[34] finds that the singlet-triplet split is strongly influenced by solvent and the emission disappears in benzene, although it is quite strong in $CHCl_3$. The emission was not due to some kind of abstraction from $CHCl_3$ (by the alkyl radical generated from ketone photolysis) because the emission is strongly attentuated in solvents containing 10% benzene. Apparently the zero field states are much closer together in benzene and the singlet-triplet splitting smaller, so that T_0-S mixing induces fast intersystem crossing, drowning out the field induced $T_{-1} \rightarrow S$ mixing. Indeed, the $T_{-1} \rightarrow S$ mixing is expected to be lower in higher fields since the T_{-1} state is stabilized by a field in Z direction and therefore drops in energy. In ABN thermolysis, an increase in k_{isc} could reduce cage recombination fractions, and that could be one reason why we find such significant deviation of the F′ values obtained in carbon tetrachloride. In fact this could explain the entire F′ vs. $\sqrt{\eta}$ plot. More realistically, one would expect the variation of k_{isc} as well as the variation of $A_D A_V^{\alpha}$ to be responsible for the observed dependence of F′ on η.

Magnetic Field Effects on Cage Recombination Fraction

These reports appeared after we made our observations[35,36] but our reasonings were similar. We expected the intersystem crossing rate to increase inside a magnetic field, and since the radical pair was initially a singlet, we expected the cage recombination fraction to be reduced inside a magnetic field. The experimental setup is described in the next section. Table III gives the data obtained. The errors in these experiments tended to be larger than those in the thermolysis data reported above. The amount of solution that could be irradiated inside the field was < 0.5 ml and we had to use 2 mm path length cells for spectrophotometric determination of the disappearance of the scavenger. The amount of light incident was reproducible only to ± 10%, since the highly curved tube surface allowed relatively unpredictable fractions of light to pass through. The placement of the tube in the esr cavity was thus a critical operation. Duplication of the optics was not a difficult problem, but periodic fluctuation of the intensity of the lamp posed additional problems.

Nothing is known about the behavior of ABN excited states in the presence of I_2, or perhaps $I_3\cdot$, since iodine must have been absorbing some light. We hoped that most of the errors could be eliminated by using the zero field experiments as a standard. A few experiments done at lower fields indicate that $P\,[P = (dI_2/dt)_{H=0}/(dI_2/dt)_{H=Ho}]$ is closer to unity at lower field strengths. The drop in cage efficiency (recombination) is roughly 19 ± 5% of the cage efficiency at zero field.

This experiment will have a surer interpretation if the corresponding keteneimine is photosensitized in and out of a magnetic field. One would expect increased cage recombination due to enhanced intersystem crossing in that case.

TABLE III

Effect of a Magnetic Field on Cage Recombination Rates

Concn. of ABN (moles/lt)	$dI'_2/dt^{1,2}$	$dI''_2/dt^{3,2}$	P^4
0.035	5.4×10^{-5}	6.67×10^{-5}	1.23
0.062	1.53×10^{-4}	2.05×10^{-4}	1.34
0.076	1.66×10^{-4}	1.98×10^{-4}	1.19
0.051	8.6×10^{-5}	9.90×10^{-5}	1.15

1. Rate of iodine disappearance at zero field.
2. Measured in O.D. units sec^{-1} (cell path length 2.0 ± 0.2 mm).
3. Rate of iodine disappearance at field strength 9 kG.
4. $P = dI'_2/dt/dI''_2/dt$.

Experimental

Materials:

Iodine:	Baker and Adamson reagent grade was used as received.
ABN:	Obtained from Aldrich Chemicals; it was purified by two recrystallizations from ethanol (absolute).
ACC:	It was synthesized by Dr. U. Nandi. It was purified by two recrystallizations from ethanol.
Di-t-butyl nitroxide:	It was synthesized by the method of Kornblum and Hoffmann.[24,25] It was purified by distillation in vacuo.
t-butylstyryl nitroxide:	It was synthesized by Dr. T. L. Penner.
2-methylpentane:	Obtained from Aldrich Chemicals (spectroquality). It was distilled over P_2O_5.
2,3-dimethylbutane:	Obtained from Aldrich Chemicals (spectroquality). It was distilled over P_2O_5.
n-nonane, n-octane and n-heptane:	Obtained from Aldrich Chemicals. They were used as received.
Toluene:	Spectroquality toluene from M.C. and B. was used as received.
Benzene:	Spectroquality benzene (M.C. and B.) distilled over P_2O_5 was used in the initial runs. In the latter runs it was purified by the

photochlorination technique of Saltiel, Metts, and Wrighton (Ref. 54, Sec. I).

Chlorobenzene: Spectroquality chlorobenzene was obtained from M.C. and B. and was distilled before use.

Carbon Tetrachloride: Spectroquality carbon tetrachloride was obtained from M.C. and B. and was used as received.

Isooctane: This was obtained from M.C. and B. (spectroquality). It was distilled from P_2O_5 after being passed through an alumina-$AgNO_3$ column, and was stored under N_2.

Procedures

The cage escape efficiency determinations were carried out in sealed, degassed tubes. The tubes were suspended in a thermostat in which the temperature did not drift more than 0.25 °C in one day. Iodine absorbance was measured using a Cary-14 spectrometer. The magnetic field effect experiments were performed inside the cavity of a Varian E-12 esr spectrometer. The solutions were degassed and sealed in esr tubes. The temperature was kept constant (and monitored occasionally) by a stream of N_2 at room temperature flowing through the cavity. The Varian 12" electromagnet could give a maximum field strength of 8-10 kG. Our field strength was in this range. The tubes were irradiated in the cavity using light from a 2.5 kw high pressure Hg lamp. The light was appropriately filtered and collimated using quartz optics. Times of irradiation varied from 20 min to 30 min.

Viscosities were mostly obtained from American Insitute of Physics tables. However a few of the viscosities could not be found in the literature and an Ostwald's viscosimeter was used to measure these viscosities. It was set up in a large thermostat containing water at the appropriate temperature. A liquid with known viscosity was used as a calibrator. Reproducibility was better than 0.5%, and absolute error (estimated by measuring the viscosity of a liquid whose viscosity was in the literature) was never more than 1%.

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CHAPTER II

QUENCHING OF EXCITED STATES OF AROMATIC MOLECULES THROUGH EXCIPLEX FORMATION

Introduction

Quenching of fluorescence of aromatics by conjugated dienes continues to be an intriguing problem in photochemistry. Extensive reviews have recently appeared in this field[1-4] and therefore, in this work attention will be focused on two aspects of the quenching mechanism: (a) the nature of interactions between the quencher and the quenchee, and (b) the possibility of intersystem crossing being induced through such interactions.

The charge transfer mechanism has been generally accepted in the case of singlet quenching by amines. The absorption spectra of charge transfer exciplexes have been recorded using laser flash photolysis techniques.[5,6] Bands in such transient absorption spectra have been assigned to transitions such as $^1(D^+A^-)^* \xrightarrow{h\nu} (A^1D^*)$ and $^1(D^+A^-)^* \xrightarrow{h\nu} (^1A^*D)$. There is a satisfactorily large solvent effect on such quenching rates, and dissociation of the charge-transfer exciplex into free ions has been directly observed in polar solvents through flash photoconductivity studies.[7] Not unexpectedly, attempts have been made to rationalize fluorescence quenching by conjugated dienes in terms of the charge-transfer model. Thus Solomon, Steel, and Weller[8] have postulated that the quenching of naphthalene and substituted naphthalene singlets by norbornadiene takes place through the intermediacy of an exciplex to be formulated as follows:

$$(AD)^* \equiv (A^*D) \longleftrightarrow (A^-D^+) \quad .$$

They write the wavefunction of the complex as

$$^1\psi_{\text{complex}} = C_1\, {}^1\psi_{A^*D} + C_2\, {}^1\psi_{A^-D^+} \quad .$$

In order for C_1 and C_2 to be of comparable magnitude, the process ${}^1A_g^* + D_g \rightarrow (A_g^-D_g^+)$ should be roughly thermoneutral. This is achieved in the case of naphthalene (A) and norbornadiene (D), if the distance between A^- and D^+ is 3.5 Å. The calculation ignores the stabilization due to exciplex formation, i.e., $A^* + D \rightarrow A^*D$, as well as stabilization of either the exciplex or the charge-transfer state due to solvation.

The free energy of the above process can be written as $\Delta F \simeq {}^1\Delta E_A + IP_D - EA_A - C - E_S$ when E_A is the singlet energy of the aromatic, IP_D is the adiabatic ionization potential of the donor (quencher), EA_A is the electron affinity of the quenchee, C is the coulomb term representing energy released on bringing A^- and D^+ toward each other from infinity to a certain distance r, and E_S is the energy of stabilization by the solvent. Modification of this model has been proposed by Evans[9] and by Rehm and Weller.[10] These modifications principally introduce a 'proximity pair' formed by diffusion and held together inside the solvent cavity. This model is given in Scheme I. Since the proximity pair has no binding energy of its own, the quenching rate is totally controlled by the reversible conversion of the proximity pair into an ion-pair.

$$A \longrightarrow A^{1*} \rightsquigarrow A^{3*}$$

$$A^{1*} \longrightarrow A + h\nu_0$$

$$A^{1*} + D \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} [A^{1*}D] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [A^-/D^+] \xrightarrow{k_2} A + D$$

Scheme I

If k_q is the observed rate of quenching, then,

$$k_q = \frac{k_d}{1 + \frac{k_{-d}}{k_1} + \frac{k_d}{k_2} \times K_1} , \quad \text{when } K_1 = \frac{k_1}{k_{-1}} = \exp(-\Delta G/RT) .$$

When $\Delta G = 23.06\,(E[D/D^+] - E(A^-/A) - e_0^2/\epsilon x) - \Delta E_{0,0}$ where $E(D/D^+)$ is the ionization potential of the donor, $E(A^-/A)$ is the electron affinity of the acceptor $e_0^2/\epsilon x$ is the coulomb energy in bringing A^- and D^+ toward each other from infinity to x, and $\Delta E_{0,0}$ is the singlet energy of the aromatic.

This scheme is a more limited form of the scheme originally proposed by Stephenson[11] and later by Taylor *et al.*[12] (Scheme II).

$$A \xrightarrow{h\nu} A^{1*} \longrightarrow A + h\nu_0$$

$$A^{1*} + Q \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [AQ]^{1*}$$

$$[AQ]^{1*} \xrightarrow{k_2} A + Q$$

$$[AQ]^{1*} \equiv [A^+Q^-] \longleftrightarrow [A^-Q^+] \longleftrightarrow [A^{1*}Q] \longleftrightarrow [AQ^{1*}]$$

Scheme II

Here k_q (observed quenching rate) $= \frac{k_2 k_1}{k_2 + k_{-1}}$.

Scheme I does not include any process that would allow the quenching rate to be modulated by the structure of the donor or the acceptor, except for variation in x. A considerable amount of experimental evidence indicates that while the correlation of log k_q with the electron affinities of a series of acceptors of approximately similar structures or with the ionization potentials of a series of similar donors is good, the correlation lines are strikingly different for different classes of compounds.[12,13] This variation is far larger than could be reasonably predicted on the basis of variation of x. Scheme II is of greater utility from this point of view, because it has no difficulty in rationalizing variation of k_q arising out of structural differences. At the same time it does not rule out charge resonance stabilization resulting in some charge separation, hence it can also account for the correlations observed with electron affinities of acceptors and ionization potential of donors. On further analysis it is found to operate between two limits as follows:

(a) fast equilibrium between $A^{1*} + Q$ and $[AQ]^{1*}$; then $k^q \simeq k_2K$, when $K = k_1/k_{-1}$.

(b) $k_2 \gg k_{-1}$; then $k_q \simeq k_1$.

We can reasonably anticipate k_2 to be roughly constant for a series of quenchers with approximately similar structures. Therefore $\log k_q = \text{const.} + \log k_1$. Since the stabilization of the exciplex is expected to be through both charge and excitation resonance, log k_q

will correlate with $E(A^-/A)$ and $E(D/D^+)$. On the other hand, using a series of quenchers with the same structure but suitably different isotopic composition, we can ensure that K remains approximately constant, and k_2 undergoes systematic change. An investigation of this nature revealed that C—H bonds do not play a significant role in radiationless decay of the exciplex [naphthalene-piperylene].[12] Perhaps C^{14} or O^{18} substituted quenchers will show significantly different quenching rates.

Intersystem Crossing from Singlet Exciplexes

One of the decay modes of the singlet exciplex is S_1-T_0 intersystem crossing of the quenchee. Direct evidence of such intersystem crossing has been obtained in amine-aromatic systems and in systems involving quenchers with strong electron withdrawing substituents, such as dicyanobenzene.[14-16] Nanosecond flash photolysis techniques enabled Ottolenghi et al. to obtain the rise time of such transient triplet absorption.[17] This was found to be equal to the decay time of the exciplex emission. Hence triplet generation seems to compete with exciplex fluorescence and therefore the triplets are assumed to arise from the thermalized exciplex. Land observed intersystem crossing in anthracene when anthracene singlets are quenched by diethylaniline.[18] In polar media the amine-aromatic exciplexes dissociate to produce free ions and triplets are generated on ion recombination.[19] Two closely similar mechanisms therefore emerge, which could explain the data in both polar and nonpolar solvents. In nonpolar solvents the 'ion-pair' or the thermalized exciplex produces some aromatic triplets on recombination. In polar solvents, the ion pair dissociates on solvation and the free ions recombine to produce triplets of the quenchee. Ottolenghi recently reported triplet production with a much shorter rise time in both polar and nonpolar solvents.[17,59] When anthracene singlets are quenched by dimethylaniline, anthracene triplet transient absorption is visible less than 20 nsec after the laser has been fired. The absorbance increase at 430 nm stops before any significant portion of the exciplex has decayed. Ottolenghi suggests that this intersystem crossing could take place in the vibrationally excited exciplex or the 'proximity pair'. Induced singlet-triplet absorption may be ruled out because there is no evidence of a ground state complex.

Again, it seems that in order to satisfactorily explain all the results discussed above as well as our own observations we have to move beyond the charge-transfer formalism. According to McGlynn and Christodoules[20] the spin forbiddenness may be reduced by the following two mechanisms: (a) the ground state of the exciplex ${}^1\psi({}^1D^1A)$ is admixed with ${}^3\psi({}^1D^3A)$; (b) depending on the spin orbit coupling in the donor the transition ${}^1\psi({}^1A^1D) \rightarrow {}^3\psi({}^3A^1D)$ may take place in which the excitation is localized mainly on the acceptor. In our system it is not clear whether naphthalene or trans β-ethyl-styrene can act as the donor. Perhaps in the weakly bound naphthalene-styrene exciplex, excitation remains localized on the naphthalene moiety and the spin orbit coupling mechanism that causes efficient intersystem crossing in naphthalene also causes the exciplex to intersystem cross. Radiationless decay rates become much more rapid and the quantum yields are probably controlled by the extent of binding in the exciplex. Exciplex formation presumably also increases intersystem crossing rate due to additional spin orbit coupling. That could explain why the fast radiationless decay modes operating in the exciplex can wipe out the emission but not the intersystem crossing. It is also not clear whether any quencher triplet is produced. The system was designed such that the quencher triplet is approximately isoenergetic with the triplet of the quenchee (for reasons that are elaborated below), and the chemical triplet trapping and counting technique used in our study could not distinguish between naphthalene and trans β-ethyl styrene triplets, assuming that styrene triplets are quenchable. A detailed discussion is deferred until the next section.

Triplet Quenching and Exciplex Formation

While singlet quenching mechanisms are dominated by processes leading to the formation and decay of the exciplex, intermediacy of a triplet exciplex (or excimer) is postulated with much greater reluctance and far more caution. The reason is that in triplet excimers the coulombic term of the excitation resonance interaction vanishes due to spin orthogonality, leaving only small exchange terms. However, models taking into account configuration interaction between charge and excitation resonance come much closer to predicting the observed red shift.[21, 22] Excimer phosphorescence has been observed from tetrahalo- and halobenzenes.[23, 24] Lim and Chakraborty[24] used rigid glass at 77 °K as medium and their report states that the maximum of the excimer phosphorescence they recorded is considerably more red-shifted than those obtained by Castro and Hochstrasser.[23] The latter group studied crystalline emissions. Langelaar et al. observed excimer phosphorescence from naphthalene and phenanthrene in ethanol solutions.[25] Interestingly, the intensity became maximum at about 170°K, 30°K higher than the melting point of alcohol which was used as the solvent. They obtained the radiative lifetime of the triplet excimer. Chandross and Thomas[26] dissociated a substituted phenanthrene dimer in a rigid glass (77°K) to obtain a sandwich pair. This sandwich pair did not show any excimer emission from the singlet state, but the phosphorescence spectrum became red-shifted and lost its structure. However the extent of the red shift was much less than that observed by Langelaar et al. Föster reviewed experimental and theoretical work done on triplet excimers prior to 1969.[27] Phillip and Schug pointed out that many optically inaccessable states are easily populated on electron impact and obtained luminescence spectra of several simple aromatics such as benzene, o- and p-xylene (monomeric), poly p-xylene, polychloro p-xylene by exciting them with 1 mev electrons.[28] The material was in a thin polymer film. Benzene exhibited singlet monomer and excimer, triplet monomer and excimer emission. Triplet excimer emission was also obtained from p-xylene. Recently Avouris and El-Bayomi[29] reported triplet excimer emission from 1, 3-diphenylpropane. The excimer emission band was red-shifted 5000 cm^{-1} from the monomer phosphorescence maximum. The stabilization energy of the triplet excimer is thus about 60-70% of the stabilization energy of the singlet excimer. The evidence for the triplet exciplex on the other hand is indirect chemical evidence, at best. The only report of triplet exciplex emission came from Roy and Whitten.[30] They identified three species each with its characteristic lifetime and absorption characteristics. They were (1) delocalized exciplex, (2) ion pair, and (3) free ions. The delocalized exciplex could be quenched, while the ion-pairs had a very short lifetime. Generally, the emission lifetime decreased drastically as a small amount of polar solvent (acetonitrile, ethanol, or DMF) was added to the benzene solution, then as the mole percent of the polar solvent increased, the lifetime increased steeply, and soon became constant. This behavior was interpreted by assuming that addition of a small amount of polar solvent produces short-lived ion pairs from the delocalized exciplex. These ion pairs dissociate when the dielectric constant of the solvent increases and then the lifetime is determined by collisional recombination of free ions.

Chemical Evidence for Triplet Exciplex Formation

Indirect chemical evidence of triplet exciplex formation comes from detection of energy wastage during triplet energy transfer (Scheme III).[31, 32] Although kinetically one does not have to postulate a discrete species $[DA]^{3*}$, it is conceptually attractive to visualize all the decay processes such as energy transfer, chemical addition to energy wastage as the decay modes of $[DA]^{3*}$, especially when collisional energy transfer is an endothermic or a thermoneutral process. This is one of the reasons why we chose trans β-ethyl styrene as the quencher; its triplet energy is approximately equal to the triplet

$$D \xrightarrow{h\nu} D^{1*} \overset{k_{isc}}{\rightsquigarrow} D^{3*} \longrightarrow D$$

$$D^{3*} + A \rightleftharpoons (DA)^{3*} \qquad (2)$$

$$(DA)^{3*} \longrightarrow D + A^{3*} \qquad (3)$$

$$(DA)^{3*} \longrightarrow D + A \qquad (4)$$

$$(DA)^{3*} \longrightarrow \underset{\bullet}{D} - \underset{\bullet}{A} \text{ (biradical)} \qquad (5)$$

$$\underset{\bullet}{D} - \underset{\bullet}{A} \longrightarrow D - A \qquad (6)$$

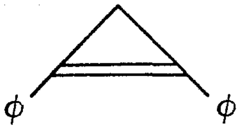
$$\underset{\bullet}{D} - \underset{\bullet}{A} \longrightarrow D + \gamma \underline{t} - A + (1-\gamma)\underline{c} - A \qquad (7)$$

$$A^{3*} \longrightarrow \alpha \underline{t} - A + (1-\alpha)\underline{c} - A \qquad (8)$$

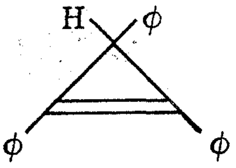
Scheme IIIa

energy of naphthalene (60 kcal mol^{-1} vs. 60.5 kcal mol^{-1}).[56] Similarly the olefins chosen to quench acetophenone triplets have much higher triplet energies than acetophenone. Similar kinetic evidence can be adduced for exciplex formation in photocycloaddition reactions. Caldwell[32] postulated a triplet exciplex on the basis of stereochemical and quantum yield studies on photocycloaddition of phenanthrene to dimethyl maleate and fumarate.

