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

Robert S. Cooke and George S. Hammond

Contribution No. 3937 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109.
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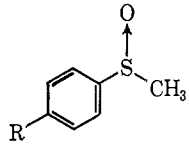
Abstract: The sensitized photoracemization of a number of alkyl aryl sulfoxides, **1a–f**, has been shown to depend on transfer of energy from the excited singlet state of naphthalene. Exothermic electronic energy transfer is ruled out. A mechanism requiring exciplex formation and subsequent radiationless decay is proposed. Substitution of the substrate shows that steric and electronic effects on the rates of fluorescence quenching or of photoracemization are small.

The thermally or catalytically induced stereomutation of sulfoxides has received considerable attention.[2] Mislow, *et al.*,[3] first demonstrated the photochemical pyramidal inversion of sulfoxides, and Hammond, *et al.*,[4] attempted to elucidate the mechanism of this reaction. Direct irradiation of alkyl aryl or diaryl sulfoxides leads to racemization with concurrent decomposition. Dialkyl sulfoxides are decomposed but not racemized by direct irradiation. Both intra- and intermolecular sensitization by naphthalene lead to stereomutation of diaryl and aryl alkyl sulfoxides with little decomposition; however, dialkyl sulfoxides are not inverted. The sensitized reaction is inefficiently quenched by the addition of piperylene.

Naphthalene sensitization of stereomutation could not be explained satisfactorily in terms of mechanistic photochemistry understood at that time. We believe that the work[5] presented below provides this explanation, as well as an example of a newly recognized type of energy transfer.

Results and Discussion

The absorption spectra of (±)-methyl *p*-tolyl sulfoxide (**1a**) in several solvents are shown in Figure 1. The



1a, R = CH_3
b, R = Br
c, R = Cl
d, R = OH
e, R = H
f, R = $C(CH_3)_3$

short wavelength transition appearing as a shoulder at 217.5 nm is assigned as the ^1L_a band of benzene.[6] The long wavelength absorption at about 243 nm is usually referred to as the benzene ^1L_b band. The solvent dependence shown by this transition indicates that it is probably a superposition of the ^1L_b band of benzene and the n–π^* band of the sulfinyl group.[6] Although it is impossible to assign a 0–0′ transition for the long wavelength absorption, we cannot imagine that it lies below 102 kcal mole^{-1}.

The approximate triplet state energy of (±)-methyl *p*-bromophenyl sulfoxide (**1b**) was determined by comparison of the phosphorescence and the singlet–triplet absorption spectra. In an ether–alcohol glass at 77°K (1:2 by volume) this compound shows weak and structureless emission. In chloroform solution (±)-methyl *p*-bromophenyl sulfoxide (**1b**), carefully purified by recrystallization, sublimation, and zone refining, showed weak, slightly structured absorption corresponding to the phosphorescence as shown in Figure 2. These results place the triplet state energy at about 79 kcal mole^{-1}.

These data 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 12 and 18 kcal mole^{-1}, respectively) and should not occur at any appreciable rate. *Any participation* of the triplet state of naphthalene was ruled out by double-sensitization experiments. Degassed solutions of 0.05 *M* benzophenone, 0.03 *M* naphthalene, and 0.05 *M* (+)-(*R*)-methyl *p*-chlorophenyl sulfoxide (**1c**) or (+)-(*R*)-methyl *p*-bromophenyl sulfoxide (**1b**) in acetonitrile were irradiated at 366 nm where only benzophenone absorbs light. Completely efficient transfer of triplet energy to naphthalene was demonstrated by the fact that no photoreduction of benzophenone occurred. The quantum yields of inversion of sulfoxide were less than 1% of those observed when naphthalene was directly irradiated and are within experimental error of zero.

The possibility of ground-state complex formation between (±)-methyl *p*-bromophenyl sulfoxide (**1b**) and naphthalene was ruled out on the basis of the absorption spectrum of a mixture which shows no anomalous bands in the 240–350-nm region. Prolonged irradiation of degassed solutions of 0.03 *M* naphthalene and 0.05–0.09 *M* (±)-methyl *p*-chlorophenyl sulfoxide (**1c**) in acetonitrile led to the disappearance of sulfoxide with a quantum yield less than 5% of that observed for the racemization under the same conditions. Frag-

(1) Part LXI: R. S. Cooke, *Chem. Commun.*, in press.
(2) For an excellent review, see K. Mislow, *Rec. Chem. Progr.*, 28, 217 (1967).
(3) K. Mislow, M. Axelrod, D. R. Rayner, H. Gotthardt, L. M. Coyne, and G. S. Hammond, *J. Am. Chem. Soc.*, 87, 4958 (1965).
(4) G. S. Hammond, H. Gotthardt, L. M. Coyne, M. Axelrod, D. R. Rayner, and K. Mislow, *ibid.*, 87, 4959 (1965).
(5) For a preliminary account, see R. S. Cooke and G. S. Hammond, *ibid.*, 90, 2958 (1968).
(6) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1965, p 491 ff.

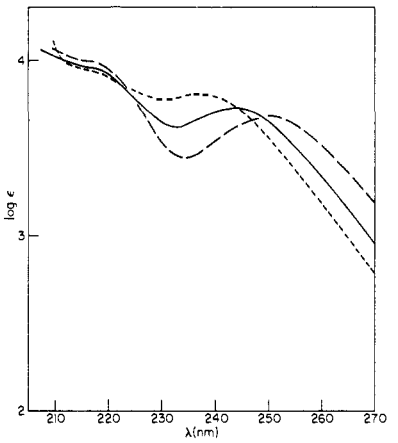


Figure 1. Absorption spectra of (±)-methyl *p*-tolyl sulfoxide in various solvents: — — —, in cyclohexane; ———, in acetonitrile; --------, in ethanol.

