ane was found to be 0.005. Since most of the acenaphthylene triplet species is quenched in the presence of oxygen, this experiment establishes the maximum singlet dimerization efficiency of acenaphthylene at 0.5%.

(8) The quantum yield of dimerization of acenaphthylene (0.10 *M*) in oxygen-saturated 10 mol % ethyl iodide was found to be 0.01. This experiment both establishes the maximum singlet dimerization efficiency and demonstrates that more than 90% of the dimerization in this solvent occurs from the triplet state.

(9) J. Pancir and R. Zahradnik, *Theor. Chim. Acta*, **14**, 426 (1969).

(10) N. Mataga and K. Nishimoto, *Z. Phys. Chem.* (*Frankfurt am Main*), **13**, 140 (1967).

(11) J. P. Doering, *J. Chem. Phys.*, **51**, 2866 (1969).

(12) G. W. Robinson and R. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962); *ibid.*, **38**, 1187 (1963).

(13) Calculated from atomic spectral data.

(14) (a) Data from fluorenone-sensitized dimerization in 10 mol % ethyl iodide indicate that $\Phi_{isc} = 0.8 \pm 0.2$. Because of the large uncertainty in this value, we have assumed for the purposes of discussion that $\Phi_{isc} = 1.0$. Although this assumption may produce a systematic error in the calculated rate constants, it does not affect our conclusions. (b) The linearity of the plot in Figure 1 precludes any large chances in Φ_{isc} at concentrations of ethyl iodide greater than 10 mol %.

(15) Since the two concentration dependence intercepts given in Table V should be equal, the experimental values were averaged.

(16) J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Amer. Chem. Soc.*, **84**, 297 (1962).

(17) K. Dziewonski and C. Paschalski, *Ber.*, **46**, 1986 (1913).

Mechanisms of Photochemical Reactions in Solution. LXXIX.[1] Production of Triplets in the Quenching of the Fluorescent State of Naphthalene by an Unsaturated Hydrocarbon

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Abstract: The fluorescence of naphthalene is quenched by *trans*-β-ethylstyrene. Counter experiments using *cis*-piperylene as a monitor show that triplets are produced as a part of the process of quenching the excited states. The triplet yield varies in different solvents and in all cases studied is smaller than the triplet yield when naphthalene decays without the assistance of a perturbing quencher. In the absence of piperylene there is a significant amount of isomerization of the quencher even when it is present in sufficiently high concentration to quench all of the excited singlets of naphthalene, an indication that triplets of either the quencher, the quenchee, or both are produced. Little isomerization of β-ethylstyrene is observed in the presence of piperylene (0.066–0.198 *M*). We believe that a singlet exciplex is formed and decays rapidly to give either both molecules in their ground states or to give naphthalene triplets and β-ethylstyrene in its ground singlet state.

Several groups have studied the quenching of fluorescence of naphthalene and other aromatic hydrocarbons by conjugated dienes.[2-7] Models to account for the quenching include two features: formation of an exciplex from the quencher and the fluorescent species, and rapid nonradiative decay of the exciplex. There has been a good deal of speculation as to the mechanisms of intermolecular interaction which leads to binding in the exciplex.[4-6] The mechanism of nonradiative decay has been discussed less and is not an easily studied phenomenon although it seems likely that some vibrational modes in the quencher must serve as especially efficient energy sinks in the internal conversion process. We now report a study of quenching of naphthalene fluorescence by a hydrocarbon, *trans*-β-ethylstyrene, in which the decay process leads to formation of naphthalene triplets in substantial yield.

Results

The fluorescence of naphthalene is quenched by *trans*-β-ethylstyrene with moderate efficiency. Series of quenching measurements with varying concentrations of quencher were carried out in four different solvents. Plots of $\Phi_F{}^0/\Phi_F$ were linear. The results are summarized in Table I.

