1070 (1971).
(47) F. Ramirez, K. Tasaka, and R. Hershberg, *Phosphorus*, **2**, 41 (1972).
(48) F. Ramirez, G. V. Loewengart, E. A. Tsolis, and K. Tasaka, *J. Am. Chem. Soc.*, **94**, 3531 (1972).
(49) W. C. Archie, Jr., and F. H. Westheimer, *J. Am. Chem. Soc.*, **95**, 5955 (1973).
(50) G. Aksness and A. I. Eide, *Phosphorus*, **4**, 209 (1974).
(51) The stereochemistry of the formation (and decomposition) of octahedral six-coordinate phosphorus from (and to) trigonal bipyramidal phosphorus is not considered in this discussion.
(52) F. Ramirez, S. L. Glaser, P. Stern, I. Ugi, and P. Lemmen, *Tetrahedron*, **29**, 3741 (1973).
(53) F. H. Westheimer in *Adv. Enzymol.*, **25**, 441 (1961).
(54) (a) S. J. Benkovic and K. J. Schray, "The Enzymes", 3d ed, Vol. 7, P. D. Boyer, Ed., Academic Press, New York, N.Y., 1973; (b) D. C. Watts, *ibid.*, Vol. 8, Chapter 12; (c) V. P. Hollander, *ibid.*, Vol. 4, Chapter 19; (d) S. Pantremoli, E. Grazi, and A. Accorsi, *J. Biol. Chem.*, **242**, 61 (1967).
(55) D. A. Usher, D. I. Richardson, Jr., and D. G. Oakenfull, *J. Am. Chem. Soc.*, **92**, 4699 (1970).
(56) A. P. Mathias and B. R. Rabin, *Biochem. J.*, **103**, 62P (1967).
(57) W. Stillwell, G. Steinman, and R. L. McCarl, *Bioorg. Chem.*, **2**, 1 (1972), and references cited therein.
(58) The extraction was carried out with diethyl ether in the particular case of $[[(CH_3)_2CH]_2CHO](C_6H_5CH_2O)P(O)ONa$ to avoid the loss of some salt in the dichloromethane.
(59) F. Ramirez, B. Hansen, and N. B. Desai, *J. Am. Chem. Soc.*, **84**, 4588 (1962).
(60) (a) D. M. Brown and D. A. Usher, *J. Chem. Soc.*, 6547 (1965); (b) D. S. Frank and D. A. Usher, *J. Am. Chem. Soc.*, **89**, 6360 (1967).
(61) NOTE ADDED IN PROOF. The pyrophosphate **1** is normally prepared from *N*-methylpyridinium (1,2-dimethylethenylene) phosphate (analogous to **3**) by reaction with 0.5 mol equiv of phosgene. If this salt is allowed to react with an excess of phosgene for an extended period, the product is 1,2-dimethylethenylene phosphorochloridate[18] instead of **1**. This observation facilitates the preparation of the highly reactive phosphorochloridate reagent which can be used for the preparation of **2**.

Quenching of Aromatic Hydrocarbon Singlets and Aryl Ketone Triplets by Alkyl Disulfides

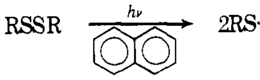
William L. Wallace,[1a] Richard P. Van Duyne,* [1b] and Frederick D. Lewis* [1c]

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received September 19, 1975*

Abstract: Quenching of aromatic hydrocarbon fluorescence and aryl ketone phosphorescence by alkyl disulfides has been investigated. Two quenching mechanisms, charge-transfer stabilized exciplex formation and electronic energy transfer, have been considered. Charge transfer appears to be unimportant for the aromatic hydrocarbons and ketones studied. Endothermic singlet–singlet energy transfer is more efficient than predicted by the Arrhenius equation. Excitation of vibrationally excited ground-state disulfide molecules provides a possible explanation for efficient endothermic quenching. Low-temperature uv spectroscopy indicates that the long-wavelength absorption of disulfides consists predominately of hot-band transitions.

Introduction

The spectroscopic[2,3] and photochemical[4-9] properties of disulfides have attracted substantial interest. The optical rotatory properties of chiral disulfides provide a probe of protein structure and environment.[3] Photochemical cleavage of the sulfur–sulfur bonds can result in inactivation of sulfur-containing proteins.[5] Since disulfides do not absorb strongly in the near ultraviolet,[2] photochemical inactivation of proteins may involve quenching of aromatic amino acid excited states by disulfide. Walling and Rabinowitz[6] demonstrated that sulfur–sulfur homolysis of alkyl disulfides can be sensitized by aromatic hydrocarbons (eq 1); however, the mechanism of sensitization was not investigated. In a recent series of papers, Hayon and co-workers[7] have established that quenching of triplet tyrosine and tryptophan by the cyclic disulfide thioctic acid in aqueous solution occurs by an electron transfer mechanism to form the disulfide radical anion (eq 2). The radical anion subsequently undergoes sulfur–sulfur cleavage (eq 3).[10]



$$\mathrm{RSSR} \xrightarrow{h\nu} 2\mathrm{RS}\cdot \qquad (1)$$

$$^3\mathrm{Trp} \text{ or } {}^3\mathrm{Tyr} + \mathrm{RSSR} \rightarrow \mathrm{Trp}\cdot^{+} \text{ or } \mathrm{Tyr}\cdot^{+} + \mathrm{RSSR}\cdot^{-} \qquad (2)$$

$$\mathrm{RSSR}\cdot^{-} \rightarrow \mathrm{RS}\cdot^{-} + \mathrm{RS}\cdot \qquad (3)$$

Quenching of aromatic ketone $^3n,\pi^*$ excited states by disulfides,[8] sulfides,[11] and thiols[12] has been postulated to involve partial charge transfer from sulfur to the half-vacant carbonyl n orbital. Kampmeier[8b] has proposed a charge-transfer stabilized exciplex mechanism for the ketone-sensitized carbon-sulfur homolysis of benzyl disulfide.

$$\begin{aligned} &{}^3\mathrm{Ketone} + \mathrm{RSSR} \\ &\longrightarrow [{}^3\mathrm{Ketone}\cdots\mathrm{RSSR} \longleftrightarrow \mathrm{Ketone}\cdot^{-}\ \mathrm{RSSR}\cdot^{+}] \\ &\qquad\qquad\downarrow \\ &\mathrm{Ketone} + \mathrm{R}\cdot + \cdot\mathrm{SSR} \end{aligned} \qquad (4)$$

The ability of disulfides to act as either electron donors or acceptors is consistent with their high electron affinities[2b,10] and low ionization potentials.[13]

Disulfides have been observed to quench the fluorescence of proteins and their constituent amino acids,[4c,6a,8] aromatic hydrocarbons, and biacetyl.[7a] Unlike the quenching of triplet tyrosine, quenching of singlet tyrosine does not result in electron transfer.[7a] A singlet–singlet energy transfer mechanism for tyrosine quenching

$$^1\mathrm{Tyr} + \mathrm{RSSR} \rightarrow \mathrm{Tyr} + {}^1\mathrm{RSSR} \qquad (5)$$

and an electron transfer mechanism (eq 2) for tryptophan quenching have been proposed by Shafferman and Stein.[5c] Fluorescence quenching of tyrosine and tryptophan containing peptides requires close approach of fluorescer and disulfide, leading Cowgill[9b] to propose vibrational dissipation of the excitation energy.

