Competitive Processes in Retardation by Mercaptans of Photoreduction by Alcohols

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Abstract: Reactions of mercaptans and disulfides have been studied in photoreduction of benzophenone by 2-propanol and by benzhydrol, and of acetophenone by α-methylbenzyl alcohol, and by the deuterated alcohols. In photoreduction of benzophenone by 2-propanol, the rate is halved by 0.001 M 2-mercaptomesitylene, and a decrease in rate is greater in the deuterio than in the protio system. Retardation is due in part to light absorption and quenching of triplet, and largely to hydrogen-transfer reactions from mercaptan to 2-hydroxy-2-propyl radical and from benzophenone ketyl to thiyl radical. Measured formation of 2-propanol-*2-d* is consistent with calculation of the relative importance of hydrogen transfer. This retardation depends on competition between transfer of hydrogen from mercaptan to the alcohol-derived radical and from this radical to ground-state ketone. The ratio of rate constants for these two reactions of the 2-hydroxy-2-propyl radical is ~150. Photoreduction of acetophenone by α-methylbenzyl alcohol is retarded by diphenyl disulfide, and carbon-bound deuterium is introduced into the carbinol. The acetophenone ketyl radical is both reduced by mercaptan and oxidized by thiyl. This retardation is less efficient in the deuterio system and depends on competition between reduction of ketyl by mercaptan and coupling of ketyl radicals. In benzophenone-benzhydrol the rate is halved by 0.01 M 2-mercaptomesitylene and carbon-bound deuterium is not introduced into the carbinol. This retardation is due predominantly to quenching of triplet by mercaptan and disulfide, in small part to masking, and is the same in the protio and deuterio systems. Photoreduction of benzophenone by 2-mercaptomesitylene, initial quantum yield ~0.1, leads to benzpinacol and disulfide. Benzhydrol is not found, confirming that transfer of hydrogen from mercaptan to benzophenone ketyl is too slow to compete with ketyl coupling. Mesityl disulfide is photoreduced by benzhydrol, $\varphi \sim 0.06$; such reduction is increased in the presence of benzophenone, presumably by reduction of disulfide and/or thiyl radical by benzophenone ketyl.

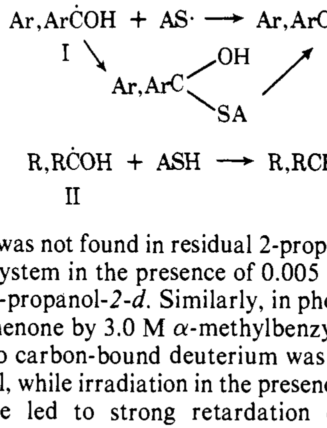
The photoreduction of benzophenone by alcohols proceeds via abstraction of hydrogen from the carbinol carbon by the ketone triplet and formation of the ketone and alcohol-derived ketyl radicals I and II (eq 1). The alcohol-derived radical transfers hydrogen to ground-state ketone, forming a second ketone-derived radical and the alcohol-derived ketone (eq 2).[1-5] Reaction 2 also occurs in reduction by diaryl carbinols, so that, initially, all pinacol is derived from the ketone.[6] Rate constants for the abstraction of hydrogen, eq 1, have been obtained from the effects of diffusion-controlled quenchers[5,7] and from quenching by the alcohols of the phosphorescence of the ketone.[8]

$$\mathrm{Ar,ArC{=}O}\ (T_1) + \mathrm{R,RCHOH} \xrightarrow{k_1} \underset{\mathrm{I}}{\mathrm{Ar,Ar\dot{C}OH}} + \underset{\mathrm{II}}{\mathrm{R,R\dot{C}OH}} \qquad (1)$$

$$\mathrm{Ar,ArC{=}O}\ (S_0) + \mathrm{II} \rightarrow \mathrm{I} + \mathrm{R,RC{=}O} \qquad (2)$$

$$\mathrm{I} + \mathrm{I} \rightarrow \mathrm{Ar,ArC(OH)C(OH)Ar,Ar} \qquad (3)$$

The photoreduction of 0.5 M benzophenone by 2-propanol was strongly retarded for an indefinite period by <0.01 M mercaptobenzene, 2-mercaptomesitylene, and their disulfides. The mesityl sulfur compounds were not consumed and were converted to a photostationary equilibrium composition of the two oxidation states.[9] Inhibition by the sulfur compounds of photoreduction of benzophenone by optically active 2-octanol was accompanied by extensive continuing loss in activity, which did not occur during irradiation of the alcohol in the presence of the sulfur compounds or benzophenone separately.[9] The inhibition was attributed to cyclical oxidation of I by thiyl radical and reduction of II by mercaptan, regenerating the starting materials in a chain inhibition of the nonchain reduction, eq 4 and 5. The observed rate of racemization appeared to account for about one-half of the retardation,[9b] indicating that the sulfur compounds had additional effects beyond their hydrogen-transfer reactions.



$$\mathrm{Ar,Ar\dot{C}OH} + \mathrm{AS\cdot} \longrightarrow \mathrm{Ar,ArC{=}O} + \mathrm{ASH} \qquad (4)$$
$$\mathrm{I} \searrow \mathrm{Ar,ArC(OH)(SA)} \nearrow$$

$$\underset{\mathrm{II}}{\mathrm{R,R\dot{C}OH}} + \mathrm{ASH} \longrightarrow \mathrm{R,RCHOH} + \mathrm{AS\cdot} \qquad (5)$$