Introduction of *cis*-piperylene (1,3-pentadiene) into the solutions led to isomerization of the diene to the *trans* isomer, indicating formation of triplets having sufficient excitation energy to transfer energy to the diene. Since naphthalene is a well-known triplet sensitizer for diene isomerization,[8,9] the reaction was to be expected in unquenched solutions. Addition of β-ethylstyrene reduced the triplet yield as expected, but *the limits approached at high concentrations of the quencher were nonzero.* The quenching act itself must produce some triplets.[10] We assume the following to be the mechanism for sensitized isomerization and quenching.

$$\mathrm{N} \xrightarrow{h\nu} {}^1\mathrm{N} \tag{1}$$

$$^1\mathrm{N} \xrightarrow{k_f} \mathrm{N} + h\nu' \tag{2}$$

$$^1\mathrm{N} \xrightarrow{k_1} {}^3\mathrm{N} \tag{3}$$

$$^1\mathrm{N} + \textit{trans}\text{-E} \xrightarrow{k_2} \alpha\,{}^3\mathrm{N} + (1-\alpha)\mathrm{N} + \textit{trans}\text{-E} \tag{4}$$

$$^1\mathrm{N} + \textit{cis}\text{-P} \xrightarrow{k_q} \mathrm{N} + \textit{cis}\text{-P} \tag{5}$$

$$^3\mathrm{N} + \textit{cis}\text{-P} \xrightarrow{k_q'} \beta\,{}^3\mathrm{P} + (1-\beta)\textit{cis}\text{-P} + \mathrm{N} \tag{6}$$

$$^3\mathrm{N} \xrightarrow{k_3} \mathrm{N} \tag{7}$$

$$^3\mathrm{P} \longrightarrow \gamma\,\textit{trans}\text{-P} + (1-\gamma)\textit{cis}\text{-P} \tag{8}$$

N = naphthalene, E = β-ethylstyrene, P = piperylene

We have omitted nonradiative decay of excited naphthalene singlets to the ground state since that process is known to be relatively unimportant.[11] The yield of naphthalene triplets is determined by the intersystem crossing efficiency for naphthalene singlets in the absences of quenchers [$\Phi_{ISC} = k_1/(k_1 + k_f)$] and α, the efficiency of triplet production in the quenching of naphthalene singlets by β-ethylstyrene. We measured relative fluorescence intensities: (1) in the absence of any quencher (F^0), (2) in a series of solutions containing varying concentrations of β-ethylstyrene but no piperylene (F'), and (3) in a series of solutions containing vary-

Table I. Rates of Quenching of Naphthalene Fluorescence by *trans*-β-Ethylstyrene

Solvent	$k_q\tau$, l. mol$^{-1\,a}$	τn, sec	k_q, l. mol^{-1} $\times 10^{-8}$ sec^{-1}
Benzene	04.3	96.5	4.5
n-Hexane	02.5	95	2.6
Ethyl ether	03.1	96.5	3.2
Acetonitrile	01.8	92.5	1.9

[a] Slopes of Stern-Volmer plots.

ing amounts of β-ethylstyrene and a constant concentration of *cis*-piperylene. We also measured the rates of production of *trans*-piperylene in a series of solutions in which the concentration of β-ethylstyrene was (Y_T) varied and in the absence of alkene (Y_T'). In some of these experiments isomerization was allowed to proceed to rather high conversions (*i.e.*, 14%). Equation 9 was used to calculate initial rates of conversion by correcting for back reaction. Repeat runs in which conversion was kept below 6% gave good agreement.

$$b = 2.303a \log a/(a - b') \quad (9)$$

where

a = conversion at photostationary state,

b = conversion that would have occurred without back reaction, and

b' = measured conversion

In some measurement series relative fluorescence intensities and isomerization rates were determined over different, but overlapping, concentration ranges because the regions of maximum sensitivity of measurement were different. All samples in runs to measure isomerization rates were subjected to identical radiation doses. Under these conditions the relationship among the relative fluorescence intensities and the relative quantum yields for isomerization is given by eq 10.

$$\Phi_{\text{ISC}}\left(\frac{Y_T F'}{Y_T' F} - 1\right) = \alpha \frac{F^0}{F}\left(\frac{F'}{F} - 1\right) \quad (10)$$

Equation 10 is a form of the relationship developed by Carroll and Quina to treat enhancement of intersystem crossing by xenon.[11a] In their work they assumed that α is unity and used the results to determine Φ_{ISC}. We assume that Φ_{ISC} has the previously measured value of 0.80 and use the equation to determine α. Figure 1 shows a plot of $\alpha((Y_T F'/Y_T' F) - 1)$ against $F^0/F'(F'/F - 1)$. In this case the slope is 0.08 although the best value obtained by averaging the results from several runs was 0.10 ± 0.02. This indicates that 10% of the quenching acts in benzene solution produce triplets. Table II summarizes the results of measurements carried out in four solvents.

