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Quenching and Radical Formation in the Reaction of Photoexcited Benzophenone with Thiols and Thioethers (Sulfides). Nanosecond Flash Studies

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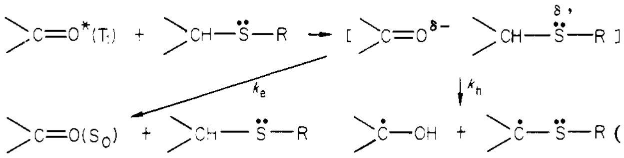
Abstract: Laser flash measurements have been made of rate constants and primary radical yields in the reactions of triplet benzophenone with aliphatic and aromatic thiols and with dialkyl and aryl alkyl sulfides. Reaction with *n*-pentylthiol in benzene leads mainly to quenching, with $k_{ir} = 9 \times 10^6$ M^{-1} s^{-1} and $\varphi_{ketyl} = 0.14$; with mesitylene-2-thiol in benzene, $k_{ir} = 7 \times 10^8$ M^{-1} s^{-1} and hydrogen transfer is efficient, $\varphi_{ketyl} \sim 1.0$. In reactions with both *p*-chlorophenyl ethyl and diisopropyl sulfides, k_{ir} increases and φ_{ketyl} decreases with increasing solvent polarity. Values of k_{ir} are higher and those of φ_{ketyl} are lower for the dialkyl than for the aryl alkyl sulfide. Results are discussed in terms of rapid interaction of the triplet with S, followed by quenching and/or hydrogen transfer. Quenching without hydrogen transfer occurs to a much greater extent with sulfides and aliphatic thiols than with amines.

Rate constants, k_{ir}, for primary interaction of triplet benzophenone and acetophenone with thioethers[1] (sulfides) and thiols[1,2] and quantum yields of photoreduction[1,3] were examined previously in steady irradiation studies. Values of k_{ir} with sulfides were determined by quenching of phosphorescence and retardation of photoreduction processes; k_{ir} is high, 8×10^8 M^{-1} s^{-1} for di-*n*-butyl sulfide in benzene,[1] and values for other dialkyl sulfides are about twice as high in acetonitrile[1] and in water.[4] Values are lower by an order of magnitude for phenyl methyl sulfide, still lower for diphenyl sulfide, and are decreased by electronegative substituents.[1] Quantum yields for photoreduction of benzophenone by sulfides are low, 0.05–0.2, and rise with decreasing values of k_{ir}. In contrast to the effect of aryl groups in sulfides, arylthiols react more rapidly than aliphatic,[1,2] with $k_{ir} > 10^8$ M^{-1} s^{-1} and $\sim 10^7$ M^{-1} s^{-1}, respectively. Like sulfides, thiols are inefficient photoreducing agents. However, they may strongly affect photoreduction reactions, catalyzing, inhibiting, or changing their course by thermal hydrogen atom transfer processes following the initial formation of free radicals.[3,5-8]

The high values of k_{ir} and low reduction quantum yields and effects of substituent and ionization potential[9] indicated[1] that, as had been proposed for amines,[10] triplet carbonyls react with sulfides via initial charge transfer, k_{ir}, followed by quenching, k_e, or by transfer of α-H to form ketyl and α-alkylthioalkyl radicals, k_h, eq 1. Reactions with thiols would be similar, leading either to quenching or to abstraction of H from S, to form thiyl radical, k_h', eq 2.