The hydrogen-transfer mechanism of retardation was supported in studies with deuterium label.[10] In photoreduction of 0.5 M benzophenone by 2-propanol-*O-d*, carbon-bound deuterium was not found in residual 2-propanol, while irradiation of the system in the presence of 0.005 M 2-mesityl disulfide led to 2-propanol-*2-d*. Similarly, in photoreduction of 0.5 M acetophenone by 3.0 M α-methylbenzyl alcohol-*O-d* in benzene, no carbon-bound deuterium was found in the residual carbinol, while irradiation in the presence of 0.01 M 2-mesityl disulfide led to strong retardation of reduction and to α-methylbenzyl-α-*d* alcohol. In this system, only one intermediate radical was formed, and it was oxidized by thiyl and reduced by mercaptan, and the sulfur compounds were again used repeatedly (eq 6-8). The rate was halved by 0.006 M thiyl, and optically active α-methylbenzyl alcohol was racemized in the retarded reduction. The rate of photoreduction of acetophenone by 2-propanol was halved by 0.001 M 2-mesitylthiyl, while photoreduction of benzophenone by benzhydrol was less sensitive, and 0.01 M thiyl group was required to halve the rate.[10]

$$\mathrm{C_6H_5COCH_3}\ (T_1) + \mathrm{C_6H_5CH(OH)CH_3} \longrightarrow 2\,\mathrm{C_6H_5\dot{C}(OH)CH_3} \qquad (6)$$

$$\mathrm{C_6H_5\dot{C}(OH)CH_3} \xrightarrow{\mathrm{AS\cdot}} \mathrm{C_6H_5COCH_3} + \mathrm{ASH} \qquad (7)$$

$$\mathrm{C_6H_5\dot{C}(OH)CH_3} \xrightarrow[\mathrm{ASH}]{} \mathrm{C_6H_5CH(OH)CH_3} + \mathrm{AS\cdot} \qquad (8)$$

Mercaptans and disulfides are also efficient quenchers.[11-13] Values of k_q have been reported for several systems in benzene: 1.4×10^7 and $3.4 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$ for quenching of acetophenone triplet by 1-butanethiol[12] and benzyl disulfide,[13] respectively, and 1.3×10^7, 2.6×10^8, 6.8×10^8, and $1.5 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$ for quenching of benzophenone triplet by 1-propanethiol,[11] mercaptobenzene,[11] 2-mercaptomesitylene,[11] and benzyl disulfide,[13] respectively.

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Mercaptans and disulfides have been used to decrease radiation damage from ultraviolet and high-energy radiation,[9] and it was of interest to assess, in some photochemical systems, the relative contributions to retardation and protection of direct quenching of excited states which prevent chemical reaction, and the free-radical hydrogen-transfer repair reactions which may restore radical intermediates to their initial molecular states. We wished also to ascertain whether stabilized organic radicals might be formed by reactions of thiyl radicals in such systems, and whether stabilized radicals would abstract hydrogen from mercaptan in competition with the dimerization. This report addresses these questions, the latter by study of benzophenone-benzhydrol benzophenone ketyl systems. These had not been examined in the past by deuterium labeling,[10] and there was reason to believe[14,15] that thiyl radical might abstract α hydrogen, eq 9, in a reverse of a key step in the repair mechanism, eq 5.

$$(C_6H_5)_2CHOH + AS\cdot \rightarrow (C_6H_5)_2\dot{C}OH + ASH \quad (9)$$

Experimental Section

Materials. Acetophenone, Fisher Certified Reagent, was distilled, bp 48 °C (0.2 mm). Argon, Airco welding grade, was passed over Drierite. Benzene, Eastman Spectrograde, was dried by distillation. Benzhydrol, Eastman, was crystallized from cyclohexane, mp 67–68 °C. Benzophenone was Fisher Certified Reagent, mp 47–48 °C. *tert*-Butyl alcohol was from Matheson Coleman and Bell. Deuterium oxide was from Merck Sharpe and Dohme, 99.7% isotopic purity. Lithium aluminum deuteride was from Metal Hydrides. α-Methylbenzyl alcohol, Eastman, was distilled under nitrogen, bp 55 °C (0.25 mm). 2-Propanol was Fisher Certified Spectroanalyzed.

tert-Butyl alcohol-*O-d* was prepared by addition of D_2O to potassium *tert*-butoxide, bp 82 °C, strong O–D stretch at 2650 cm^{-1}. Comparison of the weak O–H band at 3580 cm^{-1} with a standard indicated 95% *tert*-butyl alcohol-*O-d*. 2-Propanol-*O-d*, Aldrich, showed strong O–D bands at 2650 and 2580 cm^{-1}. Comparison of the weak O–H band at 3590 cm^{-1} with 2-propanol indicated 0.7% O–H. Benzhydrol-*O-d*, mp 67–68 °C, was prepared by treatment of benzhydrol twice with *tert*-butyl alcohol-*O-d*. The spectrum in benzene showed a weak O–H band at 3562 cm^{-1}, and a strong O–D band at 2640 cm^{-1}, and indicated 80% deuteration. α-Methylbenzyl alcohol-*O-d*, 85% deuterated, was prepared from the alcohol and D_2O, stirred overnight, extracted with ether, and distilled. 2-Propanol-*2-d* was prepared by reduction of acetone by lithium aluminum deuteride:[16] bp 79–81 °C; C–D bands at 2180 and 2090 cm^{-1}; C–H septet at τ 6.04 absent in the NMR spectrum. The extinction coefficient of the C–D peak at 2090 cm^{-1}, determined on a Perkin-Elmer Model 257 IR spectrophotometer, ϵ 15.4 M^{-1} cm^{-1}, was used in calculation of concentration of 2-propanol-*2-d* in residual 2-propanol after photoreduction of benzophenone by 2-propanol-*O-d*.

2-Mercaptomesitylene was prepared from mesitylene-2-sulfonyl chloride[15] by reduction with lithium aluminum hydride,[17] bp 57–59 °C (0.4 mm). Benzyl mercaptan, Eastman, was distilled, bp 194–196 °C. *n*-Propyl mercaptan, Eastman, showed one peak on GLC and was used as received. Benzyl disulfide was prepared from the mercaptan as described previously,[15] mp 71–72 °C, from ethanol. Mesityl disulfide, mp 125–126 °C, was available from previous work.[10] Phenyl disulfide was from Eastman, mp 60 °C. *n*-Propyl disulfide, Eastman, was purified by GLC.

