formed by weak interaction of the excited sensitizer with quadricyclene. Reactions 5 and 6 are two paths for nonradiative decay of the exciplex. Both nonradiative processes must be very fast since no new fluorescence is observed in the presence of the quencher. Reactions 5 and 6 may involve a common first step, production of a vibrationally excited form of **2**, which then partitions between relaxation paths that produce **1** and **2**. The internal conversion reaction must depend in a critical way on coupling between the vibrational modes of the quencher and the electronic excitation of the complex. This conclusion is compelled especially strongly by comparison of the behavior of **1** and **2**. We presume that the binding energy of an exciplex containing **1** would be lower than that of the exciplex from **2**, since the singlet excitation energy of **2** is higher than that of **1**. However, **1** is much less efficient as a quencher and undergoes no significant chemical change when it does quench naphthalene singlets. If the entire 90 kcal mole^{-1} energy available in excited naphthalene singlets were transferred to the quenchers, the latter would be endowed with energy far in excess of that required to produce the transition state involved in the thermal isomerization of **2** to **1**.[8] A common species cannot be produced from the two isomers during the quenching process.

We have observed a number of other cases of singlet sensitization in cases in which the energy acceptor has no known excited singlet states lying below the lowest excited singlet of the sensitizer. Many other aromatic hydrocarbons sensitize the conversion of **2** to **1** in parallel with quenching of fluorescence,[10] and the accompanying report[2] shows that sensitized isomerization of sulfoxides can follow the same mechanism. An especially interesting example is the sensitized *cis–trans* isomerization of the 1,2-diphenylcyclopropanes. In early reports we have shown that the reaction can be effected using sensitizers having low triplet excitation energies[11] and that the use of an optically active napththalene derivative as a sensitizer leads to considerable asymmetric induction.[12] We now find that sensitization by naphthalene and its derivatives requires interaction between substrates and the excited singlet states of the sensitizers. The demonstration follows the same lines as those described above. The quantum yield for the sensitized reaction, although lower than in the sensitized conversion of **2** to **1**, quantitatively parallels quenching of the fluorescence of the sensitizers. Furthermore, piperylene, which can be isomerized by naphthalene by the triplet mechanism, has only a very weak quenching effect on the sensitized isomerization of the diphenylcyclopropanes; however, 2,5-dimethyl-2,4-hexadiene, a much more powerful singlet quencher than piperylene,[3b] quenches the isomerization of the diphenylcyclopropanes very stongly.

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[7] G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belges*, 71, 781 (1962).

[8] The activation energy[9] is 38.3 kcal mole^{-1} and the enthalpy of reaction, as determined by Professor R. B. Turner in unpublished measurements of the enthalpies of hydrogenation, is -23.9 kcal mole^{-1}.

[9] J. R. Edman, *J. Org. Chem.*, 32, 2920 (1967).

[10] S. Murov, unpublished results.

[11] G. S. Hammond, P. Wyatt, C. D. De Boer, and N. J. Turro, *J. Am. Chem Soc.*, **86**, 2532 (1964).

[12] G. S. Hammond and R. S. Cole, *ibid.*, **87**, 3256 (1965).

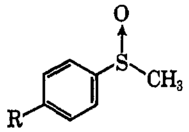
[13] National Institutes of Health Postdoctoral Fellow, 1967–1968.

Mechanisms of Photochemical Reactions in Solution. LV.[1] Naphthalene-Sensitized Photoracemization of Sulfoxides

Sir:

Mislow, *et al.*,[2] first observed that the pyramidal inversion of some aryl alkyl sulfoxides could be effected photochemically using naphthalene as a sensitizer. Reinvestigation of these results has lead to a rather different mechanism from the one originally proposed.[3]

The energy levels of **1** have been determined spectroscopically. The first excited singlet state of racemic **1a** is placed at about 113 kcal mole^{-1} based on the maximum of the $^{1}L_{b}$ band[4] occurring at 2530 Å. The energy of the first triplet state of racemic **1b** was determined from the weak and structureless phosphorescence in an ether–alcohol glass (1:2 by volume) and the structured singlet–triplet absorption spectrum of this compound in chloroform solution. The phosphorescence and singlet–triplet absorption are mirror images and place the triplet state at 79 kcal mole^{-1}. These results imply that electronic energy transfer from either the singlet or the triplet state of naphthalene to the sulfoxide to produce the corresponding excited state of the latter is highly endothermic (by 23 and 18 kcal mole^{-1}, respectively) and should not occur at any appreciable rate.



1a, R = CH$_3$
b, R = Br
c, R = OH

The possibility of ground-state complex formation between racemic **1b** and naphthalene has been ruled out on the basis of the absorption spectrum of a mixture which shows no anomalous bands in the 2400–3500-Å region. Irradiation of degassed solutions of naphthalene and either **1b** or **1c**, with light absorbed only by naphthalene (λ 3130 Å), led to formation of new products, but the quantum yield was only 1% of that for sensitized racemization. The only isolated products were the corresponding sulfides.

These observations limit the mechanisms to be considered for the sensitized racemization of **1**. Other results from this laboratory[5] suggested that the mechanism

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[1] Part LIV: S. L. Murov, R. S. Cole, and G. S. Hammond, *J. Am. Chem. Soc.*, **90**, 2957 (1968).

[2] K. Mislow, M. Axelrod, D. R. Rayner, H. Gotthardt, L. M. Coyne, and G. S. Hammond, *ibid.*, **87**, 4958 (1965).

[3] G. S. Hammond, H. Gotthardt, L. M. Coyne, M. Axelrod, D. R. Rayner, and K. Mislow, *ibid.*, **87**, 4959 (1965).

