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Effects of Structure on Rates and Quantum Yields in Photoreduction of Fluorenone by Amines. Catalysis and Inhibition by Thiols[‡]

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Abstract: Rate constants, k_{ir}, quantum yields, φ_{red}, and effects of thiol have been studied in the photoreduction of fluorenone by amines in benzene. Hydroxyethylamines show increased φ_{red} as compared with unsubstituted ethyl analogues, $\varphi_{red} \sim 0.8$ with triethylamine, but ~ 2, the maximum theoretical value, with triethanolamine and 2-(diethylamino)ethanol. Abstraction is predominantly from unsubstituted ethyl groups in the latter, and increased k_{ir} and φ_{red} are attributed to solvation by hydroxyl, present only at the reaction site, of polar intermediates or transition states. Secondary amines have high k_{ir} and low φ_{red}, 0.01–0.2, attributed to predominant abstraction of H from N and disproportionation of ketyl and aminyl radicals. This reduction is strongly catalyzed by aliphatic thiol, as aminyl radical abstracts H from S and thiyl radical abstracts H from α-C of amine. Primary amines have low k_{ir} and low φ_{red}. This reduction is not catalyzed by thiol, indicating that H is not abstracted by triplet fluorenone from N of primary aliphatic amines. Aniline inhibits this reduction, but aniline plus thiol leads to strong catalysis. Triplet fluorenone abstracts H from N of aniline, anilino radical abstracts H from S of thiol, and thiol abstracts H from α-C of amine, leading to effective reduction. Thiol catalysis may be diagnostic for the formation of aminyl radicals. Inhibition and catalysis by thiols are discussed.

Fluorenone is not photoreduced by aliphatic alcohols[1,2] or by cyclohexane. This marked difference from benzophenone reflects its low triplet energy, 53 as compared with 69 kcal/mol,[3] and possibly the lower inherent reactivity of a π,π^*[4] than an n,π^* triplet.[5] Effective photoreducing agents for both classes of ketones are found among aliphatic amines.[2,6] Reduction by amines may proceed via charge-transfer interaction with the n electrons of N, which facilitates hydrogen transfer and makes possible the reduction of π,π^* and charge-transfer triplets, which are not photoreduced by alcohols.[6-8]

In photoreduction of fluorenone by aliphatic amines, rate constants, k_{ir}, are highest for tertiary and lowest for primary amines. They rise with decreasing ionization potential in a broad range, from $\sim 10^4$ M^{-1} s^{-1} for a primary to $>10^7$ M^{-1} s^{-1} for a tertiary amine.[9,2] Similarly, in reactions of fluorenone with ring-substituted anilines and *N*-alkyl- and *N,N*-dialkylanilines, rate constants range from 10^6 M^{-1} s^{-1} to 10^{10} M^{-1} s^{-1}, low with electron-withdrawing and high with electron-donating substituents. The rate constants correlate with σ functions, further supporting charge transfer in the transition states.[10,11]

Quantum yields for overall photoreduction of fluorenone by low concentrations of triethylamine (TEA) in cyclohexane and benzene approach a value of ~ 1,[2,12] as compared with a maximum value of 2, which may be achieved if an amine-derived radical reduces ground-state ketone. Values fall at concentrations of TEA >0.2 M due to quenching of excited singlet.[12-14] Polar solvents may also decrease quantum yields, as they decrease intersystem crossing and triplet yields.[15,16] However, in a preliminary study, a low concentration (0.05 M) of acetonitrile in cyclohexane did not decrease triplet yield, and substantially increased the quantum yield of reduction by 0.005 M TEA.[17] In acetonitrile as the solvent, the triplet yield is about half that in cyclohexane,[15-17] while the reduction quantum yield was decreased less than that.[17] Photoreduction of fluorenone by TEA in alcohols has been reported.[18] In 2-propanol the triplet yield was decreased by an order of magnitude and the quantum yield for reduction by TEA nearly as much.[17] Therefore, the triplet is not less and may be more reactive in polar solvents, where the configuration is clearly π,π^*.[4,16,19] Thus, electron transfer, favored by solvent polarity, may facilitate photoreduction. However, in the photoreduction by substituted *N,N*-dimethylanilines,[10] while the rate constants rise uniformly with substitutent electron-donating power, reduction quantum yields are decreased by both strongly electron-donating and -withdrawing substituents. Although charge transfer appears important for photoreduction of fluorenone, either too much or too little may be deleterious, both possibly leading to quenching.[10]

Primary and secondary aliphatic amines are inefficient photoreducing agents for fluorenone,[2,12] and the analogous aromatic amines, anilines and mono-*N*-alkylanilines, react rapidly but lead to essentially no overall reduction.[11] Low reactivity of the primary aliphatic amines may be due to low rate constants, but the secondary amines have high rate constants.[2,12] Low reduction yields may arise by abstraction of H from N, in competition with abstraction from α-C, followed by disproportionation of the ketyl and N-centered radicals (eq 1).[11,20] This mechanism has been demonstrated in photoreduction of benzophenone by aliphatic amines and generally replaces quenching in an initially formed charge–transfer complex as the major mode of loss of efficiency of those reactions.[21] This effect was largely negated by low