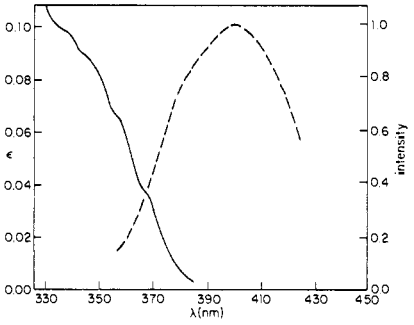


Figure 2. Triplet state spectra of (±)-methyl *p*-bromophenyl sulfoxide: ———, singlet-triplet absorption spectrum in chloroform; — — —, phosphorescence spectrum in ether–alcohol glass at 77°K.

mentary evidence obtained in prolonged irradiation of (±)-methyl *p*-bromophenyl sulfoxide (**1b**) or (±)-methyl *p*-hydroxyphenyl sulfoxide (**1d**) indicates that the corresponding sulfide is the only product. No sulfone, which is stable under the reaction conditions, was found in either case. Because of the inefficiency of this process, the decomposition of sulfoxide was neglected in the kinetic analysis of the photoracemization.

These observations limit the mechanisms to be considered for the sensitized racemization of alkyl aryl sulfoxides. Other results from this laboratory[7,8] suggested that the mechanism might depend upon activation of the substrate by the excited singlet state of the sensitizer as shown by Scheme I, where ϕ_{f_0} = quantum

Scheme I

$$N \xrightarrow{h\nu} N^1 \quad (1)$$

$$N^1 \xrightarrow{k_f} N + h\nu' \quad (2)$$

$$N^1 \xrightarrow{k_1} N \quad (3)$$

$$N^1 \xrightarrow{k_{ic}} N^3 \quad (4)$$

$$N^3 \xrightarrow{k_2} N \quad (5)$$

(7) S. L. Murov, R. S. Cole, and G. S. Hammond, *J. Am. Chem. Soc.*, 90, 2957 (1968).
(8) S. Murov and G. S. Hammond, *J. Phys. Chem.*, 72, 3797 (1968).

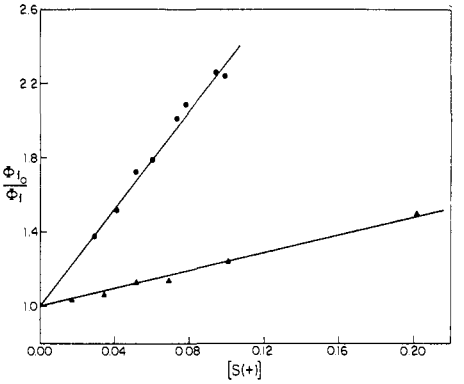


Figure 3. Quenching of naphthalene fluorescence by sulfoxides: ●, methyl *p*-chlorophenyl sulfoxide; ▲, methyl *p*-tolyl sulfoxide.

$$N^1 + S(+) \underset{k_{-q}}{\overset{k_q}{\rightleftharpoons}} [N \cdot S(+)]^1 \quad (6)$$

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

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

$$\frac{\phi_{f_0}}{\phi_f} = 1 + \frac{[k(+) + k(-)]k_q\tau_s[S(+)]}{k_{-q} + k(+) + k(-)} = 1 + k_Q\tau_s[S(+)]$$

$$\frac{1}{\phi_{inv}} = \left[1 + \frac{1}{\tau_s k_Q[S(+)]}\right]\left[\frac{k(+) + k(-)}{k(-)}\right]$$

yield of naphthalene fluorescence, ϕ_f = quantum yield of naphthalene fluorescence with added sulfoxide, ϕ_{inv} = quantum yield of inversion of sulfoxide, τ_s = singlet lifetime of naphthalene, 78 ± 5 nsec for 0.03 *M* naphthalene in acetonitrile, and $k_Q = [k(+) + k(-)]\cdot k_q/[k_{-q} + k(+) + k(-)]$.

Steps 1–5 show the normal photophysical processes for naphthalene in solution. Step 6 represents the formation of the hypothetical exciplex, while steps 7 and 8 show its radiationless decay to naphthalene and sulfoxide of retained or inverted stereochemistry.

A test of the mechanism is provided by correlation of the rate of inversion with the quenching of the naphthalene fluorescence. Experiments were performed in which either the intensity or lifetime of the fluorescence from 0.03 *M* naphthalene in degassed acetonitrile was measured as a function of sulfoxide concentration. Representative data for (±)- or (+)-(*R*)-methyl *p*-tolyl sulfoxide (**1a**) and (±)- or (+)-(*R*)-methyl *p*-chlorophenyl sulfoxide (**1c**) are shown in Figure 3. The quantum yield of inversion sensitized with 0.03 *M* naphthalene in degassed acetonitrile was measured as a function of sulfoxide concentration. The data for (+)-(*R*)-methyl *p*-tolyl sulfoxide (**1a**) and (+)-(*R*)-methyl *p*-chlorophenyl sulfoxide (**1c**) are shown in Figure 4. Included in Table I are the data from the inversion and fluorescence quenching experiments for the compounds studied. The correlation between the rate constants determined in these two independent experiments is reasonably good. The error limits quoted are average deviations of a number of runs and the actual limits may be somewhat larger. We feel that the data observed for the five optically active sulfoxides strongly support the proposed mechanism.

It should be pointed out that *there is no direct evidence for the postulated exciplex.* However, invoking

Table I

Sulfoxide	Fluorescence k_Q, M^{-1} sec^{-1}	Inversion k_Q, M^{-1} sec^{-1}
Methyl *p*-tolyl	$(3.2 \pm 0.2) \times 10^7$	$(3.4 \pm 0.3) \times 10^7$
Methyl phenyl	$(4.8 \pm 0.5) \times 10^7$	$(5.8 \pm 0.9) \times 10^7$
Methyl *p*-*t*-butylphenyl	$(3.4 \pm 0.2) \times 10^7$	$(4.6 \pm 0.3) \times 10^7$
Methyl *p*-bromophenyl	$(7.3 \pm 1.0) \times 10^8$	$(1.3 \pm 0.3) \times 10^9$
Methyl *p*-chlorophenyl	$(2.0 \pm 0.4) \times 10^8$	$(2.7 \pm 0.2) \times 10^8$
Methyl *p*-hydroxyphenyl	$(5.0 \pm 0.2) \times 10^7$	
Chloromethyl *p*-tolyl	$(2.8 \pm 0.1) \times 10^7$	

such a species in our mechanism provides a useful framework in which to consider the observed phenomena. Our discussion of the individual steps which produce or destroy the exciplex must be largely speculative, but it may provide a basis for further experimental work. Other mechanisms which fit the kinetics equally well are considered in the discussion of the intramolecular quenching observed in the case of (+)-(*R*)-*p*-tolyl 2-(1-naphthyl)ethyl sulfoxide (**2**).