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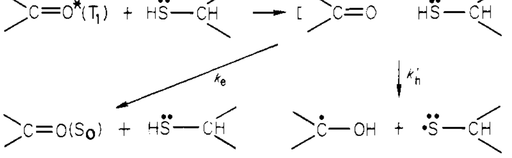
However, laser-flash studies have shown that in reaction with common amines triplet benzophenone is converted efficiently to ketyl radical, $\varphi \sim 1$, by abstraction of H from α-C and/or N.[11] The quenching process, k_e, does not generally occur in these amine reactions, and low product quantum yields arise from disproportionation of initially formed radicals. On the other hand, a low deuterium kinetic isotope effect, <1.1, in the quenching of excited acetophenone by –SH and –SD aliphatic thiol indicates that the k_e process, eq 2, may be dominant and the S–H bond is not involved in that process.[2a] Further, a preliminary flash photolysis experiment indicated low ketyl radical yield in reaction with a dialkyl sulfide.[1] Thus it was of interest to carry out further flash studies in thiol and sulfide systems.



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Materials and Methods

p-Chlorobenzenethiol (27.5 g) was stirred with 100 mL of 10% sodium hydroxide for 30 min. Diethyl sulfate (38.5 g) was added over ~1 h and the mixture was boiled for 6 h. The lower layer was distilled, leading to *p*-chlorophenyl ethyl sulfide: 26 g; 80% yield; bp 110 °C (15 mm). Anal. Calcd for C_8H_9SCl: C, 55.65; H, 5.21. Found: C, 55.94; H, 5.32 (Galbraith).

Diisopropyl sulfide, K&K Laboratories, 1-pentanethiol, Aldrich, and mesitylene-2-thiol[12] were distilled. Trifluorotrichloroethane, Burdick and Jackson, acetonitrile, Burdick and Jackson, benzene, Eastman spectrograde, cyclohexane, Fisher certified, and acetone, Fisher certified, were used directly. Water was triply distilled.

Flash photolysis was carried out using 347-nm excitation from a pulsed frequency-doubled ruby laser, as described previously.[13] Solutions of 0.004 M benzophenone, with and without thiol or disulfide, were degassed in several freeze–thaw cycles and placed under 1 atm of argon in 1 × 1 cm Pyrex cells fitted with Teflon closures. Transient absorptions were followed over the range 360–700 nm. In the absence of reductant only a short-lived (3–4 μs) transient was observed, with a spectrum corresponding to that of benzophenone triplet.[14,15] Addition of reductant shortened the triplet lifetime and led in some cases to a longer-lived intermediate with a spectrum the same as that of the ketyl radical.[14,16]

Rate constants, k_{ir}, for interaction of benzophenone triplet with reductants were obtained from the dependence of the effective pseudo-

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Table I. Pulsed Laser Photolysis of Benzophenone–Reductant Systems. Rate Constants, k_{ir}, for Triplet–Donor Interaction

reductant			
compd	mM	solvent	k_{ir}, M^{-1} s^{-1}
$(C_6H_5)_2CHOH$		C_6H_6	$9.0 \times 10^{6\,a}$
toluene	50–500	C_6H_6	3.0×10^5
MesSH		C_6H_6	$6.8 \times 10^{8\,c}$
n-$C_5H_{12}SH$	10–30	C_6H_6	8.8×10^6
p-Cl-$C_6H_4SC_2H_5$	5–200	$C_2Cl_3F_3$	2.4×10^7
p-Cl-$C_6H_4SC_2H_5$	5–200	C_6H_6	3.6×10^7
p-Cl-$C_6H_4SC_2H_5$	1–50	CH_3CN	1.6×10^8
p-Cl-$C_6H_4SC_2H_5$	0.3–1.0	$CH_3CN:H_2O^b$	5.2×10^9
$(i$-$C_3H_7)_2S$	5–500	C_6H_{12}	9×10^7
$(i$-$C_3H_7)_2S$	2–40	$C_2Cl_3F_3$	1.4×10^8
$(i$-$C_3H_7)_2S$	0.4–4.0	C_6H_6	1.9×10^8
$(i$-$C_3H_7)_2S$	0.4–4.0	CH_3CN	5.9×10^8
$(i$-$C_3H_7)_2S$	0.2–4.0	$CH_3CN:H_2O^b$	3.1×10^9

[a] Reference 22. [b] 1:1 v/v. [c] Reference 1.