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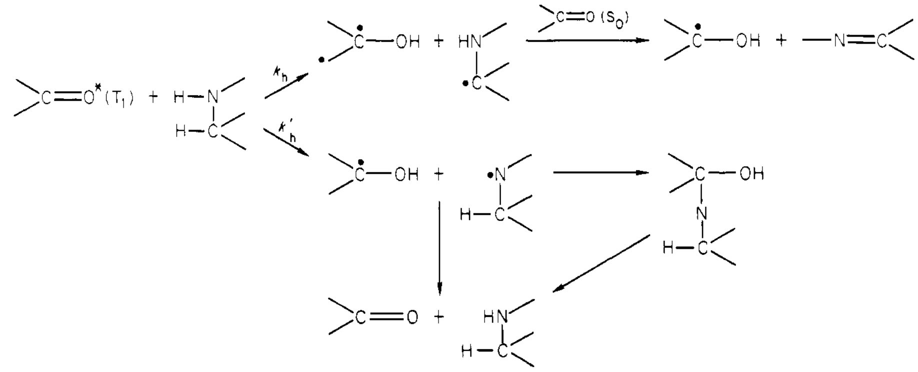
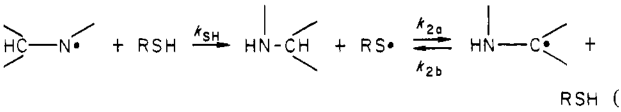


(1)

concentrations of aliphatic thiol, which convert alkylaminyl to α-aminoalkyl radicals by a catalytic reaction sequence (eq 2),



(2)

abstraction by aminyl radical of H from S of thiol, with rate constant $k_{SH} > 10^5$ M^{-1} s^{-1}, and by thiyl radical from α-C of amine $k_{2a} > 10^3$ M^{-1} s^{-1}.[22] We discuss effects of thiol and structure of reductant in fluorenone–amine photochemistry.

Experimental Section

Fluorenone, Aldrich, was crystallized from petroleum ether, mp 83–84 °C. Amines and the thiol, obtained from Aldrich unless otherwise stated, were distilled under nitrogen: 2-aminobutane, bp 63 °C; hydroxyethylamine, bp 170 °C; *n*-pentylamine, bp 104 °C; di-*n*-propylamine, bp 109–110 °C; diisopropylamine, Eastman, bp 83 °C; *N*-methyl-2-aminobutane, K and K, bp 78 °C; 2-(ethylamino)ethanol, bp 169–170 °C; *N*,*N'*-dimethyl-1,4-diaminobutane, bp 119 °C; *N*-methylaniline, bp 45–49 °C (2–3 mm); *n*-isopropylaniline, bp 50 °C (2 mm); aniline, Fischer Certified, bp 184 °C; triethylamine, Eastman, bp 89–90 °C; 2-(diethylamino)ethanol, bp 163 °C; triethanolamine, bp 165 °C (2 mm); 2-(diethylamino)ethylamine, bp 144–146 °C; 2-(dimethylamino)ethylamine, bp 108 °C; 1-pentanethiol, bp 126 °C; benzenethiol, Eastman, bp 50 °C (0.2 mm); benzene, Eastman Spectrograde, bp 82 °C. Acetonitrile, Burdick and Jackson, was used as received.

Values of k_{ir} for reaction of fluorenone triplet with amines in benzene were determined from retardation by *trans*-stilbene of reduction by the amines, based on $k_q = 1.29 \times 10^9$ M^{-1} s^{-1} for the photostationary ratio of *trans*-/*cis*-stilbene, 86.7% cis.[23] Data follow for concentrations of fluorenone, amine, and quencher, values of φ_0/φ, slope and intercept (S and I) of plots of φ_0/φ vs. concentration of quencher, and k_{ir}.

2-Aminobutane: 0.070 M fluorenone; 1.38 M amine; 4.16×10^{-5} M stilbene, φ_0/φ 1.83; 8.32×10^{-5} M, φ_0/φ 2.48; 1.25×10^{-4} M, φ_0/φ 3.33; $S = 1.83 \times 10^4$ M^{-1}; $I = 1.01$; $k_{ir} = 3.9 \times 10^4$ M^{-1} s^{-1}.

Triethylamine: 0.058 M fluorenone; 0.116 M amine; 8.5×10^{-4} M stilbene, φ_0/φ 1.39; 1.89×10^{-3} M, φ_0/φ 1.78; 2.36×10^{-3} M, φ_0/φ 1.99; $S = 417$ M^{-1}; $I = 0.997$; $k_{ir} = 2.8 \times 10^7$ M^{-1} s^{-1}.