Isomerization of Ethylstyrene. We carried out a limited study of the sensitized isomerization of *trans*-β-ethylstyrene. We do not have direct information concerning the triplet excitation energy of the substance but it should be close to that of *trans*-β-methylstyrene to which a value of 59.8 kcal mol^{-1} was assigned from the oxygen-perturbed absorption spectrum.[12] This would make the triplets nearly isoenergetic with naphthalene triplets[13] (E_T = 60.9 kcal mol^{-1}). Triplet quenching rates measured by the flash kinetic method[14] and by induced phosphorescence of biacetyl[15] have been found to be about one order of magnitude below the diffusion-controlled limit in other cases in which donor and acceptor are essentially isoenergetic. Irradiation of solutions containing 0.132 *M* *trans*-β-ethylstyrene and 0.066 *M* *cis*-piperylene led to the formation of small, but detectable, amounts of *cis*-β-ethylstyene under conditions where 10% or more *trans*-piperylene was produced. Although we have not attempted to measure the relative reactivities of the two energy acceptors with precision, the result allows us to assume that in solutions containing as much as 0.01 *M* ethylstyrene most naphthalene triplets will be intercepted before they undergo first-order decay.[14,15] The simplest mechanism for description of triplet-sensitized ismerization of *trans*-β-ethylstyrene involves competition between triplet energy transfer and quenching of naphthalene triplets without energy transfer.

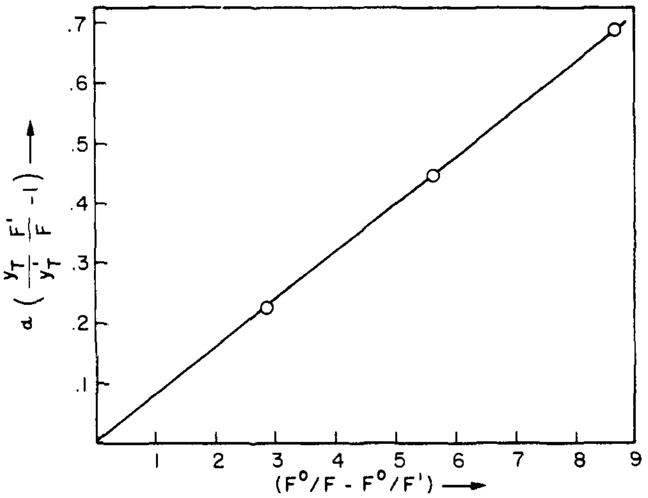

Figure 1. Plot of yield functions for naphthalene-*trans*-β-ethylstyrene-*cis*-piperylene in benzene solution.

Table II. Triplet Yields in Quenching of Naphthalene Fluorescence by *trans*-β-Ethylstyrene

Solvent	α	Solvent	α
n-Hexane	0.20 ± 0.04	Benzene	0.10 ± 0.02
Ether	0.25 ± 0.05	Acetonitrile	0.24 ± 0.03^a

[a] From two determinations only.

$$^3\text{N} + trans\text{-E} \longrightarrow \delta\,^3\text{E} + (1 - \delta)trans\text{-E} + \text{N} \quad (11)$$

$$^3\text{E} \longrightarrow \epsilon\, cis\text{-E} + (1 - \epsilon)trans\text{-E} \quad (12)$$

This mechanisms predicts that fluorescence quenching will be related to isomerization of β-ethylstyrene by eq 13

$$\Phi_i' = \delta\epsilon[(1 - F/F^0)\alpha + F\Phi_{\text{ISC}}/F^0] \quad (13)$$

where

Φ_i' = quantum yield for isomerization

Quantum yields for isomerization were measured in each of the four solvents used in this study with three different concentrations of *trans*-β-ethylstyrene. As would be anticipated, quantum yields decreased as the concentration of the substrate was increased. The values of quenching constants measured in the various solvents and the value of 0.80 for α were used to calculate the quantity within brackets in eq 13. The results are summarized graphically in Figure 2. As expected, the quenching and triplet counting data do an adequate job of accounting for the way in which the quantum yield for sensitized isomerization changes with quencher concentration in any given solvent since the quantity $\Phi_i'/[(1 - (F/F^0))\alpha + F\Phi_{\text{ISC}}/F^0]$ becomes independent of concentration. However, these constant values are different in the different solvents.