As has been pointed out above, kinetically one cannot distinguish between an exciplex undergoing radiationless decay and a donor undergoing a bimolecular energy wastage process with an acceptor. However, the evidence becomes much more compelling when the exciplex is quenched by another molecule of a quencher. In that case, the only alternative to an exciplex is inclusion of a termolecular process in the scheme. An example is DeBoer's investigations on compound 1, 2, and a carboxy substituted isomer.[33]



1



2

The predominant triplet reaction is dimerization. When 2 is sensitized with low energy triplet sensitizers, one would expect the ϕ^{-1}_{dimer} vs. [sens.] plot to be linear, because of back transfer. However the plots with sensitizers such as fluorenone, benzanthracene curve upward substantially, indicating the necessity of proposing a termolecular step as follows:

$$[\text{sens.}]^{3*} + 2 + \text{sens.} \longrightarrow 2\ \text{sens.} + 2 \qquad (9)$$

or an exciplex quenching process:[14]

$$[\text{sens.}]^{3*} + 2 \rightleftharpoons [\text{sens. } 2]^{3*} \qquad (10)$$

$$[\text{sens. } 2]^{3*} \longrightarrow \text{sens.} + 2^{3*} \qquad (11)$$

$$2^{3*} \longrightarrow \text{dimers} \qquad (12)$$

$$2^{3*} + \text{sens.} \longrightarrow 2 + [\text{sens.}]^{3*} \qquad (13)$$

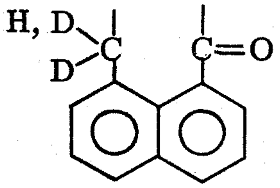
$$[\text{sens. } 2]^{3*} + \text{sens.} \longrightarrow \text{sens.} + [\text{sens.}]^{3*} + 2 \qquad (14)$$

Scheme IIIb

We made attempts to quench the acetophenone-olefin exciplex as well as the naphthalene-styrene exciplex. The results will be discussed in the next section. Among other chemical evidence for triplet exciplexes and excimers are:

1. Self-quenching of Π-Π^* ketone triplets and a reported observation of self-quenching by benzophenone triplets.

Chapman and Wamfler[34] showed that triplet yields from aromatic carbonyl compounds with low lying Π-Π^* triplets are strongly concentration dependent. Schuster and co-workers as well as Wamser[35, 36] extended the observations to Michler's ketone and benzophenone. The self-quenching could arise either from an excimer or from a bimolecular quenching process. DeBoer[37] reported mixed ketone triplet quenching. He found that type II elimination from compound 3 is sensitized by Michler's ketone or thioxanthone at low concentration, but the sensitization efficiency drops drastically as sensitizer concentration is increased.



3

The decrease in sensitization yield is more than an order of magnitude larger than what would be expected on the basis of self-quenching by the sensitizers. 3 has a triplet energy lower than either of the two sensitizers mentioned above, therefore back transfer is not important.

2. Additional evidence of an "excited state complex" has been presented by Wagner[38, 39a] and Caldwell.[40] As Caldwell points out the energy

wastage argument is persuasive but not conclusive. The biradical intermediate (which is not electronically excited) could be so short-lived that bond rotation about $C_2—C_3$ bonds would be competitive with decay _via_ dissociation. Although triplet biradicals generated by Norrish type II abstraction in ketones have been shown to attain complete rotational equilibrium before decaying to products,[41] additional chemical evidence is desirable in this matter. This was provided by Caldwell when he reported isotopic substitution studies on the system benzophenone-olefin. The isotope effects on rates of isomerization of the olefin and oxetane formation were roughly equal and were suggestive of an excited state complex. He investigated both intramolecular discrimination and intermolecular competition by measuring _cis_-_trans_ isomerization and oxetane formation rates on benzophenone sensitization of _cis_ 2-butene 2, 3-d_2, _cis_ 2-butene and _trans_ 2-butene 2-d. There was a small direct isotope effect when the dilabeled butene competed with unlabeled butene (1.02 ± 0.01). This is much smaller than would be expected if the isomerization took place _via_ excitation transfer. The oxetanes were analyzed by nmr and mass spectrometry and they gave a product isotope effect of 1.02 ± 0.01 when the dilabeled olefin competed with unlabeled olefin competed for benzophenone triplet. Since both these isotope effects are direct, there is a definite anomaly here if the biradical is the primary product of triplet ketone and olefin interaction, since biradical formation is expected to be accompanied by an inverse isotope effect.

Other arguments are presented by Wagner and Kochevar[38] in this matter. A considerable body of data indicates that triplet ketones have similar reactivity as alkoxy radicals. However, radical addition to olefins is 2-3 orders of magnitude slower than quenching of ketones by olefins. Secondly, the reactivity sequence of addition rate of radicals to olefins is almost the inverse of the order of quenching rate on variation of olefin structure.

Wagner used a charge-transfer model to rationalize his quenching rate data. A fair correlation is obtained if log k_q is plotted against ionization potential of the olefins. Wagner did not report any solvent dependence of quenching rates in this system. Our observations on a closely related system (acetophenone-olefins) indicate that there is a modest (~150%) quenching rate increase as we go from benzene to acetonitrile. This is the same solvent effect as Wagner observed in the photoreduction rates of acetophenone and $\underline{\alpha}$-trifluoro acetophenone by substituted benzenes.[39b] Using Weller's model,[10] Wagner estimates that the (acetophenone-subst. benzene) exciplex has a modest amount (20%) of charge transfer character. Application of the charge transfer model to benzene quenching of benzophenone triplets yields a rate that is at least three orders of magnitude higher than the observed rate. Here again, I believe as in the case of singlet quenching, it will be an over simplification to try to fit all quenching data into the Weller model. Charge resonance is bound to be an important source of stability in triplet exciplexes, but the extent of charge separation will depend on the structure of the quencher and the quenchee. Thus Cohen and Davis[42] report more than an order of magnitude increase in the rate of photo reduction of benzophenone by a secondary amine as the solvent is changed from benzene to acetonitrile. Clearly, here the charge separation is more complete than when an olefin is the quencher.

This account of work done on exciplexes and excimers does not pretend to be a review on the subject. It helps to put our own investigations on quenching of naphthalene excited states by trans β-ethylstyrene and quenching of acetophenone triplets by certain t-butyl substituted olefins in a perspective from which the conclusions I draw from our data can be appreciated.

Results and Discussion

Choice of A Suitable Singlet and Triplet Quencher

Trans β-ethyl styrene (I) was chosen as a singlet quencher for several reasons. Taylor and Hammond suggest that dienes owe their unique singlet quenching ability to their flexible C=C bonds which act as efficient sinks of vibrational energy.[12] Consistent with this argument is the fact that aromatic rings do not generally quench singlets. However, a weakly bound exciplex was recently reported between naphthalene and 9-methylanthracene.[43] I possesses an energy absorbing flexible C=C bond and also an aromatic nucleus. Therefore some quenching ability was expected of this compound.

Singlet Quenching Rate Constants

Table I gives the quenching rates in different solvents. The quenching rates were obtained by constructing Stern-Volmer plots ϕ^0/ϕ *vs*. [I], where ϕ^0 is the quantum yield of naphthalene fluorescence in absence of quencher, ϕ is the quantum yield in the presence of quencher of concentration [I]. The slope of this line is $k_q\tau$, when τ is the singlet lifetime. The singlet lifetimes in all the solvents were determined using a pulsed lamp (pulse lifetime: 2 or 14 nsec) and a fast rise Tektronix scope. Singlet lifetimes remain essentially constant, but the quenching rate varies in an unpredictable manner, and is generally *low* for polar solvents. Using the Taylor-Hammond scheme as a basis of rationalization of these rate constants, we start off with an assumption: The equilibration of the exciplex is fast compared to

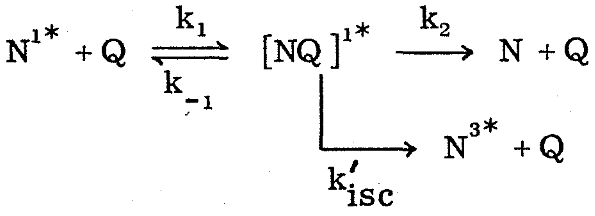
TABLE I

Fluorescence Quenching Rates by trans-β-Ethyl Styrene and Singlet Lifetimes of Naphthalene Measured in Various Solvents

Solvents	$k_q\tau$	$\tau^{1,3}$	$k_q{}^2$
Benzene	43	95	4.5×10^8
Acetonitrile	18	91.5	2.0×10^8
Diethyl ether	31	96.5	3.3×10^8
n-Hexane	25	96.5	2.6×10^8

1. nsec. 2. lt $\text{mole}^{-1}\text{sec}^{-1}$. 3. Error ± 3%.

its decay. This is equivalent (given the magnitude of our rate constants) to making the assumption that k_1 is diffusion controlled.



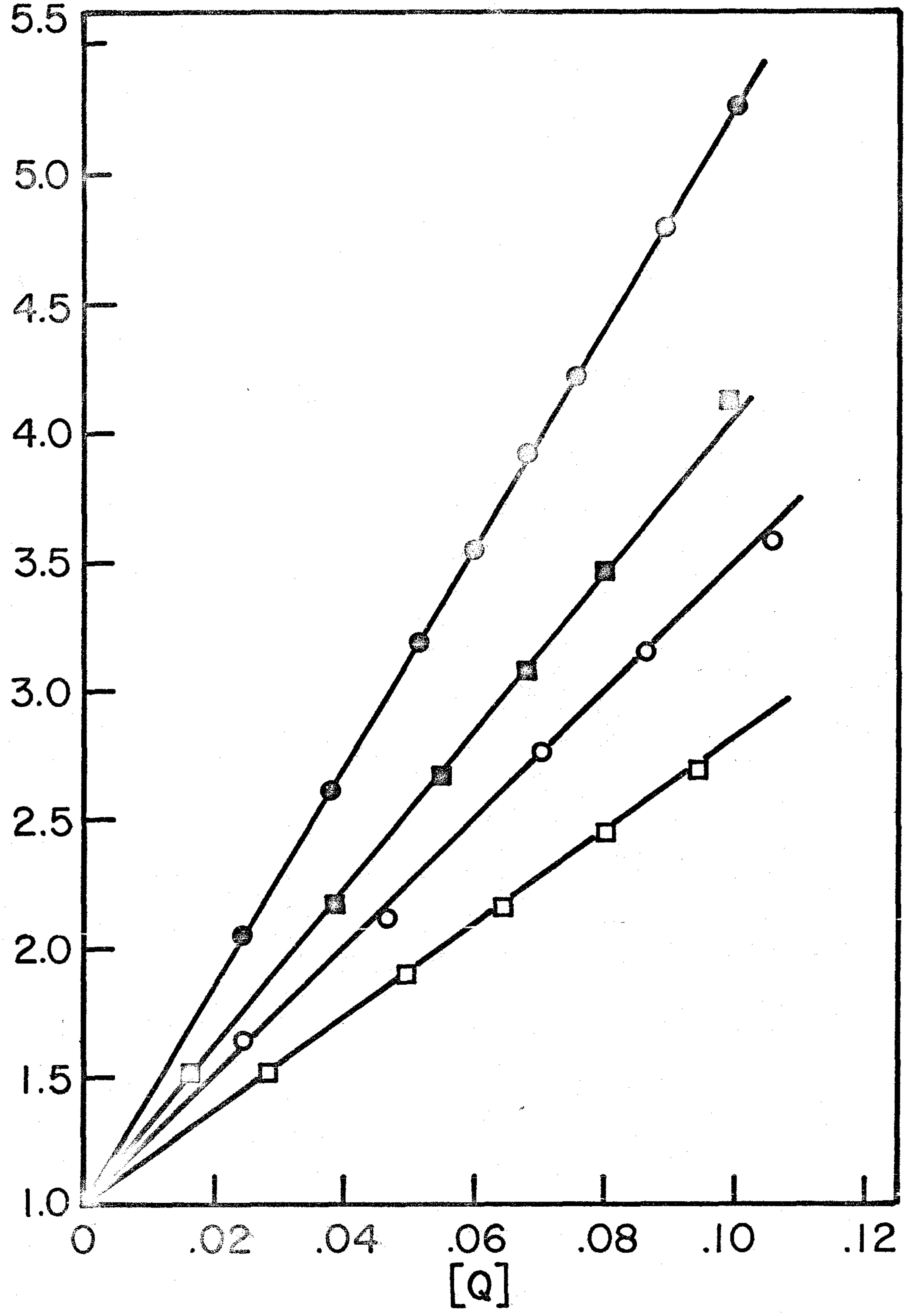
Scheme IV

Then $k_q = K(k_2 + k'_{isc})$ when $K = k_1/k_{-1}$. If we assume that K remains essentially constant in all solvents, we find that $k_2 + k'_{isc}$ is largest and $\phi'_{isc} = k'_{isc}/k_2 + k'_{isc}$ is smallest in benzene. Indeed, a rough inverse correlation between the total quenching rate and ϕ'_{isc} can be found, although the errors in the estimated values of ϕ'_{isc} are too

FIGURE 1

Quenching of naphthalene fluorescence by *trans*-β-ethyl-styrene.

In benzene	●
diethyl ether	■
n-hexane	○
acetonitrile	□


5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ϕ^0/ϕ
0
.02
.04
.06
.08
.10
.12
[Q]

large to make this correlation more precise. This could be rationalized by observing that the increase in the rate of intersystem crossing (through an increased spin orbit coupling) cannot keep pace with the increase in the rate of internal conversion which determines the overall quenching rate. The clearest deviation from such a correlation is shown by ether, where both the quenching rate and the rate of intersystem crossing are high. One can speculate at this point that perhaps there are two or more mechanisms of stabilization of the exciplex, each of which in turn has a certain effect on k_2 and k_{isc}. Perhaps the charge resonance mechanism is not very effective in promoting internal conversion, but has a significant effect on k_{isc}. Excitation resonance, on the other hand strongly affects k_2 and also k_{isc} to a lesser degree. The different ratios of k_2 and k_{isc} seen in different solvents is a consequence of the variation of effectiveness of these two mechanisms in stabilizing the exciplex.

Intersystem Crossing from the Styrene-Naphthalene Exciplex

We then considered the possibility that the singlet exciplex $[NQ]^{1*}$ was undergoing intersystem crossing to produce either N^{3*} or Q^{3*}, or both. To obtain the intersystem crossing yield of the exciplex we used the modified Quina-Carroll equation as described by Quina.[44, 45] This technique uses a triplet quencher (called the triplet counter) to trap all triplets generated during irradiation; the rate of isomerization of the counter is then proportional to the triplet yield. The following scheme was used:

$$N \xrightarrow{h\nu} N^{1*} \rightsquigarrow N^{3*} \tag{1}$$

$$N^{1*} \longrightarrow N + h\nu_0 \tag{2}$$

$$N^{1*} + Q \longrightarrow [NQ]^{1*} \tag{3}$$

$$[NQ]^{1*} \longrightarrow N + Q \tag{4}$$

$$[NQ]^{1*} \longrightarrow N^{3*} + Q \tag{5}$$

$$[NQ]^{1*} \longrightarrow N + Q^{3*} \tag{6}$$

$$[NQ]^{1*} + C \longrightarrow N + Q + C \tag{7}$$

$$N^{1*} + C \rightleftharpoons [NC]^{1*} \tag{8}$$

$$[NC]^{1*} \longrightarrow N + C \tag{9}$$

$$N^{3*} + C \longrightarrow N + C^{3*} \tag{10}$$

$$Q^{3*} + C \longrightarrow Q + C^{3*} \tag{11}$$

$$N^{3*} + Q \rightleftharpoons [NQ]^{3*} \tag{12}$$

$$[NQ]^{3*} + C \longrightarrow N + Q + C^{3*} \tag{13}$$

$$[NQ]^{3*} \longrightarrow N + Q \tag{14}$$

$$[NQ]^{3*} \longrightarrow N + Q^{3*} \tag{15}$$

$$C^{3} \longrightarrow \alpha\underline{t} - C + (1-\alpha)\,\underline{C} - C \tag{16}$$

$$Q^{3*} \longrightarrow \gamma\underline{t} - Q + (1-\gamma)\,\underline{t} - Q \tag{17}$$

Scheme V

Use of a Triplet Counter

Some comments need to be made before we use this scheme. (1) We explored the possibility of cis-piperylene (the counter) quenching the singlet exciplex $[NQ]^{1*}$, (process 7), by measuring quenching rates k_{q_1}, k_{q_2}, and k_{q_3} when k_{q_1} is the rate of quenching of naphthalene singlets by the counter, k_{q_2} is the quenching rate by the quencher (trans β-ethyl-styrene), and k_{q_3} is the quenching rate by the quencher in the presence of a certain concentration of the counter. It was found that $k_{q_3} = k_{q_1} + k_{q_2}$, indicating that the exciplex $[NQ]^{1*}$ is unquenchable by cis-piperylene. No conclusion can be drawn from this observation, except perhaps the speculative one that its lifetime is too short to be quenched by the counter, at the counter concentrations used.

(2) Since the chemical method of triplet counting used here cannot distinguish between N^{3*}, Q^{3*}, and $[NQ]^{3*}$, we performed other experiments to find out if the counter was being isomerized by $[Q]^{3*}$ or $[NQ]^{3*}$. Monitoring rate of isomerization of the quencher during the triplet counting experiments revealed that greater than 94% of the triplet energy was being quenched by the counter, which indicates that either the exciplex $[NQ]^{1*}$ intersystem crosses to produce almost exclusively N^{3*} and almost no Q^{3*}, or that Q^{3*} are entirely quenchable, a hypothesis difficult to accept in view of the rapid modes of decay (cis-trans isomerization preceded by twisting) available to the quencher triplet. If we accept the first premise, it has to be followed up with another assumption, a safer one to make this time: in a competition for N^{3*}, the counter easily wins out over the quencher. This

hypothesis received further support from our photostationary state experiments.

Photostationary States of the Counter

We allowed the counter to be sensitized by naphthalene to its photostationary state in the presence and absence of the quencher. Table II gives the photostationary state isomer ratios. We deduced that the quantum yield of disappearance of the counter was less than or equal to 0.04. This slow disappearance of the counter was perhaps responsible for the slow shift of the photostationary state to a cis-rich isomer ratio at longer irradiation times. When $[C] = 0.060\,\underline{M}$ and $[Q] = 0.132\,\underline{M}$, the quencher captured 19% of the triplets in n-hexane. When $[C] = 0.100\,\underline{M}$ and $[Q] = 0.132\,\underline{M}$, the quencher captured ~ 4% of the triplets in the same solvent, as measured by its isomerization. However, in these photostationary state experiments we used an isomer ratio of trans : cis ≡ 68 : 32,[46] so that the effective concentration of cis-piperylene in these experiments was even lower. Cis-piperylene is expected to be a more effective quencher of naphthalene triplets than trans-piperylene, as indicated by the photostationary state isomer ratio. If a substantial number of $[NQ]^{3*}$ or Q^{3*} were being produced and quenched by piperylene, one would expect the photostationary state to be different when the quencher was present. This is especially true for $[NQ]^{3*}$, for its very existence implies a certain stabilization which would make its triplet energy less than that of naphthalene. One could make the dubious assumption that the triplet energy of Q is the same as that of naphthalene, so that Q^{3*} produces the same photostationary state

TABLE II

Photostationary States of the Counter in Presence and Absence of the Quencher

Solvent	[Piperylene]$^{1, 2, 3}$	[I]^{1}	$t_{irr.}$^{4}	% Cis Found
Benzene	0.060	0.132	88 hr	34.2
Benzene	0.060		88 hr	34.5
n-Hexane	0.060	0.132	112 hr	35.2
n-Hexane	0.060		112 hr	35.4
Acetonitrile	0.060	0.132	112 hr	34.0
Acetonitrile	0.060		112 hr	34.0
Diethyl ether	0.060	0.132	112 hr	35.0
Diethyl ether	0.060		112 hr	35.6

1. moles lt^{-1}. 2. Initial isomer ratio = 69 : 31 (t : c).
3. Quantum yield of disappearance of naphthalene was estimated to be in the range 0.02-0.06. The disappearance is smaller in tubes containing I, indicating that the quencher has a smaller quantum yield of reaction with naphthalene then piperylene has. Naphthalene concentration was 0.05 M.
4. Light input = 8×10^{-8} E min^{-1}.

ratio of piperylenes as N^{3*} does. This is unlikely, although the triplet energies are probably close: ($E_{T_{naph}}$ = 60.9 ± 0.1 kcal $\underline{M}^{-1}$, E_{T_Q} ≃ 60.1 ± 0.2 kcal.[46])

We now go back to Scheme V, and write

$$\phi^{0}_{isc}\left(\frac{y_T}{y_{T'}}\frac{F'}{F} - 1\right) = \phi'_{isc}\frac{F^0}{F'}\left(\frac{F'}{F} - 1\right)$$

when ϕ^{0}_{isc} = intersystem crossing yield of naphthalene, assumed to be 0.80[48, 47]

ϕ'_{isc} = intersystem crossing yield of the exciplex;

$\phi'_{isc} = k_5/(k_4 + k_5 + k_6 + k_7)$, and since $k_7 \simeq k_6 \simeq 0$ (vide supra),

$\phi'_{isc} = k_5/(k_4 + k_5)$. (See also, Scheme IV.)

y_T = triplet yield (expressed as percent isomerization) of cis-piperylene in presence of quencher

$y_{T'}$ = triplet yield of cis-piperylene in absence of quencher

F^0 = fluorescence intensity of naphthalene in absence of quencher and counter

F' = fluorescence intensity in presence of counter but in absence of quencher

F = fluorescence intensity in presence of both quencher and counter.

The experiments were typically performed by keeping the counter concentration constant (0.066 M and 0.132 M) and varying the quencher concentration. Then

$$\phi^{0}_{isc}\left(\frac{y_T}{y_{T'}}\frac{F'}{F} - 1\right)$$

is plotted against

$$\frac{F^0}{F'}\left(\frac{F'}{F} - 1\right) \quad .$$

The slope is ϕ'_{isc}. Table III gives the values of ϕ'_{isc} obtained in four solvents. Figure II presents the data graphically.