2-(Diethylamino)ethanol: (a) 0.060 M fluorenone; 0.110 M amine; 1.10×10^{-3} M stilbene, φ_0/φ 1.21; 2.20×10^{-3} M, φ_0/φ 1.38; 3.30×10^{-3} M, φ_0/φ 1.51; 4.40×10^{-3} M, φ_0/φ 1.85; $S = 193$ M^{-1}; $I = 0.988$; $k_{ir} = 6.0 \times 10^7$ M^{-1} s^{-1}; (b) 0.058 M fluorenone; 0.120 M amine; 1.45×10^{-3} M stilbene, φ_0/φ 1.28; 2.40×10^{-3} *M*, φ_0/φ 1.52; 2.78×10^{-3} M, φ_0/φ 1.63; $S = 225$ M^{-1}; $I = 0.984$; $k_{ir} = 4.7 \times 10^7$ M^{-1} s^{-1}.

Triethanolamine: (a) 0.058 M fluorenone; 0.203 M amine; 1.07×10^{-3} M stilbene, φ_0/φ 1.43; 2.14×10^{-3} M, φ_0/φ 1.77; 3.21×10^{-3} M, φ_0/φ 2.08; 4.28×10^{-3} M, φ_0/φ 2.41; $S = 304$ M^{-1}; $I = 1.10$; $k_{ir} = 2.3 \times 10^8$ M^{-1} s^{-1}; (b) 0.057 M fluoreneone; 0.0220 M amine; 1.10×10^{-3} M stilbene, φ_0/φ 1.30; 2.20×10^{-3} M φ_0/φ 1.61; 3.3×10^{-3} M, φ_0/φ 1.95; 4.4×10^{-3} M φ_0/φ 2.29; $S = 287$ M^{-1}; $I = 0.99$; $k_{ir} = 2.0 \times 10^8$ M^{-1} s^{-1}.

Reduction quantum yields were determined in two procedures, (a) on a rotating wheel with a secondary fluorenone actinometer and (b) with monochromatic irradiation and the Aberchrome-540 actinometer.[24]

(a) Stock solutions of the components (ketone, amine, and thiol when used) were prepared, aliquots were transferred to and made up to volume in 10-mL volumetric flasks, and 5-mL portions were transferred to photolysis cells, 1.0-cm^2 Pyrex cuvettes fitted with sealed-on degassing bulbs, 1-mm quartz cuvettes, and Teflon valves. The cells were degassed in several freeze–thaw cycles, closed under argon, and irradiated on a wheel 8 cm from a G.E. H85 A3 lamp. For experiments using anilines, a Corning 7380 filter was used (passing light > 320 nm). A solution of 0.05 M fluorenone and 0.1 M triethylamine was irradiated simultaneously as a secondary actinometer, φ 0.44. Concentration of fluorenone was followed by determination of the absorbance at 405 nm, $\epsilon = 233$ M^{-1} cm^{-1} in benzene. Linear decrease with time of irradiation was observed.

(b) Aliquots, 3.0 mL, of a solution of 0.013 g of Aberchrome-540 in 10.0 mL of Baker Scintillation grade toluene were irradiated in 1.0-cm^2 cuvettes with stirring, on a Bausch and Lomb 38-86-01 monochromator, 200-W high-pressure Hg lamp. Absorbance at 494 nm increases on irradiation at 310–370 nm, and studies at 334 and 366 nm were carried out. Increase in absorbance was followed for several periods of irradiation, 0.50–1.00 min each. From the rate of increase, $\epsilon = 8225$ M^{-1} cm^{-1} and φ 0.20, the light flux was calculated. Identical volumes of the actinometer and fluorenone solution were irradiated successively.

In analyses for products, benzene solutions (~100 mL) of fluorenone and reductant in round-bottom flasks were degassed in 3–4 freeze–thaw cycles, closed off under argon, and photolyzed for ~20 h, essentially to complete reduction.

(a) A solution (80 mL) of 0.012 M fluorenone and 0.022 M 2-(diethylamino)ethanol in benzene was photolyzed, washed with water containing HCl to neutralize the amine and with water and brine, and then dried and concentrated under vacuum. The residue was crystallized from ethanol–water, leading to fluorenone pinacol: 0.147 g; 85% yield; mp 186 °C dec; mixture with an authentic sample mp 184–188 °C dec.

(b) A solution (97 mL) of 0.0102 M fluorenone and 0.021 M 2-(diethylamino)ethanol in benzene was degassed and photolyzed. An aliquot (15.0 mL) was shaken with 10.0 mL of triply distilled water. Five milliliters of the aqueous layer was transferred to a 10-mL volumetric flask, 1.00 mL of a standard aqueous solution of acetone was added as internal standard, and the flask was filled to the mark. The solution was analyzed by GLC on a 10 ft × $^1/_8$ in. 10% UCON on Chrom W 60/80 column; injection temperature, 160 °C; column, 35 °C; detector, 160 °C. Acetaldehyde was detected, corresponding to 0.0166 g in the original solution, after correction for the distribution between benzene and water and the response factors of acetaldehyde and acetone, both determined by GLC. This is a 74% yield based on reduction to fluorenone pinacol.