The discrepancy might be attributed to variations in the value of ϵ, the fraction of ethylstyrene triplets which decay to the cis isomer. This would be an unexpected phenomenon but the point was checked by measuring quantum yields for

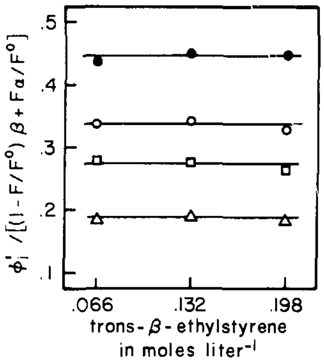

Figure 2. Correlation of quantum yields for isomerization of β-ethylstyrene in the presence of naphthalene with fluorescence quenching.

Table III. Partition Factors for Energy Transfer and Energy Wastage in Reaction of Naphthalene Triplets with *trans*-β-Ethylstyrene

Solvent	δ^a	Solvent	δ^a
Benzene	0.90 ± 0.10	Ether	0.66 ± 0.07
n-Hexane	0.54 ± 0.05	Acetonitrile	0.36 ± 0.04

[a] Error limits reflect the variation in results of measurement of ϵ using benzophenone.

isomerization sensitized by benzophenone. The values were constant at 0.50 ± 0.05 in the four solvents. Apparently δ varies, indicating that there is a solvent effect on the competition between energy transfer and energy wastage. The values of ϵ calculated from the data, using $\epsilon = 0.50$, are listed in Table III.

Stationary State Composition. The mechanism is formulated involves quenching of excited naphthalene singlets with formation of naphthalene triplets which then transfer energy to the triplet counter. At the high concentrations of *cis*-piperylene used in the experiments, one can imagine another mechanism in which energy is transferred from a triplet exciplex of naphthalene and β-ethylstyrene. If this were to occur, and if the exciplex had an excitation energy significantly different from that of naphthalene triplets, one might expect to see a change in the relative reactivities of *cis*- and *trans*-piperylene as acceptors. This follows from the fact that naphthalene falls in a sensitive region in the Saltiel plot (E_T *vs.* photostationary state composition) for the piperylenes.[8] Consequently we measured photostationary states produced in the presence and absence of β-ethylstyrene. Mixtures containing 68:32 *trans*:*cis*-piperylene, the previously reported photostationary ratio with naphthalene as the sensitizer,[16] were prepared and irradiated for long periods of time. The isomeric ratio was essentially invariant for times long in comparison with those required to effect extensive isomerization in experiments using pure *cis*-piperylene. Very long irradiation resulted in a slow change of the isomer ratio to more cis-rich mixtures. The drift rate in all solvents appeared to be essentially identical in solutions containing ethylstyrene and those in which the quencher was absent. The phenomenon may be associated with the fact that the system is not entirely photochemically "clean." Analyses by vapor chromatography and absorption spectrophotometry showed slow decrease in the total concentrations of the piperylenes and naphthalene. Quantitative assays indicated that the quantum yields for these side reactions are 0.04 or less. It is possible that products of the photochemical side reactions slowly accumulate and undergo decomposition in the heated inlet of the vapor chromatograph to produce relatively large amounts of *cis*-piperylene. Such an explanation would be more readily acceptable if results in the presence and absence of ethylstyrene were not so close to identical.

Irrespective of the cause of the time variable results, the principal implication for this discussion is the conclusion that introduction of ethylstyrene does not change the characteristics of the triplet which transfer energy to the piperylenes. Consequently, we conclude that this triplet is very naphthalene like, irrespective of whether or not it has an ethylstyrene molecule as a close neighbor.

The conclusion that energy transfer to ethylstyrene is considerably slower than transfer to *cis*-piperylene is consistent with other facts. Fluorescence quenching leads to formation of triplets which can be counted with piperylene. This would not be possible if triplet energy transfer from naphthalene to ethylstyrene were fast enough to compete effectively with diffusive separation of the partners in the original quenching complex. Energy transfer within the original solvent cage may be responsible for some of the isomerization of ethylstyrene observed in the presence of piperylene, but that rate is much lower than either the rates of piperylene isomerization or isomerization of ethylstyrene in the absence of piperylene.