Investigations of disulfide quenching mechanisms have been hindered by the absence of information about the singlet and triplet excited states of disulfides. Neither fluorescence nor phosphorescence has been detected for disulfides. The broad,

Table I. Singlet Quenching Data for Di-*tert*-butyl Disulfide

Aromatic hydrocarbon (M)	Solvent	τ_0, ns	$k_q \times 10^{-8}$, $M^{-1}\,s^{-1}$
Naphthalene (4×10^{-2})	C_6H_6	106	27 ± 2
Triphenylene (1×10^{-2})	C_6H_6	38.6	1.6 ± 0.1
	CH_3CN	37.0	2.7 ± 0.2
Phenanthrene (3×10^{-3})	C_6H_6	57.4	1.2 ± 0.1
	CH_3CN	57.5	2.2 ± 0.1
Chrysene (2.7×10^{-4})	C_6H_6	44.4	0.31 ± 0.02
	CH_3CN	44.3	0.74 ± 0.1
Pyrene (1.2×10^{-4})	C_6H_6	304	0.14 ± 0.01
	CH_3CN	282	0.28 ± 0.01
Fluoranthene (2.8×10^{-4})	C_6H_6	47.8	0.17 ± 0.01

Table II. Singlet Quenching Data for Various Disulfides in Benzene

Aromatic hydrocarbon[a] (M)	Disulfide	$k_q \times 10^{-8}$, $M^{-1}\,s^{-1}$
Triphenylene (1×10^{-2})	Di-*n*-butyl	5.7 ± 0.2
Phenanthrene (3×10^{-3})	Di-*n*-butyl	3.6 ± 0.1
Chrysene (2.5×10^{-4})	Di-*n*-butyl	1.1 ± 0.2
Pyrene (1.0×10^{-4})	Di-*n*-butyl	0.69 ± 0.04
Fluoranthene (2×10^{-4})	Di-*n*-butyl	0.78 ± 0.02
	Diisopropyl	0.23 ± 0.02
	Diphenyl	3 ± 1
	Thioctic acid	40 ± 1

[a] See Table I for aromatic hydrocarbon singlet lifetimes.

long-wavelength absorption bands of disulfides are composed of two nearly degenerate transitions and are devoid of vibrational structure.[2] In order to provide information about the mechanism(s) of disulfide quenching and the energies of disulfide excited states, we have investigated the kinetics of disulfide quenching for a series of singlet aromatic hydrocarbons and several triplet aryl ketones.

Experimental Section

Materials. Diisopropyl, di-*tert*-butyl, and di-*n*-butyl disulfide were obtained from Aldrich Chemical Co. and were distilled under vacuum before use. Their purity was checked by GLC and was found to be equal to or greater than 99%. Racemic 6,8-dithiooctanoic acid (thioctic acid) was obtained from Aldrich Chemical Co. and was recrystallized twice from cyclohexane (mp 58.0–59.5 °C). Diphenyl disulfide was recrystallized four times from ethanol (mp 59–60 °C). Methyl *n*-butyl disulfide was synthesized according to a published procedure[14a] and was purified by vacuum distillation in the absence of light. Its purity was determined to be greater than 99% by GLC. Benzophenone was obtained from Aldrich Chemical Co. and was recrystallized four times from ethanol. Acetophenone was recrystallized twice from ethanol–water and vacuum distilled. Photosensitizer grade benzil from Baker was used without further purification. Anthraquinone was recrystallized twice from benzene and then vacuum sublimed twice at 120 °C and 0.15 Torr (mp 283–284 °C). 2-Methylanthraquinone was recrystallized twice from ethanol and vacuum sublimed twice at 150 °C and 0.1 Torr (mp 174–175 °C). Zone-refined naphthalene and fluoranthene were purchased from Aldrich Chemical Co. and were used without further purification. Photosensitizer grade chrysene was obtained from Baker, recrystallized from ethanol, and then vacuum sublimed. The purification of triphenylene, phenanthrene, and pyrene has been described.[14b] Fisher spectrograde benzene was refluxed twice over phosphorus pentoxide for 24 and 12 h, respectively, and a center 70% cut taken. Burdick and Jackson spectroquality acetonitrile was used as received for singlet quenching studies but was distilled from phosphorus pentoxide under nitrogen with a center cut taken for triplet quenching studies. Matheson, Coleman, and Bell EPA suitable for phosphorimetry was used as received for the low-temperature absorption studies.

Apparatus. Singlet lifetimes were measured using the time-correlated single-photon counting technique as described by Ware.[15] Triplet lifetimes were measured using a flash apparatus that has previously been described.[16] Where possible, triplet lifetimes were measured using both techniques and the lifetimes were found to agree within the error limits quoted. All fluorescence spectra and relative fluorescence intensity measurements were made using the Perkin-Elmer Model MPF-2A fluorescence spectrophotometer. A Polyscience Model 80 temperature controller used with a Model 1818 Beckman thermocirculator low temperature accessory provided the variable temperature capability necessary to obtain the Arrhenius parameters. The accuracy and precision of the system were estimated at ±0.5 °C for temperatures below 50 °C and ±1 °C for temperatures above 50 °C. All uv spectra both at 25 °C and 77 K were taken with a Cary 14 recording spectrophotometer. Low-temperature spectra at 77 K using clear EPA glasses were measured using a 0.8 cm o.d. quartz sample tube which was inserted into a liquid nitrogen filled quartz tube (1.0 cm i.d. and 1.2 cm o.d.) surrounded by a Dewar filled with liquid nitrogen above the optical path and evacuated to prevent water condensation in the optical path. All GLC disulfide analyses were carried out using a 6 ft × 0.125 in. column packed with 5% FFAP on Chromasorb G 70–80 mesh. Both isothermal and programmed temperature analyses were made using a Hewlett-Packard Model 5750 research chromatograph with a dual flame ionization detector.

Methods. All solutions prepared for this study were degassed either by several freeze–pump–thaw cycles or by bubbling prepurified nitrogen through the solution for at least 20 min. Singlet lifetimes measured using solutions degassed by either technique differed by less than 1%. The overall precision of the singlet lifetimes reported in this paper is ± 4%.

Quantum yields for the formation of di-*n*-butyl disulfide from methyl *n*-butyl disulfide upon direct photolysis were obtained by irradiating 0.1 M degassed benzene solutions of the asymmetric disulfide with the output of a 450-W Hanovia medium-pressure mercury-vapor lamp filtered by a potassium chromate solution to isolate the 313-nm mercury line. Quantum yields for the sensitized formation of di-*n*-butyl disulfide in benzene and acetonitrile were measured by irradiating degassed 0.1 M methyl *n*-butyl disulfide solutions with a 200-W Hanovia medium-pressure mercury-vapor lamp using overlapping Corning CS 0-52 and CS 7-54 filters to isolate the 365-nm mercury line. All tubes were irradiated on a Rayonet Model MGR-500 merry-go-round apparatus and benzophenone–benzhydrol actinometers were used to measure light intensities.[17]

Results

Singlet Quenching. The fluorescence of a series of aromatic hydrocarbons is quenched by alkyl disulfides. Rate constants for singlet quenching (Tables I and II) were determined from the variation of fluorescer lifetime (τ_F) with the quencher concentration using the Stern–Volmer equation

$$\tau_F{}^0/\tau_F = 1 + k_q\tau_F[Q] \tag{6}$$

Lifetimes in the presence and absence of quencher were measured by the time-correlated single-photon counting technique on highly degassed solutions. Fluorescence lifetimes in the absence of quencher are comparable to literature values[18] indicative of the purity of solvents and fluorescers. Comparison of emission spectra with literature spectra[18] indicates that excimer formation can be eliminated as a complicating factor. Values of k_q were obtained from linear Stern–Volmer plots (five or more points, correlation coefficients >0.99). Quenching rate constants are highly reproducible, having a precision of ±10%. The conventional technique of fluorescence intensity quenching could not be used for most of the aromatic hydrocarbons due to competitive absorption (Figure 1) by the disulfides at the wavelengths necessary for fluorescence excitation. Competitive absorption does not affect lifetimes measured by single-photon counting.