(c) A solution (100 mL) of 0.011 M fluorenone and 0.0125 M 2-(diethylamino)ethylamine in benzene was photolyzed, extracted with 40 mL of water containing 2.5 mL of concentrated HCl, washed with water until neutral, and concentrated under vacuum. The residue was crystallized from ethanol–water–Norite, leading to the pinacol: 0.184 g; 92% yield; mp 185–189 °C; mmp 187–192 °C dec.

(d) A solution (100 mL) of 0.0089 M fluorenone and 0.022 M 2-(diethylamino)ethylamine in benzene was photolyzed, treated with water, and analyzed for acetaldehyde as described above in reduction by 2-(diethylamino)ethanol. Acetaldehyde was detected in 99% yield.

(e) A solution (89.5 mL) of 0.031 M fluorenone and 0.025 M triethanolamine in C_6H_6 was photolyzed and extracted with two 20-mL portions of 4:1 water–acetic acid. The benzene layer was further washed with water, sodium bicarbonate, and brine, dried, and concentrated under vacuum. The residue was washed with cold carbon tetrachloride and dried, leading to fluorenone pinacol: 0.44 g; 89% yield; mp 180–183 °C;

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Table I. Rate Constants, k_{ir}, for the Reaction of Triplet Ketones with Amines in Benzene

amine	fluorenone k_{ir} M^{-1} s^{-1}	benzophenone[a] k_{ir} M^{-1} s^{-1}
2-$C_4H_9NH_2$	3.9×10^4	2.5×10^8
2-$C_4H_9NHCH_3$	2.2×10^6 [b]	1.4×10^9
$(C_2H_5)_3N$	2.3×10^7; 1.7×10^7 [b]	2.3×10^9
$(C_2H_5)_2NCH_2CH_2OH$	5.4×10^7	
$(HOCH_2CH_2)_3N$	2.2×10^8	
$C_6H_5NH_2$	2.2×10^9 [c]	
$C_6H_5NHCH_3$	7.1×10^9 [c]	

[a] Reference 27. [b] Reference 2, in cyclohexane. [c] Reference 11, in cyclohexane.

Table II. Photoreduction of Fluorenone by Tertiary Amines in Benzene and the Effects of Hydroxyethyl Groups and Added Thiol

fluorenone, M	amine compound	amine concn, M	quantum yield
0.005, 0.010	$(C_2H_5)_3N$	0.013	0.80[a,b]
0.005, 0.010	$(C_2H_5)_3N$	0.10	0.74[a,c]
0.080	$(C_2H_5)_3N$	0.05	0.50
0.080	$(C_2H_5)_3N$	0.10	0.44[a]
0.080	$(C_2H_5)_3N$	0.50	0.20
0.005	$HOCH_2CH_2N(C_2H_5)_2$	0.010	1.8[a]
0.010	$HOCH_2CH_2N(C_2H_5)_2$	0.010	2.0[a]
0.082	$HOCH_2CH_2N(C_2H_5)_2$	0.010	0.9[a]
0.050	$HOCH_2CH_2N(C_2H_5)_2$	0.010	1.1
0.050	$HOCH_2CH_2N(C_2H_5)_2$	0.10	0.77[c]
0.004	$(HOCH_2CH_2)_3N$	0.010	1.9[a]
0.008	$(HOCH_2CH_2)_3N$	0.010	2.0[a]
0.060	$(HOCH_2CH_2)_3N$	0.020	1.2
0.060	$(HOCH_2CH_2)_3N$	0.050	1.0
0.060	$H_2NCH_2CH_2N(CH_3)_2$	0.10	0.78[d]
0.063	$H_2NCH_2CH_2N(C_2H_5)_2$	0.10	0.78
0.063	$H_2NCH_2CH_2N(C_2H_5)_2$	0.05	0.94[e]

[a] Determined with Aberchrome-540 actinometer, 334-nm irradiation; all others on rotating wheel. [b] Mesitylene-2-thiol, 0.017 M, decreased quantum yield to 0.27. [c] 1-Pentanethiol, 0.03 and 0.3 M, had no effect on quantum yield. [d] 1-Pentanethiol, 0.03 M, decreased quantum yield to 0.64. [e] 1-Pentanethiol, 0.10 M, decreased quantum yield to 0.74.