Table II. Pulsed Laser Photolysis of 0.004 M Benzophenone–Reductant Systems. Quantum Yields of Ketyl Radical

reductant					
compd	M	solvent	% triplet trapped	$\Delta D_R^\infty / \Delta D_T^\circ$	φ_{ketyl}
$(C_6H_5)_2CHOH$	0.60	C_6H_6	95	0.77	2.0^a
$(C_6H_5)_2CHOH$	0.60	CH_3CN	94	0.84	2.0^a
c-C_6H_{12}	neat		90	0.36	1.0
$MesSH^b$	0.01	C_6H_6	95	0.39	1.0
n-$C_5H_{11}SH$	0.30	C_6H_6	93	0.053	0.14
p-Cl-$C_6H_4SC_2H_5$	0.10	$C_2F_3Cl_3$	90	0.27	0.69
p-Cl-$C_6H_4SC_2H_5$	0.20	C_6H_6	95	0.17	0.46
p-Cl-$C_6H_4SC_2H_5$	0.02	CH_3CN	96	0.11	0.26
p-Cl-$C_6H_4SC_2H_5$	0.02	CH_3CN: H_2O^c	98	~0	<0.05
$(i$-$C_3H_7)_2S$	0.02	$C_2F_3Cl_3$	93	0.09	0.22
$(i$-$C_3H_7)_2S$	0.004	C_6H_6	84	~0	<0.05
$(i$-$C_3H_7)_2S$	0.01	CH_3CN	95	~0	<0.05
$(i$-$C_3H_7)_2S$	0.004	CH_3CN: H_2O^c	97	~0	<0.05

[a] Standard. [b] Mesitylene-2-thiol. [c] 1/1 v/v.

Table III. Pulsed Laser Photolysis of 0.004 M Benzophenone–Diisopropyl Sulfide in Cyclohexane. Quantum Yields of Ketyl Radical from Reaction with the Sulfide

			% triplet trapped		
$[(i$-$C_3H_7)_2S]$, M	k_d, $s^{-1} \times 10^{-6}$	O.D.$_{ketyl}$ at 530 nm	by C_6H_{12}	by $(i$-$C_3H_7)_2S$	φ_{ketyl} from $(i$-$C_3H_7)_2S$
	5.6	0.0925	95		
0.02	7.8	0.078	68	28	0.42
0.05	9.9	0.069	54	43	0.39
0.10	15.0	0.057	35	63	0.37

Table IV. Pulsed Laser Photolysis of 0.004 M Benzophenone–1.0 M Diisopropyl Sulfide in Cyclohexane–Acetone. Effect of Acetone on Yield of Ketyl from Reaction of Triplet with Sulfide

	% triplet trapped		O.D.$_{ketyl}$ at 530 nm		
% acetone	by C_6H_{12}	by $(i$-$C_3H_7)_2S$	total	from $(i$-$C_3H_7)_2S$	φ_{ketyl} from $(i$-$C_3H_7)_2S$
0	94.6^a		0.083^a		
0	6	94	0.031	0.026	0.30
4	6	94	0.024	0.019	0.22
10	5	95	0.017	0.012	0.14
20	5	95	0.015	0.011	0.12
40	4	96	0.012	0.008	0.09

[a] No diisopropyl sulfide present. 1.0 M diisopropyl sulfide present in all other experiments.

first-order triplet decay constant on concentration of reductant (R), eq 3.

$$k_{eff} = k_0 + k_{ir}(R) \qquad (3)$$

Yields of benzophenone ketyl radical were determined, as described previously,[17,11] from the absorbance of triplet and ketyl at 530 nm in the presence of sufficient reductant to trap at least 90% of the triplet. The yield of ketyl radical from the triplet is proportional to the ratio $r = \Delta D_R^\infty / \Delta D_T^0$, where ΔD_T^0 and ΔD_R^∞ are the transient absorbances corresponding, respectively, to initial formation of triplet and to total formation of radical. The measured ratios, r, were converted to quantum yields by comparison with the r value for complete trapping of triplet by benzhydrol, for which $\varphi_{ketyl} = 2.0$.[18] Corrections to the yields were applied for the fraction of untrapped triplet.