Results for quenching of several aromatic hydrocarbons by di-*tert*-butyl disulfide in benzene and acetonitrile are given in Table I. The observed rates are all less than the rate constants for diffusion-controlled quenching in benzene ($k_{diff} \sim 5 \times 10^9$ $M^{-1}\,s^{-1}$)[19] and acetonitrile ($k_{diff} \sim 1.5 \times 10^{10}$ $M^{-1}\,s^{-1}$).[20] Rate constants are faster in acetonitrile than in benzene by a

Table III. Triplet Quenching Data

Aryl ketone	Solvent	τ_0, μs	Disulfide	$k_q \times 10^{-8}$ $M^{-1}\,s^{-1}$
Benzophenone	C_6H_6	5 ± 1	Di-*tert*-butyl	1.4 ± 0.4
	C_6H_6	5 ± 1	Di-*n*-butyl	4.8 ± 0.8
	CH_3CN	50 ± 1	Di-*tert*-butyl	2.7 ± 0.3
	CH_3CN	50 ± 1	Di-*n*-butyl	8.4 ± 0.9
Acetophenone	CH_3CN	43 ± 1	Di-*n*-butyl	12 ± 4
Benzil	C_6H_6	58 ± 2	Di-*n*-butyl	0.0053 ± 0.0005

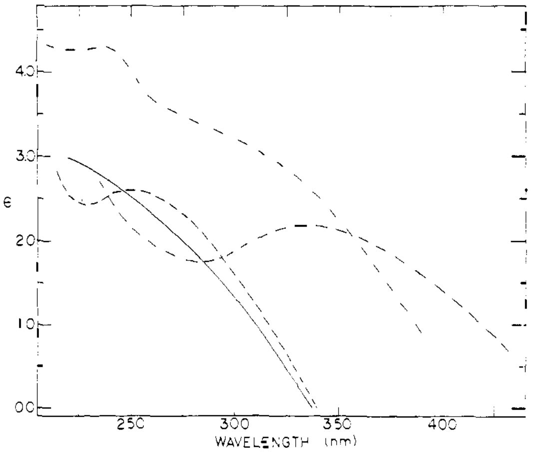


Figure 1. Absorption spectra of (—) di-*tert*-butyl disulfide, (- - - -) di-*n*-butyl disulfide, (-·-·-·-) thioctic acid, and (-··-··-··-) diphenyl disulfide in acetonitrile at room temperature.

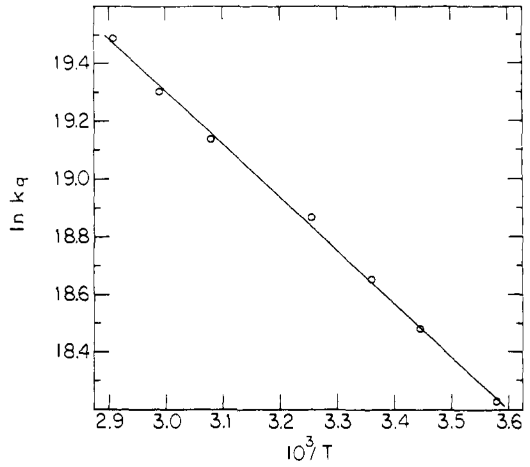


Figure 2. Arrhenius plot for the quenching of pyrene by di-*n*-butyl disulfide in acetonitrile.

factor of 2.0 ± 0.3, which is independent of the magnitude of the quenching constant. The rate constants for singlet quenching by di-*n*-butyl disulfide in benzene (Table II) are consistently faster than those for quenching by di-*tert*-butyl disulfide by a factor of 3.8 ± 0.9. The rate constant for quenching of fluoranthene by diisopropyl disulfide is intermediate between the values for di-*n*-butyl and di-*tert*-butyl disulfide; whereas substantially faster rate constants were observed for quenching by diphenyl disulfide and thioctic acid.

The alkyl disulfides and aromatic hydrocarbons are stable under the conditions used for lifetime measurements. The exclusive photochemical reaction of di-*n*-butyl disulfide is highly reversible sulfur-sulfur cleavage (vide infra).[4] Di-*tert*-butyl disulfide undergoes moderately efficient carbon-sulfur cleavage;[8b,c] however, radical recombination may predominate in inert solvents. Thioctic acid undergoes polymerization upon irradiation[4] and thus the quenching rate constant in Table II is subject to some uncertainty.

The temperature dependence of the fluorescence quenching rate constant was determined for pyrene and di-*n*-butyl disulfide in acetonitrile. Since pyrene can be excited at wavelengths where there is no competitive absorption, fluorescence intensity quenching could be utilized. An Arrhenius plot for quenching data obtained between 6 and 71 °C is given in Figure 2. Rate constants are corrected for changes in the pyrene singlet lifetime. Activation parameters from the least-squares fit of the data in Figure 2 are $E_a = 3.65 \pm 0.06$ kcal/mol and $\Delta S^{\ddagger} = -11.2 \pm 0.3$ eu.

Triplet Quenching. Several aromatic ketones with lowest n,π* triplet states display room-temperature phosphorescence in purified, highly degassed solvents.[21] Room-temperature phosphorescence can be quenched by added disulfide. Rate constants for triplet quenching (Table III) were determined from the variation of room-temperature phosphorescence intensities as a function of disulfide concentration. The extremely low concentrations of disulfide needed to quench ketone triplets, 10^{-4}–10^{-6} M, made it unnecessary to correct for competitive absorption. Quenching of benzophenone by either di-*n*-butyl or di-*tert*-butyl disulfide is faster in acetonitrile than in benzene by a factor of 1.9 ± 0.1. The ratio of rate constants for benzophenone quenching by di-*n*-butyl vs. di-*tert*-butyl disulfides is 3.3 ± 0.1 in both solvents. The rate constant for di-*n*-butyl disulfide quenching of acetophenone is greater than that for quenching of benzophenone; whereas quenching of benzil is substantially slower.

In view of Kampmeier's report[8b] of rapid disulfide quenching of 2-methylanthraquinone, an effort was made to investigate it in this present study. Room-temperature emission can be observed from anthraquinone and 2-methylanthraquinone; however, the emission appears to have two components and the ratio of their intensities is highly sensitive to irradiation.[22,23] Thus we have been unable to obtain reliable results for the anthraquinone or 2-methylanthraquinone-disulfide systems.

Irradiation of Methyl *n*-Butyl Disulfide. Irradiation of mixtures of alkyl disulfides is known to result in disproportionation to a nearly statistical mixture of asymmetric and symmetric disulfides.[4,14a]

$$\mathrm{RSSR} + \mathrm{R'SSR'} \xrightarrow{h\nu} \underset{1}{\mathrm{RSSR}} + \underset{2}{\mathrm{RSSR'}} + \underset{1}{\mathrm{R'SSR'}} \tag{7}$$

We employed the reverse of this process to determine whether triplet quenching results in disulfide sulfur-sulfur cleavage. Direct irradiation (313 nm) of 0.1 M methyl *n*-butyl disulfide leads to the same steady-state mixture of symmetric and asymmetric disulfides as is obtained by irradiating an equimolar mixture of the symmetric disulfides alone. There is no decrease in the total disulfide concentration, even when irradiation is continued for five times the duration required to obtain the steady state. Thus sulfur-sulfur cleavage must be the exclusive primary process for primary alkyl disulfides. An

Table IV. Quantum Yields for Methyl *n*-Butyl Disulfide Disproportionation

Aryl ketone	Solvent	Time, s	Φ[a]
None	C_6H_6	650	6.5
Acetophenone	C_6H_6	650	2.9
Benzophenone	C_6H_6	915	2.8
	CH_3CN	915	3.1
Benzil	C_6H_6	915	0.5

[a] Quantum yield for di-*n*-butyl disulfide formation.