The excited complexes are visualized as being loosely bound, and we expect that they would be formed on nearly every encounter in solution. Since quenching rates are well below diffusion controlled, we infer that reactions 7 and 8 are rate limiting and that $k_{-q} \gg [k(+) + k(-)]$. These assumptions simplify the expression for k_Q, the measured rate constant for quenching, and indicate that quenching reactivity is controlled both by the stability of the exciplex, measured by k_q/k_{-q}, and by the radiationless decay rate, measured by $k(+) + k(-)$. The binding energy of the complex may result from exciton and charge-transfer interactions.[8] Our use of electron-donating and -withdrawing substituents on the benzene ring failed to show a clear trend or a large variation in the quenching rate constants which would support the hypothesis that charge-transfer interactions are dominant. It is also surprising that steric bulk has no obvious effect on the rate constants. However, electronic and steric effects on the value of k_q/k_{-q} may compensate for inverse effects on the value of $k(+) + k(-)$. At present we have no way of separating these controlling factors.

Steps 7 and 8 show the radiationless decay of the exciplex to the ground states of the components. 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. In this decay some of the 90 kcal mole^{-1} electronic excitation energy appears in the sulfoxide molecule in the form of vibrational energy. The partitioning must be such that at least 38.4 kcal mole^{-1}, the activation energy for the thermal pyramidal inversion process,[9] is localized in the sulfinyl group. This is shown by the values obtained for $[k(+) + k(-)]/k(-)$ given in

Table II

Sulfoxide	$[k(+) + k(-)]/k(-)$
Methyl *p*-tolyl	2.7 ± 0.2
Methyl phenyl	2.3 ± 0.3
Methyl *p*-*t*-butylphenyl	2.5 ± 0.2
Methyl *p*-chlorophenyl	2.2 ± 0.1
Methyl *p*-bromophenyl	6.5 ± 0.3

(9) D. R. Rayner, A. J. Gordon, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4854 (1968).

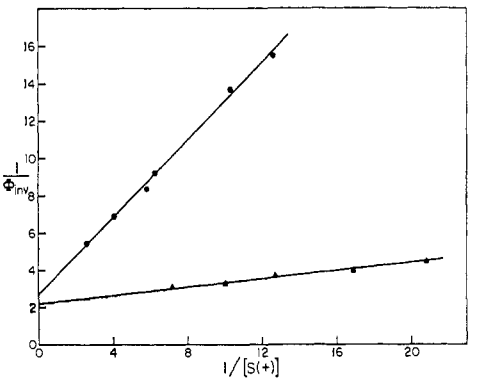


Figure 4. Quantum yield of sulfoxide inversion sensitized by naphthalene: ●, (+)-(*R*)-methyl *p*-tolyl sulfoxide; ▲, (+)-(*R*)-methyl *p*-chlorophenyl sulfoxide.

Table II. Neglecting for the moment the data from (+)-(*R*)-methyl *p*-bromophenyl sulfoxide (**1b**), we note that 37–45% of the time the exciplex decays to give sulfoxide with inverted stereochemistry. The value of $[k(+) + k(-)]/k(-)$ is expected to be a number greater than two since vibrational deactivation of the sulfoxide will very likely be sufficiently rapid to compete with loss of the original chirality of the substrate. We can think of no mechanism leading to reversal of chirality.

The value of $[k(+) + k(-)]/k(-) = 6.5$ for (+)-(*R*)-methyl *p*-bromophenyl sulfoxide (**1b**) indicates an interesting change of mechanism which was not totally unexpected. Wilkinson[10] has pointed out that molecules such as bromobenzene are able to catalyze the conversion of the excited singlet states of aromatic hydrocarbons to their triplet states. In the mechanism for (+)-(*R*)-methyl *p*-bromophenyl sulfoxide (**1b**) it is necessary to include a step represented by 9. Since the

$$N^1 + S(+) \xrightarrow{k_c} N^3 + S(+) \qquad (9)$$

singlet–triplet splitting for naphthalene is only 30 kcal mole^{-1}, the vibrational energy produced in intersystem crossing is 8 kcal mole^{-1} less than would be required to cross the barrier to inversion of the sulfoxide. Analysis of the mechanism including step 9 indicates that the value of $1/\phi_{inv}$ at infinite sulfoxide concentration is equal to $(1 + k_c/k_Q)[k(+) + k(-)]/k(-)$. Assuming a normal partitioning factor for the vibrationally excited sulfoxide, it is found that k_c/k_Q is about 1.7. From the observed fluorescence quenching rate constant of 7.3×10^8 M^{-1} sec^{-1}, the values $k_Q = 2.7 \times 10^8$ M^{-1} sec^{-1} and $k_c = 4.6 \times 10^8$ M^{-1} sec^{-1} are obtained. We have determined that the rate constant for quenching of naphthalene fluorescence by bromobenzene under identical conditions is $k_c = (3.1 \pm 0.1) \times 10^8$ M^{-1} sec^{-1}. This value is in excellent agreement with our calculated value of k_c.

The observation[3] that it is not possible to sensitize the inversion of dialkyl sulfoxides with naphthalene was explained by fluorescence quenching measurements. The intensity of fluorescence of 0.03 M naphthalene in degassed acetonitrile was measured as a function of dimethyl sulfoxide concentration. The rate constant for quenching was found to be $k_Q = (7.5 \pm 0.3) \times 10^5$ M^{-1} sec^{-1}. The quenching rate is at least 20 times

(10) T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, **61**, 620 (1965).