Discussion

Substantial yields of naphthalene triplets are produced when the fluorescent state of naphthalene is quenched by *trans*-β-ethylstyrene. The extent to which this process competes with decay to form both quencher and quenchee in their ground singlet states is a function of the solvent. A second phenomenon, extensive energy wastage when naphthalene triplets are quenched by ethylstyrene, also shows solvent dependence. The two processes share a common feature since both involve competition between rapid, nonradiative relaxation processes one of which requires intersystem crossing in each case. One might hope that the high sensitivity to the nature of the medium would provide some unifying bridge between the process involving crossing from excited singlet to triplet and that involving crossing from triplet to ground singlet. As is shown by the data in Tables II and III, there is a limited consistency. In benzene the intersystem crossing processes, formation of triplets in fluorescence quenching, and energy wastage in triplet quenching are less important than in the other solvents. Ether and *n*-hexane appear to show roughly consistent behavior. However, triplet quenching without energy transfer is predominant in acetonitrile whereas that solvent appears to be similar to ether and hexane in its effect on the triplet yield in fluorescence quenching.

If a singlet exciplex is formed when ethylstyrene quenches the fluorescent state of naphthalene, the latter probably remains the principal site of excitation and, as a first approximation, we can think about the process as involving weak interaction with the quencher which, however, is sufficient to produce some mixing of states in the naphthalene increasing the probability of nonradiative transitions. Thayer and Yardley[17] have recently presented a discussion of bimolecular quenching which builds upon and updates many previous treatments. The model, which does not deal with intersystem crossing, depends entirely upon instantaneous dipole-dipole interactions for a mixing mechanism. This leads to prediction of especially high quenching efficiency for molecules having permanent dipole moments, which is consistent with the author's data for quenching of the fluorescence of propynal at low pressure. Dispersion interaction is proposed to be the principal mixing mechanism with nonpolar quenchers. An interesting feature of this approach is prediction that quenching reactivity will depend upon the ionization potential of the quencher. Such correlations are regularly observed in quenching of the fluorescence of aromatic compounds by unsaturated hydrocarbons[2-7] and have been used to support the inference that "charge transfer" occurs during quenching.[4,5] The limited success of the Thayer-Yardley treatment suggests caution in dedicated adherence to the charge-transfer model.

The very fact that intersystem crossing occurs during quenching can be construed as evidence in favor of charge transfer in an exciplex. If full electronic charge were transferred from the quencher to the aromatic molecule, two ion radicals would be produced. The singlet-triplet splitting in the radical pair would become small and intersystem crossing would be expected to occur at the very rapid rates known from the radical pair mechanism for production of chemically induced dynamic nuclear polarization.[18] The situation is probably realized in quenching of aromatic hydrocarbons by amines, a process known to produce substantial yields of triplets.[19,20] We are still reluctant to assign large amounts of charge-transfer character to exciplexes formed from two hydrocarbons but a contribution from such a structure to the total state of the system may help to account for rapid intersystem crossing.

The solvent effects do not point the way to any simple resolution of the problem. For example, if solvent polarity or polarizability were to dominate by increasing charge transfer one would expect intersystem crossing to be less in *n*-hexane than in any of the other solvents included in our study. The data in both Tables II and III show it to be intermediate in its influence. On the other hand, the existence of substantial solvent effects shows that models to account for the dynamics of internal conversion based only on consideration of quencher and quenchee molecules will be inadequate.

Experimental Section

Materials. Zone-refined naphthalene from Aldrich Chemicals was used as received. The emission spectrum, singlet lifetime, and melting point agreed with literature values. *trans*-β-Ethylstyrene, 99% pure, was obtained from Chemical Samples. It was occasionally subjected to bulb-to-bulb distillation. Gas chromatographic analysis, using SE-30 and β,β′-oxydipropionitrile columns, showed a trace of the cis isomer as the only significant impurity. Spectroquality benzene was supplied by Matheson Coleman and Bell. It was purified by photochlorination[21] and was twice distilled before use with the middle ⅔ fraction being accepted each time. *cis*-Piperylene (1,3-pentadiene) was supplied by Chemical Samples.