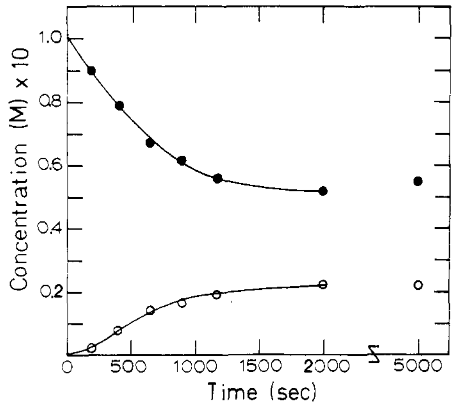


Figure 3. Concentration vs. time for the disappearance of 0.1 M methyl *n*-butyl disulfide (●) and the formation of di-*n*-butyl disulfide (○) upon photolysis at 313 nm in benzene.

induction period of several minutes is observed for disulfide disproportionation. The quantum yield for formation of di-*n*-butyl disulfide (Table IV) increases from 3.6 at 200 s to a maximum value of 6.5 at 400 s and then remains constant until the solution approaches the steady state (Figure 3). The high quantum yields are indicative of the chain mechanism previously proposed for disulfide disproportionation.[14a] The induction period is similar to that recently reported for acid-catalyzed disproportionation of an asymmetric disulfide[24] and (presumably) is due to the presence of a free-radical scavenger which is consumed in the early stages of the photolysis.

The benzophenone-sensitized photolysis (365 nm) of 0.1 M methyl *n*-butyl disulfide in benzene gives results similar to those obtained for direct photolysis, except that the maximum quantum yield for di-*n*-butyl disulfide formation is 2.8 (Table IV). Assuming a similar triplet quenching rate for methyl *n*-butyl and di-*n*-butyl disulfides, 0.1 M disulfide should quench all of the benzophenone triplets. Furthermore, the light intensities for direct and sensitized irradiation are nearly identical. Thus there is no obvious explanation for the lower quantum yield for sensitized vs. direct irradiation. The quantum yield for acetophenone sensitized di-*n*-butyl disulfide formation is similar to that for benzophenone sensitization. The lower quantum yield for benzil sensitization reflects the failure of 0.1 M methyl *n*-butyl disulfide to quench all of the benzil triplets. The effect of solvent on the benzophenone-sensitized quantum yield is small.

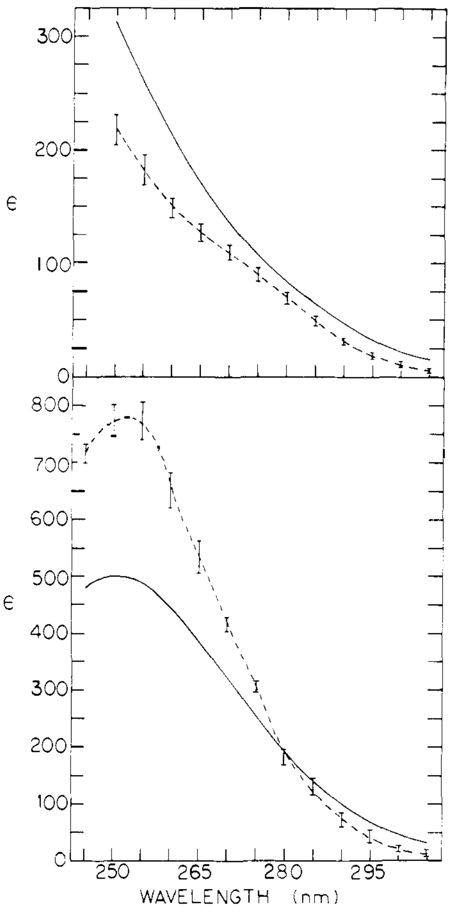


Figure 4. Absorption spectra of di-*tert*-butyl disulfide (top) and di-*n*-butyl disulfide (bottom) at 25 °C (—) and 77 K (- - - - -) in EPA.

Disulfide Absorption Spectra. Room-temperature absorption spectra of several disulfides in acetonitrile are shown in Figure 1. The broad long-wavelength absorption bands are devoid of structure as previously reported for solution[2a] and vapor-phase spectra.[25] Absorption spectra of di-*tert*-butyl and di-*n*-butyl disulfide were recorded at room temperature and 77 K in EPA solvent (Figure 4). Low-temperature spectra are corrected for solvent volume contraction.[26] Both disulfides show decreased long-wavelength absorption at 77 K, indicative of hot-band contributions to the room-temperature spectra. A weak shoulder at 270 nm is barely discernible in the 77 K spectrum of di-*tert*-butyl disulfide. This shoulder may correspond to the low oscillator strength transition at 277 nm predicted by Boyd;[2c] however, this assignment cannot be made with certainty due to the experimental error involved in measuring the low-temperature spectra.

Discussion

Singlet Quenching. Several mechanisms for singlet quenching via full or partial electron transfer (eq 2 and 4) and long-range or collisional energy transfer (eq 5) will be considered. Weller and co-workers[27] have extensively studied the fluorescence quenching of aromatic hydrocarbons by amines and attributed quenching to the formation of an exciplex by transfer of an electron from a ground-state amine to the excited aromatic hydrocarbon. Rate constants for fluorescence quenching are dependent upon the free-energy change for electron transfer, which can be calculated from the donor oxidation potential, the acceptor reduction potential, and the fluorescer singlet energy according to

$$\Delta G_{\mathrm{et}} = E(\mathrm{D/D^+}) - E(\mathrm{A^-/A}) - E_{\mathrm{s}} + \mathrm{const} \tag{8}$$

where the constant term is the energy required to bring the radical ion pair to the encounter distance. Fluorescence quenching rate constants increase with decreasing ΔG_{et} until a limiting value near the diffusion-controlled limit is reached when $\Delta G_{\mathrm{et}} \leq -5$ kcal/mol.

If exciplex formation is responsible for fluorescence quenching, rate constants for fluorescence quenching should be dependent upon the electron donor and acceptor properties of the aromatic hydrocarbon excited state (Table V) and the disulfide ground state.[8b,11b,27-29] Comparison of the kinetic

Table V. Charge Transfer Parameters for Aromatic Hydrocarbons and Aryl Ketones

Aromatic hydrocarbon or ketone	$^{1,3}E$, eV (kcal/mol)	$E(D/D\cdot^+)$,[f] eV	$E(A\cdot^-/A)$,[f] eV	$-^{1,3}E + E(D/D\cdot^+)$ eV	$-^{1,3}E - E(A\cdot^-/A)$, eV
Naphthalene	3.92 (90.2)[a]	1.77	−2.45	−2.15	−1.47
Triphenylene	3.61 (83.2)[a]	1.72	−2.40	−1.89	−1.21
Phenanthrene	3.58 (82.4)[b]	1.67	−2.35	−1.91	−1.23
Chrysene	3.44 (79.2)[a]	1.57	−2.27	−1.87	−1.17
Pyrene	3.34 (76.9)[a]	1.33	−2.01	−2.01	−1.33
Acetophenone	3.21 (74.0)[c]	2.55[c]	−1.99[g]	−0.66	−1.22
Benzophenone	2.99 (68.9)[c]	2.37[c]	−1.72[g]	−0.62	−1.27
Benzil	2.33 (53.7)[d]		−1.04[g]		−1.29
Anthraquinone	2.71 (62.4)[d]		−0.89[h]		−1.82
2-Methylanthraquinone	2.73 (63)[e]		−0.89[i]		−1.82

[a] I. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", Academic Press, New York, N.Y., 1965. [b] R. N. Nurmukhametov, *Russ. Chem. Rev.*, **35,** 473 (1966). [c] R. O. Loufty and R. O. Loufty, *J. Phys. Chem.*, **77,** 336 (1973). [d] J. G. Calvert and J. N. Pitts, "Photochemistry", Wiley, New York, N.Y., 1966. [e] Reference 8b. [f] V. D. Parker, *J. Am. Chem. Soc.*, **96,** 5656 (1974). [g] C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems", Marcel Dekker, New York, N.Y., 1970. [h] M. Peover, "Electroanalytical Chemistry", Vol. 2, A. J. Bard, Ed., Marcel Dekker, New York, N.Y., 1967. [i] Value for anthraquinone assumed.