General Procedures. Extinction coefficients of the disulfides and benzophenone in benzene were determined on a Cary 14 spectrophotometer.

In the study of the effects of sulfur compounds on rates of photoreduction, solutions, with and without sulfur compound additives, were degassed in four freeze–thaw cycles, closed under argon with Teflon valves, and irradiated simultaneously on a turntable, 8 cm from a G.E. H85/A3 UV lamp, in 1-cm square tubes fitted with 1-mm side-arm cuvettes. Disappearance of carbonyl was followed (a) in the ultraviolet in the side-arm cuvettes, or (b) in the infrared in 0.49-mm NaCl cells, by tenfold dilution with benzene, scanning at 1660 cm^{-1}, and comparison with a standard curve.

In studies of rates of formation of 2-propanol-*2-d*, benzene and 2-propanol were distilled from the irradiated solution, the distillate was analyzed for 2-propanol and 2-propanol-*O-d* in the infrared against standards, and for C–D by scanning at 2500–2000 cm^{-1} and comparison with the authentic sample. In some cases deuterium incorporation was also determined by NMR. Dilution of the 2-propanol–benzene distillate with CCl_4 moved the OH band to τ 6.87, away from the methine CH multiplet at τ 6.04. The ratio of the integrated areas due to the methine-*h* and the methyl doublet at τ 8.80 allowed estimation of methine-*d*.

Quenching by mesityl disulfide of phosphorescence of 0.0085 M benzophenone in benzene was studied on a Perkin-Elmer MPF-4L spectrofluorimeter: excitation, 340 nm; emission, 420 nm.

Benzophenone–2-Propanol. A solution of 0.2 M benzophenone in 1 M 2-propanol or 2-propanol-*O-d* in benzene was irradiated and photoreduction was followed for 1–2 h, 20–40% reduction. Retarded reactions were followed for 4–17 h, 15–50% reaction. Rates were zero order over the extent followed. In a study of incorporation of C–D, solutions of 0.2 M benzophenone, 1.0 M 2-propanol-*O-d*, and varying concentrations of 2-mercaptomesitylene in benzene were irradiated for up to 20 h and analyzed for extent of reduction and for C–D. In a system without benzophenone, a solution of 1.0 M 2-propanol-*O-d*, 0.0031 M mesityl mercaptan, and 0.005 M mesityl disulfide in benzene was irradiated for 15 h. Recovered 2-propanol showed no absorption at 2000–2200 cm^{-1}.

In study of incorporation of C–D into 1 M 2-propanol in irradiation in *tert*-butyl alcohol-*O-d* as solvent, the alcohols were collected by distillation; *tert*-butyl alcohol was converted to the chloride by hydrochloric acid, and separated; 2-propanol was distilled from the aqueous layer, isolated by GLC, and analyzed for C–D. Irradiation of benzophenone alone or mercaptan alone in the 2-propanol–*tert*-butyl alcohol-*O-d* led to no C–D in the 2-propanol.

Acetophenone–α-Methylbenzyl Alcohol. Solutions of 0.20 M acetophenone, 1.00 M α-methylbenzyl alcohol-*O-h* or -*O-d*, and 2.0 M *tert*-butyl alcohol-*O-h* or -*O-d* in benzene, with and without 0.005 M phenyl disulfide, were irradiated. Rates of reduction were followed in the infrared for 3.4 h in the absence of the disulfide, 30% reduction, and for 9.33 h in the presence of the disulfide, 38% reduction. The extinction coefficient of the carbonyl band of acetophenone in benzene containing 2 M *tert*-butyl alcohol was 615 M^{-1} cm^{-1} at 1686 cm^{-1}. The remainder of the deuteriodisulfide system, after irradiation, was distilled. The high boiling fraction was collected, bp 38–40 °C (0.2 mm), dissolved in benzene, and examined in the infrared against α-methylbenzyl alcohol-*O-d* in benzene. It showed C–D absorption at 2130 cm^{-1}.

Benzophenone–Benzhydrol. (i) In studies of rates of reduction, solutions of 0.2 M benzophenone and 1.00 M benzhydrol or benzhydrol-*O-d*, in *tert*-butyl alcohol or *tert*-butyl alcohol-*O-d*, with and without 0.01 M 2-mercaptomesitylene, were irradiated for 30 and 65 min, respectively, and analyzed at 1660 cm^{-1} against *tert*-butyl alcohol or *tert*-butyl alcohol-*O-d* in benzene, with use of a calibration curve. The extinction coefficient for benzophenone in these solutions was 440 M^{-1} cm^{-1}.

(ii) (a) For examination of introduction of deuterium in recovered benzhydrol, a solution of 0.2 M benzophenone, 1.00 M benzhydrol-*O-d*, and 0.01 M mesityl mercaptan in *tert*-butyl alcohol-*O-d* was irradiated for 5.75 h. The mixture was centrifuged, benzpinacol, 55% yield, was separated and washed with methanol, and the supernatant and washings were concentrated. The residue was dissolved in benzene, and the infrared spectrum, taken against benzhydrol and *tert*-butyl alcohol-*O-d* in benzene, showed no C–D bands between 2040 and 2220 cm^{-1}. The hydrol was extracted from the residue with cold methanol and crystallized from cyclohexane, mp 65–67 °C. A spectrum of 1.7 M solution of this recovered hydrol in benzene, against a similar solution of authentic hydrol, showed no absorption at 2040–2220 cm^{-1}. Further extraction of the initial pinacol precipitate led to no material with CD absorption.

(b) A similar solution, containing 0.05 M *n*-propyl disulfide instead of 0.01 M mesityl mercaptan, showed 75% retardation. After irradiation for 6.5 h, recovered benzhydrol showed no C–D absorption.