An Independent Confirmation of the Exciplex Intersystem Crossing Yield In Benzene

The values of ϕ'_{isc} are found to be solvent dependent, with the value in benzene rather low, and the values in other solvents bunched together in the range 0.15-0.30. This naturally cast suspicions on the benzene data, particularly since it was quite low. Apart from normal repetitions, we performed another experiment: one that uses the quencher as a counter. This experiment has inherent sources of error, such as energy wastage during energy transfer from N^{3*} to Q. For that reason, use of a counter with better known behavior is preferred. However, we had been studying the naphthalene-quencher triplet energy transfer characteristics and had come to the conclusion that energy wastage is minimum in benzene among the four solvents studied, and is quite small (vide infra). The experiment was performed as follows:

Enough quencher was added to quench $> 97\%$ of the naphthalene singlets. A parallel tube was made up of benzophenone and the quencher. The tubes were simultaneously irradiated with the 3130 Å Hg line in a merry-go-round apparatus, and analyzed for the cis-isomer of the quencher. In absence of intersystem crossing of the exciplex $[NQ]^{1*}$ one would expect the rate of isomerization sensitized by benzophenone to be at least 45 times faster than the rate of isomerization sensitized by naphthalene. A value of ϕ'_{isc} can be calculated by

TABLE III

Intersystem Crossing Yields of the Singlet Exciplex in Different Solvents

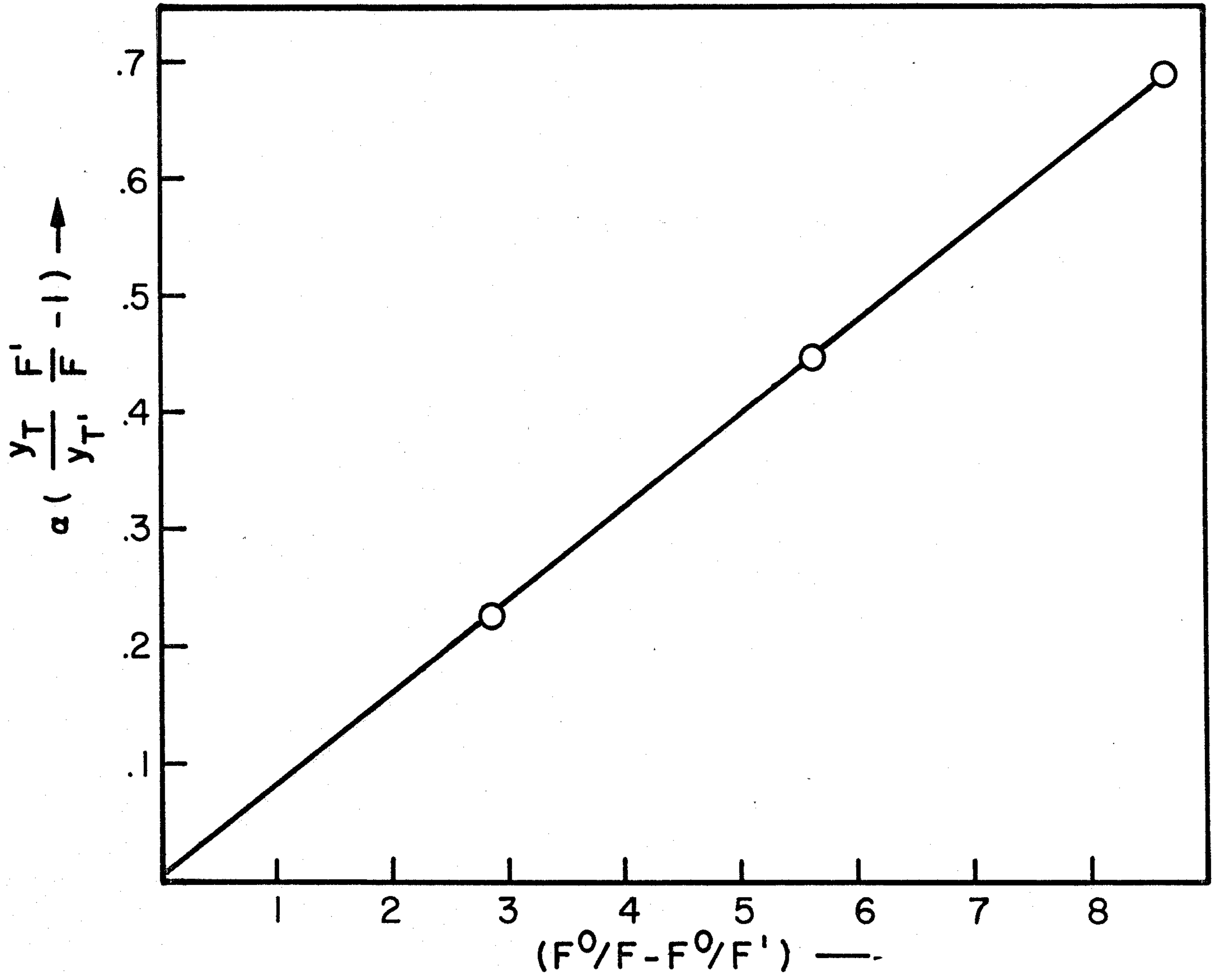
Solvent	ϕ'_{isc} [1]
Benzene	0.10 ± 0.02
Acetonitrile	0.28 ± 0.05
Diethyl ether	0.25 ± 0.06
_n_-Hexane	0.24 ± 0.04

1. The errors are estimated by adding the scatter of different determinations (reproducibility) to the estimated error due to incomplete quenching of N^{3*} by the counter and an assumed error of 2% in g.c. analysis.

comparing these two rates, and it came to 0.14. It was expected to be a little higher than the actual value, for the quencher was absorbing some light directly at the concentration (0.66 _M_) it was used. We cannot correct this value for this extra isomerization, for the quantum yield of isomerization on direct isomerization is not known. Then there is the additional complication of singlet energy transfer from I to naphthalene. However the amount of light being absorbed by the quencher directly was probably between 4-7% of the total light intensity, and therefore the ϕ'_{isc} determined through the use of counter is seen to be essentially confirmed.

FIGURE 2

Intersystem crossing in the exciplex.


$\alpha\left(\frac{y_T}{y_{T'}}\frac{F'}{F}-1\right)$ →
.1
.2
.3
.4
.5
.6
.7
1
2
3
4
5
6
7
8
$(F^0/F - F^0/F')$ →

Triplet Energy Transfer from Naphthalene to the Quencher

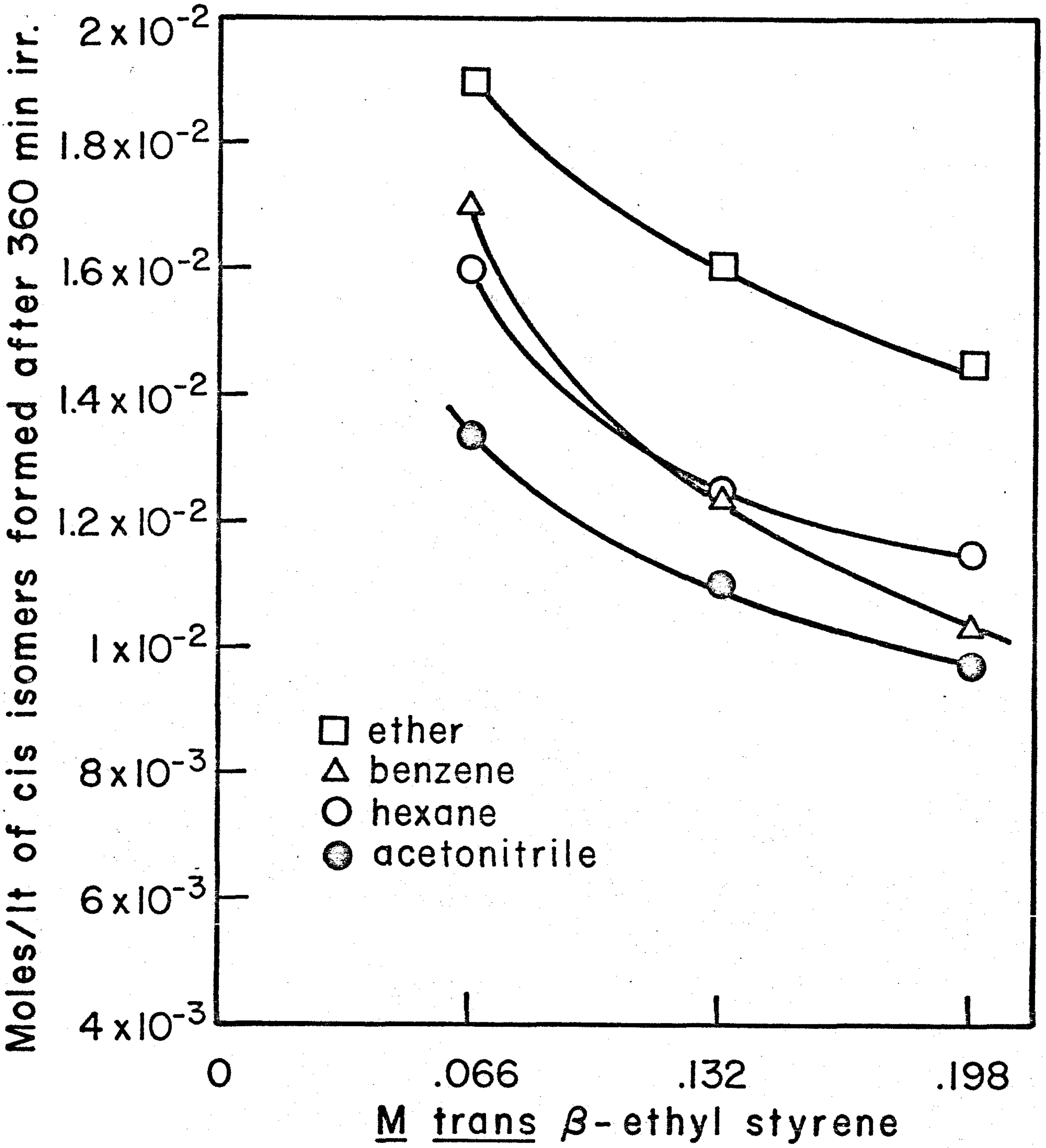
After the quantum yields of intersystem crossing of the singlet exciplex were obtained, it became possible to estimate the total triplet yield in any given naphthalene-quencher system. This in turn made it possible to study the efficiency of triplet energy transfer from naphthalene to the quencher. Caldwell[49] has recently studied energy transfer to trans-β-methyl styrene, and he found no evidence of energy wastage in his system. However he studied only one condensed aromatic as a donor: chrysene. Our data indicates substantial energy wastage in solvents other than benzene. The quantum yield of isomerization in benzene is 0.45 ± 0.05, which is close enough to the decay ratio to make energy wastage a relatively unimportant process in this solvent.

Measurement of Inefficiency During Energy Transfer and Quantum Yield of Triplet Energy Transfer

We obtained rates of isomerization of the quencher in different solvents on simultaneous irradiation of tubes containing identical concentrations of naphthalene and quenchers and constructed plots of yield of cis-isomer vs. quencher concentration in all solvents. The plots are shown in Figure III. The isomerization yield decreases as the quencher concentration increases, because of increased singlet quenching. Correcting for this singlet quenching and allowing for triplet generation through intersystem crossing of the exciplex should yield a horizontal line when the corrected triplet yield is plotted against quencher concentration. This is a reasonably safe prediction

FIGURE 3

Triplet sensitization of I.


Moles/lt of cis isomers formed after 360 min irr.
2 x 10⁻²
1.8 x 10⁻²
1.6 x 10⁻²
1.4 x 10⁻²
1.2 x 10⁻²
1 x 10⁻²
8 x 10⁻³
6 x 10⁻³
4 x 10⁻³
0
.066
.132
.198
M trans β-ethyl styrene
□ ether
△ benzene
○ hexane
● acetonitrile

because although energy transfer may not be diffusion controlled, naphthalene triplet lifetime is long enough to allow all naphthalene triplets to be quenched by styrene. In fact, the nature (and slope) of these plots can be used as a further test of the ϕ'_{isc} values obtained earlier. These plots are shown in Figure IV. They are indeed roughly horizontal, the scatter probably being no more than what would be expected taking the errors of the two corrections into account. However, the four solvents yield four different horizontal lines, indicating triplet yield is different in different solvents. We call $\phi_{t\rightarrow c}$ the isomerization efficiency $=(k_{14}/k_{14}+k_{15})\cdot(1-\gamma)$. If the total light input is I we can write $I[(1 - F'/F^0)\phi^0_{isc} + F'/F^0\ \phi'_{isc}]\times \phi_{t\rightarrow c}$ = molecules of <u>cis</u>-isomer produced.

Using the above formula we estimated $\phi_{t\rightarrow c}$ for benzene to be 0.45 ± 0.05. Assuming that the decay ratio is 0.5, we get $\phi_{It} = \phi_{t\rightarrow c}/(1-\gamma) \simeq 0.9 \pm 0.10$. ϕ_{It} for other solvents can be calculated using the following equation:

$$\phi_{It(sol)}/\phi\ \text{(benzene)} = \phi_{t\rightarrow c(sol)}/\phi_{t\rightarrow c(benzene)}$$

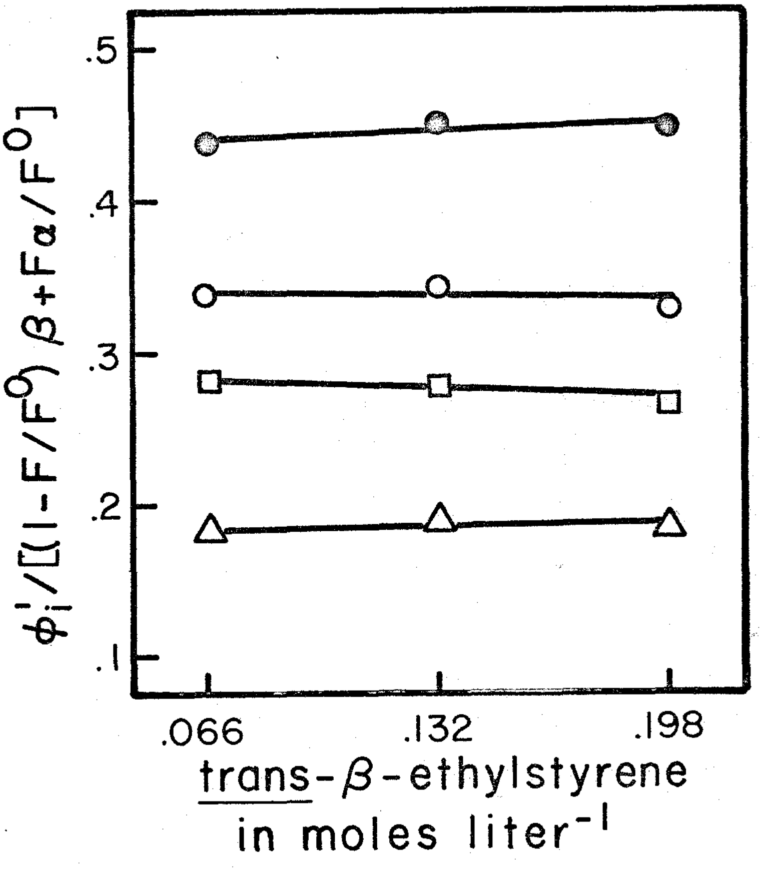
and

$$\phi_{t\rightarrow c(sol)}/\phi_{t\rightarrow c(benzene)} = y_{T(sol)}/y_{T'(benzene)}$$

which incorporates the assumption that the decay ratio γ remain solvent independent.

FIGURE 4

Energy wastage in the naphthalene-I system.


$\phi_i'/[(1-F/F^0)\beta+F\alpha/F^0]$
.5
.4
.3
.2
.1
.066
.132
.198
trans-β-ethylstyrene
in moles liter^{-1}

Solvent Independence of Decay Ratio of I

The solvent independence of the decay ratio was demonstrated by measuring the rates of isomerization of quencher I when a high energy aromatic ketonic sensitizer (benzophenone) is used. Clearly if the solvent dependence of rates of isomerization of I could be due to either different amounts of energy wastage in different solvents or due to variation of decay ratio. However since the rates do not vary within limits of experimental error (~10%) it would be a striking coincidence if the variation in the degree of inefficiency of energy transfer just compensated for a variation of the decay ratio. Besides Caldwell[49] has shown that there is no inefficiency of energy transfer from benzophenone to trans-β-methyl styrene. The observed lack of variation of rates of isomerization was thus interpreted to indicate that the decay ratio is solvent independent (see Table IV).

Table V gives ϕ_{It} for three solvents, assuming ϕ_{It} to be 0.9 ± 0.1 for benzene, obtained with the assumption that the decay ratio is 0.50. The relatively large inefficiency in acetonitrile can perhaps be thought of as partly being due to the slight lowering of naphthalene triplet energy. A half kilocalorie decrease might reduce the energy transfer rate two-fold and make radiationless decay of the triplet exciplex competitive. Our results, taken in conjunction with Caldwell's observations point out the danger of labeling a quencher a 'vertical' quencher or a 'nonvertical' quencher. Nonvertical quenching or quenching through chemical interaction accompanied by energy wastage takes place when certain structural requirements are satisfied by the quencher and the quenchee. While trans-β-methyl styrene acts as a

TABLE IV

Relative Rates of Isomerization of I Sensitized by Benzophenone

Solvent	Percent Isomerization[1, 2]	$1 - \gamma$[3]
Benzene	5.7	0.53 ± 0.05
Diethyl ether	5.5	0.51 ± 0.05
n-Hexane	5.9	0.54 ± 0.06
Acetonitrile	6.3	0.56 ± 0.06

1. For the same (arbitrary) period of irradiation.
2. Error: ± 10% of recorded value.
3. Calculated assuming that there is no energy wastage in energy transfer from benzophenone. γ = (moles of cis-isomer produced)/I(in einsteins) $\times t_{irr}$ since the intersystem crossing yield of benzophenone is unity, and all benzophenone triplets are quenched.

TABLE V

Quantum Yields of Energy Transfer from Naphthalene to the Quencher

Solvent	ϕ_{It}[1]
Benzene	0.90 ± 0.10
n-Hexane	0.56 ± 0.05
Acetonitrile	0.40 ± 0.08
Diethyl ether	0.70 ± 0.07

1. Error in all except one case assumed to be equal to the error in benzene. This assumes that the decay ratio is known with high accuracy to be 0.5. Error in acetonitrile computed separately.

vertical quencher when quenching benzophenone, fluorenone, and chrysene triplets it is established that trans-β-ethyl styrene acts as as nonvertical quencher of naphthalene in hexane, ether, and acetonitrole but not in benzene.

Quenching of Acetophenone Triplets by Olefins

The above conclusion is also drawn from our data on quenching of acetophenone triplets by olefins. The olefins used in this experiment were substituted in such a way that in the exciplex the olefin-ketone distance would be large. This ought to increase the effect of any charge transfer on the dipole moment of the exciplex and magnify the dependence of quenching rates on solvent polarity. One experimental problem which we anticipated was that the overall quenching rates would be lower. Tablex VI and VII give the relative rates of isomerization of olefins I-VIII in five different solvents. These relative rates were determined by monitoring per cent isomerizations of identical acetophenone-olefin mixtures in five different solvents after they had been simultaneously irradiated with 313 nm radiation in a merry-go-round apparatus. All rates have been expressed relative to benzene which is thus taken to be unity for each olefin.

Solvent Dependence of Isomerization Rates

The data indicate that the rate of isomerization increases approximately one and a half times as the solvent is changed from benzene to acetonitrile. This rules out any significant participation by charge-transfer processes in stabilizing the exciplex. What is striking,

TABLE VI

Relative Rates of Isomerization of Olefins
Sensitized by Acetophenone[1, 2]

Solvent	I	II	III	IV
Benzene[4]	1	1	1	1
n-Hexane	0.5	0.9	0.7	0.6
Acetonitrile	1.6	1.5	1.8	1.5
Diethyl ether[3]	0.09	0.10	0.08	0.21
Anisole	0.8	0.95	0.8	0.8

I: cis-2, 2-dimethyl-3-hexene.
II: cis-2, 2-dimethyl-3-heptene.
III: cis-4, 4-dimethyl-2-pentene.
IV: cis-3, 4-dimethyl-2-pentene.

---

[1] Acetophenone concentration varied from 0.1 M to 0.25 M.

[2] Per cent isomerization never exceeded 6%, and was always more than 0.2%.

[3] The error in measurement in this solvent was larger because of the reasons discussed in text, and because the total percentages of isomerization were often very low (0.2%-1.5%).

[4] See text. No horizontal correlation is implied here.

TABLE VII

Relative Rates of Isomerization of Olefins Sensitized by Acetophenone[1]

Solvent	V	VI	VII	VIII
Benzene[2]	1	1	1	1
n-Hexane	0.6	0.7	0.7	0.65
Acetonitrile	1.3	1.5	1.6	1.7
Diethyl ether	0.3	0.33	0.2	0.25
Anisole	0.8	0.9	0.8	0.85

V: trans-2, 2-dimethyl-3-hexene.
VI: trans-2, 2-dimethyl-3-pentene.
VII: trans-4, 4-dimethyl-2-pentene.
VIII: trans-3, 4-dimethyl-2-pentene.