A different procedure was used in studying diisopropyl sulfide in cyclohexane, CH, where the solvent reacts competitively with the excited ketone. In this system, the effective pseudo-first-order triplet decay rate is the sum of the rates of its "intrinsic" decay, k_d^0, H-atom abstraction from CH, and interaction with added sulfide. Assuming that the intrinsic decay in CH is the same as that in weakly polar trichlorotrifluoroethane, $k_d^0 = 3 \times 10^5\ s^{-1}$, and that the reaction rate with CH remains constant in dilute sulfide (<0.1 M), the fractions of ketone reacting respectively with CH and with sulfide were obtained from the measured triplet lifetimes in the absence of sulfide ($\tau \sim 200$ ns) and at varying sulfide concentrations. The ketyl radical quantum yield from the CH reaction is unity.[11] The quantum yield from the sulfide reaction, f, may then be found from the measured total radical absorbance, according to the relation

$$f = \frac{1}{P}\left[\frac{AC_0}{A_0} - C\right] \qquad (4)$$

in which P = percent triplet trapped by the sulfide, A = absorbance due to ketyl radical in the presence of sulfide, A_0 = absorbance due to ketyl radical in the absence of sulfide, C = percent triplet trapped by cyclohexane in the presence of sulfide, and C_0 = percent triplet trapped by cyclohexane in the absence of sulfide. Radical absorbances at 530 nm were obtained at each sulfide concentration from the averages of about seven measurements, normalized to constant flash energy and agreeing to ±3%.

In experiments in mixed cyclohexane–acetone solvent, the ratio of benzophenone triplet lifetime in pure CH to that in 60/40 v/v CH–acetone was 0.64, and the radical yield, corrected for untrapped triplet, was unity in both of these solvents. Thus, acetone did not quench the triplet under these conditions. Ketyl radical yields from the diisopropyl sulfide reaction in this mixed solvent were then determined over the range 0–40% acetone directly from the normalized radical absorption at 530 nm, using such a high sulfide concentration, 1.0 M, that 95% of the triplet was trapped by the sulfide.

Results

Primary Rate Constants, k_{ir}, and Ketyl Quantum Yields. Oscillograms of triplet absorption decay in the absence and presence of n-pentylthiol and mesitylene-2-thiol and of the absorption due to ketyl radical, at 530 nm, are given in Figure 1. Oscillograms relating to formation of ketyl radical from reaction with p-chlorophenyl ethyl sulfide in several solvents are shown in Figure 2. Rate constants, k_{ir}, for interaction of benzophenone triplet with these compounds, determined by their effects on triplet lifetimes, and of quantum yields for formation of ketyl radical in these reactions are listed in Tables I–IV.

The value of k_{ir} for n-pentylthiol in benzene, $8.8 \times 10^6\ M^{-1}\ s^{-1}$ (Table I), is similar to that found for aliphatic thiols by phosphorescence quenching.[1,2] However, the reaction led largely to quenching, with minor abstraction of H, $\varphi_{ketyl} = 0.14$, Table II, Figure 1. Mesitylene-2-thiol, on the other hand, with a much higher k_{ir}, $6.8 \times 10^8\ M^{-1}\ s^{-1}$, gave ketyl radical with $\varphi \sim 1$, Figure 1.