(iii) Masking and quenching were evaluated in irradiation of 0.57 M benzophenone and 1.1 M benzhydrol in benzene, (a) in the absence and (b) in the presence of 0.0031 M mesityl disulfide. Aliquots were degassed and irradiated for 96 min. Reduction of benzophenone was followed at 344 nm, and in (a) the rate was 7.7×10^{-4} M min^{-1}, $\varphi = 0.99$, and in (b) 5.1×10^{-4} M min^{-1}, $\varphi = 0.66$. A decrease in absorbance of disulfide was followed at 400 nm, ϵ 50 M^{-1} cm^{-1}. It was rapid initially, 6.4×10^{-5} M min^{-1}, $\varphi \simeq 0.08$, and reached half the total decrease in 20 min. A sample was irradiated for 20 h and analyzed for disulfide by GLC on a 5-ft column, 10% QF-1 on Chromosorb W, column temperature 185 °C. The concentration of disulfide was 0.00056 M. The average concentration of disulfide during the irradiation was calculated from the plot of absorbance at 400 nm against time and was 0.00124 M.

(iv) Reaction of excited ketone with mercaptan was examined. (a) A solution of 0.093 M benzophenone and 0.14 M 2-mercaptomesitylene in benzene was degassed, irradiated for 15 h, and concentrated in vacuo. The residue was dissolved in chloroform and examined on EM Reagent precoated silica gel F-254 sheets with benzene as eluent. Benzophenone, R_f 0.28, mesityl mercaptan, R_f 0.57, and benzpinacol, R_f 0.37, were found; no evidence of benzhydrol, R_f 0.13, was detected. (b) A solution of 0.11 M benzophenone and 0.057 M 2-mercaptomesitylene in benzene was degassed and irradiated. The initial rate of formation of disulfide, followed for 20 min at 400 nm, was 4×10^{-5} M min^{-1}; it was 8×10^{-5} M min^{-1} for oxidation of mercaptan, $\varphi = 0.10$, relative to a benzophenone–benzhydrol actinometer. Analysis by GLC after 16.5-h irradiation indicated 0.0064 M disulfide, 22% conversion of thiol to disulfide. Irradiation of 0.18 M benzophenone and 0.005 M mesityl disulfide in benzene for 2 h led to no change in concentration of disulfide.

(v) Reaction of excited disulfide with benzhydrol was examined. (a) A solution of 0.012 M mesityl disulfide and 0.69 M benzhydrol in benzene was degassed and irradiated, and disappearance of disulfide was followed by measurement of absorbance, in a 1-mm quartz side arm, at 370 nm, ϵ 480. Disappearance was zero order, 4.5×10^{-5} M min^{-1}, 0.0047 M decrease in disulfide after 106 min, $\varphi = 0.058$. The solution was analyzed for mercaptan by GLC on a 4-ft column, 5% QF-1, 10% DC-200 on Chromosorb W, column temperature 110 °C; the concentration of 2-mercaptomesitylene was 0.0090 M, 95% yield. Irradiation of 0.014 M mesityl disulfide in benzene for 25 min led to no decrease in absorbance.

(b) Solutions in benzene of (i) 0.073 M mesityl disulfide and 0.46 M benzhydrol, and (ii) 0.079 M mesityl disulfide, 0.48 M benzhydrol, and 1.06 M benzophenone were irradiated through a 7380 (CS 0-52) filter which passed the 366-nm and absorbed the 313- and 334-nm bands. In (ii), 67% of the light was absorbed by the ketone and 96% of the excited ketone was quenched by disulfide and mercaptan. Reduction of disulfide was followed for 125 min by the decrease in absorption at 400 nm. The reduction was zero order and in (i) was 4.8×10^{-5} M min^{-1}, $\varphi = 0.062$, and in (ii), 5.6×10^{-5} M min^{-1}, $\varphi = 0.073$.

(c) Solutions of 0.020 M mesityl disulfide and 0.50 M benzhydrol in benzene (i) alone and (ii) with 0.50 M benzophenone were irradiated through Pyrex. In (ii), 67% of the light was absorbed by the ketone, and 87% of the excited ketone was quenched by disulfide. Rates of reduction of disulfide were followed for 103 min at 400 nm, 5.3×10^{-5} M min^{-1}, $\varphi = 0.069$ in (i), and 7.5×10^{-5} M min^{-1}, $\varphi = 0.097$ in (ii).

Results

Solutions of each of the ketone–alcohol pairs, with and without mercaptan or disulfide retarder, were irradiated simultaneously, and unretarded and retarded rates, related as the quantum yields, were followed spectrophotometrically. Studies were made in protium (OH) and deuterium (OD) systems, and introduction of carbon-bound deuterium was examined. Photoreductions of benzophenone by mercaptan and of disulfide by benzhydrol were also studied.

In photoreduction (Table I) of 0.2 M benzophenone by 1 M 2-propanol in benzene, the quantum yield was halved by ~0.001 M, and decreased to less than one-tenth by 0.008 M 2-mercaptomesitylene. Similar retardations were observed in *tert*-butyl alcohol and in neat 2-propanol. The aliphatic *n*-propyl disulfide was less effective by a factor of about seven. Retardation of reduction by 2-propanol was *more* effective in deuterio than in protio systems, about 20% greater in the retardation by 0.001 M 2-mercaptomesitylene. In photoreduction (Table II) of acetophenone by α-methylbenzyl alcohol, retardation by phenyl disulfide was slightly *less* efficient in the deuterio than in the protio system. In reduction of 0.2 M benzophenone by 1 M benzhydrol in *tert*-butyl alcohol, 0.01 M 2-mercaptomesitylene was required to halve the rate and the retardation was the same in the deuterio and protio systems. These differing relative efficiencies of retardation in deuterio and protio systems appear to be related to the differing competing radical processes in the three systems.