Table VI. Quenching Data and Ionization Potentials for Alkyl Sulfides

Aromatic hydrocarbon or ketone	Quencher	IP,[a] eV	$k_q \times 10^{-8}$, $M^{-1} s^{-1}$ [b]
Naphthalene	Diethyl sulfide	8.44	0.05
Naphthalene	Di-*tert*-butyl sulfide	8.07	0.06
Benzophenone	Diethyl sulfide	8.44	4
Benzophenone	Di-*n*-butyl sulfide	8.22	4 (8)[c]
Benzophenone	Di-*tert*-butyl sulfide	8.07	1 (0.5)[c]

[a] Data from ref 13. [b] J. V. Auping and F. D. Lewis, unpublished results. [c] Data from ref 11b.

data in Table I with the charge-transfer parameters in Table V show poor correlations with either excited-state donor ($-E_s + E(D/D^+)$) or acceptor ($-E_s - E(A^-/A)$) ability. Charge transfer from disulfide to excited aromatic hydrocarbons is clearly incompatible with the faster rate constants for singlet quenching for di-*n*-butyl vs. di-*tert*-butyl disulfide, in light of the lower ionization potential for di-*tert*-butyl disulfide (8.17 vs. 8.61 eV).[13,30] Alkyl sulfides have lower ionization potentials than the corresponding disulfides;[13] however, rate constants for quenching of naphthalene fluorescence by diethyl or di-*tert*-butyl sulfide (Table VI) are significantly slower than the rate constant for di-*n*-butyl disulfide quenching. Further evidence against electron-transfer quenching is provided by the modest increase in rate constant with solvent polarity (Table I).[21a] The small solvent effect may only reflect the faster rate of diffusion in acetonitrile vs. benzene.

The absence of a correlation between fluorescence quenching kinetics and charge-transfer parameters apparently rules out either full electron transfer or charge-transfer stabilized exciplex formation as the mechanism for singlet quenching. Calculation of ΔG_{et} according to eq 8 gives values which are at least several kilocalories/mole endothermic for all the energy transfer systems studied. Thus our results do not rule out electron-transfer quenching in cases where ΔG_{et} is exothermic. Some biological energy-transfer systems probably meet this qualification.[5c]

Singlet-singlet energy transfer (eq 5) can occur via long-range or short-range (collisional) mechanisms,[31] both of which require that rate constants be dependent upon spectral overlap of donor fluorescence and acceptor absorption. Spectral overlap is in turn related to singlet energy. Figure 5 shows the linear dependence of log k_q for di-*tert*-butyl and di-*n*-butyl disulfide

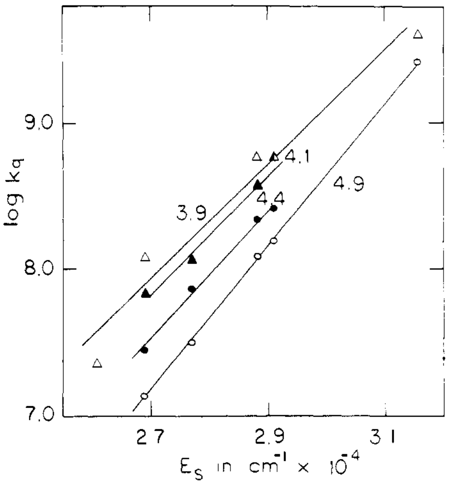


Figure 5. Log of quenching rate constants vs. donor singlet energy to: △, hexyl azide in benzene; ○, di-*tert*-butyl disulfide in benzene; ●, di-*tert*-butyl disulfide in acetonitrile; and ▲, di-*n*-butyl disulfide in benzene. Numbers are slopes in cm mol × 10^4.

quenching upon fluorescer singlet energy. The observed increase in k_q values for fluoranthene[32] quenching by alkyl disulfides < diphenyl disulfide < thioctic acid (Table II) is consistent with decreasing quencher singlet energy, as judged by the positions of the onset of absorption (Figure 1). Singlet-singlet energy transfer also requires that a singlet excited state of the disulfide be populated. The conditions used by Walling and Rabinowitz[6] for naphthalene-sensitized sulfur-sulfur cleavage of diisobutyl disulfide (0.2 M) should ensure that >95% of the naphthalene singlets are quenched by disulfide. Since the initial rate of product formation is independent of the fraction of light absorbed by the disulfide or fluorescer, singlet quenching must result in efficient population of the disulfide singlet excited state. Shafferman and Stein[5c] have also demonstrated that singlet sensitization of dithioglycolic acid by tyrosine results in the same product ratios as direct photolysis.

The weak ultraviolet absorption of the alkyl disulfides at the wavelengths of aromatic hydrocarbon fluorescence (Figure 1) allows both the long-range Förster[33] and "trivial" emission-reabsorption[31] mechanisms for singlet-singlet energy transfer to be ruled out. Thus energy transfer must require close approach or collision of aromatic hydrocarbon and disulfide. Cowgill[9b,c] has demonstrated that fluorescence quenching of tryptophan and tyrosine residues by disulfides requires an encounter distance of less than 7 Å. Short-range singlet-singlet or triplet-triplet energy transfer can also occur via an exchange interaction mechanism (vide infra).[34] Sandros[35] has observed that rate constants for triplet-triplet exchange energy transfer between many energy donor-acceptor pairs obey the empirical relationship

$$k_q = k_{\text{diff}} \exp(-\Delta E/RT)/(1 + \exp(-\Delta E/RT)) \qquad (9)$$

where k_{diff} is the diffusion-controlled rate constant and ΔE is the difference in acceptor and donor singlet or triplet energies. For endothermic energy transfer ($\Delta E > 0$) the energy deficiency can be provided by ground-state vibrational energy. The slope of a plot of log k_q vs. ΔE is predicted to be 21.0×10^{-4} cm mol. This predicted slope differs substantially from the results for alkyl disulfide quenching shown in Figure 5.

Endothermic energy transfer has been observed to be more rapid than predicted by the Arrhenius equation for a number of cases in which the energy donor or energy acceptor has substantially different ground- and excited-state geometries.[14a,31,36-42] Such behavior has been called "nonclassical" energy transfer by Hammond.[36] Most cases of nonclassical energy transfer involve molecules which differ in ground- and excited-state geometry by virtue of torsion about a double bond (*cis*-stilbene and its derivatives,[36] conjugated polyenes,[37] oxime ethers,[38] azomethine dyes[39]) or single bond (biphenyl,[40] benzil[41]). Extended Hückel molecular orbital calculations[2c] show that the energies of the two highest occupied molecular orbitals (HOMO) of dimethyl disulfide vary considerably with CSSC dihedral angle (Figure 6). The total ground-state energy is minimized for dihedral angles of about 90°, where the highest occupied molecular orbitals are nearly degenerate. The energy of the lowest unoccupied molecular orbital (LUMO) decreases slowly with dihedral angle. The absence of disulfide emission could result from the large difference in ground-state and excited-state equilibrium geometries or the dissociative nature of the excited state. Unfortunately the quantum yield for sulfur-sulfur cleavage could not be determined due to the complication of thiyl radical recombination. The high quantum yield for disulfide disproportionation (Table IV) requires a moderate to high (≥6.5) chain length, but the quantum yield for the initial sulfur-sulfur cleavage step could be significantly less than unity.