---

[1] For a discussion of errors, see preceding table. Usually errors (reproducibility) were ± 0.3 units, except for ether. To this must be added errors due to quenching by photoproducts, but the maximum error is not expected to be more than ± 50% of the observed rate.

[2] The absolute values of quantum yields were typically more than an order of magnitude smaller than the quantum yields of isomerization of corresponding cis-olefins. There is no horizontal correlation implied in this table; see text.

however, is the extraordinary decrease in rate of isomerization observed in diethyl ether. Before discussing the probable causes of an order of magnitude decrease in rate of isomerization in this solvent, a few comments need to be made about the possible sources of error in measuring these relative rates. Wagner[39b] has discussed the problems of getting the olefins free from oxidation products and dienes. All olefins were purchased in sealed ampoules, packed under N_2. They were all bulb-to-bulb distilled over $LiAlH_4$. Their purity was tested by glpc before and after the bulb-to-bulb distillation and they never gave any peak with retention times a diene would be expected to have. The solvents were purified by conventional techniques (see experimental techniques). As an added precautionary measure, quantum yields of isomerization were determined for cis-pentene-2 and cis-hexene-2 using benzophenone as the sensitizer. The quantum yields were in good agreement with Caldwell's data.[40] It should be noted that the relative rate decrease observed in either cannot be produced by an impurity either in the sensitizer or in the olefin; impurity quenching of acetophenone triplets can at most introduce an error equivalent to the difference of bimolecular diffusive rate constants in the two solvents, ether and benzene. At the same time one would expect a correspondingly large rate increase in anisole which is much more viscous than benzene. This was not observed.

Another potential explanation of the observed drop in rates was that acetophenone was disappearing at a faster rate in ether, and therefore was not absorbing all the light during the whole period of irradiation. It was difficult to follow the loss of acetophenone by spectrophotometry, since an unidentified product had an absorption maximum around 365 nm. Hence loss of acetophenone was calculated by determining the decrease of absorbance at twelve suitable wavelengths between 320 and 366 nm and plotting the percent decrease in absorbance (expressed as loss of acetophenone) against wavelength. This curve leveled off around 330 nm, indicating minimum absorption by the product at this region. This maximum value of loss of acetophenone agreed with the estimated loss as determined by glpc. The concentration of acetophenone was maintained such that at all times acetophenone absorbed greater than or equal to 95% of the light at 313 nm. The rate of appearance of the product was only slightly less rapid in anisole, an observation that rules out the rate decrease in ether as being due to quenching of acetophenone triplets by the product.

Sensitization by m-Methoxy Acetophenone

We used *m*-methoxy acetophenone as a sensitizer in an attempt to study the effect of variation of sensitizer structure on the solvent dependence of isomerization rates. The triplet energy of m-methoxy acetophenone is 1-3 kcal/mole higher than that of acetophenone. The lowest triplet is Π-Π^*, indicating much greater delocalization of the triplet energy on the aromatic ring. Table VIII gives the relative rates determined for the *cis*-olefins. The rates were approximately 30-50 times slower and too slow to be accurately measured for the *trans*-olefins. The 'ether effect' disappears entirely. This is perhaps an indication that the 'ether effect' is more closely associated with the

TABLE VIII

Relative Rates of Isomerization of Olefins Sensitized by m-Methoxy Acetophenone[1]

Solvent	I	II	III
Benzene[2]	1	1	1
Acetonitrile	1.3	1.4	1.6
n-Hexane	0.7	0.8	0.7
Diethyl ether	0.66	0.6	0.7
Anisole	0.8	0.66	0.8

I: cis-4, 4-dimethyl-2-pentene.
II: cis-2, 2-dimethyl-3-Hexene.
III: cis-2, 2-dimethyl-3-pentene.

---

[1] For a discussion of errors, see text.

[2] Rates of isomerization of each olefin in all solvents expressed relative to the rate in benzene.

structure of the sensitizer, since the observed solvent dependence was largely constant over all the olefins studied, although the drop in isomerization rate in ether was perceptibly smaller for the trans-olefins. The error in measuring the rates of sensitization by m-methoxy acetophenone was perhaps slightly larger because a certain small percentage of the triplets was decaying through self-quenching. The sensitizer concentration was maintained at such a level that self-quenching was expected to be negligible. This put an upper limit on the total period of irradiation depending on the rate of disappearance of the sensitizer.

The 'ether effect' can be interpreted in two ways: (a) radiationless decay of the exciplex is more efficient in ether, and (b) the sensitizer triplet has a shorter lifetime in this solvent. We measured the lifetimes of acetophenone triplets at room temperature in some of these solvents.

Measurement of Acetophenone Triplet Lifetimes

The adopted method was sensitization of biacetyl phosphorescence. Biacetyl phosphoresces at room temperature either on direct irradiation or on sensitization. Phosphorescence quantum yield at room temperature is 0.08.[53] The following scheme was used to obtain the triplet lifetime. A more detailed version of the same scheme has been used by Sandros[50] who allowed for sensitization of biacetyl singlets, and fluorescence emission from biacetyl contributing to the total emission intensity.

$$\begin{aligned}
A &\xrightarrow{h\nu} A^{1*} \rightsquigarrow A^{3*} \\
A^{3*} &\xrightarrow{k_d} A \\
A^{3*} + B &\xrightarrow{k_{It}} A + B^{3*} \\
B^{3*} &\xrightarrow{k_p} B + h\nu_0 \\
B^{3*} &\xrightarrow{k'_d} B
\end{aligned}$$

Scheme VI

Then

$$I_p \text{ (phorescence intensity)} = \frac{k_p}{k'_d + k_p} \times \frac{k_{It}[B]I}{k_{It}[B] + k_d}$$

when I is the intensity of exciting light.

$$I_p(\text{lim}) = \frac{k_p \times I}{k'_d + k_p} \quad ,$$

when all triplets are quenched by biacetyl.

$$I_p(\text{lim})/I_p = 1 + \frac{k_d}{k_{It}} \times \frac{1}{[B]} \quad .$$

A plot of $I_p(\text{lim})/I_p$ vs. $1/[B]$ is therefore expected to be linear, and the slope equal to k_d/k_{It}. It was assumed that acetophenone intersystem crosses with unit efficiency, and does not transfer singlet energy to biacetyl. The concentrations of the sensitizer and biacetyl were such that biacetyl absorbed less than 1% of the light. However a broad band was seen at ~420-460 nm that could be acetophenone phosphorescence, biacetyl fluorescence, or both. We would rather say it was acetophenone phosphorescence as well as biacetyl fluorescence, since the intensity of this band showed no clear concentration (of quencher) dependence, but underwent erratic changes. The solutions were photostable to different degrees depending on the solvent. The acetonitrile solution was most photostable and the ether solution was the least. Figures 5, 6, and 7 show the plots of $I_p(\mathrm{lim})/I_p$ vs. $1/[B]$. In one case $I_p(\mathrm{lim})$ had to be obtained by extrapolating a plot of $1/I_p$ vs. $1/[B]$ to infinite biacetyl concentration. Table IX gives the lifetimes obtained from the slopes. The relatively large variations are a reflection of the large errors inherent in such a technique. What stands out, however, is the extraordinarily short lifetime found in ether. The rate of disappearance of the sensitizer in ether is relatively high, but not anywhere close to the rate of decay. Clearly, the acetophenone triplet undergoes some kind of interaction with ether which opens up a new channel of radiationless decay. The k_{It} values used in computing the lifetimes were obtained from the equation of Porter and Osborne:[51] $k_{diff} = 8\,RT/3000\,\eta$, when η is the viscosity of the solvent, as well as from the work of Sandros[50] and Wagner.[38] Normal precautions were taken to ensure that adventitious quenchers were not present in the solvents. The sensitizer for the lifetime determination and isomerization studies came from the same bottle. This reduces the absolute validity of our data, because impurities present even in trace amounts would reduce the lifetime. However, we were more interested in the lifetime of the triplet acetophenone we used in the first part of our work, rather than absolute lifetimes on which there is some data.[52] Figures 5-7 indicate the scatter in our Stern-Volmer plots.

TABLE IX

Lifetime of Acetophenone Triplets Determined by Sensitized Phosphorescence of Biacetyl[1]

Solvent	$k_d/k_{It}\tau$	k_{It}[2]	$k_d = 1/\tau$
Benzene	1/2500	6×10^9	2.2×10^6
Acetonitrile	1/20, 000	1.6×10^{10}	8.0×10^5
Diethyl ether	1/150	2×10^{10}	1.3×10^8

1. The literature value of k_d in benzene is 3.8×10^5.[52] However, this may be just the first order decay rate of the triplet-triplet absorption spectrum. In that case, the actual decay rate is probably somewhat larger. k_d in our experiments will be overestimated, as pointed out by Sandros,[50] if photoproducts from biacetyl quench acetophenone triplets. If this is true, then the observed difference between the lifetimes in benzene and ether is probably larger than the actual difference of lifetimes in these two solvents.
2. These values have no special theoretical or experimental significance, and are educated guesses on my part. They are in line with the values used widely in literature.

FIGURE 5

Biacetyl quenching of acetophenone triplets

Solvent: Ether

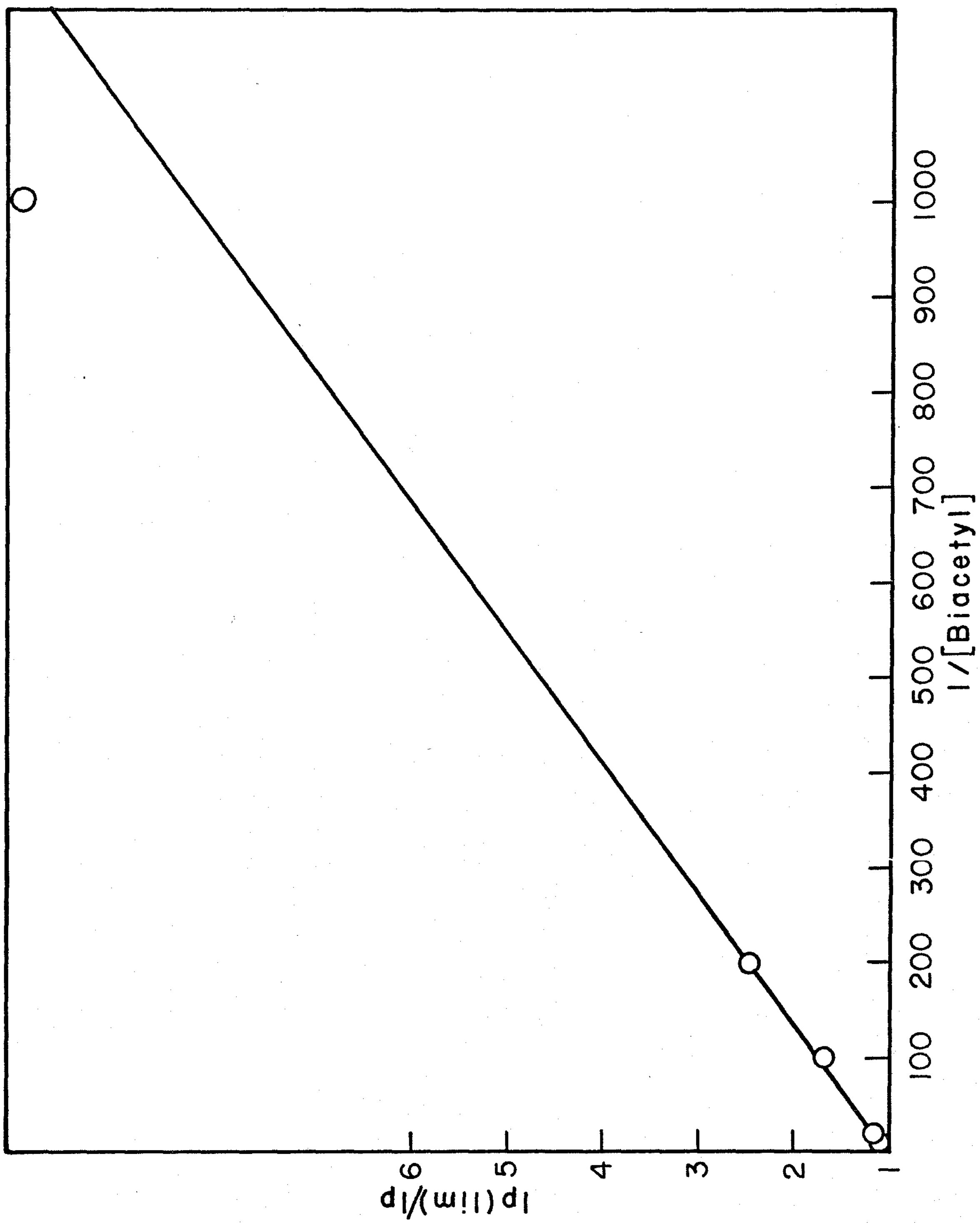

Ip(lim)/Ip
1
2
3
4
5
6
100
200
300
400
500
600
700
800
900
1000
1/[Biacetyl]

FIGURE 6

Biacetyl quenching of acetophenone triplets.

Solvent: Benzene

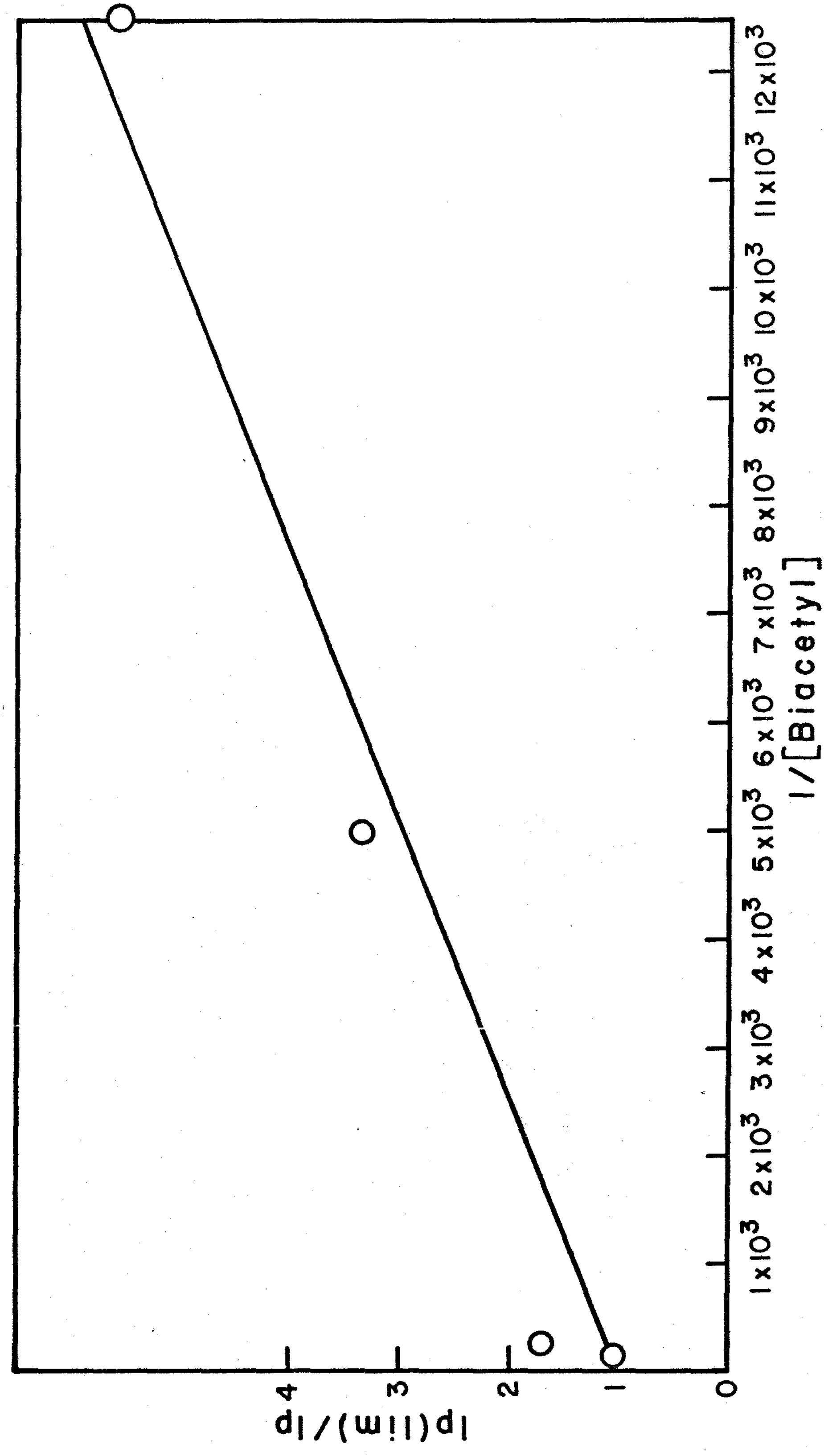
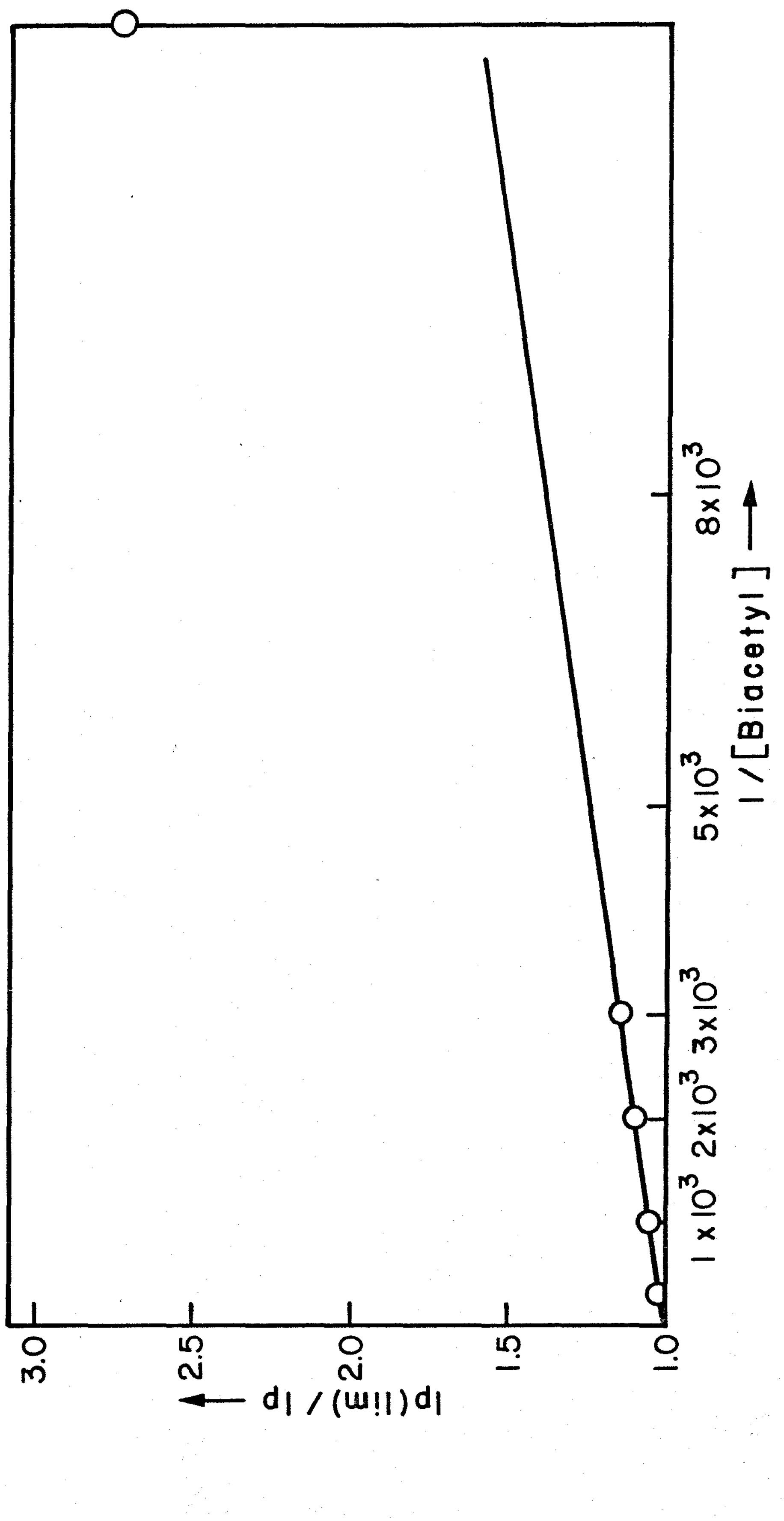

Ip(lim)/Ip
0
1
2
3
4
1/[Biacetyl]
1x10^3
2x10^3
3x10^3
4x10^3
5x10^3
6x10^3
7x10^3
8x10^3
9x10^3
10x10^3
11x10^3
12x10^3

FIGURE 7

Biacetyl quenching of acetophenone triplets.