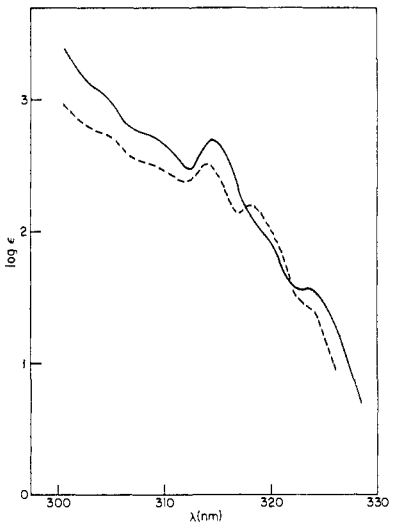
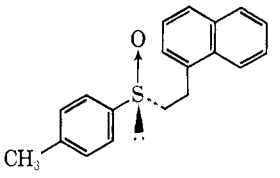


Figure 5. Absorption spectra of (+)-(*R*)-*p*-tolyl 2-(1-naphthyl)-ethyl sulfoxide (————) and 1-ethylnaphthalene (-------).

slower than that of aryl alkyl sulfoxides, and under normal irradiation conditions the amount of inversion would be too small to detect.

Mislow[3,4] has shown that (+)-(*R*)-*p*-tolyl 2-(1-naphthyl)ethyl sulfoxide (**2**) undergoes efficient stereomutation when irradiated at wavelengths where only the



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naphthalene chromophore is expected to absorb. The absorption spectra of this compound and 1-ethylnaphthalene are shown in Figure 5. The differences observed indicate a small amount of ground-state interaction not found in mixtures of sulfoxides and naphthalene. The compound has a fluorescence spectrum very similar to that of 1-ethylnaphthalene except that the quantum yield is estimated to be 0.06 by comparison with the emission from naphthalene. These facts show that the excited state from which emission occurs is probably one in which excitation is still located in the naphthalene unit. This inference is further fortified by the observation that the fluorescence of **2** is quenched by *cis*-piperylene with almost the same rate constant, $(7.2 \pm 0.6) \times 10^7\ M^{-1}\ \text{sec}^{-1}$, as that observed[11] in the quenching of 1-methylnaphthalene by *trans*-piperylene, $7.9 \times 10^7\ M^{-1}\ \text{sec}^{-1}$. However, the quantum yield for photoinversion of **2** is 0.451 ± 0.004, indicating that radiationless decay with transfer of energy to the sulfoxide unit is extremely efficient. The aryl sulfinyl group is intimately involved in an accelerated nonradiative decay mechanism, but apparently not in the radiative process or in quenching by piperylene. This behavior is most easily rationalized by Scheme II involving two excited states, one in which the excitation is localized in the naphthalene unit and another in which delocalization between the two chromophoric units occurs, where ϕ_{inv_0} = quantum yield of inversion of **2**, ϕ_{inv} = quantum yield of inversion of **2** with added quencher, and τ_s = singlet lifetime of **2**, 9.5 ± 1.0 nsec as determined by the Berlman method[12] under our experimental conditions.

Scheme II

$$\text{N—S(+)} \xrightarrow{h\nu} \text{N}^1\text{—S(+)} \tag{10}$$

$$\text{N}^1\text{—S(+)} \xrightarrow{k_f} \text{N—S(+)} + h\nu' \tag{11}$$

$$\text{N}^1\text{—S(+)} \xrightarrow{k_0} \text{N—S(+) or N}^3\text{ — S(+)} \tag{12}$$

$$\text{N}^1\text{—S(+)} \underset{k_{-q}}{\overset{k_q}{\rightleftharpoons}} [\text{N—S(+)}]^1 \tag{13}$$

$$[\text{N—S(+)}]^1 \xrightarrow{k(+)} \text{N—S(+)} \tag{14}$$

$$[\text{N—S(+)}]^1 \xrightarrow{k(-)} \text{N—S(—)} \tag{15}$$

$$\text{N}^1\text{—S(+)} + \text{Q} \xrightarrow{k_Q} \text{N—S(+)} + \text{Q} \tag{16}$$

$$\frac{\phi_{\text{inv}_0}}{\phi_{\text{inv}}} = \frac{\phi_{f_0}}{\phi_f} = 1 + \tau_s k_Q[\text{Q}]$$

Steps 10–12 represent the normal photophysical processes available to naphthalene derivatives and step 13 is the reversible formation of the species with delocalized excitation. The mechanism indicates that the effect of piperylene on the photoinversion should be parallel to its fluorescence quenching effect.

The quantum yield of inversion of a 0.006 *M* solution of **2** in degassed cyclohexane was measured as a function of added piperylene and a value of $k_Q = (7.7 \pm 1.0) \times 10^7\ M^{-1}\ \text{sec}^{-1}$ was determined. The excellent agreement between the numbers measured by quenching of fluorescence and of the chemical reaction indicates that the same quenching step (or steps) interferes with both radiative and nonradiative decay of the excited state of **2**. Irreversible formation of an excited state that both undergoes stereomutation and can be quenched by piperylene is ruled out. However, we cannot rigorously exclude the possibility that the delocalized excited state, $[\text{N–S(+)}]^1$, is subject to quenching if it is equilibrated with the fluorescent state as shown in eq 13. All we know is that the net reactivity of the two species is similar to that of a 1-alkylnaphthalene. Actually, an embarrassing plethora of mechanisms will accommodate our observations. Three that are immediately obvious are (1) reversible formation of the delocalized complex, quenching of only $\text{N}^1\text{–S(+)}$ which is the principal species present at equilibrium; (2) reversible formation of the delocalized complex, quenching of both $\text{N}^1\text{–S(+)}$ and $[\text{N–S(+)}]^1$ with comparable rate constants, the two excited species present in comparable amounts; and (3) irreversible formation of the delocalized complex, quenching of $\text{N}^1\text{–S(+)}$ only.

We have a preference for mechanism 1 based on nonrigorous arguments. If mechanism 2 were correct, the concentration and lifetime of $[\text{N–S(+)}]^1$ would have to be comparable to those of $\text{N}^1\text{–S(+)}$ and we would expect to see some new fluorescence at least slightly red shifted from that of 1-alkylnaphthalenes. If mechanism 3 is correct, we can estimate the value of k_q. We infer from the quantum yield for stereomutation that at least 90% of the material decays by way of the de-

(11) L. M. Stephenson, Jr., Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1968.