The schematic energy-level diagram shown in Figure 6 provides a possible explanation for the efficient endothermic energy transfer observed for alkyl disulfide quenchers (Figure 5). Excitation of vibrationally excited disulfide ground-state molecules is energetically advantageous, since an increase in HOMO energy upon sulfur-sulfur torsion is accompanied by a decrease in LUMO energy (Figure 6). The decrease in LUMO energy with dihedral angle may be greater for di-*n*-butyl and di-*tert*-butyl disulfide than for dimethyl disulfide, due to increased steric repulsion of the alkyl groups.[43] Similar "hot-band" models for nonclassical energy transfer[31] have previously been proposed to explain results for azides[36a,14b] and benzil.[41]

According to Dexter's theory, the rate constant for exchange-induced energy transfer, k_{et} (s^{-1}), is determined by the exchange interaction energy, U_e (cm^{-1}), and the spectral overlap integral, J (cm),

$$k_{\text{et}} = (4\pi^2/h)U_e^2 \int f_D(\nu)\epsilon_A(\nu)d\nu = (4\pi^2/h)U_e^2 J \qquad (10)$$

Unfortunately, U_e cannot be expressed in terms of experimentally measurable parameters[34] and its quantum mechanical evaluation is extremely tedious and subject to large error.[46] Engel and Steel[44] have evaluated U_e experimentally using eq 10 and measured values of k_{et} and J for the quenching of aromatic hydrocarbon singlets by azoalkanes. Using a different approach, Hoytink[45] has estimated values of U_e for the quenching of aromatic hydrocarbon singlets by oxygen ($^3\Sigma_g^-$). These results indicate, at least for the energy donor-acceptor systems studied, that typical values of U_e fall in the range of 10-100 cm^{-1}. Using the approach applied to azoalkanes by Engel and Steel, a value of 200 ± 50 cm^{-1} for U_e was calculated using an extrapolated value for k_q of $5 \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$ for naphthalene quenched by di-*n*-butyl disulfide in benzene as derived from Figure 5. This energy donor-acceptor system was chosen because it exhibited the greatest spectral overlap ($J = 11.9 \times 10^{-7}$ cm) of the aromatic hydrocarbon-acyclic alkyl disulfide systems examined. Measurement of J for additional systems is impractical, since either J is too small to be measured accurately or the full spectral band for the lowest-energy uv transition of the disulfide energy acceptor cannot be measured experimentally. We view a value of 200 ± 50 cm^{-1} for U_e as being compatible with an exchange interaction quenching mechanism in light of the range of U_e values previously quoted for azoalkane and oxygen quenching. In addition an exchange mechanism provides a possible explanation for the faster quenching rates for di-*n*-butyl disulfide vs. di-*tert*-butyl disulfide, since spectral overlap is slightly greater for di-*n*-butyl disulfide (Figure 1).

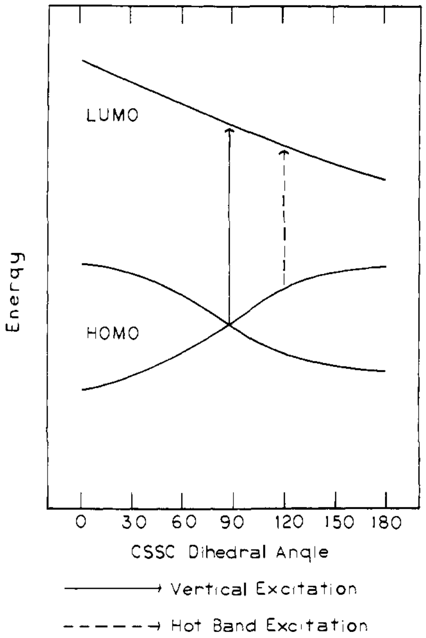


Figure 6. Schematic diagram showing the energy variation of the two highest occupied and lowest unoccupied molecular orbitals of the disulfide chromophore with the CSSC dihedral angle.

An alternative explanation for the slower rate constants for singlet and triplet quenching by di-*tert*-butyl vs. di-*n*-butyl disulfide involves steric hindrance of exchange energy transfer. There is conflicting evidence concerning the importance of steric effects upon the rates of triplet-triplet energy transfer.[47,48] Wagner[47] observed no difference in the rate constant for quenching of *n*-alkyl vs. *tert*-alkyl phenyl ketones. Wamser and Chang[48] attributed the 20-fold slower rate constant for quenching of triplet triphenylene by azo-*tert*-butane vs. azo-*n*-butane to steric hindrance. Inspection of space-filling molecular models indicates that a *tert*-butyl group should not hinder overlap of the disulfide n orbitals with the fluorescer π orbitals, assuming a CSSC dihedral angle of ~110°.[2c] Evidence based on molecular models is suggestive at best; however, lacking substantial information on steric hindrance of electronic energy transfer we prefer to attribute the slower quenching rate constants for *tert*-butyl vs. *n*-butyl disulfide to a decrease in spectral overlap.

The singlet and triplet energies of nonemitting molecules are frequently estimated from kinetic data, such as that shown in Figure 5.[31,36,39] It is assumed that quenching is diffusion controlled as long as the excitation energy of the quencher is several kilocalories/mole lower than that of the singlet or triplet donor. For an exchange mechanism, this assumption is valid only if the quencher 0,0 absorption band has a high oscillator strength. For nonrigid molecules, rate constants for exothermic energy transfer could be substantially slower than diffusion controlled. Thus the extrapolated singlet energies obtained from Figure 5 for di-*n*-butyl (92 ± 5 kcal/mol) and di-*tert*-butyl disulfide (95 ± 5 kcal/mol) should be interpreted as upper limits and may substantially overestimate the actual values. We suspect that previous estimates[36-42] of singlet and triplet energies for nonrigid molecules which have substantially different equilibrium ground-state and excited-state geometries may also be too large.

The Arrhenius activation parameters measured for pyrene quenched by di-*n*-butyl disulfide in acetonitrile do not unequivocally support any one energy transfer mechanism. The low activation energy of 3.65 ± 0.06 kcal/mol is much too low to account for an estimated energy gap, ΔE, of ~ 13 kcal/mol, which would be the Arrhenius activation energy in a conventional collisional energy-transfer mechanism. The entropy of activation (-11.2 ± 0.3 eu) is consistent with a bimolecular collisional process and may be sufficiently large to implicate an orientational requirement for the energy transfer process. Orientational requirements for intermolecular exchange energy transfer have been postulated previously,[49a] but conflicting data[49b,c] make it difficult to determine the extent of the requirement. There is also a general lack of data concerning the activation parameters of systems known to undergo exchange energy transfer. It is interesting to note, however, that activation energies and entropies similar in magnitude to the ones here have been found for singlet[50] and triplet exciplex[51] formation.