Isomerization rates were determined by irradiating the samples in a merry-go-round apparatus[22] fitted with appropriate filters to isolate the 313-nm line from a medium pressure mercury arc. Analyses were carried out with Hewlett-Packard 700 or 5750 gas chromatographs. The columns used were: for naphthalene and ethylstyrene, 7 ft × ⅛ in. 10% SE-30 on Chromosorb P; for piperylenes in either solution a 30 ft × ⅛ in. column of 25% β,β′-oxydipropionitrile on Chromosorb P and a 20 ft × ⅛ in. column of 10% Carbowax 20M on Chromosorb W in tandem; for piperylenes in other solvents, a 30 ft × ⅛ in. column of 25% β,β′-oxydipropionitrile on Chromosorb P. Retention time differences for the piperylene isomers were optimized to 7.0 min at 45°. Analysis of material received from Chemical Samples before distillation showed the presence of 0.75% of *trans*-piperylene and a trace of cyclopentene as impurities. After bulb-to-bulb distillation over lithium aluminum hydride the percentage of trans isomer was reduced to 0.5%. *trans*-Piperylene (99+% pure) was obtained from Chemical Samples and bulb-to-bulb distilled over lithium aluminum hydride. The purity was monitored by gas chromatography. Spectroquality acetonitrile obtained from Matheson Coleman and Bell was distilled twice from anhydrous potassium carbonate and stored under nitrogen. "Pesticidiquality" ether obtained from Matheson Coleman and Bell was always distilled from lithium aluminum hydride and stored under nitrogen just prior to use. *n*-Hexane, Phillips Pure Grade, was passed through an alumina column before use.

Procedures. Fluorescence quenching experiments were performed with solutions degassed by three freeze-pump (10^{-4} Torr)-thaw cycles in sealed Pyrex tubes. A Hitachi MPF 2 spectrofluorimeter was used to record emission spectra. In quantum yield determinations both the ferrioxalate and benzophenone-piperylene systems were used as actinometers with concordant results.

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References and Notes

(1) Part LXXVIII is A. Gupta and G. S. Hammond, *J. Amer. Chem. Soc.*, submitted for publication.

(2a) L. M. Stephenson, D. G. Whitten, and G. S. Hammond, in "The Chemistry of Ionization and Excitation," G. R. A. Johnson and G. Scholes, Ed., Taylor and Francis, Ltd., London, 1967, pp 35–42; L. M. Stephenson, D. G. Witten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 3665 (1966); (b) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968).

(3) S. Murov and G. S. Hammond, *J. Phys. Chem.*, **72**, 3797 (1968).

(4) B. S. Solomon, C. Steel, and A. Weller, *Chem. Commun.*, 927 (1969).

(5) T. R. Evans, *J. Amer. Chem. Soc.*, **93**, 2081 (1971).

(6) G. N. Taylor and G. S. Hammond. *J. Amer. Chem. Soc.*, **94**, 3684 (1972).

(7) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3687 (1972).

(8) G. S. Hammond, *et al.*, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

(9) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(10) We reject the alternative possibility that triplets are formed from the initially produced excited state before it decays to the fluorescent state. Irradiation was in the first naphthalene absorption band so excitation produced principally S_1, the B_{1u} state of naphthalene. The excitation spectrum for naphthalene fluorescence follows the absorption spectrum closely indicating that both vibrational and electronic relaxation are fast compared with the process that we are studying.

(11) (a) F. A. Carroll and F. H. Quina, *J. Amer. Chem. Soc.*, **94**, 6246 (1972); (b) A. R. Horrocks and F. Wilkinson, *Proc. Roy. Soc., Ser. A*, **306**, 257 (1968).

(12) R. E. Kellogg, private communication.

(13) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(14) W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).

(15) K. Sandros, *Acta Chem. Scand.*, **23**, 2815 (1969).

(16) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(17) C. A. Thayer and J. T. Yardley, *J. Chem. Phys.*, **57**, 3992 (1972).

(18) R. Kaptein, *J. Amer. Chem. Soc.*, **94**, 6251 (1972).

(19) N. Orbach, R. Potashnik, and M. Ottolenghi, *J. Phys. Chem.*, **76**, 1138 (1972).

(20) L. Molina and F. Quina, unpublished studies from this laboratory.

(21) J. Saltiel, private communication.

(22) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, 1, 245 (1969).