Table III. Photoreduction of Fluorenone by Secondary Amines in Benzene and Catalysis by 1-Pentanethiol (PSH)

fluorenone, M	amine compound	amine concn, M	PSH, M	quantum yield
0.008	$(2\text{-}C_3H_7)_2NH$	0.012		~0.01[a]
0.008	$(2\text{-}C_3H_7)_2NH$	0.012	0.03, 0.10[b]	0.46[a]
0.008	$(2\text{-}C_3H_7)_2NH$	0.044		~0.02[a]
0.008	$(2\text{-}C_3H_7)_2NH$	0.044	0.01, 0.10	0.36[a]
0.065	$(2\text{-}C_3H_7)_2NH$	0.01–1.0		~0.02
0.065	$(2\text{-}C_3H_7)_2NH$	0.10	0.01–0.10	0.36
0.065	$(2\text{-}C_3H_7)_2NH$	1.0	0.02, 0.04	0.16
0.060	$(n\text{-}C_3H_7)_2NH$	0.05		0.12
0.060	$(n\text{-}C_3H_7)_2NH$	0.40		0.06
0.060	$(n\text{-}C_3H_7)_2NH$	0.05	0.06, 0.11	0.50[c]
0.060	2-$C_4H_9NHCH_3$	0.14		0.10
0.070	$HOCH_2CH_2NHC_2H_5$	0.01, 0.03		0.21
0.070	$HOCH_2CH_2NHC_2H_5$	0.03	0.01, 0.04	0.49
0.070	$CH_3NH(CH_2)_4NHCH_3$	0.12		0.15
0.070	$CH_3NH(CH_2)_4NHCH_3$	0.12	0.01, 0.10	0.40
0.060	$C_6H_5NHCH_3$	0.17		<0.01
0.006	$C_6H_5NHCH_3$	0.017		<0.01
0.0030	$C_6H_5NHCH_3$	0.010	0.01, 0.10	0.10
0.060	$C_6H_5NHCH_3$	0.012	0.01, 0.10	0.10
0.004	$C_6H_5NHCH(CH_3)_2$	0.011		~0[a]
0.004	$C_6H_5NHCH(CH_3)_2$	0.011	0.01	0.12[a]

[a] Same as footnote *a*, Table II. [b] Photoreduction of fluorenone by 0.04–1.0 M 1-pentanethiol alone in benzene is inefficient, φ ~0.03. [c] Benzenethiol, 0.002 and 0.020 M, reduces quantum yield to 0.08.

mmp 182–184 °C dec. The acetic acid extracts were combined, and portions were treated with (i) 0.5 g of phenylhydrazine or (ii) 0.25 g 2,4-dinitrophenylhydrazine and 1 mL concentrated HCl, heated for 5 min, and cooled. From portion (i) glycolaldehyde phenylhydrazone was obtained: mp 161–163 °C; reported[25] 162 °C, and from (ii) the 2,4-dinitrophenylosazone: mp 333–336 °C, lit.,[26] 330 °C.

Results

Rate Constants. Values of k_{ir} for reactions of fluorenone triplet with amines in benzene were determined from retardation by stilbene of photoreduction by the amines (Table I). k_{ir} for 2-aminobutane, 4×10^4 M^{-1} s^{-1}, is slightly higher than an earlier estimate[9] but still quite low, 2 and 3 orders of magnitude lower than for a secondary amine and for triethylamine, respectively. Hydroxyl substituents increase k_{ir}, one in 2-(diethylamino)ethanol, by a factor of >2 and 3, triethanolamine, by an order of magnitude to 2.2×10^8 M^{-1} s^{-1}. An attempt was made to determine k_{ir} for the reaction with 1-pentanethiol by pulse-laser photolysis.[16] Decay of the triplet was increased only ~2% by 0.6 M thiol; 1 M thiol appeared to increase the lifetime, possibly by a solvent effect; k_{ir} appears to be quite low, but was not determined.

Quantum Yields. Tertiary Amines (Table II). Quantum yields for the overall reduction of <0.01 M fluorenone by 0.013 and 0.10 M triethylamine in benzene are ~0.8, consistent with earlier results.[2,12] We now find that hydroxyl substituents in tertiary amines lead to a major increase in the reduction quantum yield, essentially, to the maximum theoretical values, φ 1.8–2.0 at <0.01 M fluorenone and 0.01 M 2-(diethylamino)ethanol and triethanolamine. Yields are lower at higher concentrations of fluorenone. 2-(Dimethylamino)ethylamine and 2-(diethylamino)ethylamine appear to behave like 2-(diethylamino)ethanol but were not examined in detail. An aromatic thiol, mesitylene-2-thiol, strongly retarded reduction by triethylamine, while 1-pentanethiol either had no effect or led to some retardation.

Reduction by 2-(diethylamino)ethanol led, after treatment with aqueous acid, to fluorenone pinacol and acetaldehyde in 85% and 74% yields, respectively. These products were also found in >90% yield in the reduction by 2-(diethylamino)ethylamine. Glycolaldehyde was characterized after photoreduction by triethanolamine.