Triplet Quenching. Disulfide[8b] and sulfide[11b] quenching of aryl ketone n,π^* triplet states has been postulated to occur via a charge-transfer mechanism (eq 4). We have briefly investigated the quenching of acetophenone, benzophenone, and benzil room-temperature phosphorescence by alkyl disulfides in order to assess the extent of charge transfer. As was the case for singlet quenching, the relative rate constants for di-*n*-butyl and di-*tert*-butyl disulfide quenching of benzophenone (Table IV) are the opposite of what would be expected on the basis of disulfide ionization potential. Also, the polar solvent effect is small and independent of disulfide ionization potential. Guttenplan and Cohen[11b] postulated a partial charge-transfer mechanism for alkyl sulfide quenching of triplet benzophenone; however, unlike their results for amine quenchers, rate constants for sulfide quenching (Table VI) do not correlate with sulfide ionization potential. Competing α-hydrogen transfer was postulated to account for faster quenching by di-*n*-butyl vs. di-*tert*-butyl sulfide. This rationalization does not account for the identical quenching rate constants for di-*n*-butyl and diethyl sulfide.

The three aryl triplet ketones investigated differ in excited-state electron affinity ($-E_s - (A^-/A)$) by only 0.07 eV. This variation appears to be far too small to account for the large variation in quenching rate constants (Table III). Rate constants for triplet quenching increase with ketone triplet energy in accord with an exchange mechanism for triplet-triplet energy transfer.[31] Kampmeier's proposal of a charge-transfer mechanism for disulfide triplet quenching was based on the anomalously rapid quenching of 2-methylanthraquinone by dibenzyl disulfide. Calculation of the free-energy change for electron transfer from di-*tert*-butyl disulfide to anthraquinone triplet according to eq 8 gives a value of $\Delta G_{et} = -0.27$ eV. Since anthraquinone is the only ketone in Table V for which ΔG_{et} is exothermic, quenching might be expected to occur by a charge-transfer mechanism. Kinetic data for quenching of anthraquinone (or 2-methylanthraquinone) could not be obtained due to its complex photochemical behavior.[22,23] Substantial changes are observed in the room-temperature emission of anthraquinone within the time required to record its emission spectrum in either benzene or acetonitrile. Thus the use of anthraquinone as a triplet-energy donor cannot be recommended.

Conclusion

Full and partial electron-transfer mechanisms have been proposed for quenching of singlet- and triplet-excited molecules by disulfides. Our investigation has demonstrated that charge-transfer mechanisms are incompatible with kinetic data for quenching of aromatic hydrocarbon singlets and aryl ketone triplets by alkyl disulfides. Quenching kinetics are dependent upon energy donor singlet or triplet energies, indicative of an exchange type interaction in the energy-transfer process. Exchange-energy transfer is expected to be the dominant quenching mechanism in cases where the free energy for ion-pair formation for a charge-transfer mechanism is highly endothermic. We had hoped to investigate the competition between exchange-energy transfer and charge-transfer mechanisms in cases where the free energy for ion-pair formation is exothermic. Unfortunately, triplet anthraquinone was the only obvious candidate for such an investigation and its complex photochemistry prevented the desired study. Further investigation of charge-transfer quenching by disulfides will be necessary to define the scope of this mechanism, which appears to play an important role in biological systems.

Acknowledgment. The authors wish to thank Franklin E. McCoy for measurement of the disulfide disproportionation quantum yields and Judith V. Auping for determination of the alkyl sulfide quenching data. We also thank Professors S. Fischer, E. K. C. Lee, A. Nitzan, and C. Steel for stimulating discussions of energy-transfer mechanisms. The support of this research by the National Science Foundation (MPS74-12573 A01) and the Dreyfus Foundation is gratefully acknowledged.

References and Notes

(1) (a) Northwestern University Fellow, 1972–1975; (b) Alfred P. Sloan Fellow, 1974–1976; *(c) Camille and Henry* Dreyfus Teacher–Scholar, 1973–1978.
(2) (a) G. Bergson, G. Claeson, and L. Schotte, *Acta Chem. Scand.*, **16**, 1159 (1962); (b) J. Linderberg and J. Michl, *J. Am. Chem. Soc.*, **92**, 2619 (1970); (c) D. B. Boyd, *ibid.*, **94**, 8799 (1972); (d) J. Webb, R. W. Strickland, and F. S. Richardson, *ibid.*, **95**, 4775 (1973); (e) R. W. Woody, *Tetrahedron*, **29**, 1273 (1973); (f) L. A. Neubert and M. Carmack, *J. Am. Chem. Soc.*, **96**, 943 (1974).
(3) S. Beychock, *Science*, **154**, 1288 (1966).
(4) E. Block, *Q. Rep. Sulfur Chem.*, **4**, 283 (1969).
(5) (a) R. W. Cowgill, *Biochim. Biophys. Acta*, **120**, 196 (1966); (b) S. Arian, M. Benjamini, J. Feitelson, and G. Stein, *Photochem. Photobiol.*, **12**, 481 (1970); (c) A. Shafferman and G. Stein, *ibid.*, **20**, 399 (1974).
(6) C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **81**, 1137 (1959).
(7) (a) J. Feitelson and E. Hayon, *Photochem. Photobiol.*, **17**, 265 (1973); (b) D. V. Bent and E. Hayon, *J. Am. Chem. Soc.*, **97**, 2599 (1975); (c) D. V. Bent and E. Hayon, *ibid.*, **97**, 2612 (1975).
(8) (a) G. W. Byers, H. Gruen, H. G. Giles, H. N. Schott, and J. A. Kampmeier, *J. Am. Chem. Soc.*, **94**, 1016 (1972); (b) H. Gruen, H. N. Schott, G. W. Byers, H. G. Giles, and J. A. Kampmeier, *Tetrahedron Lett.*, 3925 (1972); (c) S. M. Rosenfeld, R. G. Lawler, and H. R. Ward, *J. Am. Chem. Soc.*, **94**, 9255 (1972).
(9) (a) K. Dose, *Photochem. Photobiol.*, **6**, 437 (1967); (b) R. W. Cowgill, *Biochim. Biophys. Acta*, **140**, 37 (1967); (c) R. W. Cowgill, *ibid.*, **207**, 556 (1970); (d) J. H. Leaver, *Photochem. Photobiol.*, **21**, 197 (1975).
(10) M. Z. Hoffman and E. Hayon, *J. Am. Chem. Soc.*, **94**, 7950 (1972).
(11) (a) J. Guttenplan and S. G. Cohen, *Chem. Commun.*, 247 (1969); (b) J. B. Guttenplan and S. G. Cohen, *J. Am. Chem. Soc.*, **94**, 4040 (1972); (c) R. S. Davidson and P. R. Steiner, *Chem. Commun.*, 1115 (1971).
(12) R. G. Zepp and P. J. Wagner, *J. Chem. Soc., Chem. Commun.*, 167 (1972).
(13) H. Bock and G. Wagner, *Angew. Chem., Int. Ed. Engl.*, **11**, 150 (1972).
(14) (a) S. F. Birch, T. V. Cullum, and R. A. Dean, *J. Inst. Pet., London*, **39**, 206 (1953); (b) F. D. Lewis and J. C. Dalton, *J. Am. Chem. Soc.*, **91**, 5260 (1969).
(15) W. R. Ware in "Creation and Detection of the Excited State", A. A. Lamola, Ed., Marcel Dekker, New York, N.Y., 1971.
(16) F. D. Lewis, C. E. Hoyle, J. G. Magyar, H.-G. Heine, and W. Hartmann, *J.*