Values of k_{ir} for p-chlorophenyl ethyl sulfide increase markedly with increasing solvent polarity, from $\sim 3 \times 10^7\ M^{-1}\ s^{-1}$ in trichlorotrifluoroethane and benzene to $10^8\ M^{-1}\ s^{-1}$ in acetonitrile and $5 \times 10^9\ M^{-1}\ s^{-1}$ in 1:1 acetonitrile–water, Table I. The rate in benzene is similar to and intermediate between those for p-chlorophenyl methyl sulfide and phenyl methyl sulfide, determined previously by phosphorescence, quenching.[1] Polarity of solvent had the opposite effect on radical yields to that on k_{ir}: φ_{ketyl}

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decreased with increasing polarity from 0.69 in the chlorofluorocarbon to 0.46 in benzene, 0.26 in acetonitrile, and ~0 in 1:1 acetonitrile–water, Table II.

Values of k_{ir} for diisopropyl sulfide were greater than those for *p*-chlorophenyl ethyl sulfide by factors of 4–5 in the chlorofluorocarbon, benzene, and acetonitrile and rose from 9×10^7 M^{-1} s^{-1} in cyclohexane to 3.1×10^9 in 1:1 acetonitrile–water. The value in benzene, 1.9×10^8 M^{-1} s^{-1}, is intermediate between those of di-*tert*-butyl sulfide, 5.0×10^7 M^{-1} s^{-1}, and di-*n*-butyl sulfide, 8.3×10^8 M^{-1} s^{-1}, determined previously by phosphorescence quenching. Steric factors may cause these differences. Reaction of benzophenone triplet with this aliphatic sulfide led to little if any ketyl radical in benzene, acetonitrile, and 1:1 acetonitrile–water, $\varphi < 0.05$, and to a low yield in trichlorotrifluoroethane, $\varphi = 0.22$. Since this is a poor solvent for the ketone, a study was carried out in cyclohexane as a solvent of low polarity in which to measure quantum yields of ketyl from reaction with diisopropyl sulfide. The contributions of cyclohexane and sulfide to formation of ketyl were separated as described. Over the range of sulfide concentration, 0.02–0.10 M, in which the fraction of triplet trapped by sulfide varies from about 0.3 to 0.6, the radical yield from the sulfide reaction is constant within experimental error, $\varphi_{ketyl} = 0.40$, Table III.

The effect of polarity of the medium on yield of the ketyl radical from the reaction with diisopropyl sulfide was further examined in cyclohexane–acetone solutions containing increasing concentrations of acetone, as described above. The yield was found to decrease steadily with increasing acetone concentration, from 0.30 in pure CH to 0.09 in 40 v/v % acetone, Table IV. The yield in pure CH here is slightly less than that in Table III, determined at much lower sulfide concentration.

Spectra of Intermediates. The spectrum of the benzophenone triplet was recorded in acetonitrile solution in the absence of diisopropyl sulfide and in the presence of the sulfide immediately and at 0.5 and 1 μs after flash. All spectra were the same and identical with that of the triplet.[14,15,19] Evidence for a charge-transfer complex was not found, and no ketyl radical was observed. The spectrum of the radical, formed from reaction with 1 M diisopropyl sulfide in cyclohexane, in which 94% of triplet reacted with sulfide, was identical with that of the ketyl radical formed from reaction of benzophenone triplet with benzhydrol.[14,16]

Spectra of the ketyl radical were observed in reactions of benzophenone triplet with *p*-chlorophenyl ethyl sulfide in trichlorotrifluoroethane, benzene, and acetonitrile. However, in 1:1 acetonitrile–water the spectrum of the transient, after disappearance of the triplet, was not that of the ketyl radical, but showed absorption at 650–700 nm, resembling that of the radical anion.[16] The transient decay was first order, faster than that of the ketyl radical in the less polar solvents, and it was not converted to ketyl radical by the water. This absorption may be due to the charge-transfer complex.