Solvent: Acetonitrile


Ip(lim) / Ip ⟶
3.0
2.5
2.0
1.5
1.0
1 x 10^3
2x10^3
3x10^3
5x10^3
8x10^3
1/[Biacetyl] ⟶

Quantum Yield of Isomerization of Olefins

The following scheme was used to obtain quantum yields:

$$A \xrightarrow{h\nu} A^{1*} \rightsquigarrow A^{3*} \tag{1}$$

$$A^{3*} \xrightarrow{k_d} A \tag{2}$$

$$A^{3*} + \underline{t}\text{-}0 \longrightarrow [A\cdot \underline{t}\text{-}0]^{3*} \tag{3}$$

$$A^{3*} + \underline{c}\text{-}0 \longrightarrow [A\cdot \underline{c}\text{-}0]^{3*} \tag{4}$$

$$[A\cdot \underline{t}\text{-}0]^{3*} \longrightarrow A + \underline{t}\text{-}0 \tag{5}$$

$$[A\cdot \underline{c}\text{-}0]^{3*} \longrightarrow A + \underline{c}\text{-}0 \tag{6}$$

$$[A\cdot \underline{t}\text{-}0]^{3*} \longrightarrow A + 0^{3*} \tag{7}$$

$$[A\cdot \underline{c}\text{-}0]^{3*} \longrightarrow A + 0^{3*} \tag{8}$$

$$0^{3*} \longrightarrow \gamma\underline{t}\text{-}0 + (1-\gamma)\,\underline{c}\text{-}0 \tag{9}$$

Scheme VIIa

Here oxetane formation has been neglected. Oxetane quantum yields were quite low in benzene, the solvent in which all the quantum yield experiments were performed. Oxetane quantum yields were estimated by recording disappearance of acetophenone absorbance and varied from 0.001-0.02 for the trans-olefins and 0.03-0.06 for the cis-olefins. These values showed rather small variations with concentration of the olefins. A maximum value of 0.08 can be accepted for cis-2,2-dimethyl-3-hexene and cis-4, 4-dimethyl-3-pentene; a maximum value of 0.01 can be accepted for the corresponding trans olefins and both cis and trans 3, 4-dimethyl-2-pentenes.

All the isomerization quantum yields determined were initial quantum yields. Figures 8, 9, and 10 indicate the dependence of ϕ_{iso}^{-1} on reciprocal of the corresponding olefin concentration.

The following expressions can be derived from Scheme VIIa:

$$\frac{1}{\phi_{c\rightarrow t}} = \frac{1}{\gamma}\left(\left[1+\frac{k_6}{k_8}\right]+\frac{1}{[\underline{c}\text{-}0]}\times\frac{k_d}{k_4}\left[1+\frac{k_6}{k_8}\right]\right)$$

and

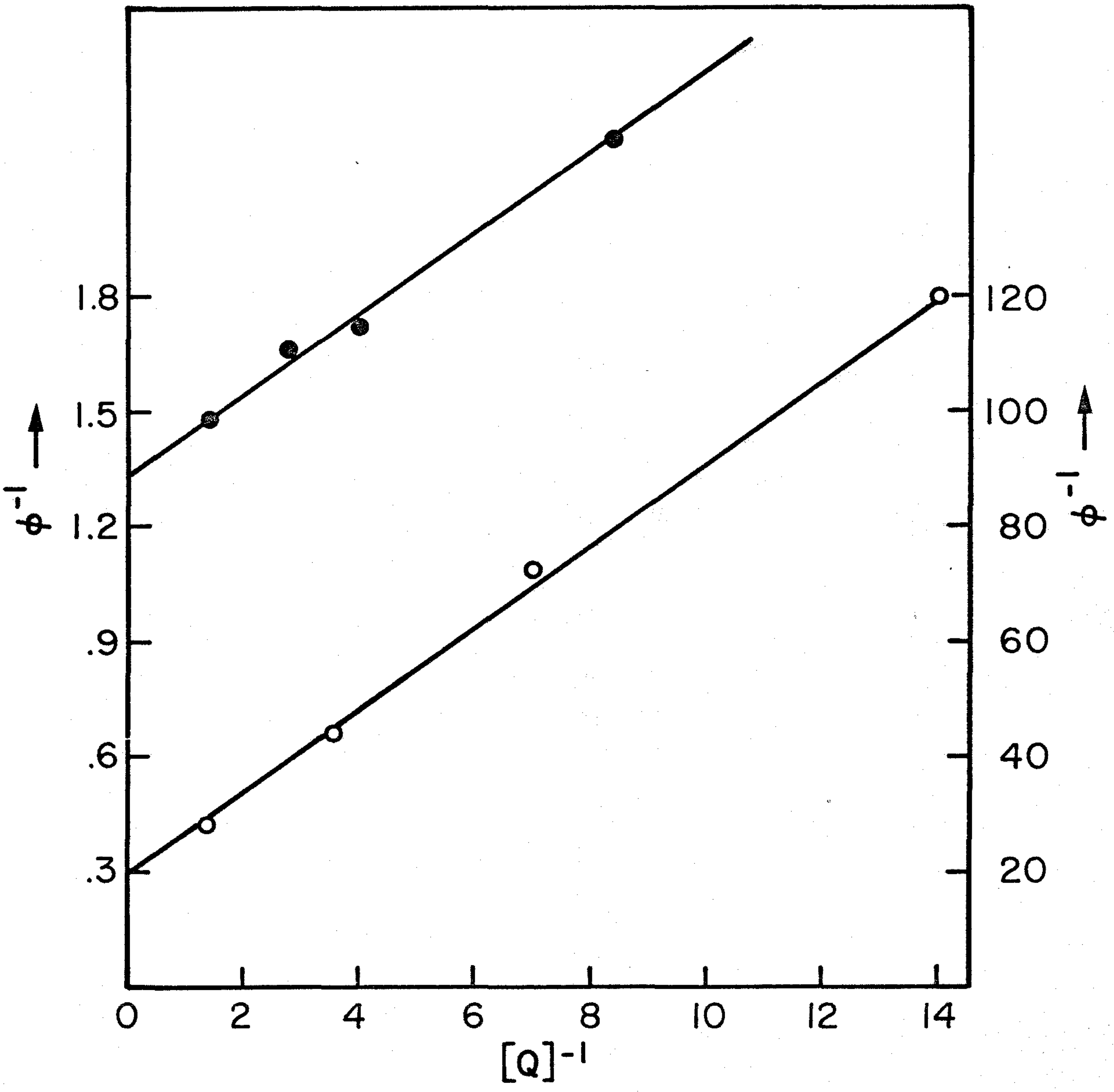
$$\frac{1}{\phi_{t\rightarrow c}} = \frac{1}{1-\gamma}\left(\left[1+\frac{k_5}{k_7}\right]+\frac{1}{[\underline{t}\text{-}0]}\times\frac{k_d}{k_3}\left[1+\frac{k_5}{k_7}\right]\right) .$$

Therefore the slope-intercept ratio of these plots give access to all the important rate constants if the decay ratios are known. The decay ratios could be determined by using a high energy sensitizer and allowing the olefins to reach photostationary states. However it is not easy to find a reliable high energy sensitizer with high triplet yield for the olefins under consideration. The assumption that the decay ratio $\gamma = 0.5$, as is found for many other olefins as well as styrenes, seems to be the safest one to make. It is possible to extract the decay ratio by monitoring competitive isomerization of a diene functioning as a triplet trap, but there is the problem of the diene quenching the triplet exciplex $[A\cdot\underline{t}-0]^{3*}$ or $[A\cdot\underline{c}-0]^{3*}$. Perhaps the decay ratio can be directly measured using a suitably substituted benzene or Hg as sensitizer. This possibility of mercury sensitization has to be investigated in the future. Table X gives the relevant rate constants.

FIGURE 8

Plot of ϕ^{-1} vs. $[\text{olefin}]^{-1}$.

4,4-dimethyl cis-2-pentene (left coordinate)	●
4,4-dimethyl trans-2-pentene (right coordinate)	○



1.8
1.5
1.2
.9
.6
.3
ϕ^{-1}
120
100
80
60
40
20
ϕ^{-1}
0
2
4
6
8
10
12
14
$[Q]^{-1}$

FIGURE 9

Plot of ϕ_{iso}^{-1} vs. [olefin]$^{-1}$.

3, 4-dimethyl cis-2-pentene	●
3, 4-dimethyl trans-2-pentene	○

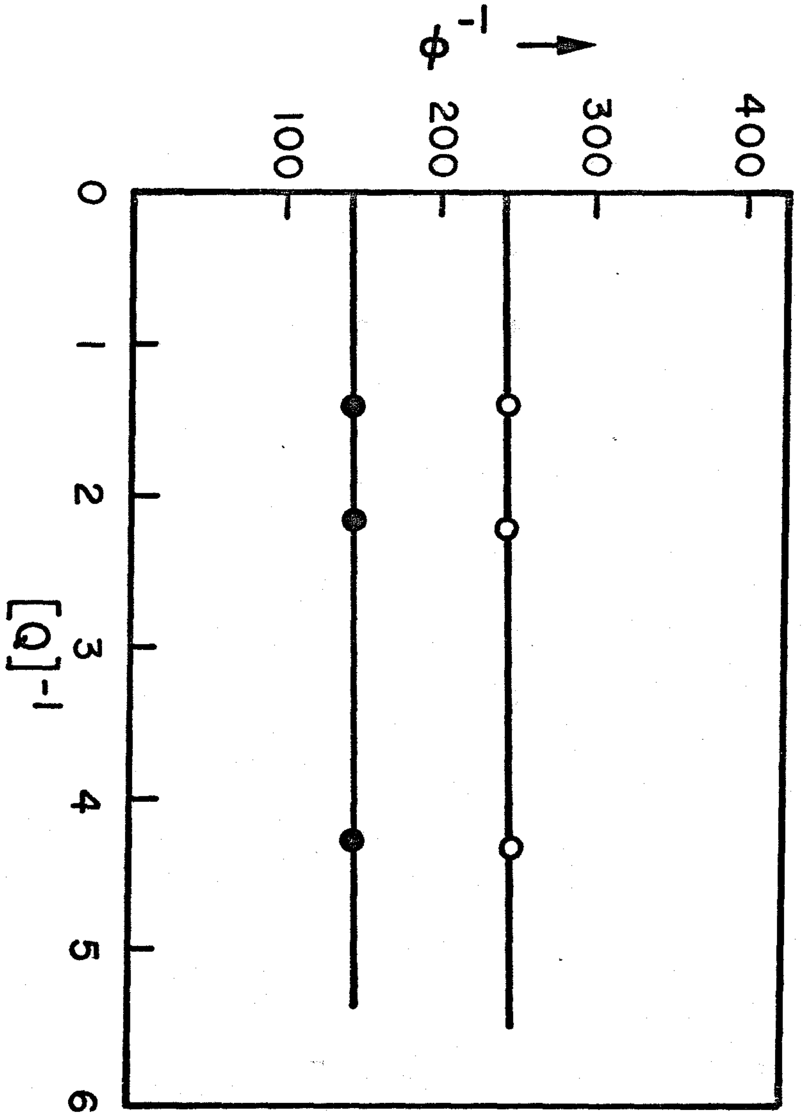

φ⁻¹ →
100
200
300
400
0
1
2
3
4
5
6
[Q]⁻¹

FIGURE 10

Plot of ϕ^{-1} vs. $[\text{olefin}]^{-1}$.

2, 2-dimethyl cis-3-hexene	● (left ordinate)
2, 2-dimethyl trans-3-hexene	○ (right ordinate)

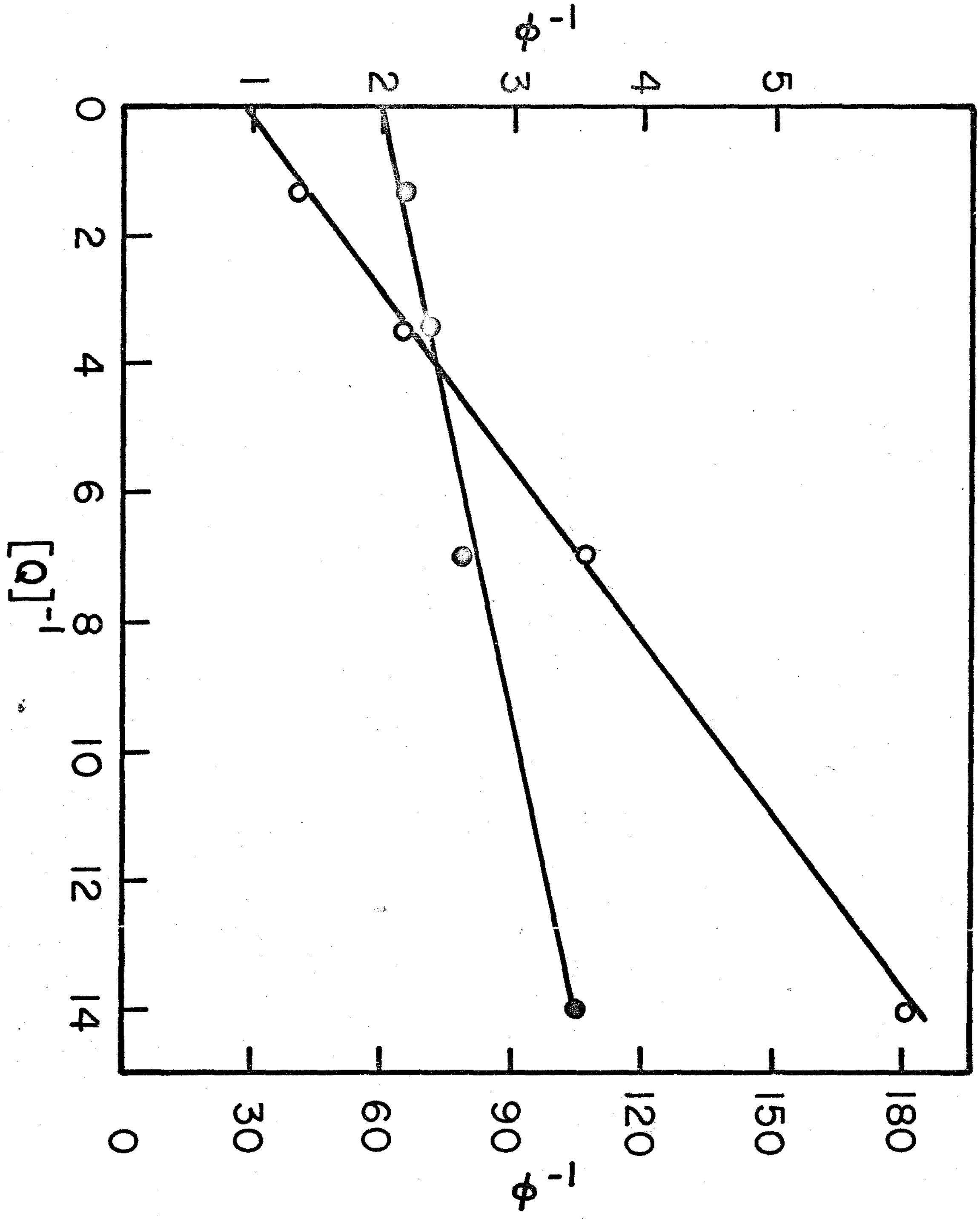

φ^{-1}
1
2
3
4
5
0
2
4
6
8
10
12
14
[Q]$^{-1}$
0
30
60
90
120
150
180
φ^{-1}

TABLE X

Rate Data for Olefins Sensitized by Acetophenone

Olefins	k_4[1]	k_3	k_6/k_8	k_5/k_7
I	4.1×10^7		0	
II	2.6×10^7		0[2]	
III	5.3×10^8		69	
IV		4.5×10^6		10.5
V		5.5×10^6		3.2
VI		2.9×10^8		119

I: cis-2, 2-dimethyl-3-hexene.
II: cis-4, 4-dimethyl-2-pentene.
III: cis-3, 4-dimethyl-2-pentene.
IV: trans-2, 2-dimethyl-3-hexene.
V: trans-4, 4-dimethyl-2-pentene.
VI: trans-3, 4-dimethyl-2-pentene.

---

1. See text.
2. Obviously γ cannot be 0.5 here, since $\phi_{\text{lim}}^{-1} = 1.32$. It has been assumed to be 0.76.

Nature of the Triplet Exciplex

There has been some controversy about the electronic state of the exciplex. We have assumed in our kinetic scheme that the exciplex formation is irreversible.[40] That assumption could bear reexamination particularly for the *trans*-olefins, with which the overall quenching rate is quite low. However, incorporation of reversibility in Scheme VIIa will not change our conclusions. Wagner also points out that this exciplex has not been quenched or made to transfer electronic energy to any acceptor. The conclusion was that the exciplex does not possess electronic energy and was therefore called an 'excited state complex'. It has already been pointed out that DeBoer's data[33] can only be explained either by postulating a termolecular quenching process or by assuming that the triplet exciplex is being quenched by the low energy sensitizer. We made attempts to quench the triplet exciplex by using a small, constant concentration of *cis*-1, 3-pentadiene.

Quenching of the Triplet Exciplex

Since the lifetime of acetophenone triplet in benzene is 4.5×10^{-7} sec, a 10^{-4} *M* solution of *cis*-piperylene is expected to quench roughly 20% of the triplets. However, as the olefin concentration increases, effective lifetime of the donor triplets would decrease, and the diene would capture fewer and fewer of the ketone triplets. At the limit of infinite olefin concentration, the diene would not have any effect on the isomerization quantum yield at all, unless it is quenching the triplet exciplex. Schematically,

$$A^{3*} + \underline{c} - p \longrightarrow A + p^{3*} \qquad (10)$$

$$[AO]^{3*} + \underline{c} - p \longrightarrow A + O + p^{3*} \qquad (11)$$

Scheme VIIb

Then

$$\frac{1}{\phi'_{c\to t}} = \frac{1}{\gamma}\left[\left(1 + \frac{k_6}{k_8} + \frac{k_{11}[\underline{c}\text{-}p]}{k_8}\right) + \frac{1}{[O]}\;\frac{k_d + k_{10}[\underline{c}\text{-}p]}{k_4}\;\frac{k_8 + k_6 + k_{11}[\underline{c}\text{-}p]}{k_8}\right] .$$

In other words, plots $\phi^{-1}_{c\to t}$ vs. 1/[olefin] should have different slopes, but the same intercept if only acetophenone triplets were being quenched. Quenching of the triplet exciplex however would produce a different intercept, as well as a different slope. Figure 11 shows that the triplet exciplex was being quenched by the diene.

We can write

$$\left[\frac{\phi_{c\to t}}{\phi'_{c\to t}}\right]_{1/[O]=0} = \frac{1 + k_6/k_8 + \dfrac{k_{11}[\underline{c}\text{-}p]}{k_8}}{1 + k_6/k_8}$$

or

$$\left[\frac{\phi_{c\to t}}{\phi'_{c\to t}}\right]_{1/[O]=0} - 1 = \frac{k_{11}[\underline{c}\text{-}p]}{k_6 + k_8} = p \;\; (\text{say}) \quad .$$

Then

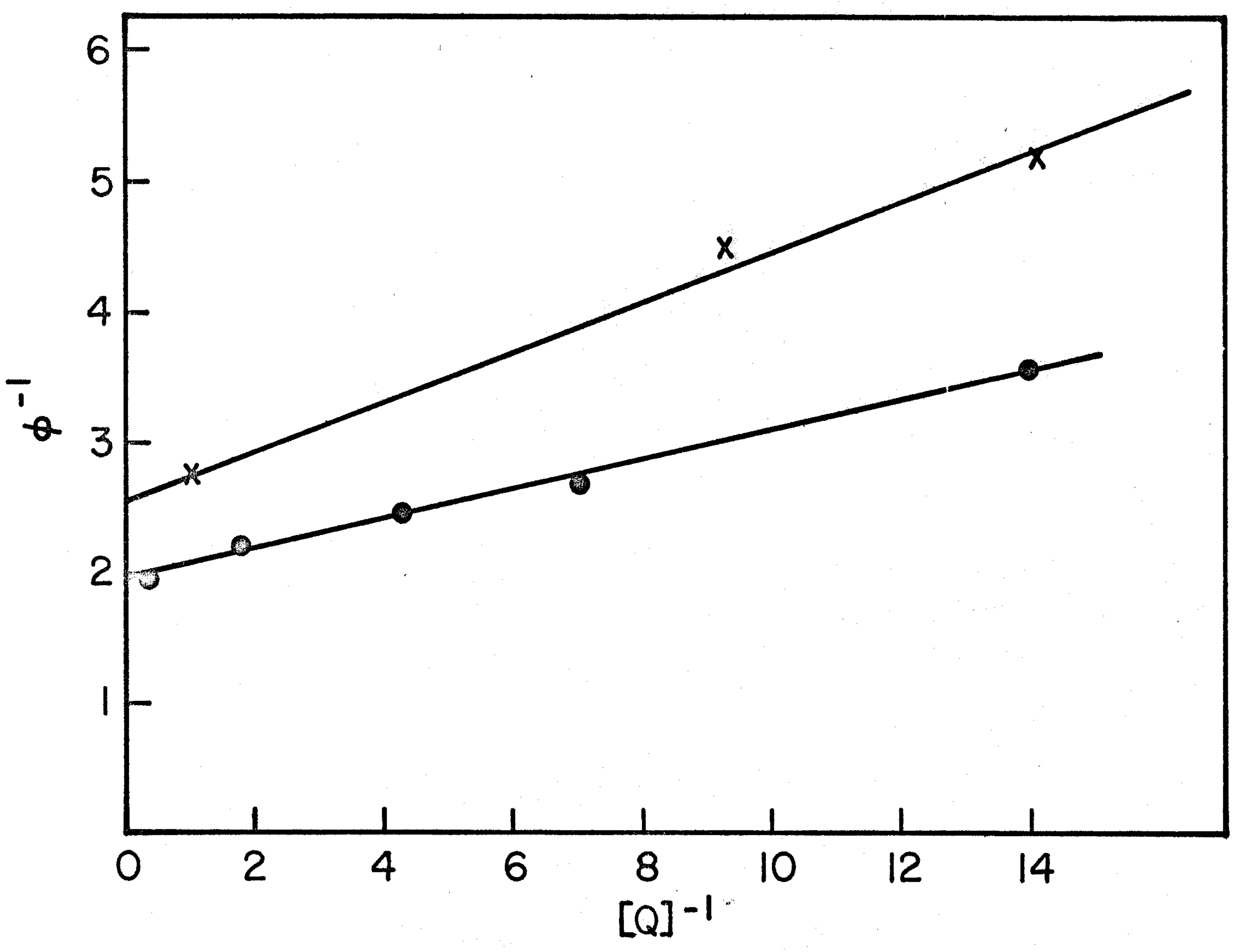
$$\frac{k_{11}[\underline{c}\text{-}p]}{k_6 + k_8 + k_{11}[\underline{c}\text{-}p]} = \frac{p}{p+1} = 0.2 \qquad (\text{from Figure 12}) \; .$$

Assuming that cis-piperylene quenches the exciplex at a diffusion controlled rate, we can estimate its lifetime from the information above.