Table I. Photoreduction of 0.20 M Benzophenone by 1.0 M 2-Propanol or 2-Propanol-*O-d* in the Presence of Mesityl Mercaptan, MesSH, and *n*-Propyl Disulfide $(PrS)_2$

	retarder		system	rel
solvent	compd	10^3 M	OH or OD	rate
C_6H_6			OH	1.00[a]
C_6H_6	MesSH	1.01	OH	0.59
C_6H_6	MesSH	2.02	OH	0.36
C_6H_6	MesSH	4.00	OH	0.19
C_6H_6	MesSH	8.00	OH	0.08
C_6H_6	$(n\text{-PrS})_2$	10.2	OH	0.25
C_6H_6			OD	1.00[b]
C_6H_6	MesSD	1.01	OD	0.49[e]
C_6H_6	MesSD	2.02	OD	0.27
C_6H_6	MesSD	8.00	OD	0.06
C_6H_6	$(n\text{-PrS})_2$	10.2	OD	0.22
2-PrOH			OH	1.00[c]
2-PrOH	MesSH	2.52	OH	0.29
2-PrOD			OD	1.00
2-PrOD	MesSD	2.52	OD	0.23
tert-BuOD			OD	1.00[d]
tert-BuOD	MesSD	4.2	OD	0.16

[a-d] Quantum yields for unretarded reactions: [a] 1.57; [b] 1.51; [c] 1.16; [d] 1.2. [e] Absolute rate 1.55×10^{-5} M s^{-1}.

Contributions to the retardation of absorption of light (masking) and quenching by the sulfur compounds were evaluated. The major emission frequencies of the GE H85/A3 lamp, passed by Pyrex, are at 313, 334, and 366 nm, with relative intensities of 38, 12, and 100, respectively. The disulfides and benzophenone show broad absorption envelopes in this range. Extinction coefficients were determined (the first number in each pair is the wavelength in nm; the second is the extinction coefficient, ϵ, in M^{-1} cm^{-1}): mesityl disulfide, 313, 2920; 334, 1970; 366, 464; phenyl disulfide, 313, 1040; 334, 430; 366, 56; *n*-propyl disulfide, 320, 10; 334, 3; benzophenone, 313, 70; 334, 124; 366, 69. From the relative emission intensities and the extinction coefficients and average concentrations of disulfide and ketone during the irradiation period, the fraction of light absorbed by the disulfide, generally small, was calculated (Table III). The mercaptan essentially does not mask in these experiments. The rate constant for quenching of benzophenone triplet by mesityl disulfide in benzene was determined by phosphorescence quenching. Values of concentration of disulfide and I_0/I were: 2.46×10^{-4} M, 5.3; 7.38×10^{-4} M, 10.6; 1.23×10^{-3} M, 15.6; 2.21×10^{-4} M, 26.9; $k_q = 1.4 \times 10^9$ M^{-} s^{-1}, based on $\tau_p = 8.0$ µs. The value of k_q for 2-mercaptomesitylene is[11] 6.8×10^8 M^{-1} s^{-1}. Values of k_r for abstraction of hydrogen from 2-propanol and benzhydrol are 1.8×10^6 and 7.5×10^6 M^{-1} s^{-1}, respectively.[8] The extent of quenching by the sulfur compounds was calculated from the values of k_q, k_r, and k_d, and the average concentrations of alcohol, mercaptan, and disulfide (72% thiyl present as mercaptan, the remainder as disulfide) during the periods of irradiation (Table III).

Contributions to the retardation of the hydrogen-transfer repair mechanism were studied by introduction of carbon-bound deuterium. In a system of 0.2 M benzophenone, 2.02×10^{-3} M 2-mercaptomesitylene, and 1.0 M 2-propanol-*O-d* in benzene, 2.4% of the light would be absorbed, and 42% of the triplet would be quenched by the sulfur compounds, these effects decreasing reduction of ketone from $\varphi = 1.51$ to $\varphi = 0.84$, and abstraction of α-H from $\varphi = 0.75$ to $\varphi = 0.42$ (Table III). In two series of experiments, photoreductions were de-

Table II. Photoreduction of 0.2 M Ketone by 1.0 M Carbinol in the Presence of Phenyl Disulfide (PhSSPh) or Mesityl Mercaptan (MesSH)

solvent	ketone	carbinol	retarder compd	retarder 10^3 M	rel rate
2 M *tert*-C_4H_9OH in C_6H_6	$C_6H_5COCH_3$	$C_6H_5CHOHCH_3$			1.00[a]
	$C_6H_5COCH_3$	$C_6H_5CHOHCH_3$	PhSSPh	5.0	0.41
2 M *tert*-C_4H_9OD in C_6H_6	$C_6H_5COCH_3$	$C_6H_5CHODCH_3$			1.00
	$C_6H_5COCH_3$	$C_6H_5CHODCH_3$	PhSSPh	5.0	0.46
tert-C_4H_9OH	$(C_6H_5)_2C{=}O$	$(C_6H_5)_2CHOH$			1.00[b]
tert-C_4H_9OH	$(C_6H_5)_2C{=}O$	$(C_6H_5)_2CHOH$	MesSH	10.0	0.53
tert-C_4H_9OD	$(C_6H_5)_2C{=}O$	$(C_6H_5)_2CHOD$			1.00
tert-C_4H_9OD	$(C_6H_5)_2C{=}O$	$(C_6H_5)_2CHOD$	MesSD	10.0	0.54[c]

[a] Quantum yield 0.32, calculated from data in ref 18. [b] Quantum yield 0.49, ref 19. [c] Absolute rate 1.68×10^{-5} M s^{-1}.