Secondary Amines (Table III) are inefficient photoreducing agents for fluorenone. Quantum yields are 0.01–0.02 over a range of concentrations of fluorenone and diisopropylamine. *N*-Isopropylaniline and *N*-methylaniline are almost totally inefficient.[11] Yields are somewhat higher for some other secondary amines: φ ~0.1–0.2 for di-*n*-propylamine, *N*-methyl-2-butylamine, *N,N'*-dimethyl-1,4-diaminobutane, and 2-(ethylamino)ethanol. However, photoreduction of fluorenone by secondary aliphatic amines is strongly catalyzed by aliphatic thiol. 1-Pentanethiol, itself an inefficient photoreducing agent (φ ~0.03 at 0.04–1.0 M thiol), increased reduction by 0.01 M diisopropylamine from φ ~0.01 to φ 0.46 and reduction by 0.10 and 1.0 M amine to 0.36 and 0.16, respectively. Reductions by di-*n*-propylamine and 2-(ethylamino)ethanolamine were increased to φ 0.5, from 0.12 and 0.21, respectively, and reduction by *N,N'*-dimethyl-1,4-diaminobutane was increased from φ 0.15 to φ 0.40. However, reductions by *N*-methylaniline and *N*-isopropylaniline were increased by thiol only to φ ~0.1 from ~0.01. Aromatic thiol did not catalyze, but reduced, quantum yield for di-*n*-propylamine from 0.12 to 0.08.

Primary Amines (Table IV). Quantum yields for photoreduction by 2-aminobutane are low at low concentration, φ ~0.03 at 0.1 M amine, rise to ~0.3 at 1 M amine, and decrease at higher concentration. As with secondary and tertiary amines, the hydroxyl substituent increased reduction efficiency. However, in contrast to the effect in secondary amine systems, 0.01 M thiol had no catalytic effect; retardation occurred at 0.05 and 0.10 M

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[25] "Tables for Identification of Organic Compounds, Supplement to Handbook of Chemistry and Physics"; Chemical Rubber Publishing Company: Cleveland, 1960; p 80.

[26] *Chem. Abstr.* **1969**, *70*, 19994μ.

Table IV. Photoreduction of Fluorenone by Primary Aliphatic Amines in Benzene: Effect of 1-Pentanethiol (PSH)

fluorenone, M	amine compound	amine M	PSH, M	quantum yield
0.010	2-$C_4H_9NH_2$	0.10		0.04[a]
0.055	2-$C_4H_9NH_2$	0.20		0.02
0.062	$HOCH_2CH_2NH_2$	0.22		0.16
0.062	$HOCH_2CH_2NH_2$	0.22	0.20	0.11
0.058	1-$C_5H_{11}NH_2$	1.2		0.24
0.055	2-$C_4H_9NH_2$	1.2		0.32[a]
0.055	2-$C_4H_9NH_2$	6.2		0.11
0.009	2-$C_4H_9NH_2$	2.0		0.13[a]
0.009	2-$C_4H_9NH_2$	1.1		0.23[a]
0.009	2-$C_4H_9NH_2$	1.1	0.01	0.23[a]
0.009	2-$C_4H_9NH_2$	1.1	0.05	0.15[a]
0.009	2-$C_4H_9NH_2$	1.1	0.10	0.10[a]

[a] Footnote *a*, Table II.

Table V. Photoreduction of Fluorenone by 2-Aminobutane (Am): Effects of Anilines and Thiols (TSH)

fluorenone, M	amine, M	C_6H_5NHR R	C_6H_5NHR M	TSH T	TSH M	quantum yield
0.070		H	0.02, 0.1			0.01
0.060	1.1	H	0.01, 0.1			~0.01
0.060	1.1	H	0.012	1-C_5H_{11}	0.10	0.62
0.060	1.1	H	0.13	1-C_5H_{11}	0.01, 0.10	0.45
0.062	1.1	H	0.020			~0
0.062		H	0.017	C_6H_5	0.02, 0.10	0.07
0.062	1.1	H	0.020	C_6H_5	0.02	0.31
0.062	0.34	H	0.020	C_6H_5	0.02	0.18
0.062	1.1	H	0.020	C_6H_5	0.10	0.22
0.061	1.1	CH_3	0.021			0.04
0.062	1.1	CH_3	0.020	1-C_5H_{11}	0.015, 0.10	0.51
0.0060	1.1	CH_3	0.014	1-C_5H_{11}	0.02, 0.11	0.51[a]
0.0060	0.70	CH_3	0.017	1-C_5H_{11}	0.010	0.31
0.0060	0.42	CH_3	0.017			<0.01
0.0060	0.42	CH_3	0.017	1-C_5H_{11}	0.010	0.26
0.0060	0.14	CH_3	0.017	1-C_5H_{11}	0.010, 0.10	0.23

[a] Footnote *a*, Table II.

thiol. Aniline and *N*-methylaniline themselves lead to essentially no photoreduction[11] and strongly inhibit the inefficient reduction by 2-aminobutane (Table V). However, addition of 1-pentanethiol negated this inhibition and catalyzed reduction strongly, from φ ~0.01 in the presence of 0.01 M aniline to φ 0.62, a value twice the maximum observed in the absence of inhibitor. The catalysis was slightly less in the presence of 0.13 M aniline. Thiol also reversed the inhibition by *N*-methylaniline, and the catalysis decreased with decreasing concentration of 2-aminobutane. Benzenethiol and aniline led to somewhat more reduction than aniline alone, and the aromatic thiol also led to significant catalysis of the aniline-inhibited reduction by 2-aminobutane from φ ~0 to ~0.3.