FIGURE 11

Quenching of the triplet exciplex [Acetophenone-Olefin].

Olefin = cis-2,2-dimethyl-3-hexene.


6
5
4
3
2
1
ϕ^{-1}
0
2
4
6
8
10
12
14
$[Q]^{-1}$

The lifetime is $1/(k_6 + k_8) = 4.1 \times 10^{-7}$ sec. That its lifetime is very close to the lifetime of acetophenone triplet should not come as too much of a surprise. The excitation is probably localized on acetophenone, since the energy of the lowest Π-Π^* triplet of the olefin is appreciably higher than the energy of the exciplex. This could also explain why the structures of olefins studied here do not seem to affect rates of isomerization very much, unless the variation of the structure is so drastic that it seriously affects the binding in the exciplex. If this is true, then the exciplex formed by quenching of acetophenone triplets by a trans-olefin should also be quenchable by piperylene and the lifetime of the corresponding exciplex should be close to that of the acetophenone triplet. Unfortunately this is not an easy prediction to verify, for the rates of isomerization of trans-olefins are ordinarily very low and addition of piperylene would further reduce these rates.

An examination of the rates in Table X indicates that the olefin structure determines how the exciplex is going to decay. For 3,4-dimethyl-2-pentenes the dominant decay made is energy wastage. The other four olefins are similar in structure and we find that decay via energy wastage is more important with the trans-isomer. Our data do not conflict with Caldwell's observations that exciplex formation is irreversible. If the stabilization of the exciplex is 6.5 kcal mole^{-1} or more, dissociation back to acetophenone triplet and olefin is expected to be slower than the observed decay rate of the exciplex. It is possible that this stabilization is produced through some relaxation of steric strain in the olefin due to reduction of bond order of the C=C bond. However irreversibility cannot be a general phenomenon.

It presumably arises from a competition of three processes: (1) dissociation back to the aromatic triplet, (2) energy wastage, and (3) energy transfer.

Conclusion

In conclusion let me say a few words about the decay ratio. It is possible that the triplet exciplex decays to a biradical instead of the olefin triplet and the ground state ketone. The biradical then could decay to give the oxetanes, as well as the *cis*- and *trans*-olefins. The decay ratio in that case would be sensitizer dependent, as was postulated by Saltiel, Neuberger, and Wrighton.[56] The energy wastage still takes place from the triplet exciplex which is the precursor of the biradical. There is no easy way to produce conclusive data in favor of either the biradical or the triplet mechanism of isomerization. Mere demonstration that apparent decay ratios obtained from ϕ_{iso}^{-1} plots *vs*. 1/[olefin] are different for different sensitizers won't suffice, for reasons explained above. Nor will photostationary state data enable us to calculate the actual decay ratios. In fact, it is doubtful if kinetic methods can distinguish between the radiationless decay of the triplet exciplex and the decay of the biradical favoring the *cis*- or the *trans*-isomer of the olefin due to steric reasons. Labelling experiments may be fruitful. Therefore our investigation was mainly concerned with the initial events that occur on encounter between an olefin and a ketone triplet. We established that the resultant interaction gives rise to an electronically excited complex which undergoes radiationless decay at varying rates depending on the structure of the olefin and the sensitizer. We reached no conclusions on whether the exciplex formation is irreversible and whether the isomerization proceeds through the intermediacy of a biradical. Quenching rates could be determined using *m*-methoxy acetophenone as a sensitizer (an experiment of dubious value, for the quantum yields are vanishingly small). If the inefficiency is found to be caused by a slow quenching rate, then one can speculate that the initial exciplex formation involves some interaction between the $n-\Pi^*$ excited state (of acetophenone) and the olefin. If the inefficiency is caused by a high rate of energy wastage, one would have to conclude that the decay mode of the exciplex leading to isomerization involves development of some interaction between the carbonyl group and the olefin.

Experimental

Materials

Naphthalene:	Zone refined naphthalene was obtained from *Aldrich Chemicals*, and was used as received. Singlet lifetime, fluorescence, and melting point data agreed with literature values.[55]
trans-β-Ethyl-styrene:	99% *trans*-β-Ethyl-styrene was obtained from *Chemical Samples* and was, on occasion, purified by bulb-to-bulb distillation. Vpc analysis showed a single peak with less than 0.1% *cis*-styrene as the main impurity.
Benzene:	Spectrograde benzene was supplied by *Matheson, Coleman, and Bell*. This was purified by the photochlorination method of Saltiel, Metts, and Wrighton.[54] The final distillation was repeated twice and each time the middle half of the distillate was collected.
cis-1, 3-Pentadiene:	99% *cis*-1, 3-Pentadiene was supplied by *Chemical Samples*. Preliminary vpc analysis showed that the main impurities were 0.75% *trans*-1, 3-pentadiene and some cyclopentene. This diene was bulb-to-bulb

distilled from $LiAlH_4$ and this operation reduced the percentage of *trans*-1, 3-pentadiene to 0. 5-0. 6%, and other impurities to negligible proportions.

Acetophenone: 'Gold labeled' acetophenone was supplied by *Matheson, Coleman, and Bell*. Analysis by vpc revealed that it was $>$ 99% pure. It was used as received.

m-Methoxy acetophenone: It was supplied by *Aldrich Chemicals* with stated purity 99+%. It was used as received, after the gc showed only one peak on both Carbowax 20 *M* and SE-30 columns. The absorption spectrum agreed with literature.[57]

cis-2, 2-Dimethyl-3-hexene: Obtained from *Chemical Samples*. It contained 0. 2% *trans*-isomer as the main impurity. It was bulb-to-bulb distilled from $LiAlH_4$.

trans-2, 2-Diemethyl-3-hexene: Obtained from *Chemical Samples*. It contained 0. 1% *cis*-isomer as the main impurity. It was bulb-to-bulb distilled from $LiAlH_4$.

cis- and trans-4, 4-Dimethyl-3-pentene: Obtained from *Chemical Samples*. They contained 0. 2% and ~ 0. 1% contaminations of *trans*- and *cis*-isomers, respectively. They were bulb-to-bulb distilled from $LiAlH_4$.

cis- and *trans*-3, 4-Dimethyl-2-pentene: Supplied by Chemical Samples. They contained 0.3% and 0.15% of *trans*- and *cis*-isomers, respectively. They were purified by bulb-to-bulb distillation over $LiAlH_4$.

trans-1, 3-Pentadiene: It was obtained from Chemical Samples; stated purity was 99%. vpc analysis showed that it had 0.5% *cis*-isomer as the main impurity. It was purified by bulb-to-bulb distillation over $LiAlH_4$.

Diethyl ether: Supplied by Malinkordt Corporation; it was freshly distilled from $LiAlH_4$ under N_2.

Acetonitrile: Spectroquality acetonitrile was obtained from Matheson, Coleman, and Bell. It was distilled from P_2O_5 and then from K_2CO_3.

n-Hexane: Phillips pure grade (99%) *n*-hexane was further purified by passing it through alumina.

Anisole: Spectroquality anisole was received from Matheson, Coleman, and Bell and was used as received after its absorption spectrum agreed with literature.[53] Injection into gc produced only one peak (> 99% purity).

Biacetyl: It was always freshly distilled (twice) under vacuum in dark. It was obtained from Aldrich Chemicals and was labeled 99+% pure.

Procedures

The fluorescence quenching experiments were performed with rigorously degassed tubes (3 freeze-thaw cycles; pressure ~ 10^{-5} nm). Emission measurements were made using a Hitachi MPF-2 spectrofluorimeter. Lifetimes were measured using a 17 nsec rise time N_2 lamp and a fast rise Tektronix scope. The decay traces were fitted to the lamp pulse and the lifetime was calculated using a computer. Irradiation was carried out in a mery-go-round apparatus equipped with filters to isolate the 3130 Å line of a medium pressure Hg lamp.[58] The band pass varied from 7 nm to 20 nm. Pyrex tubes were used for all experiments. Rates of reactions were measured through product analysis using glpc. The following columns were used for analysis: cis- and trans-piperylenes in all solvents other than ether: 25′ × ¼″ 25% $\beta\beta'$ODPN; cis- and trans-piperlyenes in ether: 50′ × ¼″ 25% $\beta\beta'$ ODPN and 20′ × ¼″ Carbowax 20M in tandem; all olefins: 25′ × ¼″ 25% $\beta\beta'$ ODPN and 7′ × ¼″ 5% SE-30 in tandem; naphthalene, m-methoxy acetophenone, and acetophenone: 7′ × ¼″ 5% SE-30; 10′ × ¼″, 10% Carbowax, 20M. The ether-piperylene separation was fair-to-good. All the other separations were excellent.

The sensitized phosphorescence of biacetyl required special precautions. All the solutions were prepared in the dark, and they were degassed (5 freeze-thaw cycles: $< 10^{-6}$ nm Hg pressure) in the dark. Doubly distilled biacetyl was used in these experiments and care was taken to expose the samples to light as little as possible. Phosphorescence spectra were recorded on a Hitachi MPF-3 spectrofluorimeter.

Use of ratio recording yielded more stable baselines. In certain cases, the excitation spectra rather than the emission spectra were recorded, to minimize competitive absorption by biacetyl.

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59. After this thesis was written, Professor A. Weller announced at the Gordon Conference in photochemistry that Dr. M. Ottolenghi's observation of prompt triplet formation in amine-aromatic systems is in error.

CHAPTER III

MAGNETIC FIELD EFFECT ON TRIPLET-TRIPLET ENERGY TRANSFER PROCESSES

Introduction

Triplet-triplet energy transfer is one of the most widely studied processes in photochemistry after Ermolaev and Terenin[1] first demonstrated its existence. Since the process is spin allowed it should proceed on every encounter of the donor and the acceptor if there is no barrier to energy transfer. However the maximum rates corresponding to exothermic energy transfer are found to be 3-10 times slower than the diffusion controlled encounter rates predicted by the equation of Porter and Osborne.[2] A similar inefficiency was observed by Rebert and Ausloos[3] in the gas phase, and the inefficiency ranged from 0.5 to 0.98, although the energy transfer was always exothermic. It is certainly possible that part or all of this inefficiency is due to small frequency factors. The source of such frequency factors could be poor overlap of the vibrational states of the triplets of the donor and the acceptor, as well as an orientation dependence of energy transfer. However orientation factors cannot explain the fifty-fold decrease in efficiency as the acceptor changes from styrene to butadiene, neither of which has any bulky substituent preventing access to the conjugated system.

The inefficiency of energy transfer in solution phase has been studied by Wagner,[3] whose model nicely accounts for the observed relationship between energy transfer rates (k_{et}) and diffusion controlled rates (k_D and k_{-D}, calculated by the equation of Osborne and Porter).

It is well known that the rate of energy transfer is slowed down when there are bulky substituents present which limit the approach of the donor toward the acceptor during an encounter.[4] However, it is a matter of conjecture to what extent this effect on the rate is due to increased separation of donor and acceptor molecules, and to what extent it is due to the substituents preventing a parallel lineup of the donor and the acceptor. Perhaps study of depolarization during energy transfer in fluid solution can give some answers to this question. A study of this kind at 77°K was carried out by Eisenthal.[4c] He found that there was no preferred angular orientation for triplet energy transfer from benzophenone to phenanthrene. On the basis of presently available data it seems attractive to postulate the formation and decay of an exciplex as the source of the inefficiencies observed both in solution and gas phase. The binding energy of the exciplex will be influenced by the extent of overlap between the triplet states of the donor and the acceptor which will be a function of the orientation (angle) between the molecular axes of the donor and the acceptor in the sandwich configuration (assuming they are planar). The binding energy will also depend on the distance between the donor and the acceptor, which will account for the retardation caused by bulky substituents.

$$D \longrightarrow D^{1*} \rightsquigarrow D^{3*} \tag{1}$$

$$D^{3*} + A \rightleftharpoons (DA)^{3*} \tag{2}$$

$$(DA)^{3*} \longrightarrow D + A^{3*} \tag{3}$$

$$A^{3*} \longrightarrow A \tag{4}$$

$$(DA)^{3*} \longrightarrow D + A \ . \tag{5}$$

Scheme I

The unimolecular decay of the donor triplet D^{3*} has been omitted because we are considering a situation in which all donor triplets are quenched by the acceptor. In that case, process (5) becomes the only path leading to energy wastage or inefficiency. This has been observed for quenching of aromatic ketone triplets by stilbenes and by isoprene.[5, 6] The exciplex lifetime must be very short (< 1 nsec) because it is unquenchable by any other quencher. We attempted to modulate the decay ratio of the exciplex using a magnetic field. The results and interpretations offered for the results are given in the next subsection.

Results and Discussion

The sensitizers used in these experiments were common aromatic ketonic sensitizers, e.g., benzophenone, acetonaphthone, Michler's ketone, and m-methoxyacetophenone. The quenchers were the isomeric pentadienes and 1, 2-diphenylethylenes. Magnetic field effects were first looked for in the initial quantum yields. Table I gives the data obtained. We expected the field effect on initial quantum yields to show up on the photostationary state ratios. In fact, the field effect on the photostationary state was expected to be directly proportional to the observed field effect on initial rates for high energy sensitizers according to the following equation:

$$\frac{[\phi_{c\to t}/\phi_{t\to c}]_{H=Ho}}{[\phi_{c\to t}/\phi_{t\to c}]_{H=O}} = \frac{[c]/[t]_{pss,\ H=O}}{[c]/[t]_{pss,\ H=HO}} \ .$$

This equation can be derived by assuming that the rates of energy transfer from the donor to both the isomers of the acceptor are approximately equal to each other. This expectation was fulfilled and Table II gives the data on photostationary states.

Kinetic Analysis of the Data

A kinetic analysis using Scheme I after incorporating into it the following process helps us reach certain conclusions.

$$A^{3*} \longrightarrow \alpha \underline{t} - A + (1-\alpha)\underline{c} - A \ . \qquad (6)$$

First of all the field effect cannot be due to the perturbation of unimolecular decay processes of either the sensitizer or the donor excited

TABLE I

Effects of Magnetic Field on Composition at Photostationary State

Substrate	Sensitizer	$([\underline{\text{trans}}]/[\underline{\text{cis}}])_{pss}$	Field[1]	pss(on)/pss(off)
Piperylenes	Benzophenone	1.32	On	1.08
		1.22	Off	
Piperylenes	m-Methoxyacetophenone	1.38	On	1.13
		1.22	Off	
Piperylenes	Fluorenone	2.20	On	1.08
		2.04	Off	
Piperylenes	2-Acetonaphthone	2.39	On	1.16
		2.06	Off	
Piperylenes	Michler's ketone[2]	1.30	On	1.07
		1.21	Off	
Stilbenes	Benzophenone	0.61	On	0.91
		0.67	Off	
Stilbenes	2-Acetonaphthone	0.42	On	0.95
		0.44	Off	

[1] Field strengths varied from 8.5-9 kG.

[2] p,p′-Dimethylaminobenzophenone.

TABLE II

Effects of Magnetic Field on Initial Conversion Rates

Substrate	Sensitizer	R^0/R^1
trans-Piperylene	Benzophenone	1.09
cis-Piperylene	Benzophenone	1.02
trans-Piperylene	m-Methoxyacetophenone	1.12
cis-Piperylene	m-Methoxybenzophenone	1.03
trans-Piperylene	Fluorenone	1.17
cis-Piperylene	Fluorenone	1.06
trans-Piperylene	2-Acetonaphthone	1.16
cis-Piperylene	2-Acetonaphthone	1.07
trans-Stilbene	Benzophenone	1.07
cis-Stilbene	Benzophenone	1.15
trans-Stilbene	2-Acetonaphthone	1.10
cis-Stilbene	2-Acetonaphthone	1.17

[1] Ratio of initial rate with field off to rate with field on as estimated by measuring conversion ($< 5\%$) to other isomer at fixed time interval under equivalent irradiation conditions. Precision is ± 2%.

states. It is possible that a combination of such perturbations can produce the observed effect but that is unlikely because the acceptor isomers possess a common triplet in each case, and one cannot easily visualize a mechanism by which the decay ratios of these triplets are altered by a magnetic field. The observed change in photostationary state rules out unimolecular decay of donor excited states as the source of the observed inefficiency. One interesting aspect of the data is that in all cases the applied magnetic field causes isomerization rates to decrease. This led to the proposition that the applied magnetic field was increasing the rate of processes such as (5). A tentative hypothesis was proposed to explain how a magnetic field could alter the decay ratio of the exciplex.[14] In passing, we note that this hypothesis is kinetically sound, in that it can explain why the field effect is dependent on the structures of both the sensitizer and the acceptor. It also rationalizes the field effect on the photostationary states, as arising from the perturbation on the initial quantum yields.

It is known that the total symmetry (product of spin and angular momentum symmetrics) is conserved when a molecule undergoes intersystem crossing.[7] The donor triplet is thus born with a nonequilibrium distribution of population among the zero field states. In the absence of a quencher, spin lattice relaxation would intervene long before the triplet underwent radiative or radiationless decay, expecially at room temperature in fluid solutions.[8] Hence the observed phosphorescence is found to be a single unimolecular process. The different decay characteristics of the zero field levels become experimentally observable at very low temperatures when the radiative lifetime albeit long, is shorter than the spin lattice relaxation lifetime[9] which shows a T^2-T^7 dependence on temperature.[10] This is the basis of the experimental technique developed by DeGroot and van der Waals, by El-Sayed and by others.[9,11] A typical investigation was carried out by Veeman and van der Waals on benzophenone and substituted benzophenones. Their data are especially helpful to us in evaluating the merit of our speculative hypothesis put forward before the data of Veeman et al. became available.[14] At 1.3°K Veeman[12] finds that the rate of population of the three triplet sublevels are 0.97 (± 0.22), 1, and 0.56 (± 0.35) for $|x\rangle$, $|y\rangle$, and $|z\rangle$ sublevels, respectively. A much greater differentiation is expected on the basis of symmetry requirements and they attribute this discrepency to the fact that excitation in a single crystal generates exciton states which undergo spin orbit relaxation before they get trapped into some defect in the crystal. Data are presented on rates of radiative and nonradiative decay from these states, and their 'steady state' populations assuming spin orbit relaxation rate to be slow. It was found that the rate of nonradiative decay of $|z\rangle$ sublevel is more than an order of magnitude larger than the rates of nonradiative decay of $|x\rangle$ and $|y\rangle$ [625 $\sec^{-1}$, 36 $\sec^{-1}$, and 54 $\sec^{-1}$]. There are similar differences in the rates of radiative decay. The upshot is that the stationary state population of $|z\rangle$ is only 3% that of $|x\rangle$ and 5% that of $|y\rangle$. It is also known that triplet-triplet energy transfer takes place through an exchange mechanism, a process that does not perturb the spin symmetry.[17] In other words, τ_x of the donor produces τ_x of the acceptor and so on.[13] Another way of looking at it is that the exciplex has too short a lifetime to permit slr processes to equilibrate the population among its triplet sublevels.

Our contention is that while the benzophenone triplet undoubtedly undergoes spin lattice relaxation before it undergoes unimolecular decay at room temperature, the situation is different when its lifetime is reduced to 10^{-8} sec or so in the presence of 0.01 M quencher such as piperylene. Rates of spin lattice relaxation cannot be estimated easily in fluid solutions at room temperature. One estimate is $\sim 10^7$ sec^{-1}. This is also the value obtained by estimating (with gross approximations) the spin lattice relaxation rate from its temperature dependence predicted by Raman process analyses. If this assumption that the quencher normally encounters a sensitizer triplet in the $|x\rangle$ or $|y\rangle$ substrate is accepted, we can see why energy wastage processes at zero field do not have high rates. The triplet exciplex $(DA)^{3*}$ has too short a lifetime (even at room temperature) to permit equilibration of the population among its triplet sublevels. The negligible number of molecules $[(DA)^{3*}]$ in the $|z\rangle$ sublevel have a faster rate of radiationless decay than the others in $|x\rangle$ and $|y\rangle$ which decay primarily through energy transfer. Application of a magnetic field produces three new sublevels $|+\rangle$, $|0\rangle$, and $|-\rangle$. Now if the reaction were carried out with the molecular axis oriented along a fixed axis, mixing would depend on the direction of the applied field relative to the molecular axis. Here we may assume that due to tumbling a sensitizer molecule experiences the applied field on all three of its axes.