Table III. Incorporation of 2-C-d in 2-Propanol. Photoreduction of 0.2 M Benzophenone by 1.0 M 2-Propanol-*O-d* in the Presence of 2-Mercaptomesitylene (MesSD)

solvent	MesSD	irrad. h	φ_{red}	mask, %	quench,[a] %	$\varphi_{H\ abst}$ calcd[b]	$\varphi_{H\ abst}$ obsd[c]	φ_{C-D} calcd[d]	φ_{C-D} obsd[e]
C_6H_6	0		1.51			0.75	0.75		
C_6H_6	2.02	4, 6, 10	0.41[f]	2.4	42	0.42	0.21	0.21	0.19
C_6H_6	2.02	4, 17	0.38	2.4	42	0.42	0.19	0.23	0.23
C_6H_6	9.90	12	0.062	12	78	0.15	0.031	0.12	0.14
tert-C_4H_9OD	21.9	7.7	0.045	22	88	0.070	0.023	0.047	0.042

[a] $100 \times k_q(Q)/[k_q(Q) + k_r(RH) + k_d]$. [b] $0.5 \times \varphi_{red.}$ in the absence of sulfur compounds, less corrections due to masking and quenching. [c] $0.5 \times \varphi_{red.}$. [d] $\varphi_{H\ abst}(calcd) - \varphi_{H\ abst}(obsd)$. [e] Calculated from incorporation of 2-C-d. [f] Absolute rate 3.9×10^{-6} M s^{-1}.

creased to $\varphi = 0.41$ and 0.38, indicating net abstractions of α-H of $\varphi = 0.21$ and 0.19, and possible repair by hydrogen (deuterium) transfer from mercaptan of $\varphi = 0.21$ and 0.23. Observed introduction of C–D, after 4, 6, 10, and 17 h of irradiation, showed $\varphi = 0.19$ and 0.23, supporting rapid exchange of deuterium between mercaptan[20] and alcohol-*O-d*, and the repair mechanism, eq 4, 5, and 10:

$$(CH_3)_2\dot{C}OD + ASD \rightarrow (CH_3)_2CDOD + AS\cdot \quad (10)$$

Similar results were obtained after single periods of irradiation, at 9.9×10^{-3} M mercaptan in benzene and 2.2×10^{-2} M mercaptan in *tert*-butyl alcohol-*O-d*, with much higher extents of quenching.

Introduction of deuterium in systems in which only one intermediate radical is formed was examined. Retardation by 0.005 M phenyl disulfide of photoreduction of 0.2 M acetophenone by 1 M α-methylbenzyl alcohol-*O-d* in 2 M *tert*-butyl alcohol-*O-d* in benzene led to recovery of α-methylbenzyl alcohol-α-*C-d*, eq 11:

$$C_6H_5\dot{C}(OD)CH_3 + ASD \rightarrow C_6H_5CD(OH)CH_3 + AS\cdot \quad (11)$$

However, this did not prove to be the case in retardation of photoreduction of benzophenone by benzhydrol. Retardation by 0.01 M 2-mercaptomesitylene of photoreduction of 0.2 M benzophenone by 1 M benzhydrol-*O-d* in *tert*-butyl alcohol-*O-d* led to recovery of benzhydrol which contained no C–D. Also, strong retardation by *n*-propyl disulfide led to no C–D in the recovered benzhydrol. The quantum yield of photoreduction of 0.57 M benzophenone by 1.1 M benzhydrol in benzene was decreased from 0.99 to 0.66 by 0.0031 M mesityl disulfide. The disulfide was reduced rapidly and levelled off at 18% of the initial concentration. The average concentration of disulfide was 0.00124 M and mercaptan was 0.0037 M during the irradiation period. Calculations indicated that 3.5% of the light was absorbed by the disulfide and 34% of excited ketone was quenched by mercaptan and disulfide. These effects would suffice to decrease the quantum yield from 0.99 to 0.63, and the hydrogen-transfer mechanism of retardation was neither required nor observed. Benzophenone ketyl radical did not abstract hydrogen (deuterium) from mercaptan, eq 12, in competition with its dimerization, eq 3.

$$(C_6H_5)_2\dot{C}OD + ASD \nrightarrow (C_6H_5)_2CDOD \quad (12)$$

Parts of the benzophenone–benzhydrol–thiyl system were examined separately. Long irradiation of 0.1 M benzophenone and 0.14 M 2-mercaptomesitylene led to partial conversion to benzpinacol and disulfide, but to no benzhydrol. The excited ketone was quenched by the mercaptan and formed ketyl and thiyl radicals, with high efficiency,[21] eq 13. These largely regenerated starting ketone and mercaptan, eq 4. Oxidation of the thiol was fairly rapid initially, $\varphi = 0.10$, but it levelled off at 22% thiyl as disulfide,

$$(C_6H_5)_2C{=}O^* + ASH \rightarrow (C_6H_5)_2\dot{C}OH + AS\cdot \quad (13)$$

Mesityl disulfide is stable to irradiation in benzene, alone and in the presence of benzophenone, but is photoreduced to the mercaptan by benzhydrol. Excited disulfide or thiyl radical from excited disulfide may abstract hydrogen from benzhydrol, eq 9, $\varphi \simeq 0.06$. The reduction becomes somewhat more efficient when benzophenone is also present and is not entirely quenched by the sulfur compounds. In a system of 0.020 M mesityl disulfide and 0.50 M benzhydrol, the presence of 0.50 M benzophenone increased reduction of disulfide from $\varphi = 0.069$ to 0.097, possibly largely via eq 14.

$$(C_6H_5)_2\dot{C}OH + ASSA \rightarrow (C_6H_5)_2C{=}O + ASH + AS\cdot \quad (14)$$

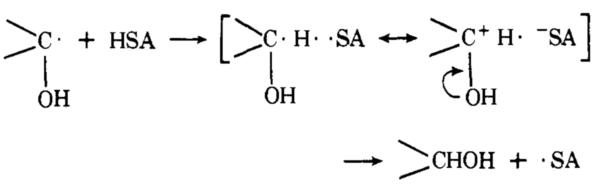
Discussion

In the benzophenone–2-propanol system, the results on introduction of deuterium, Table III, indicate that, after allowance is made for masking and quenching, the hydrogen-transfer mechanism, eq 4 and 5, does account for the retardation of photoreduction by mercaptans. In neat (13 M) 2-propanol, in our earlier studies,[9] quenching by 0.002 M 2-mercaptomesitylene is estimated to be only 6% as compared with 42% in 1 M 2-propanol in the present study. Retardation was efficient, and would be essentially the same at the same concentration of benzophenone, and due to the hydrogen-transfer mechanism. However, the difficulty in measuring small concentrations of deuterated 2-propanol in the large excess of neat solvent would be greater. Under the very low concentration conditions of flash photolysis studies,[22] 0.005 M benzophenone, 0.0001 M diphenyl disulfide in 2-propanol, no decrease in ketyl yield was observed, indicating no significant quenching, and retardation was seen in the increased rate of disappearance of ketyl in the presence of the sulfur compound, presumably largely by eq 4 and to a small extent by eq 14.