(12) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965, p 35 ff.

localized complex. From the fluorescence lifetime we then estimate that k_q would be about 9×10^7 sec^{-1}. Intuitively, we feel that this is too slow to be reasonable for the rate of establishment of the kind of weak coupling that we imagine to be involved between the chromophoric units. The reasoning is essentially the same as that which led us to expect bimolecular exciplex formation to be nearly diffusion controlled (*vide supra*). If the hypothesis of fast interaction is accepted, we would then conclude that the delocalized excited state represents only a very shallow energy trap, since the persistence of fluorescence shows that a significant population retains the localized excitation.

Finally, we should ask why we want to discuss the problem in terms of two excited species at all. Why not simply say that there is a single excited state having normal fluorescence properties which also finds an unusually rapid mechanism for internal conversion by dumping energy into the inversion vibration of the sulfinyl group? We pass by this simplest description because we cannot conceive of efficient coupling to high vibrational levels of the sulfinyl group unless some of the electronic excitation is transferred to the group before internal conversion. That the vibrational modes of the sulfinyl group are involved in the rapid radiationless decay is postulated since the rest of the molecule resembles compounds which do not serve as quenchers of aromatic hydrocarbons.

Experimental Section

Solvents and Sensitizers. **Naphthalene** (Eastman) was recrystallized twice from ethanol and sublimed at 50° (0.05 mm). **Benzophenone** (Eastman) was recrystallized twice from petroleum ether (bp 60–70°) and sublimed at 40° (0.05 mm). Purification of **1-ethylnaphthalene** (J. T. Baker) was by distillation at 135–136° (20 mm).

Acetonitrile (Matheson Coleman and Bell) was distilled three times from phosphorus pentoxide and once from anhydrous potassium carbonate. It was then distilled with no drying agent through a 60-cm column packed with glass helices. Only the middle fraction was taken. **Cyclohexane** (Matheson Coleman and Bell) was stirred at reflux with sulfuric acid under a nitrogen blanket for 3 days. The sulfuric acid was changed every 24 hr. It was then washed with sodium bicarbonate solution and water, dried over magnesium sulfate, filtered, and distilled from phosphorus pentoxide through a 60-cm column packed with glass helices. Only the middle fraction was taken. **Diethyl ether** (Mallinckrodt) for phosphorescence measurements was distilled from lithium aluminum hydride under a nitrogen blanket just prior to use. **Ethyl alcohol** (U.S. Industrial Chemicals) for phosphorescence measurements was refluxed over magnesium turnings and distilled just prior to use through a column packed with glass helices.

Sulfoxides. All infrared spectra were obtained on a Perkin-Elmer 257 spectrometer. Nmr spectra were measured on a Varian A 60-A instrument, and ultraviolet data were obtained on a Cary 14 spectrometer. The polarimetric measurements in both synthetic and kinetic work were made with a Perkin-Elmer 141 polarimeter. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

The syntheses of (±)-[13] and (+)-(*R*)-methyl *p*-tolyl sulfoxide[14] (**1a**), (±)-[15] and (+)-(*R*)-methyl phenyl sulfoxide[16] (**1e**), (±)-methyl *p*-hydroxyphenyl sulfoxide[17] (**1d**), and (+)-(*R*)-*p*-tolyl 2-(1-naphthyl)ethyl sulfoxide[3] (**2**) have been described.

(±)-**Methyl *p*-bromophenyl sulfoxide** (**1b**) was prepared in 91% yield by the sodium metaperiodate oxidation[15] of *p*-bromothioanisole (Aldrich) in methanol–water at 0° for 18 hr. Final purification was effected by recrystallization from 5% chloroform–95% toluene and sublimation at 75° (0.05 mm). The compound had a melting point of 82.5–84.0°. The infrared spectrum ($CHCl_3$) showed a strong band at 1050 cm^{-1}. The nmr spectrum ($CDCl_3$–1% TMS) showed signals at δ 2.70 (3 H, s), 7.58 (4 H, A_2B_2). The ultraviolet spectrum (CH_3CN) had λ_{max} 250.0 nm (ϵ 6750), 222.0 (11,300).

Anal. Calcd for C_7H_7BrOS: C, 38.37; H, 3.22; S, 14.63; Br, 36.47. Found: C, 38.38; H, 3.17; S, 14.62; Br, 36.50.

(±)-**Methyl *p*-chlorophenyl sulfoxide** (**1c**) was prepared in 80% yield by the sodium metaperiodate oxidation[15] of *p*-chlorothioanisole (Wateree Chemical Co.) in methanol–water at 0° for 24 hr. Purification was effected by chromatography on silica gel, recrystallization from toluene, and sublimation at 50° (0.035 mm). The compound had a melting point of 46.0–48.2°. The infrared spectrum ($CHCl_3$) showed a strong band at 1050 cm^{-1}. The nmr spectrum ($CDCl_3$–1% TMS) showed signals at δ 2.72 (3 H, s), 7.57 (4 H, A_2B_2). The ultraviolet spectrum (CH_3CN) had λ_{max} 248.5 nm (ϵ 5650), 220.0 (11,200).

Anal. Calcd for C_7H_7ClOS: C, 48.14; H, 4.04; S, 18.36; Cl, 20.30. Found: C, 48.30; H, 3.99; S, 18.41; Cl, 20.39.