Fields applied along x and y axes will mix the other states, i.e., $|z\rangle$ with $|y\rangle$ and $|z\rangle$ with $|x\rangle$, respectively. The result is an accelerated decay of the donor triplet and opening up of a fast channel of radiationless decay in the exciplex. Now, accelerated decay of the sensitizer triplet will have no effect on the lifetime of the donor triplet for it is completely determined by the quenching process. Indeed, as has been pointed out before, the unimolecular decay rates [from $|x\rangle$, $|y\rangle$ as well as $|z\rangle$] are slow enough to assure complete equilibration before decay in the absence of a quencher. The effect on the exciplex may be expected to be nonnegligible, however, since it is already known that there is some radiationless deactivation even at zero field presumably from the small population at $|z\rangle$ sublevel.[5,6] This theory predicts that if we have a low enough concentration of the acceptor the bimolecular quenching rate will be slow compared to spin lattice relaxation rate, and the field effect will disappear. Experiments were performed with 10^{-3} M and 10^{-4} M piperylene, but the errors in these experiments were too large to reach any meaningful conclusion. The field effect measured with benzophenone and *trans*-piperylene at such low concentrations was 1.03 ± 0.05. This theory also explains the small magnitude of the field effect and its dependence on the structures of the sensitizer and the acceptor. Obviously the zero-field splitting parameters in the exciplex are expected to be rather sensitive to variation of donor or structures. One would expect the splitting to also depend upon the binding energy of the exciplex which cannot be estimated easily. If the splitting is very small (as is likely) it is possible that the exciplex is partially equilibrated among the triplet sublevels even at zero field. Application of a magnetic field can only complete this equilibration (with respect to the zero field levels; transitions between $|+\rangle$, $|0\rangle$, $|-\rangle$ will be slower, since they will be more widely split) and cause a relatively small increase in population of $|z\rangle$ levels, i.e., only a relatively small number of molecules will acquire more $|z\rangle$ character inside a field. This might be the reason why we see only a 7-20% increase in radiationless decay rates inside a field, and none at all with cis-piperylene and benzophenone.

Other Theories that Attempt to Explain the Field Effect

Atkins[15] proposed that the field effect can be explained in terms of Zeeman splitting in the exciplex which acquires some biradical character through charge transfer. He showed that a 10% charge transfer could induce a 10% field effect. According to Atkins, charge transfer in the exciplex produces a 'triplet biradical', whose g values are different. As the spins of the ionic doublets precess at different rates in the magnetic field, the triplets develop singlet character. Atkins proposes that energy wastage takes place from the singlet component. He calculates the probability that the exciplex is in a singlet state as a function of t and integrates it over the lifetime of the exciplex. After making assumptions that the "singlet-triplet" energy splitting is small, the lifetime of the exciplex $\approx 10^{-8}$ sec, and the g value difference to be $\sim 10^{-3}$, Atkins obtains the expression:

$$p = \tfrac{1}{2}\lambda^2 \left\{ \frac{(2v\tau)^2}{1+(2v\tau)^2} \right\} \quad \text{when } v \simeq 10^8 \text{ rad sec}^{-1} \;.$$

For a 10% charge transfer (i.e., $\lambda^2 \simeq 0.1$) $p \sim 5\%$. This is certainly an attractive theory and we cannot make a definitive judgment about it one way or the other. However one experiment was performed on the basis of a prediction Atkin's theory makes.

CIDNP Experiments on Benzophenone-Piperylene System

Since Atkins proposes that the singlet state of the biradical (or radical pair) is responsible for radiationless decay, while the intersystem crossing takes place from the triplet state of the radical pair, one would expect that both diene (acceptor) isomers become nuclear spin polarized, and the spin polarization in the two isomers should be opposite. *Cis*- and *trans*-stilbenes were sensitized by benzophenone inside the cavity of an nmr spectrometer and the nmr spectra of the stilbenes monitored as the isomerization progressed. There was no evidence of any CIDNP developing in either of the isomers. An initial positive result was ascribed to solvent (initially CCl_4) interaction and/or intervention by impurities. However we do not regard this experiment as a definitive test against the Atkins hypothesis. Other experiments can be performed, some of which are: (1) study of the field effect in polar solvents, e.g., acetonitrile. The field effect ought to be significantly larger in polar solvents, if the exciplex lives long enough to permit stabilization through solvent rearrangements. (2) Study of the field effect using substituted benzophenones, e.g., *p*- and *o*-fluoro, *o*-chloro or *o*-methoxy benzophenones. A final evaluation of Atkin's theory must await such experiments.

We also performed some isotopic substitution experiments following advice from Professor M. Sharnoff. The sensitizers used were benzophenone and benzophenone-d_{10}, and among the quenchers used were piperylenes, and *cis*- and *trans*-piperylene d_8. Tables III and IV give the data on these isotopic experiments. It seems that while isotopic substitution of piperylene reduces the field effect by 50%, the isotopic substitution of the sensitizer does not change the field effect significantly. The theoretical significance of these results is not clear.

TABLE III

Effects of Magnetic Field on Composition at Photostationary State with Deuterated Quenchers and Sensitizers

Substrate	Sensitizer	[trans]/[cis]$_{pss}$	Field	pss(on)/pss(off)
Piperylenes	Benzophenone-d_{10}	1.30	On	1.07
		1.22	Off	
Stilbenes	Benzophenone-d_{10}	0.62	On	0.93
		0.67	Off	
Piperylenes-d_8	Benzophenone	1.26	On	1.03
		1.22	Off	

TABLE IV

Effects of Magnetic Field on Initial Conversion Rates with Deuterated Quenchers and Sensitizers

Substrate	Sensitizer	R^0/R^1
trans-Piperylene-d_8	Benzophenone	1.04
cis-Piperylene-d_8	Benzophenone	1.00
trans-Piperlyene	Benzophenone-d_{10}	1.08
cis-Piperylene	Benzophenone-d_{10}	1.02
trans-Stilbene	Benzophenone-d_{10}	1.09
cis-Stilbene	Benzophenone-d_{10}	1.16

1. Ratio of initial rate with field off to rate with field on.

Experimental

Materials

Benzophenone: It was received from *Aldrich Chemicals*. It was twice recrystallized from ethanol. The final mpt. was 48 °C.

cis- and trans-1, 3-Pentadienes: They were received from *Chemical Samples* and were bulb-to-bulb distilled from $LiAlH_4$.

trans-Stilbene: Scintillation grade *trans*-stilbene was received from *Aldrich Chemicals*, and was used as received, after verifying that it contained 0.2% of the *cis*-isomer as its main impurity.

cis-Stilbene: It was made by sensitizing *trans*-stilbene with benzil, a low energy sensitizer that produces a photostationary state containing 99% *cis*-stilbene. The irradiated mixture was passed through an alumina column and the appropriate fraction of the eluent was collected. This was purified by passing it through another alumina column. After the final low pressure distillation it was found to be 99.8% pure.

cis- and trans-Piperylene-d_8: They were synthesized by Dr. G. N. Taylor. They were purified by preparative glpc.

Benzophenone-d_{10}: Prepared in this laboratory. The mass spectrum, absorption spectrum as well as gc analysis, indicated that it was 99+% pure. It was recrystallized and sublimed before use.

Other sensitizers were purified by the methods of Lamola.[16]

Procedures

Irradiations were initially carried out in the cavity of an esr spectrometer using light from a 3 kw xenon-Hg lamp. The light was filtered through 1% $NiSO_4$ solution in water and then through a uranium glass filter. The temperature of the cavity was maintained at room temperature using a stream of N_2. Some of the experiments were done using a permanent magnet (field strength 9 kG) with wedge-shaped pole pieces and a medium pressure 450 watts Hg lamp as the source of irradiation. Solutions were degassed in 5 mm (OD) tubes by 3-5 freeze-thaw cycles and their weights determined to ensure that all tubes had the same amount of solution. Solutions were typically 0.1 M in quencher and sensitizer, and irradiation times were 5-20 min for initial quantum yield experiments and up to 24 hrs for photostationary state measurements. Analysis was done by gc. The columns used were

$25' \times \frac{1}{8}''$ 25% $\beta\beta'$ODPN on chrom P for piperylenes
$10' \times \frac{1}{8}''$ 10% UCW-98 on chrom W for stilbenes
$15' \times \frac{3}{8}''$ 25% $\beta\beta'$ ODPEN on chrom P for preparative chromatography of piperylene d-8.

Three techniques were used (not concurrently) for measuring the area of the peaks:

(1) Cutting and weighing,

(2) Disc integration,

(3) Electronic integration with printouts for areas.

The errors in these experiments were caused in the main by (1) improper line up of the nonmagnetic stage used in the latter part of the work to correspond with irradiations carried out inside the permanent magnet. This was absent when the esr cavity was used as the sample holder. (2) Lack of control of the amount of light being absorbed. The tube faces were curved and allowed a variable amount of light to pass through. The absolute error in gc measurements was estimated by making up a series of piperylene solutions of different isomer ratios and measuring the resulting peak areas and their ratios. They agreed to within 1%. It was also found that piperylenes have the same detector response. For piperylenes and stilbenes the response was found to be independent of concentration up to 0.15 M, i.e., the peak areas were directly proportional to the product of the concentration of the material and the amount injected.

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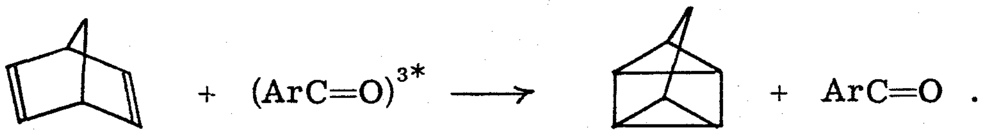
PROPOSITION I

It is proposed that norbornadiene methyl amine (III) be tested as a quencher of aromatic ketone triplets and aromatic hydrocarbon singlets.

Norbornadiene (I) is known to undergo valence isomerization on being sensitized by benzophenone.[1] This process cannot be considered to be a classical excitation transfer process since the triplet of norbornadiene is estimated to be 9 kcal/mole higher in energy than the benzophenone triplet. The quantum yield of cyclization is close to unity, but it drops rapidly as the triplet energy of the sensitizer is decreased. Presumably, a triplet exciplex is formed, which decays with transfer of a certain fraction of the energy into the appropriate vibrational modes of norbornadiene.

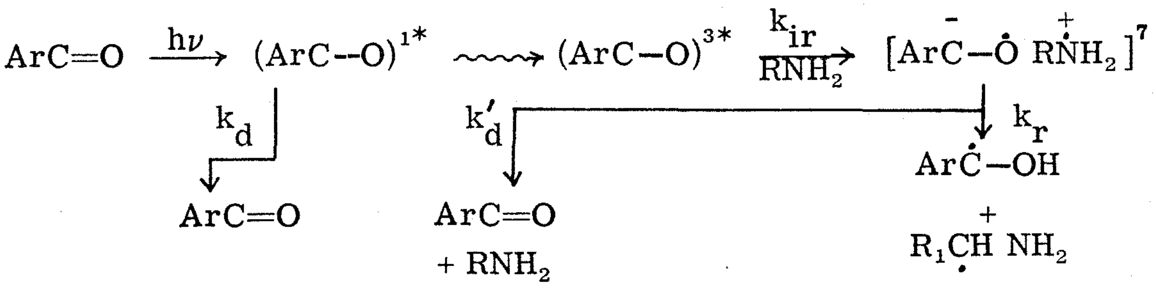


I

II

Some of the electrical energy of the ketone is thus converted into chemical energy. This chemical energy can in principle be converted into mechanical or electrical work.[2] The efficiency of recovery is dependent on the temperature at which the reconversion is carried out. However this cycle can be used to harvest solar energy only if norbornadiene is suitably substituted so that it quenches low lying ketone triplets. There is one report that 3-carboxyl norbornadiene quenches michler ketone triplets. Clearly energy requirements for the isomerization cannot be solely responsible for the decrease in quantum yield observed with fluorenone, since the activation energy requirement corresponds with an excitation energy of 620 nm. Suitable substitution could improve the fraction of energy channeled into the isomerization pathway through a change in the decay ratio of the exciplex. Norbornadiene is also found to quench naphthalene but rather inefficiently.[3] This inefficiency might also be overcome by suitable substitution.

The experiment I propose is based on my assumption that an amine substitution on norbornadiene will increase its quenching ability of both aromatic hydrocarbons and aromatic ketonic triplets. Quenching of aromatic ketonic triplets (by amines) is complicated by the rearrangement of the charge transfer exciplex to photoreduction products.[9] Cohen[5,4] and others have studied quenching and photoreduction of aromatic ketones by amines in detail. Their observations indicate that the photoreduction quantum yield is much smaller for secondary amines than for tertiary amines, while primary amines show little photoreactivity. High energy n-Π^* ketone triplets are much less discriminating, and they abstract hydrogen from all amines having hydrogens on their α-carbon. k_{ir} (Scheme I) decreases with k_r. Decreasing solvent polarity or putting electron rich substituents on the phenyl ring of the ketone also reduces k_r as well as k_{ir}.

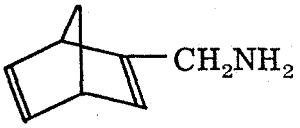


Scheme I

Table I gives some typical rates and quantum yields.

Fluorenone[6] is known to be quenched and photoreduced by amines, and here again although both k_{ir} and k_r are less for a secondary amine compared to a tertiary amine, the ratio of k'_d to k_d goes up. Other ketones that have been studied include p-methoxyacetophenone[4] and biacetyl.[7,8]

The above discussion strongly indicates that a norbornadiene such as III will quench low-lying ketonic triplets and not undergo photoreduction. Among the sensitizers I propose to use are (a) fluorenone, (2) benzil. As mentioned above, fluorenone will not be photoreduced by a primary amine such as III, and photoreduction quantum yields will be



III

expected to be even lower for benzil, if only because the total available energy is less, and the excitation is more delocalized. Unquestionably, k_{ir} will be small too, since III is a primary amine, but I still expect

TABLE I

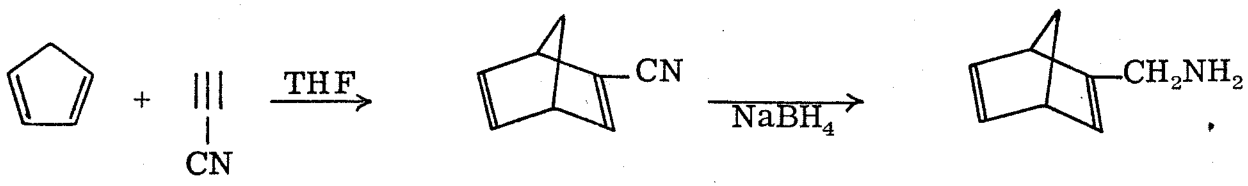
Quenching by Triethyl Amine[4]

Solvent	Ketone	k_d/k_{ir}	k_q^1/k_{ir}	k_{ir}	k_d	ϕ_{lim}^2
CH_3CN	2NA[3]	0.0006	50	8×10^6	5×10^3	1.2
t-BuOH	2NA[3]	0.0033				0.63
Benzene	2NA[3]	0.013	750	5×10^5	6×10^3	0.46
CH_3CN	2AN[4]	0.010	650	6×10^5	6×10^3	0.67
t-BuOH	2AN[4]	0.005				0.16
Benzene	2AN[4]	0.070	2800	1×10^5	7×10^3	0.05

1. k_q = quenching rate by piperylene.
2. ϕ_{lim} = limiting quantum yield of photoreduction obtained by plotting $1/\phi$ vs. $1/[RNH_2]$.
3. NA: naphthaldehyde.
4. AN: acetonaphthone.

the amine to capture about 50% of the triplets. Benzene may be used as a solvent, further reducing any possibility of loss of the amine.

A simple synthetic route for synthesizing I is proposed in Scheme II.



Scheme II

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PROPOSITION II

It is proposed that nanosecond flash photolysis be used to study the decay of singlet exciplexes produced by quenching of aromatic singlets by dienes.

Quenching of fluorescence of aromatics by amines is accompanied by emission from the singlet exciplex, provided that the solvent is nonpolar.[1,2] Study of such emission, particularly using the pulse excitation has provided a lot of information on the nature of binding in the exciplex.[3] The evidence of intermediacy of an exciplex during quenching by dienes is strong, but rests entirely on kinetic evidence.[4] It has been suggested that this exciplex must be too short-lived to undergo radiative decay. Our investigations have shown that the [naphthalene-t-β-ethyl styrene] exciplex must live long enough to intersystem cross. Saltiel's observations[5] on quenching of anthracene by hexadienes also led to an estimate of lifetime of the corresponding exciplex. The lower limit calculated by Saltiel is 30 nsec.

My proposition is to look for transient absorptions that could be ascribed to the exciplexes in such systems. Nanosecond flash photolysis seems to be a convenient technique for such measurements. Using this technique it is possible to detect emitting transients of lifetime less than 1 nsec, and absorbing transients of lifetime 1 nsec or more.

Usually a N_2 laser is employed as the source of excitation, which means we could study anthracene or dimethoxynaphthalenes as excitation donors. The relatively short lifetimes of the excited singlets of these compounds require that the quencher be relatively efficient, otherwise the fraction of singlets quenched becomes small. Hexadienes could be used as quenchers.

Decay trace of the transient absorption will directly furnish us with the exciplex lifetime. If the lifetime is not exceedingly short, lack of emission from these exciplexes will require a new interpretation. Perhaps the lifetimes can be correlated with efficiency of generation of triplets from such exciplexes.

Another important aspect of the proposed experiment is to record absorption spectra of such exciplexes. Ottolenghi[6] has shown that such absorption spectra can be useful in determining the nature of binding in the exciplex. For example, the absorption spectrum of [anthracene-N, N-diethylaniline] exciplex has bands which can be attributed to transitions as follows:

$$^1(D^+A^-)^* \xrightarrow{h\nu} {}^1(D^{+*}A^-)$$

$$^1(D^+A^-)^* \xrightarrow{h\nu} (A\,^1D^*)$$

and

$$^1(D^+A^-)^* \xrightarrow{h\nu} (^1A^*D) \quad .$$

Evans[7] and Soloman, Steel, and Weller[8] have proposed that the aromatic-diene exciplexes derive their binding energy through charge transfer interactions. This model cannot adequately explain all experimental data. Hammond et al.[4] have proposed a more general model for the exciplex, one that takes into account excitation and charge resonance. The experiment outlined above may help settle this controversy.

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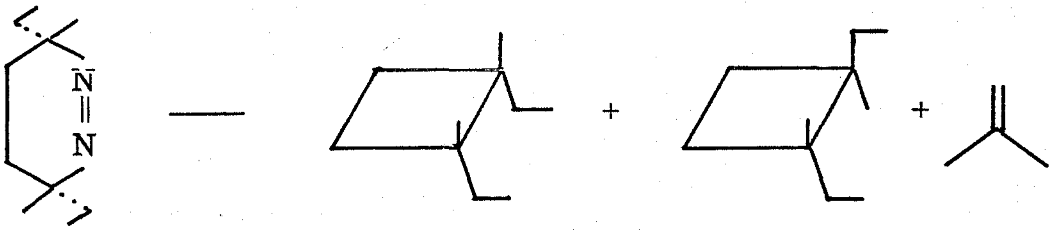
PROPOSITION III

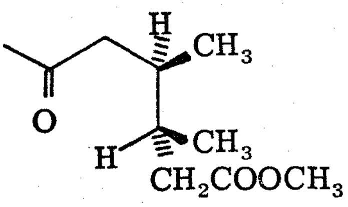
It is proposed to use CIDNP to measure the rate of spin inversion in radical pairs and biradicals.

The role of biradicals in small ring isomerizations and racemizations has recently become the subject of intensive scrutiny.[1-3] Yet no consensus has emerged on the structure and lifetime of the biradical. Activation parameters of many of these systems are accurately known,[2] and Benson and co-workers[4] made thermochemical calculations on the basis of such rate data. Their conclusion was that the biradical lies at the bottom of a potential minimum, and the barrier to closure varies from 5-10 kcal mole^{-1}. This calculation predicts a certain lifetime of the biradical which can be verified through direct or indirect experimentation. Theoretical calculations including the recent ones by Salem[5] fail to reveal any potential minimum corresponding to the biradical.