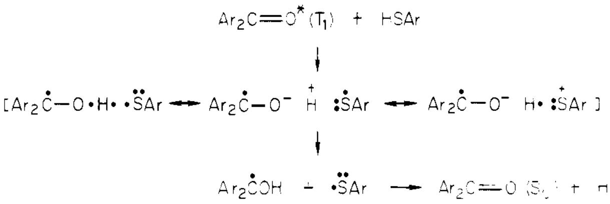
Discussion

Data on systems related to this study indicate that replacement of an alkyl by an aryl group increases the ionization potential in sulfides and decreases it in thiols; thus, aromatic thiol and dialkyl sulfide have the lowest, aryl alkyl sulfide the intermediate, and aliphatic thiol the highest ionization potentials in the range 8.3–9.3 eV.[20] The order of decreasing ionization potentials corresponds to the order of increasing k_{ir} found here. This relationship and the observed rise in k_{ir} with increasing solvent polarity are evidence for the importance of charge transfer in these reactions.

The slow reaction in this group of sulfur compounds, that with the aliphatic thiol, is as fast as reduction with benzhydrol.[21,22] However, benzhydrol gives ketyl radical with unit quantum efficiency while the alkylthiol leads mainly to quenching and to little radical. It is conceivable that this quenching proceeds via H-atom abstraction and disproportionation of the geminate radical pair within the solvent cage. Such in-cage disproportionation was suggested for a thermally generated thiyl in thiol trapping of a type II biradical.[2b] However, unit ketyl yields in light-induced reactions with other donors in this solvent[11] and the low deuterium isotope effect in thiol quenching[2a] indicate that stretching of the S–H bond is not significantly involved in the rate-limiting part of the mechanism. Thus, we conclude that thiol quenching occurs within the primary exciplex, the k_e process.

The failure of triplet benzophenone to abstract H from the alkylthiol is surprising in view of the efficiency with which thiols transfer H to radicals formed in thermal and photochemical processes.[3,5–8] However, this apparent discrepancy may be understood in terms of the time scale imposed by the rate of internal conversion, particularly in conjunction with a relatively strong S–H bond. The spin rephasing within the complex, necessary for quenching,[23] may perhaps be facilitated by a heavy-atom effect in sulfur.

On the other hand, the aromatic thiol, mesitylene-2-thiol, with its much higher k_{ir}, formed ketyl radical with unit efficiency.[24] The value of k_{ir} is about twice that of benzene thiol,[1] possibly because of the electron-donating methyl groups, and is three orders of magnitude greater than that for toluene, Table I. The hydrogen is clearly abstracted from S and not from the methyls. The differences in rate and radical yield between aryl- and alkylthiols must be related to the decrease in ionization potential and SH bond strength[25] caused by resonance stabilization by the aromatic ring of the thiyl radical species. Weakening the SH bond would favor H-atom transfer in competition with quenching. In more detail, the interaction between triplet and thiol may involve the hydrogen atom to a greater extent in the aryl than in the alkyl case, consistent with the greater acidity of the aryl SH,[26] eq 5.



(5)

This may be similar to reactions with the common amines, in which ketyl radicals are formed with $\varphi \simeq 1$ by abstraction of H from N and/or α-C depending on structure.[11]

Higher k_{ir} for the dialkyl sulfide than for alkylthiol, by more than an order of magnitude, also indicates that the H of aliphatic S–H is not substantially involved in the primary step and the second electron-donating alkyl group facilitates the interaction at S. Conversely, lower k_{ir} for aryl alkyl sulfides than for the arylthiol indicates that the H of S–H is involved in reaction of the arylthiol, eq 5; lower k_{ir} for the aryl alkyl than for the dialkyl sulfide may be attributed to electron withdrawal from S by the electronegative aryl group.