The retarding reactions, eq 4 and 5, in effect catalyze the thermodynamically favorable disproportionation of the benzophenone and 2-propanol derived radicals, which normally does not occur, as the 2-propanol derived radical is rapidly oxidized to acetone by ground-state benzophenone, eq 2.[1] Oxidations of ketyl by thiyl, eq 4 (and 7), are exothermic radical-radical reactions with high rate constant, whether they occur by hydrogen transfer or by combination followed by decomposition of the thiohemiketal. Reductions by ASH, eq 5 (and 8 and 12), are radical-molecule reactions with lower rate constants, and would be limiting steps in the retardation cycle. In the photostationary state, the concentrations of radicals and mercaptan would be such as to allow the rates of reactions 4 and 5 (and 7 and 8) to be equal. The limiting reaction, reduction of ketyl by mercaptan, may be more rapid the weaker the S–H bond which is broken and the stronger the C–H bond which is made. Thus, the aromatic mercaptan is more effective than the aliphatic, and less mercaptan is needed when the radical to be reduced is that from 2-propanol, in the photoreduction by 2-propanol, than when it is the resonance-stabilized acetophenone-ketyl radical in the photoreduction by α-methylbenzyl alcohol.

In the retarded photoreduction by 2-propanol, transfer of hydrogen or deuterium from mercaptan to 2-hydroxy-2-propyl radical II, eq 5, competes with transfer of hydrogen from radical II to the ground-state ketone, eq 2. From the quantum yields (Table III) for incorporation of deuterium by 0.0014 M 2-mercaptomesitylene, $\varphi = 0.21$, and for oxidation of 2-hydroxy-2-propyl radical by 0.2 M benzophenone, $\varphi = 0.20$, the ratio of the rate constants may be estimated, $k_5/k_2 \simeq 150$. This is lower than our previous estimate, in which masking and quenching by the sulfur compounds were not taken into account.[23] That retardation by mercaptan is generally more effective with 2-propanol *O-d* than with *-O-h* (Table I) is consistent with the deuterium kinetic isotope effect presumably being greater in the slower oxygen to oxygen hydrogen transfer of eq 2 than in the more rapid transfer from mercaptan, eq 5.

In retardation by mercaptan of the acetophenone-α-methylbenzyl alcohol system, deuterium was found in recovered carbinol, confirming the proposal[10] that the acetophenone ketyl radical is both oxidized by thiyl and reduced by mercaptan, eq 7 and 8. Retardation in this system appears somewhat less effective in the deuterium than in the protium system (Table II). Reduction of acetophenone ketyl by mercaptan competes, not with another hydrogen-transfer process, as in the benzophenone–2-propanol system, but with combination of two ketyl radicals to form the pinacol. A small normal deuterium kinetic isotope effect in transfer from sulfur to carbon may cause the retardation to be less efficient in the deuterium system. The efficient introduction of deuterium in these systems that are not totally devoid of protium also indicates that the kinetic isotope effect in the transfer reaction of eq 5 is small. There may be an important rate-enhancing polar contribution[24] to the transition state for this hydrogen transfer, eq 15:



$$>\underset{\mathrm{OH}}{\underset{|}{\mathrm{C}}}\cdot + \mathrm{HSA} \longrightarrow \left[>\underset{\mathrm{OH}}{\underset{|}{\mathrm{C}}}\cdot\mathrm{H}\cdot\cdot\mathrm{SA} \longleftrightarrow >\underset{\mathrm{OH}}{\underset{|}{\mathrm{C}}}{}^{+}\,\mathrm{H}\cdot\,{}^{-}\mathrm{SA}\right] \longrightarrow >\mathrm{CHOH} + \cdot\mathrm{SA} \quad (15)$$

In the benzophenone–benzhydrol system, retardation by mercaptan led to no introduction of deuterium into recovered benzhydrol, and, consistently, to no deuterium isotope effect. Our earlier failure to examine this aspect of this reaction led to an inappropriate interpretation in terms of hydrogen-transfer processes.[10] The highly stabilized benzophenone ketyl radical abstracts hydrogen from the mercaptan too slowly for that process to compete significantly with coupling of the radicals to form benzpinacol. This system is less sensitive than the others to retardation by mercaptan, and 10^{-2} M 2-mercaptomesitylene was required to halve the rate. Calculations of the light absorbed by disulfide and of the quenching to be expected from the mercaptan and disulfide lead to the extent of retardation which is observed, and the cyclic hydrogen-transfer mechanism of retardation, eq 4 and 5, does not operate.