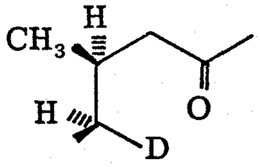
Studies on the stereochemical course of such reactions indicate that the rate of closure of such biradicals is rapid relative to the rate of bond rotation about C—C single bonds. Thus Bartlett[6] observed that thermolysis of I produces II, III, and IV with 97% retention of stereochemistry. Walters[7] found that thermal decomposition of <u>trans</u>-1, 2-dimethylcyclobutane produces 2-butenes with 90% retention of stereochemistry. Photochemically produced singlet biradicals recombine with similar retention of stereochemistry. Stephenson[8] found that Norrish type II reaction from the singlet state of the ketone V proceeds with 98% retention of stereochemistry. The above comparison of reactivities of the singlet biradicals is meaningful, since we are comparing reactivities of biradicals with similar structure at radical sites (tertiary). Similar correlation is found for secondary and primary biradicals, although the extent of retention of stereochemistry is less. A straightforward kinetic scheme can relate the rate of loss of stereochemistry (k_r) with k_{rot}, rate of rotation about C—C single bonds. For tertiary radicals we find k_c (rate of recombination) $\simeq 30\ k_{rot}$. For secondary radicals this relation is $k_c \simeq 9\ k_{rot}$. These data, taken in conjunction with Benson's hypothesis required unrealistically high barriers to rotation about C—C bonds, in order to achieve consistency. Therefore we reach the tentative conclusion that the biradical does not exist at the bottom of a potential well and it has considerably shorter lifetime than one would expect on the basis of Benson's hypothesis. Perhaps the activation energies for dissociation of the biradical precursors are experimentally underestimated, if we follow Johnston and Birk's arguments.[9] This error will be more significant in smaller molecules, e.g., cyclopropane.[12]



I II III IV



V



VI

Since the lifetime of the biradicals are very short, other fast rates such as the spin inversion rates become important in determining the lifetime of biradicals. The rate of spin inversion can be estimated (for a tertiary biradical) from the data of Bartlett.[6] When I was triplet sensitized, it was found that product formation took place with 65% retention of stereochemistry. Similar results are obtained for other triplet tertiary biradicals. We use the following scheme in order to estimate the ratio of k_{si} and k_{rot} $[k_{si} \equiv k_{spin\ inversion}]$

$$\begin{tikzcd}
A \arrow[r, "h\nu"] & B \arrow[r, "k_{si}"] \arrow[d, shift left, "k_{rot}"] & B' \arrow[r, "k_c"] \arrow[d, shift left, "k_{rot}"] & \oplus \\
 & C \arrow[r, "k_{si}"'] \arrow[u, shift left, "k_{rot}"] & C' \arrow[r, "k_c"'] \arrow[u, shift left, "k_{rot}"] & \ominus
\end{tikzcd}$$

An approximate solution of this scheme is $k_{si} \simeq k_{rot}$ using Bartlett's data on singlet and triplet biradicals from I. The approximation involves the omission of reversible production of B and C from B′ and C′, respectively. This assumption is justified in view of the large magnitude of k_c, which will make the stationary state concentrations of B′ and C′ small. Thus we see that k_{si} is somewhat larger than k_{rot} i.e., $[k_{rot} < k_{si} < 2k_{rot}]$ when the reverse paths (B′ → B and C′ → C) are switched on. Therefore one may state that spin inversion probably interferes with closure of a singlet biradical to a small but perceptible extent.

I believe that the direct measurement of spin inversion rates would be an important aid in determining rates of all other decay processes of the biradical. It is interesting to note that Stephenson and Brauman[13] attribute the loss of stereochemistry of a triplet biradical to other reasons. They believe that spin inversion is very rapid and not rate determining at all for recombination process of a triplet biradical. It is an elegant and ingenious scheme and the reader is referred to this article or a recent review[2] on this subject for more information. This experiment will be a definitive test of their hypothesis. It can also clear up several ambiguities that exist in the commonly accepted mechanisms of radical pair recombination. For example, if it is assumed that recombination rate of singlet radical pair inside a primary cage is fast relative to diffusive separation (as would be the case if the recombination process had no activation barrier opposing it) it is not clear why the escape fractions are so high. A competitive but somewhat slower intersystem crossing process seems to be a good candidate at present. Clearly the mean distance between radical centers in a nondelocalized radical pair in a solvent cage cannot be much more than the separation of radical centers in a 1,4 biradical. It is significant that almost all CIDNP measurements on caged radical pairs (in the primary cage) has been on radicals containing carbonyl groups, a group that induces spin-orbit coupling. Other, similar problems can be easily cited in the area of biradical chemistry. For example, in a recent communication Yang assumed very slow intersystem crossing in a 1:4 biradical which is a precursor to ocetanes from butenes and aldehydes.[14] Thus he determined the extent of triplet addition by using rate of loss of stereochemistry as a probe. It is entirely possible that the triplet biradical undergoes fast intersystem crossing (relative to k_{rot}) and gives products with a significant amount of retention of stereochemistry.

The experiments I propose are similar to those performed by Berson et al.[15] and Closs.[10,11] The prevailing theory of CIDNP CCKO theory does not take into account T^{-1} - S intersystem crossing. It was shown that this approximation is good provided the coupling between the radical centers is small. However, in the event of large coupling as is usually the case with a biradical, $T^{-1} \rightarrow S$ intersystem crossing induces emission from all proton, instead of emission from some and absorption from others. The extent of the enhancement is field dependent and if the signal enhancement is plotted against the applied field one can estimate the coupling between the radical centers. Intersystem crossing can then be assumed to be inversely proportional to the T - S splitting, since the splitting is small, and other factors such as density of states, Frank Condon Factors tend to remain constant.

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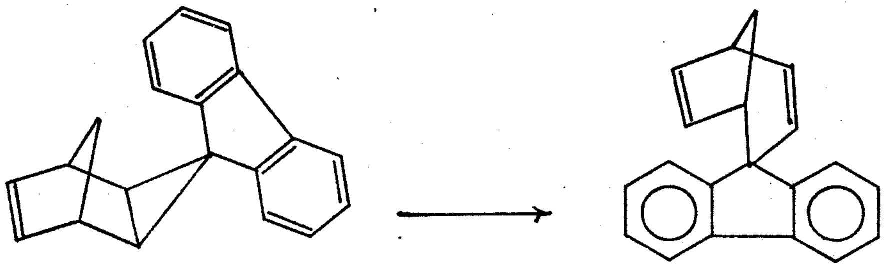
PROPOSITION IV

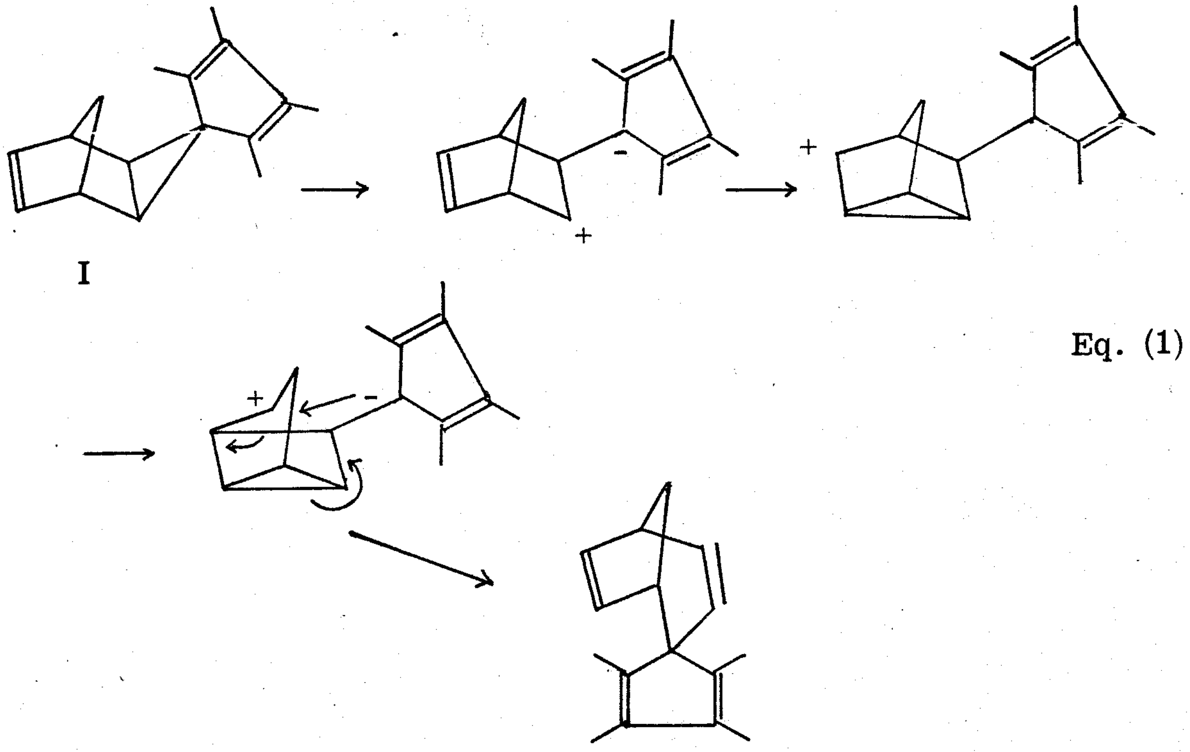
It is proposed that the mechanism of rearrangement of 3-(9′-fluorenyl)tricyclo[3.2.1 $O^{2,4}$] octene 8 (I) be investigated by studying the reaction of the title compound in acids and bases.

When Filipescu and DeMember[1] synthesized I they observed



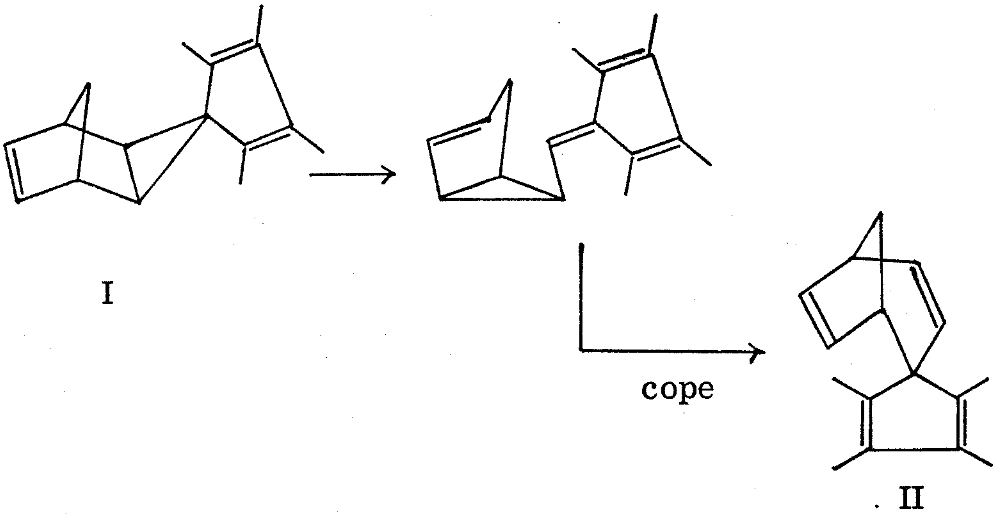
I II

that I rearranges to II thermally. They suggested an apparently implausible mechanism for this transformation (Eq. 1) when better mechanisms are available (Eq. 2).[2]



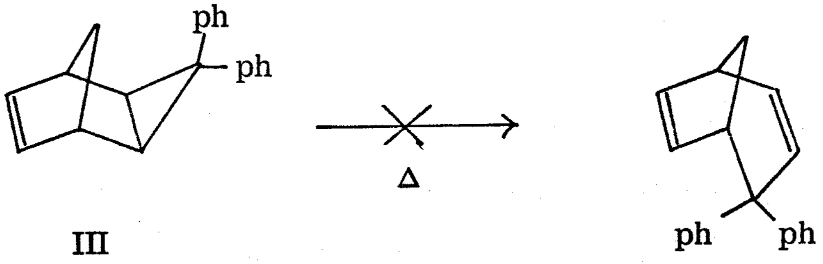
I

Eq. (1)



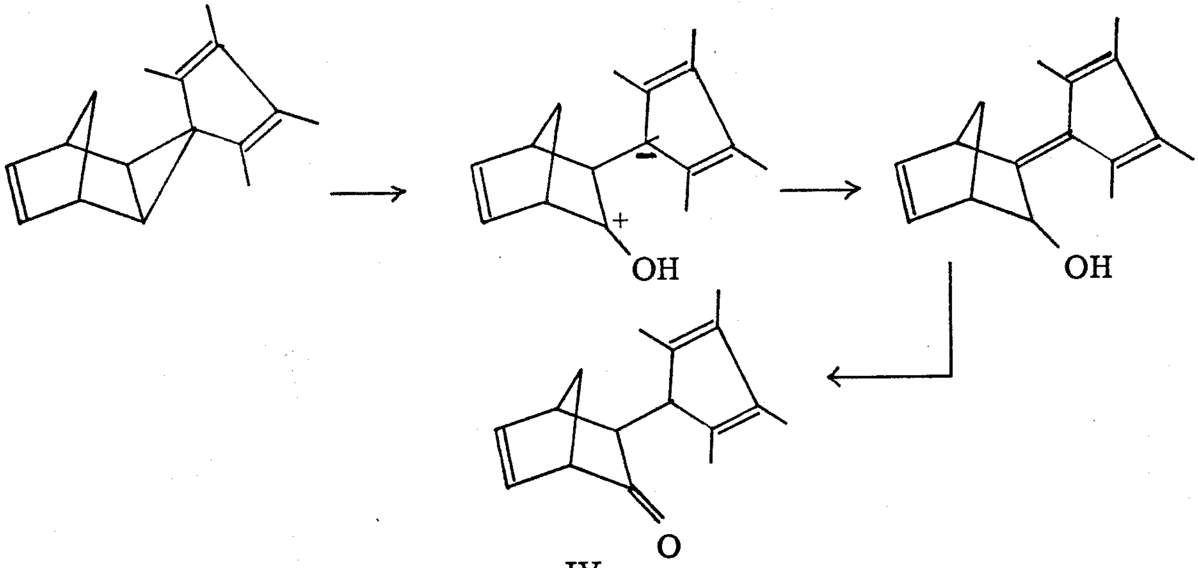
Eq. (2)

However, if Eq. (2) were correct there is no reason why III should not undergo the same rearrangement, which it does not.[3]



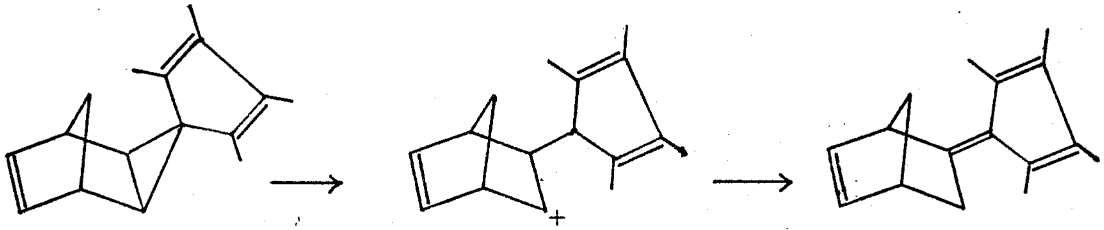
On the other hand, if Eq. (1) represents the correct mechanism, the failure of III to rearrange may be rationalized by saying that a 9-fluorenyl anion is more stable than a diphenyl carbanion.

This proposition suggests experiments to test this mechanism. If mechanism (1) is correct then on warming in alkali I ought to give IV.



IV

On the other hand, on acid hydrolysis I ought to produce V



I [illegible] V

In general, one would expect the rearrangement of I → II to be assisted by polar, aprotic solvents in case mechanism I is correct.

The second part of this proposition suggests more sensitive tests for the negative charge on the 9-fluorenyl carbon. A Hammett plot with appropriate substituents on the fluorene nucleus is expected to give a positive slope if there is a negative charge on the 9-fluorenyl carbon. Suitable substituents would be chloro, nitro, and methyl groups. Similarly, III can be prepared with a $-NO_2$ group in one of the parapositions and if the zwitterion mechanism is correct, this substituted III ought to undergo the same rearrangement as I. The synthesis of substituted I and III ought to be similar to the synthesis of unsubstituted compounds.[1,3]

References

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PROPOSITION V

It is proposed to investigate the decay modes of the excited states of $Fe(CN)_6^{4-}$.

Although photoreactions of the ferrocyanide ion has been studied since the nineteenth century, we do not yet have a consensus on the nature and mechanism of the photoprocesses.

The most definitive molecular orbital treatment on this ion was published in 1968 by Alexander and Gray.[1] Their results indicated that there were 4 ligand field transitions, $^1A_{1g} \rightarrow {}^1T_{1g}$, $^1A_{1g} \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^1T_{2g}$, $^1A_{1g} \rightarrow {}^3T_{2g}$. They also found two charge transfer bands (CTTL) with maxima at 210 and 250 nm. They do not discuss the charge transfer to solvent transitions that have been proposed repeatedly.[2,3] Such proposals originated from the observation that photoelectrons are produced on short wavelength (200-300 nm) irradiation of $Fe(CN)_6^{4-}$. A broad CTTS band with maximum around 250 nm could certainly explain the observed variation of quantum yield of photoelectron production with wavelength of excitation. This quantum yield is maximum at 254 nm ($\simeq 1.0$) and is smaller at 214 nm and 300 nm. However, it is possible that the charge transfer band with maximum at 210 nm has a faster rate of radiationless decay due to the availability of low lying unfilled metal orbitals. This proposition suggests experiments which will throw more light into this matter.[4]

If photoelectron production occurs from the charge transfer to ligand bands, an increase in solvent polarity would stabilize the ground state and would thus cause only a relatively small red shift of the band. At the same time, once the excited state is prepared it will probably be stabilized through solvent rearrangement and photoelectron production is likely to be facilitated. The general experimental observation would then be that the photoelectron production quantum yield would increase over the whole region 200-300 nm. On the other hand, if photoelectron production takes place from the CTTS band, it will be strongly red shifted in polar solvents, and the maximum of quantum yield of electron production will shift to longer wavelengths. A suitably inert solvent system could be water-acetonitrile or water-DMSO. Photoelectron production quantum yields could be determined easily by scavenging all the electrons produced with N_2O, and monitoring the nitrogen evolution rate. A more difficult problem is to devise a reliable method of measuring the light input at 200 nm. Parker[5] suggests that the ferrioxalate actinometer is capable of giving reliable and reproducible results up to 200 nm. Perhaps a linear irradiation assembly can be used and a vacuum photocell or a photomultiplier tube used to monitor the light intensity. Calibration of such phototubes is a problem and the following arrangement is suggested instead, which combines a fluorescence counter used successfully by Weber and Teale[6] at 200 nm with the ferrioxalate actinometer. The arrangement is depicted in Figure I and consists of a fully transparent (fused silica or quartz) sealed cuvette mounted inside a larger cell.

The inner cell contains the fluorescence counter which is 1 dimethylamino naphthalene 5-sodium sulfonate. The outer cell contains either a mixture of benzophenone and cis-piperylene or ferrioxalate solution. The inner cuvette could be a segment of a sphere, i.e., a spherical cell with a plane face (Figure Ic). Weber and Teale showed that the fluorescence efficiency of the above mentioned counter is independent of excitation energy up to 200 nm. The actual (absolute) value of the light intensity will be $\theta I'/\phi_f$, when I′ is the light intensity measured by the actinometer and ϕ_f is the quantum yield of fluorescence of the counter and $1/\theta$ is the fraction of emitted light absorbed by the actinometry solution. Although this can be accurately measured, we do not need it for the experiments suggested above.

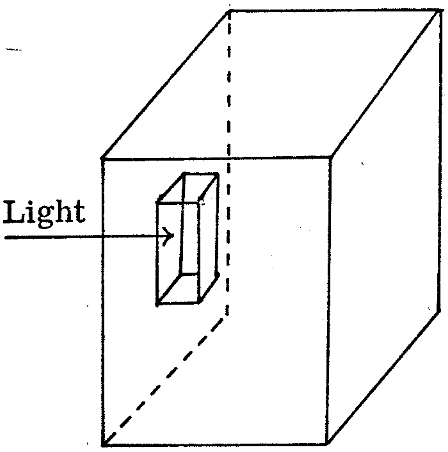

Figure Ia

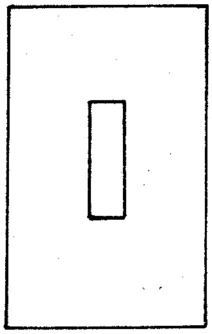

Figure Ib

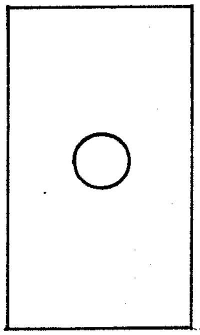

Figure Ic

Another important photoreaction that the ferrocyanide ion undergoes is the aquation reaction. Aquation quantum yield is 0.4 from both the ligand field bands, and is smaller from the CT bands.[7] It is possible that the ligand field bands undergo dissociation as their principal/only mode of decay, and 0.4 is the fraction of cyanide ions that do not recombine with the five coordinate intermediates. On the other hand it is possible that radiationless decay competes with dissociation from the ligand field bands. If the latter is the case, intersystem crossing can be probably induced from these states by carrying out the irradiation in concentrated solutions of LiBr ($\geqslant 5\underline{M}$) or in a LiBr glas at 77 °K. Even if dissociation is the principal mode of decay at room temperature, it will be slowed down at 77 °K (if the ligand field states are not dissociative) and intersystem crossing will be favored. Emission from the resulting triplet can be looked for around 440 nm, where the singlet-triplet absorption has been recently located.[8] If LiBr has a pronounced effect on either the triplet emission at room temperature or reduces the aquation (or photosubstitution) quantum yield substantially, the conclusion would be that radiationless decay is a principal mode of deactivation, and dissociation quantum yield cannot be unity or close to unity. These conclusions can be verified by studying the photosubstitution or photoaquation process in concentrated solutions of $KC^{14}N$. If the quantum yield of labelling of the complex is significantly higher than 0.4, one has to attach greater importance to the dissociative mechanism of relaxation of the ligand field states.

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