(±)-**Methyl *p*-*t*-Butylphenyl Sulfoxide** (**1f**). To a solution of 16.6 g of *p*-*t*-butylbenzene thiol (Matheson Coleman and Bell) (0.10 mole), 30 ml of water, and 4.0 g of sodium hydroxide (0.10 mole) were added with stirring 14.2 g of methyl iodide (0.10 mole) over the course of 30 min. The two-phase system was stirred 1 additional hr making sure that the aqueous layer remained basic. The reaction mixture was extracted with ether, and the extracts were washed with brine, dried over magnesium sulfate, filtered, and flash evaporated to give 16.8 g of **methyl *p*-*t*-butylphenyl sulfide** (94%). The compound had a boiling point of 50.0–56.0° (0.10 mm). The nmr spectrum ($CDCl_3$–1% TMS) showed δ 2.37 (3 H, s), 1.27 (9 H, s), 7.23 (4 H, A_2B_2). (±)-**Methyl *p*-*t*-butylphenyl sulfoxide** (**1f**) was prepared in 65% yield by the sodium metaperiodate oxidation[15] of the sulfide in methanol–water at 0° for 19 hr. The product was purified by column chromatography on silica gel, recrystallization from 5% toluene–95% hexane, and sublimation at 70° (0.05 mm). The compound had a melting point of 76.0–77.0°. The infrared spectrum ($CHCl_3$) showed a strong band at 1047 cm^{-1}. The nmr spectrum ($CDCl_3$–1% TMS) showed signals at δ 2.71 (3 H, s), 1.34 (9 H, s), 7.60 (4 H, s). The ultraviolet spectrum (CH_3CN) had λ_{max} 244.0 nm (ϵ 5890), λ_{sh} 217.5 (10,100).

Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22; S, 16.33. Found: C, 67.36; H, 8.28; S, 16.38.

(±)-**Chloromethyl *p*-Tolyl Sulfoxide.** A solution of 8.58 g of thionyl chloride (0.072 mole) in 20 ml of methylene chloride was placed in a three-necked flask equipped with a magnetic stirrer, a reflux condensor, and an addition funnel. The solution was heated to reflux and a solution of 9.27 g of (±)-methyl *p*-tolyl sulfoxide (**1a**) (0.060 mole) in 30 ml of methylene chloride was added over the course of 1 hr. The reaction mixture was heated under reflux for an additional 2 hr. The solvent was flash evaporated, and the residual oil was distilled under vacuum to give 9.27 g of pale yellow **chloromethyl *p*-tolyl sulfide** (89%). Attempted oxidation of this sulfide using sodium metaperiodate led to extensive decomposition. A solution of 3.00 g of **chloromethyl *p*-tolyl sulfide** (0.0174 mole) in 80 ml of chloroform was added to a round-bottomed flask equipped with a magnetic stirrer. The solution was cooled to −5° and 3.88 g of 85% *m*-chloroperbenzoic acid (0.0191 mole) was added at a rate such that the temperature of the reaction mixture did not exceed 0°. The mixture was stirred at room temperature overnight, washed with saturated sodium bicarbonate solution followed by water, dried over magnesium sulfate, filtered, and flash evaporated. The residual oil was chromatographed on silica gel, recrystallized from 50% hexane–50% xylene, and sublimed at 50° (0.035 mm) to give 2.928 g of (±)-**chloromethyl *p*-tolyl sulfoxide** (89%). The compound had a melting point of 59.8–61.0°. The infrared spectrum ($CHCl_3$) showed a strong band at 1056 cm^{-1}. The nmr spectrum ($CDCl_3$–1% TMS) showed signals at δ 2.40 (3 H, s), 4.40 (2 H, AA′), 7.48 (4 H, A_2B_2). The ultraviolet spectrum (CH_3CN) showed λ_{max} 247.5 nm (ϵ 6000), λ_{sh} 219.0 (9800).

Anal. Calcd for C_8H_9ClOS: C, 50.93; H, 4.81; S, 16.99; Cl, 18.79. Found: C, 50.88; H, 4.89; S, 17.01; Cl, 18.81.

(+)-(*R*)-**Methyl *p*-Bromophenyl Sulfoxide** (**1b**). Using the procedure of Gattermann,[18] *p*-bromoaniline (Matheson Coleman and Bell) was converted to ***p*-bromobenzenesulfinic acid.** The crude acid was purified by conversion to the ferric sulfinate salt by addi-

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tion of saturated ferric chloride solution to an aqueous suspension of the acid. The salt was triturated with cold water and treated with a concentrated solution of sodium hydroxide. The ferric hydroxide was filtered and the filtrate was acidified with concentrated sulfuric acid. The acid was recovered by ether extraction, drying over magnesium sulfate, filtration, and flash evaporation of the solvent. The yield of purified **p-bromobenzenesulfinic acid** was 68%. The compound had a melting point of 104–110°. The infrared spectrum (Nujol) showed a strong band at 1057 cm^{-1}. The acid was converted to **p-bromobenzenesulfinyl chloride** and then directly to **(−)-menthyl-(±)-p-bromobenzene sulfinate** by a procedure analogous to that of Herbrandson.[19] A solution of the diastereomers in petroleum ether (bp 60–70°) was treated with anhydrous hydrogen chloride, flash evaporated, and crystallized from acetone. The procedure was repeated several times with the mother liquors until a 61% yield of **(−)-menthyl (−)-p-bromobenzenesulfinate** was obtained. Final purification was effected by recrystallization from petroleum ether (bp 60–70°) to constant rotation. The material had a melting range of 108.0–113.5°. The specific rotation of the ester was $[\alpha]^{25}D$ −159.8° (*c* 2.7, chloroform). The infrared spectrum (CCl_4) showed a strong band at 1145 cm^{-1}. The nmr spectrum ($CDCl_3$–1% TMS) showed (*inter alia*) signals at δ 4.22 (1 H, m), 7.67 (4 H, s). Treatment of the menthyl sulfinate with methylmagnesium iodide by a procedure analogous to that of Andersen[20] gave **(+)-(*R*)-methyl p-bromophenyl sulfoxide (1b)** in 56% yield. Final purification was effected by column chromatography on silica gel and sublimation at 70° (0.05 mm). The compound had a melting point of 73.5–78.0°. The specific rotation was $[\alpha]^{25}D$ +103.7° (*c* 1.2, acetone). The infrared spectrum (CCl_4) showed a strong doublet at 1061 and 1069 cm^{-1}. The nmr spectrum ($CDCl_3$–1% TMS) showed signals at δ 2.73 (3 H, s), 7.62 (4 H, A_2B_2).