[4] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N.Y., 1965, p 491.

[5] Reference 1 and references cited therein.

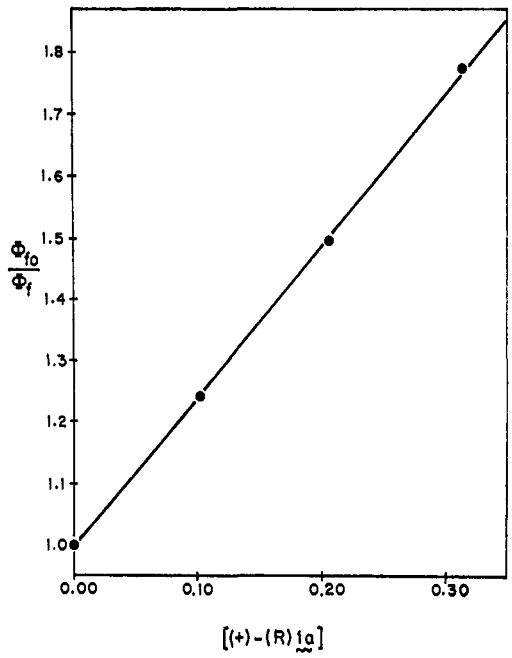

Figure 1. Fluorescence of naphthalene as a function of added sulfoxide.

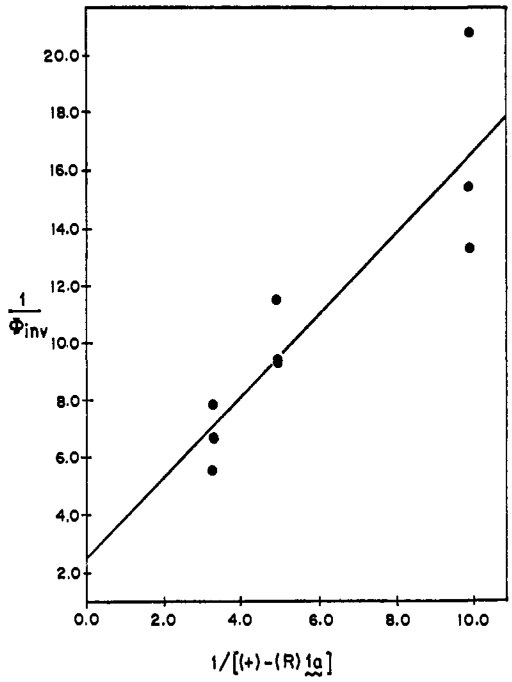

Figure 2. Quantum yield of inversion as a function of sulfoxide concentration.

might depend upon activation of the substrate by the excited singlet state of the sensitizer as shown by the following equations

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

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

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

$$\mathrm{N}^1 \xrightarrow{k_{ic}} \mathrm{N}^3 \tag{4}$$

$$\mathrm{N}^3 \xrightarrow{k_2} \mathrm{N} \tag{5}$$

$$\mathrm{N}^1 + \mathrm{S}(+) \xrightarrow{k_q} [\mathrm{N}\cdot\mathrm{S}(+)]^1 \tag{6}$$

$$[\mathrm{N}\cdot\mathrm{S}(+)]^1 \xrightarrow{k(+)} \mathrm{N} + \mathrm{S}(+) \tag{7}$$

$$[\mathrm{N}\cdot\mathrm{S}(+)]^1 \xrightarrow{k(-)} \mathrm{N} + \mathrm{S}(-) \tag{8}$$

$$\frac{\Phi_{f_0}}{\Phi_f} = 1 + \tau_s k_q[\mathrm{S}(+)]$$

$$\frac{1}{\Phi_{inv}} = \left[1 + \frac{1}{\tau_s k_q[\mathrm{S}(+)]}\right]\left[\frac{k(+) + k(-)}{k(-)}\right]$$

where Φ_{f_0} = quantum yield of naphthalene fluorescence, Φ_f = quantum yield of naphthalene fluoroescence with added sulfoxide, Φ_{inv} = quantum yield of inversion of sulfoxide, and τ_s = singlet lifetime of naphthalene.[6]

An intermediate exciplex is presumed to be formed although there is no direct evidence for the species. A test of the mechanism is provided by correlation of the rate of racemization with quenching of the naphthalene fluorescence.

Experiments were performed in which the intensity of fluorescence from 0.03 *M* naphthalene in degassed acetonitrile solutions with various concentrations of racemic **1a** was measured. These results are shown in Figure 1. A value of $k_q = 3.2 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$ is obtained in this experiment.

The quantum yield of inversion sensitized with 0.03 *M* naphthalene in degassed acetonitrile solution as a function of the concentration of (+)-(*R*)-**1a** was determined. These results are shown in Figure 2. A value of $k_q = 2.3 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$ is obtained. The considerable error in these determinations is undoubtedly the result of difficulties in determining absolute light intensities and of magnification of errors in determining small differences between large rotations. We believe that the values of k_q determined in the two experiments are the same within experimental error, in agreement with the proposed mechanism.

In steps 7 and 8 of the mechanism, much of the 90 kcal mole^{-1} excitation energy originally carried by naphthalene must be converted to vibrational energy distributed between the two partners in the complex. An amount equal to at least 43 kcal mole^{-1}, the activation energy for the thermal inversion reaction,[7] must appear in the sulfinyl group.

Work in progress has shown that intramolecular sensitization[2] involves the same mechanism.

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[6] τ_s = 78 ± 3 nsec for 0.03 *M* naphthalene in acetonitrile, as determined directly from fluorescence decay curves.

[7] D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *J. Am. Chem. Soc.*, **88**, 3138 (1966).