Discussion

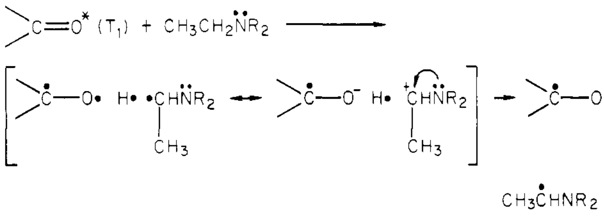
Reactivity of Triplet Fluorenone. A measure of the low reactivity of fluorenone may be seen in k_{ir} with 2-aminobutane, 4 orders of magnitude lower than for benzophenone[27] (Table I). The differences are smaller with secondary and tertiary amines, decreasing with rising k_{ir}. However, the reaction of benzophenone may be approaching diffusion control, and any intrinsically greater reactivity would not be revealed. If, then, the reactivity of fluorenone toward 2-propanol should also be 10^{-4} that of benzophenone, k_{ir} would be $\sim 10^2$ M^{-1} s^{-1} as compared with $\sim 10^6$ M^{-1} s^{-1}. This, combined with low triplet yield in 2-propanol[17] and a decay constant of $\sim 10^4$ s^{-1},[28,29] would lead to essentially no abstraction of H from the alcohol. As will be noted below, the reaction of fluorenone with a primary amine may follow a course similar to that of benzophenone with an alcohol.

Reaction with Tertiary Amines. The high rate constant for the reaction with TEA, although lower than that for benzophenone, indicates a large component of charge transfer in the transition state, favored by the low ionization potential of TEA and reduction potential of fluorenone.[30] This is supported by the relationship between log k_{ir} and donor ionization potential in excited fluorenone–amine systems and by the increase in k_{ir} with increasing polarity of solvent.[9] The fluorenone ketyl radical is formed with unit quantum efficiency from TEA,[31] and if the reaction proceeds via initial electron transfer, this is followed entirely by proton transfer, with no return to the ground state (eq 3). The overall

$$>C{=}0^*(T_1) + CH_3CH_2NR_2 \rightarrow [>\dot{C}{-}O^- \; CH_3CH_2\dot{N}R^+] \rightarrow >\dot{C}{-}OH + CH_3\dot{C}H\ddot{N}R_2 \quad (3)$$

reduction yield is not higher than the initial ketyl yield, indicating that if reduction of ground-state ketone by TEA-derived radicals occurs, this is compensated for by regeneration of starting materials by disproportionation. The product of cross-coupling of fluorenone ketyl and TEA-derived radical has been isolated,[2] indicating that reduction of a second ground-state molecule is not very rapid in comparison with the radical combination process.

The electronegative hydroxyl groups in the two hydroxyethyl tertiary amines decrease their basicity substantially, by ~1 pK_a unit per hydroxy.[32] Despite this decreased reactivity toward protons in water, the hydroxyls increase k_{ir}, possibly as they provide a polar microenvironment at the reaction site. This may facilitate formation of a charge-transfer complex (eq 3) or the polar contributor to the transition state for a hydrogen abstraction (eq 4).



(4)

To this end, they need be present only at the reaction site and, thus, would not decrease intersystem crossing as solvent alcohol does.[17] Most remarkably, the hydroxyl substitutents increase overall reduction yields more than twofold, essentially to the maximum possible value of 2, an uncommon result in photoreduction by amines. Since TEA itself leads to ketyl radical with unit efficiency, the hydroxyl substitutents must increase reduction yields by causing rapid reduction of ground-state ketone by the α-aminoalkyl radical. This differs from catalysis by methanol of the reaction of excited singlet benzene with tertiary amines, in which the effect appears to be on the proton transfer in the initial exciplex.[33] In our work ethanol retards the reduction of fluorenone by TEA.