Anal. Calcd for C_7H_7BrOS: C, 38.37; H, 3.22; S, 14.63; Br, 36.47. Found: C, 38.46; H, 3.22; S, 14.69; Br, 36.41.

(+)-(*R*)-Methyl p-Chlorophenyl Sulfoxide (1c). Using the procedure analogous to that of Gattermann[18] *p*-chloroaniline (Eastman) was converted to **p-chlorobenzenesulfinic acid** in 59% yield after purification through the ferric sulfinate salt. The compound had a melting point of 96.0–99.0°. The infrared spectrum (Nujol) showed a strong band at 1050 cm^{-1}. The acid was converted first to **p-chlorobenzenesulfinyl chloride** and then to **(−)-menthyl (±)-p-chlorobenzenesulfinate** by a sequence analogous to that of Herbrandson.[19] By a procedure identical with that used for (−)-menthyl (−)-*p*-bromobenzenesulfinate a 69% yield of **(−)-menthyl-(−)-p-chlorobenzenesulfinate** was isolated. Final purification was by recrystallization to constant rotation from petroleum ether (bp 60–70°). The material had a melting range of 82.5–86.0°. The specific rotation was $[\alpha]^{25}D$ −183.6° (*c* 5.5, chloroform). The infrared spectrum (CCl_4) showed a strong band at 1145 cm^{-1}. The nmr spectrum ($CDCl_3$–1% TMS) showed (*inter alia*) signals at δ 4.14 (1 H, m), 7.57 (4 H, A_2B_2). The sulfinate was converted to **(+)-(*R*)-methyl p-chlorophenyl sulfoxide (1c)** in 92% yield with methylmagnesium iodide by a method analogous to that of Andersen.[20] Final purification was effected by column chromatography on silica gel and sublimation at 45° (0.035 mm). The compound had a melting point of 45.5–48.0°. The specific rotation was $[\alpha]^{25}D$ +124.7° (*c* 7.8, acetone). The infared spectrum ($CHCl_3$) showed a strong band at 1049 cm^{-1}. The nmr spectrum ($CDCl_3$–1% TMS) showed absorptions at δ 2.72 (3 H, s), 7.58 (4 H, A_2B_2).

Anal. Calcd for C_7H_7ClOS: C, 48.14; H, 4.04; S, 18.36; Cl, 20.30. Found: C, 48.23; H, 4.04; S, 18.36; Cl, 20.38.

(+)-(*R*)-Methyl p-t-Butylphenyl Sulfoxide (1f). Conversion of *t*-butylbenzene (Matheson Coleman and Bell) to **p-t-butylnitrobenzene** was effected in 56% yield using the nitration procedure of Brown[21] followed by separation of isomers by spinning band distillation at 10 mm. The isomeric purity was shown to be greater than 99% by vpc analysis. The compound had a boiling point of 78–83° (0.08–0.06 mm). The infrared spectrum (liquid film) showed strong bands at 1525 and 1350 cm^{-1}. The nmr spectrum ($CDCl_3$–1% TMS) showed signals at δ 1.35 (9 H, s), 7.83 (4 H, A_2B_2). A mixture of 147.5 g of **p-t-butylnitrobenzene** (0.825 mole) and 75 ml of ethanol was placed in a 500-ml Parr Shaker bottle with 1.50 g of 85% platinum oxide. Hydrogenation was carried out over the course of 8 hr at pressures of 3.4–1.0 atm of hydrogen. The reaction mixture was filtered through Celite and flash evaporated. Distillation of the residual oil gave 113.4 g of **p-t-butylaniline** (92%). The compound had a boiling point of 55.0–56.0° (0.04–0.03 mm). The infrared spectrum (liquid film) showed bands at 3450, 3350, and 3210 cm^{-1}. The nmr spectrum ($CDCl_3$–1% TMS) showed signals at δ 1.23 (9 H, s), 3.38 (2 H, s), 6.80 (4 H, A_2B_2). The amine was converted to **p-t-butylbenzenesulfinic acid** in 42% yield using a procedure analogous to those of Gattermann[18] followed by purification through the ferric sulfinate salt. The acid had a melting point of 59.0–63.0°. The infrared spectrum ($CHCl_3$) showed a strong band at 1082 cm^{-1}. The acid was converted to **p-t-butylbenzenesulfinyl chloride** and then to **(−)-menthyl (±)-p-t-butylbenzenesulfinate** by a sequence analogous to that of Herbrandson.[19] The mixture of diastereomers was treated with anhydrous hydrogen chloride in petroleum ether (bp 60–70°) and crystallized from this solvent. The procedure was repeated several times on the mother liquors giving a 73% yield of **(−)-menthyl (−)-p-t-butylbenzenesulfinate**. Final purification was effected by careful recrystallization from petroleum ether (bp 60–70°) to constant rotation. The melting point of the compound was 99.5–102.5°. The specific rotation was $[\alpha]^{25}D$ −171.9° (*c* 1.9, chloroform). The infrared spectrum (CCl_4) showed a strong band at 1146 cm^{-1}. The nmr spectrum ($CDCl_3$–1% TMS) had signals (*inter alia*) at δ 4.15 (1 H, m), 1.33 (9 H, s), 7.61 (4 H, A_2B_2). Treatment of the sulfinate with methylmagnesium iodide in a procedure analogous to that of Andersen[20] gave **(+)-(*R*)-methyl p-t-butylphenyl sulfoxide (1f)** in 66% yield after purification by column chromatography on silica gel and sublimation at 56° (0.05 mm). The compound had a melting point of 51.0–54.0° The specific rotation was $[\alpha]^{25}D$ +107.9° (*c* 2.4, acetone). The infrared spectrum ($CHCl_3$) showed a strong absorption at 1050 cm^{-1}. The nmr spectrum ($CDCl_3$–1% TMS) showed signals at δ 2.71 (3 H, s), 1.35 (9 H, s), 7.62 (4 H, s).

Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22; S, 16.33. Found: C, 67.44; H, 8.27; S, 16.25.