In a retarded reduction proceeding at a rate of 1.68×10^{-5} M s^{-1} (Table II), the concentration of benzophenone ketyl radical is 2.8×10^{-7} M, based on a dimerization rate constant of 2.2×10^8 M^{-1} s^{-1} in 2-propanol.[25] Abstraction of deuterium by benzophenone ketyl from 0.007 M mercaptan did not compete detectably with this dimerization, and may be less than one-tenth as rapid, leading to a maximum value of $k_{12} \leq 9 \times 10^2$ M^{-1} s^{-1}, and perhaps lower than this by an order of magnitude. Under comparable conditions of retarded reduction by 2-propanol, 2-hydroxy-2-propyl radical abstracted deuterium from 0.0014 M mercaptan with high efficiency (Table III). The concentration of this ketyl radical is low, due to rapid oxidation by ground-state ketone, eq 2, and may be estimated to be no greater than one-tenth that of the benzophenone ketyl radical, $\leq 1.3 \times 10^{-8}$ M, leading to a minimum value of $k_5 \geq 1 \times 10^5$ M^{-1} s^{-1}, with the true value possibly significantly greater. These values are consistent with those from studies of chain transfer in polymerization.[26,27] In this calculation, the values are derived from the radical coupling rate constant, and indicate that radical reactions with rate constants less than $\sim 10^2$ M^{-1} s^{-1} may not be observed in competition with coupling.

The sulfur compounds also enter directly into light-induced reactions in these systems. Flash photolysis studies of benzophenone and 2-mercaptomesitylene in benzene, currently in progress,[21] indicate efficient formation of benzophenone ketyl radicals, quantum yield ~ 1, eq 13. The low quantum yield for formation of disulfide from steady-state irradiation of benzophenone and 2-mercaptomesitylene in benzene, $\varphi \sim 0.1$, indicates that regeneration of starting materials by disproportionation and/or cross-coupling is about an order of magnitude more rapid than homocoupling to pinacol and disulfide, and this step in the repair mechanism, eq 4, is thus essentially diffusion controlled. That no benzhydrol was formed from benzophenone ketyl and the high concentration (0.14 M) of 2-mercaptomesitylene of this experiment substantiate the relative slowness of the reaction of eq 12, and its failure to occur significantly in the steady-state studies. The conversion of mercaptan to disulfide slowed down and appeared to level off during prolonged irradiation. The disulfide is stable to irradiation, alone and in the presence of benzophenone and benzpinacol. Direct excitation or energy transfer from excited ketone may dissociate the disulfide, but the thiyl radicals recombine in the absence of a hydrogen donor. A reaction that may lead to a leveling in the yield of disulfide is reduction of disulfide by ketyl, eq 14, the latter formed from excited ketone and mercaptan, eq 13.

Disulfide is reduced to mercaptan when irradiated with benzhydrol in benzene. The quantum yield is low, $\varphi = 0.06$ for 0.012 M disulfide and 0.69 M benzhydrol. A similar quantum yield has been reported for irradiation of diaryl disulfides in a variety of solvents.[28] Reduction may result from reaction of excited disulfide with hydrol, or of thiyl radicals from excited disulfide with hydrol, eq 9. If the latter, it is not clear whether the yield of thiyl radicals is low, most of the excited disulfide decaying to ground state, or the yield is high, with most of the thiyl radicals dimerizing. When benzophenone is also present, and is largely quenched by disulfide but in part reacts with benzhydrol to form ketyl radicals, the efficiency of reduction of the disulfide is increased. If direct and sensitized[29] excitation of disulfide lead to similar reactivity, it may be estimated that formation of ketyl radical with $\varphi = 0.17$ increased reduction of disulfide with $\varphi = 0.034$, 40% of the ketyl radicals reducing disulfide, eq 14, and/or thiyl radicals which might otherwise have dimerized.

In the benzophenone–benzhydrol system, containing a retarding concentration ($\sim$0.01 M) of mercaptan disulfide, masking and quenching by the sulfur compounds are sufficient to account for all the observed retardation. Reduction of benzophenone ketyl radical to benzhydrol by mercaptan is not observed in competition with dimerization to benzpinacol. In radiation-induced reactions, products of radiolysis of solvent, reactive radicals, may be largely scavenged by mercaptans, leading to thiyl radicals. The reactive radicals and the thiyl radicals may also react with sensitive solutes, converting them in part to stabilized radicals which may not be repaired by mercaptan. These may enter into coupling reactions and lead to biological damage.

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1,2-Di(9-anthryl)ethane. Crystal and Molecular Structure of the Photoisomer. Conformational Effects in the Photophysics and Photochemistry

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Abstract: Photodissociation of the photoisomer crystal (AEAPI) gives a number of conformations of the 1,2-di(9-anthryl)ethane with different photophysical and photochemical properties. Weakly absorbed light produces two nonfluorescent conformations, with slightly different orientations in the crystal, and two fluorescent conformations which are thermally related. Both sets can be photoisomerized with different rates, at liquid helium temperature. Other, more relaxed, sandwich conformations are produced by more strongly absorbed light and possible conformational arrangements of the two chromophores have been identified by polarized absorption spectra. The crystal and molecular structure of the photoisomer has been determined from single-crystal X-ray diffraction data collected on a Picker FACS-1 diffractometer. Crystals of AEAPI are monoclinic, with $a = 10.095$ (2) Å, $b = 12.471$ (2) Å, $c = 8.340$ (1) Å, $\beta = 111.20$ (1)°, and $Z = 2$. The packing arrangement is strongly pseudocentrosymmetric, approximating space group $P2_1/c$. The structure was solved using the MULTAN programs and has been refined successfully in space group $P2_1$, with one additional (noncrystallographic) constraint, viz., that the two anthracene-derived moieties in each molecule are exactly related by inversion symmetry. Agreement between observed and calculated structure factor amplitudes for the terminal scattering model is only moderate, with weighted and unweighted R factors of 0.36 and 0.08, respectively, for 1776 observed unique data. Nevertheless, bond lengths and bond angles are all close to their expected values, and a number of spectral features can be correlated with the crystal packing arrangement.

Introduction

The reversible photoisomerization of 1,2-di(9-anthryl)ethane (AEA) was studied by Livingston and Wei,[2] although a description of the two isomers (AEA and its photoisomer AEAPI) was given first by Roitt and Waters.[3] More recently,[4-9] there have been studies of the photophysical and photochemical properties of both isomers.

The feature of recent interest is the photodissociation of AEAPI to form AEA, in which the two anthracene chromo-

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