Increase in k_{ir} with solvent polarity is also found in reactions with amines.[9,27] However, sulfides show highest values in aqueous systems, while hydrogen bonding to N reduces k_{ir} with amines. The increase in k_{ir} with solvent polarity is accompanied by lower φ_{ketyl}, Tables I and II, and lower overall reduction yields.[1] It is conceivable that quenching at S and abstraction of α-H of sulfides are separate processes which occur at comparable rates in nonpolar solvents and that quenching increases more rapidly with rising

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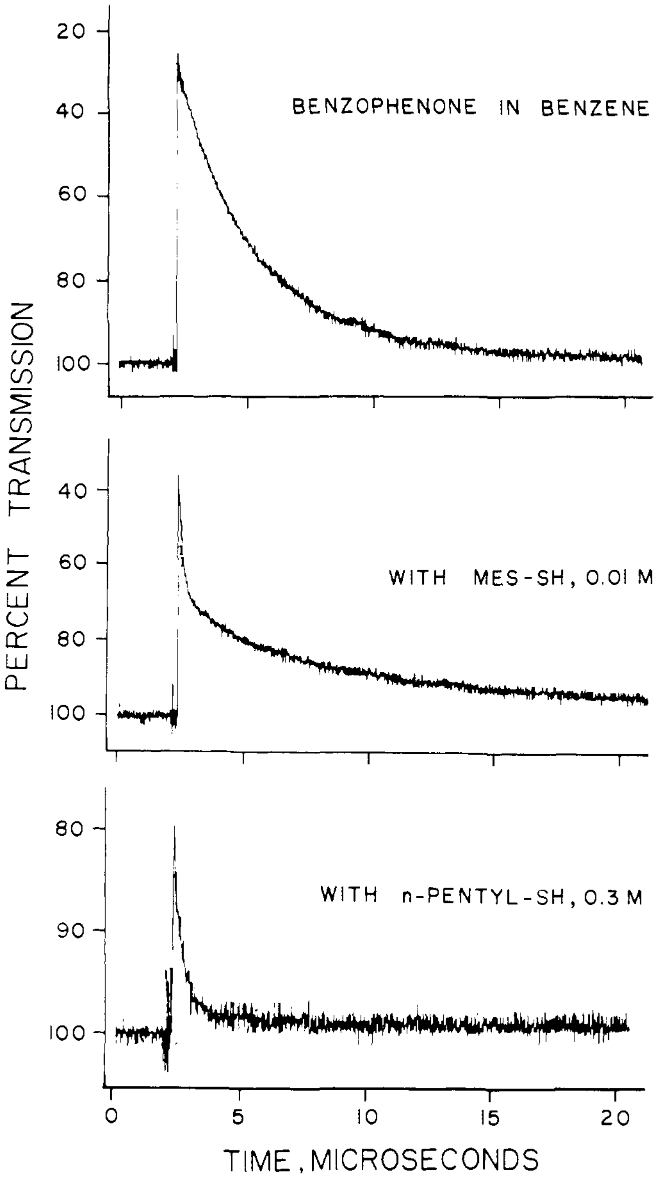

Figure 1. Reaction of benzophenone triplet with thiols; oscillograms showing light absorption vs. time, for flash-illuminated benzophenone (0.004 M) solutions in benzene: upper, no added thiol; middle, with 0.01 M mesitylenethiol; lower, with 0.3 M *n*-pentylthiol. λ = 525 nm.

solvent polarity. However, initial interaction at S followed by channeling into quenching and abstraction pathways, eq 1, does not require comparable rates for quite different processes, and seems preferable. Initial interaction at S followed by reaction at a distant site is seen in photoreduction by methionine.[4] Solvent may associate to a lesser or greater extent with a dipolar charge-transfer complex[28] and this may favor quenching over radical formation with an increasing dielectric constant.[29] Charge transfer generally facilitates transfer of α-H,[10] but with increasing development and stabilization of charge in sulfide systems, quenching, k_e, competes more favorably with k_h. A similar situation may obtain in fluorenone–dimethylaniline systems, where strongly electron donating substituents lead to very high k_{ir} and very low overall reduction.[30] Inefficient overlap of the orbitals of α-C with those of higher principal quantum number on S leads to less stabilization of the α-alkylthioalkyl radical and its less ready formation than in the case of analogous α-alkylaminoalkyl radicals.