Measurement of Fluorescence Quenching. Solutions for fluorescence quenching experiments were prepared in 10-ml volumetric flasks by the addition of an aliquot of a stock solution of naphthalene and weighed portion of substrate. Aliquots of 3.0 ml were delivered into 13 mm o.d. Pyrex test tubes which had been washed carefully with Orvus (Proctor and Gamble), rinsed thoroughly, dried, and preconstricted to facilitate sealing. The samples were degassed by three freeze–pump–thaw cycles at 5×10^{-4} mm and sealed. If the fluorescence quenching experiments were to be done by the intensity method, the fluorescence spectra were obtained on an Aminco Bowman spectrophotofluorimeter exciting at 320 nm. If the experiments were to be done by the lifetime method, the fluorescence lifetimes were obtained on a TRW Model 75 A decay time fluorimeter. The data were then plotted as in Figure 3.

Absolute singlet lifetimes were measured directly on the TRW Model 75 A decay time fluorimeter or by employing the method of Berlman[11] on the Aminco Bowman spectrophotofluorimeter.

Measurement of Quantum Yields. Solutions for irradiation were prepared in 10-ml volumetric flasks as above. Aliquots of exactly 3.0 ml were delivered into each of two preconstricted 13 mm o.d. Pyrex test tubes and the remainder of the solution was placed in a third tube kept as a blank. The tubes were degassed and sealed as above. Irradiations were carried out in a merry-go-round apparatus. For irradiations at 366.0 nm Corning 737 and 052 glass filters were used to isolate the desired wavelength. For irradiations at 313.0 nm a Corning 757 glass filter and a circulating solution filter of 2.38 g of potassium chromate in 4500 ml of 1% sodium carbonate were employed. Potassium ferrioxalate actinometry[22] was used to measure light intensities. The literature procedure was modified slightly by the use of stock solutions of ferrioxalate rather than preparing it by precipitation.

In experiments to determine the quantum yield of disappearance of (±)-methyl *p*-chlorophenyl sulfoxide (**1c**), the sample tubes contained an internal standard of 0.005 *M* hexaethylbenzene. The disappearance of sulfoxide was determined by vpc analysis of samples and blanks on a Loenco Model 160 flame ionization gas chromatograph. Separation was effected on a 2 ft column of 10% Carbowax 20M at a temperature of 187°.

In experiments measuring the kinetics of the racemization reaction, the percentage of inversion of sulfoxide was determined by the comparison of the rotations of irradiated solutions and blanks on a Perkin-Elmer 141 polarimeter. Conversion was less than 6%

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and was corrected for back reaction. The data were plotted as in Figure 4.

Conclusion

The sensitized photoracemization of alkyl aryl sulfoxides has been shown to result from energy transfer from the singlet state of naphthalene. The possibility of exothermic electronic energy transfer has been ruled out spectroscopically. It is postulated that an exciplex is formed from an excited singlet state naphthalene molecule and a ground state molecule of the sulfoxide. This excited complex then undergoes radiationless decay converting electronic energy to vibrational energy partitioned between the two components of the exciplex. Enough vibrational energy appears in the aryl sulfinyl center to effect thermal pyramidal inversion with high efficiency. Steric and electronic effects on the rates of fluorescence quenching or photoracemization are small.

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Photochemistry of Quinoline and Some Substituted Quinoline Derivatives[1]

F. R. Stermitz, C. C. Wei, and C. M. O'Donnell

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80521. *Received September 5, 1969*

Abstract: Irradiation of quinoline and 8-methylquinoline in acidic ethanol yielded the 2- and 4-ethylquinolines. Irradiation in 95% ethanol yielded the 2-α-hydroxyethylquinolines together with the corresponding 1,2,3,4-tetrahydroquinolines. Irradiation of quinoline in *t*-butyl alcohol yielded 2-(2-hydroxy-2-methylpropyl)quinoline. Photoalkylation did not proceed in 2-propanol but instead a low yield of a reduced quinoline dimer occurred. If 2-substituted quinolines containing a γ-hydrogen were irradiated in inert solvents, an elimination corresponding to ketone type II cleavage would occur with quantum yields varying from 0.014 to 0.29 depending upon the structure of the starting quinoline. This reaction was shown (by quenching studies) to proceed through an excited singlet, probably of n–π^* configuration. The photoelimination had a McLafferty rearrangement counterpart in the electron-impact fragmentations of the 2-substituted quinolines.

Systematic studies on the photochemistry arising from the C=N portion of aza aromatic molecules are infrequent in the chemical literature in spite of the fact that ample evidence indicates that this should be a fruitful area of investigation. Indeed, electronic spectroscopy of aza aromatics, both in theory and in experiment, has developed side by side with that of the carbonyl group and the similarities obtaining between the two have been pointed out.[2] With few exceptions, however, the literature of organic photochemistry is lacking in studies which compare C=N photoreactivity in aza aromatics with knowledge of the excited states of these molecules.[3] One exception has been in the case of acridine, whose physical and organic photochemistry has been somewhat thoroughly investigated.[5] Surprisingly, this large body of work has not led to similar studies on other N-heteroaromatics. A second exception is the case of riboflavin, a very complex molecule whose photochemistry has engaged the attention of numerous groups of workers[6] over a considerable span of years. Our original interest[7] in this area arose from an accidental observation on the photolability in alcohol solution of the alkaloid papaverine. However, it was soon apparent that, beyond the discovery[7,8] of a somewhat novel variant of C=N photochemistry, the importance of future work lay in establishing the individual mechanistic details and generality[9] of aza aromatic photochemistry involving

(1) Photochemistry of N-Heterocycles. V. Previous Paper: F. R. Stermitz and C. C. Wei, *J. Amer. Chem. Soc.*, **91**, 3103 (1969). This work was supported in part by Grant GM-14525 from the National Institute of General Medical Sciences, U. S. Public Health Service.

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(3) The voluminous work on nucleic acid derivatives[4] up to the present time has almost invariably dealt with two basic reactions (exemplified by thymine dimerization and uracil hydration) which do not appear to involve the C=N of these molecules directly. However, purine and pyrimidine bases do undergo the type of reaction we are here discussing although such reactivity has not yet been demonstrated in the more complex biologically important derivatives.

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