Org. Chem., **40**, 488 (1975).
(17) W. M. Moore and M. Ketchum, *J. Am. Chem. Soc.*, **84**, 1368 (1962).
(18) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", 2d ed, Academic Press, New York, N.Y.
(19) P. J. Wagner and I. Kochevar, *J. Am. Chem. Soc.*, **90**, 2232 (1968).
(20) N. J. Turro, N. E. Schore, H.-C. Steinmetzer, and A. Yekta, *J. Am. Chem. Soc.*, **96**, 1936 (1974).
(21) (a) C. A. Parker and T. A. Joyce, *Trans. Faraday Soc.*, **65**, 2823 (1969); (b) W. D. K. Clark, A. D. Litt, and C. Steel, *J. Am. Chem. Soc.*, **91**, 5413 (1969); (c) F. D. Lewis and C. E. Hoyle, *Mol. Photochem.*, **6**, 235 (1974).
(22) (a) S. A. Carlson and D. M. Hercules, *J. Am. Chem. Soc.*, **93**, 5611 (1971); (b) S. A. Carlson and D. M. Hercules, *Photochem. Photobiol.*, **17**, 123 (1973); (c) S. A. Carlson and D. M. Hercules, *Anal. Chem.*, **45**, 1794 (1973).
(23) D. M. Hercules and S. A. Carlson, *Anal. Chem.*, **46**, 674 (1974).
(24) J. L. Kice and G. E. Ekman, *J. Org. Chem.*, **40**, 711 (1975).
(25) S. D. Thompson, D. G. Carroll, F. Watson, M. O'Donnell, and S. P. McGlynn, *J. Chem. Phys.*, **45**, 1367 (1966).
(26) R. Passerini and I. G. Ross, *J. Sci. Instrum.*, **30**, 274 (1953).
(27) (a) H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **67**, 791 (1963); (b) H. Knibbe, D. Rehm, and A. Weller, *ibid.*, **72**, 257 (1968); (c) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).
(28) J. B. Guttenplan and S. G. Cohen, *Tetrahedron Lett.*, 2163 (1972).
(29) T. R. Evans, *J. Am. Chem. Soc.*, **93**, 2081 (1971).
(30) Reduction potentials have not been reported for alkyl disulfides, preventing comparisons of kinetic data with disulfide acceptor properties.
(31) A. A. Lamola, "Technique of Organic Chemistry", Vol. 14, Interscience, New York, N.Y., 1969, Chapter 2.
(32) Fluoranthene data is not included in Figure 3 due to the difficulty in assigning an effective singlet energy. The weak component (71.7 kcal/mol) and strong second transition (79.3 kcal/mol) are coupled by vibronic mixing: J. Kolc, E. W. Thulstrup, and J. Michl, *J. Am. Chem. Soc.*, **96**, 7188 (1974).
(33) T. Förster, *Discuss. Faraday Soc.*, **27**, 7 (1959).
(34) D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).
(35) K. Sandros, *Acta Chem. Scand.*, **18**, 2355 (1964).
(36) (a) W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966); (b) D. G. Whitten, P. D. Wildes, and C. A. DeRosier, *ibid.*, **94**, 7811 (1972).
(37) A. Sykes and T. G. Truscott, *Trans. Faraday Soc.*, **67**, 679 (1971).
(38) A. Padwa and F. Albrecht, *J. Am. Chem. Soc.*, **96**, 4849 (1974).
(39) (a) W. G. Herkstroeter, *J. Am. Chem. Soc.*, **97**, 3090 (1975); (b) **97**, 4161 (1975).
(40) P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 2820 (1967).
(41) K. Sandros, *Acta Chem. Scand.*, **27**, 3021 (1973).
(42) (a) F. D. Lewis and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **90**, 7033 (1968); (b) J. L. Leyshon and A. Reiser, *J. Chem. Soc., Faraday Trans., 2*, 1918 (1972).
(43) The presence of a steric effect on the barrier to rotation about sulfur–sulfur bonds has been established: R. R. Fraser, G. Boussard, J. K. Saunders, J. B. Lambert, and C. E. Mixan, *J. Am. Chem. Soc.*, **93**, 3822 (1971).
(44) P. S. Engel, L. D. Fogel, and C. Steel, *J. Am. Chem. Soc.*, **96**, 327 (1974).
(45) G. J. Hoytink, *Acc. Chem. Res.*, **2**, 114 (1969).
(46) N. Filipescu, J. R. DeMember, and F. L. Minn, *J. Am. Chem. Soc.*, **91**, 4169 (1969).
(47) P. J. Wagner, J. M. McGrath, and R. G. Zepp, *J. Am. Chem. Soc.*, **94**, 6883 (1972).
(48) C. C. Wamser and P. L. Chang, *J. Am. Chem. Soc.*, **95**, 2044 (1973), and references cited therein.
(49) (a) K. B. Eisenthal, *J. Chem. Phys.*, **50**, 3120 (1969); (b) S. Siegel and L. Goldstein, *ibid.*, **43**, 4185 (1965); (c) J. K. Roy and M. A. El-Sayed, *ibid.*, **40**, 3442 (1964).
(50) F. D. Lewis and C. E. Hoyle, submitted for publication.
(51) J. K. Roy, F. A. Carroll, and D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 6349 (1974).

Solid-State Chemistry of Organic Polyvalent Iodine Compounds. 8. Solid-State Chemistry and Molecular and Crystal Structures of Two Polymorphs of 1-Methoxy-1,2-benziodoxolin-3-one[1a]

Margaret C. Etter[1b]

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received August 25, 1975*

Abstract: 1-Methoxy-1,2-benziodoxolin-3-one crystallizes in two polymorphic forms: **I**-α, orthorhombic diamond-shaped crystals, space group *Pbca*, $a = 15.440\ (15)$ Å, $b = 8.097\ (2)$ Å, $c = 13.532\ (12)$ Å, $\rho_m = 2.17$ g/cm^3, $Z = 8$; and I-β, monoclinic acicular crystals which are metastable in solution relative to **I**-α, space group $P2_1/a$, $a = 7.73\ (1)$ Å, $b = 10.06\ (1)$ Å, $c = 12.60\ (1)$ Å, $\beta = 118.3\ (1)°$, $\rho_m = 2.16$ g/cm^3, $Z = 4$. The molecular structures are the same for both polymorphs and they both exhibit a stereospecific intermolecular coordination interaction between trivalent iodine and the carbonyl oxygen of a neighboring screw-related molecule. The geometry of the chains of coordinated molecules are different, resulting in unique molecular packing properties. Single crystals of both polymorphs can be hydrolyzed quantitatively to give *o*-iodosobenzoic acid and reduced quantitatively by x-ray radiation to give *o*-iodobenzoic acid. The reaction products formed are in both an amorphous and a preferentially oriented crystalline phase. The chemistry of these transformations is presented in this paper and the topotactic relationships between crystalline reactant and product lattices are discussed in the following paper in this series.

Introduction

1-Methoxy-1,2-benziodoxolin-3-one (I) crystallizes in two polymorphic modifications (orthorhombic I-α and monoclinic I-β), both of which are readily hydrolyzed and reduced in the solid state. The two polymorphs, which crystallize with the same molecular structures and conformations, undergo the same chemical reactions but at different rates. The most striking aspect of these reactions is the growth of preferentially oriented crystalline product phases, a phenomenon commonly observed in single-crystal transformations of organic polyvalent iodine compounds.[2] In order to understand the significance of molecular packing modes, intermolecular coordination interactions, and geometrical lattice parameters of the reactant matrix on nucleating and directing the growth of a product lattice, the molecular and crystal structures of the two polymorphs have been determined. In addition, the chemical aspects of the reactions of I have been investigated in both solution and solid-state samples, leading to the discovery of a novel photolytic reaction of benziodoxole compounds.

Experimental Section

Compound Preparation. I was prepared according to a procedure of Baker[3] by methanolysis of 1-acetoxy-1,2-benziodoxolin-3-one (IV). An alternative esterification procedure was also developed which gave comparable yields of I by refluxing a solution of 1 g of *o*-iodosobenzoic acid (II), 0.12 ml of acetic acid, and 10 ml of methanol for 24 h. After filtration, the filtrate was allowed to sit for about 4 h until crystallization was complete. A 60% yield of I, in the form of diamonds and