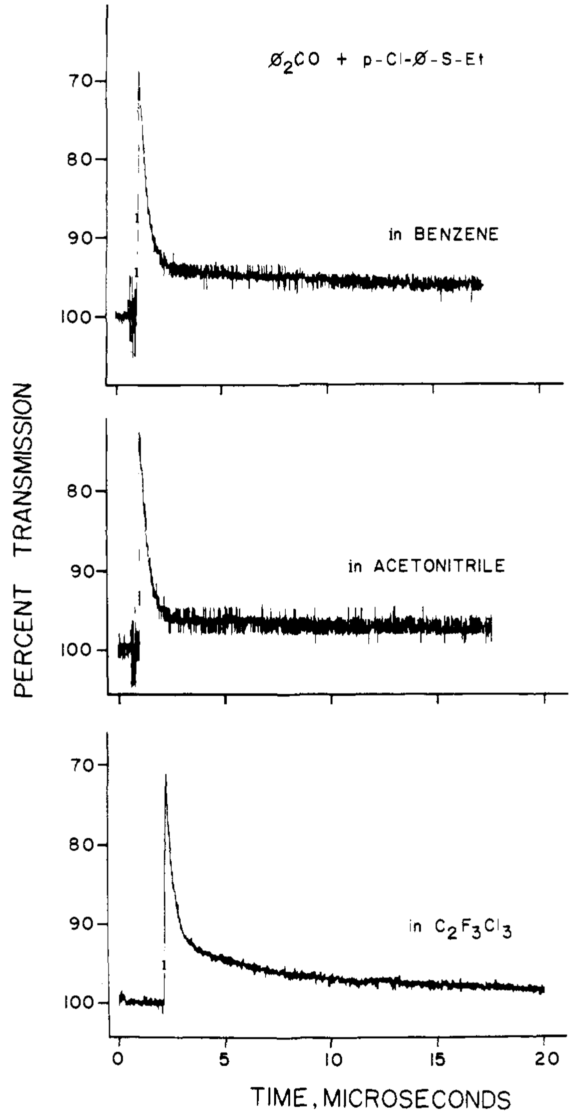

Figure 2. Oscillograms showing solvent effects on ketyl radical yield in triplet benzophenone (0.004 M) reaction with *p*-chlorophenyl ethyl sulfide: upper, 0.2 M sulfide in benzene; middle, 0.02 M sulfide in acetonitrile; lower, 0.1 M sulfide in $C_2F_3Cl_3$. λ = 525 nm.

However, when favorable orbital overlap is prevented in amines by steric factors, as with a bridgehead bicyclic amine, diazabicyclo[2.2.2]octane, Dabco, efficient quenching and inefficient hydrogen transfer occur,[11,31] much as with the sulfides.

While initial charge transfer is strongly indicated and spectra of the triplet and ketyl radical are readily obtained, spectral evidence for a charge-transfer complex is generally not observed in these systems. However, such evidence was found in reaction of the aryl alkyl sulfide in 1:1 CH_3CN-H_2O, as noted above. This had been previously observed in the benzophenone–Dabco system in acetonitrile[11b] and attributed to the charge-transfer complex. Thus in systems in which the charge-transfer complex or a solvent-shared ion pair[29] may be most stabilized, spectral evidence for such species is found, and the ketyl yield is eliminated or decreased via the k_e process.

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Registry No. Benzophenone, 119-61-9; toluene, 108-88-3; MesSH, 1541-10-2; $(C_6H_5)_2CHOH$, 91-01-0; *n*-$C_5H_{11}SH$, 110-66-7; *p*-$ClC_6H_4SC_2H_5$, 5120-72-9; (*i*-$C_3H_7)_2S$, 625-80-9; *c*-C_6H_{12}, 110-82-7.

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