Thus, the second reduction also may proceed via a charge-transfer mechanism and be facilitated by solvation by the hydroxl. Charge transfer would be followed either by proton transfer and

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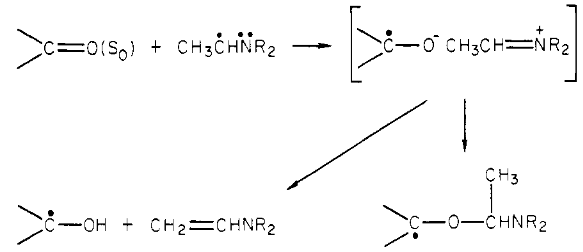
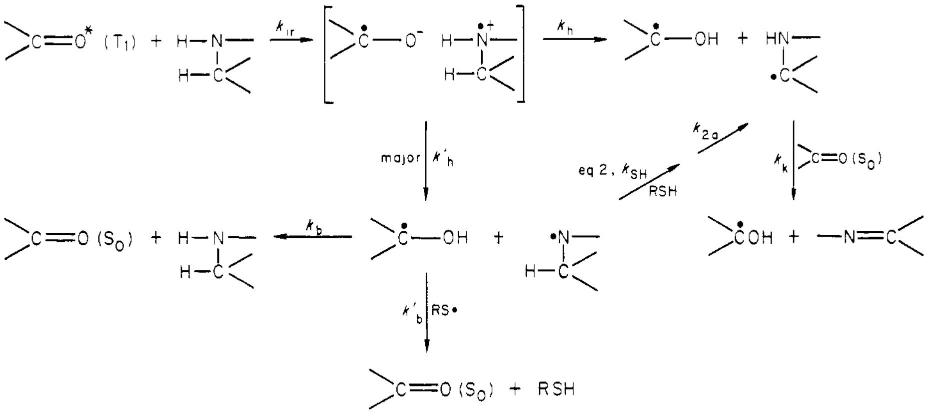
formation of ketyl radical and enamine or by ion-pair combination, an addition reaction equivalent to reduction (eq 5). Products corresponding to combination of the radicals formed by the addition route have been observed in the photoreduction of fluorenone by N,N-dimethylaniline.[10] Alternatively, the reduction may be a hydrogen transfer facilitated by polar contributions to the transition state as in eq 4. The hydrogen transfer and addition courses both lead to fluorenone pinacol and aliphatic aldehyde after treatment with water, and these products were obtained in high yield. It is of interest that acetaldehyde was obtained in greater than statistical yield in reductions by 2-(diethylamino)ethanol and 2-(diethylamino)ethylamine. Thus, abstraction is predominantly from the unsubstituted ethyl groups, and the polar β substituent does not facilitate the reduction by causing the initial abstraction to occur from its own alkyl group. It may be noted that hydroxyl substituents in amines do not appear to facilitate reduction of benzophenone as they do with fluorenone.


(5)


(6)

The observed decrease in reduction quantum yield at higher concentrations of fluorenone is unexpected. At high concentrations light may be absorbed largely near the face of the cell, leading to high local concentration of triplet and radical and, thus, to quenching. Quenching of triplet by ground-state ketone may also decrease yields. If this is the sole effect of concentration, a quenching constant of $\sim 10^7$ M^{-1} s^{-1} would be indicated.

Secondary Amines. High k_{ir} and the relation of k_{ir} to ionization potential support a charge-transfer mechanism.[9] The triplet is largely trapped at the lowest concentrations of diisopropyl- and di-n-propylamines, where little quenching of singlet occurs.[12] Nevertheless, reduction quantum yields are quite low; the catalysis by thiol indicates that this is due to predominant abstraction of H from N rather than from α-C. Somewhat higher quantum yields with secondary amines containing primary and secondary, as compared with tertiary, α-H support initial charge transfer with more favorable abstraction of the more acidic α-H in competition with abstraction of H from N. Steric and stereoelectronic factors also favor abstraction from less substituted carbon.[6,34,35] In the absence of thiol, the dialkylaminyl radicals disproportionate with ketyl to regenerate starting materials. Thiol catalyzes the reduction by a sequence of hydrogen atom transfers. Aminyl radical abstracts H from S in competition with the disproportionation, and thiyl radical abstracts α-H from amine, also in competition with its disproportionation with ketyl, converting alkylaminyl to a product-forming aminoalkyl radical (eq 2 and 6). This mechanism precludes catalysis by thiol in the reduction by tertiary amines, and none is observed.

Effective catalysis by thiol depends on concentrations of thiol, ketone, and amine such that (a) alkylaminyl radical abstracts H from thiol faster than it disproportionates with ketyl, (b) ground-state ketone oxidizes aminoalkyl radical faster than thiol reduces it, and (c) thiyl radical abstracts H from amine faster than it disproportionates with ketyl (eq 7–9) These inequalities call for high concentrations of ketone and amine and optimum intermediate concentration of thiol, and these dependencies were observed in benzophenone–amine–thiol systems.[22] The fluorenone systems differ in that the excited singlet is quenched by moderate concentrations of secondary (and tertiary) amines,[12-14] and quantum yields are also reduced by high concentration of the ketone. Thus, the less effective catlaysis at 1 M than at 0.01 M diisopropylamine may be caused by singlet quenching[12] and the consequent lower yield of aminyl radical. Increased retardation at high concentration of thiol is seen with primary amines (Table IV).

$$k_{SH}(>CH\dot{N}-)(RSH) > k_b(>CH\dot{N}-)(>\dot{C}OH) \tag{7}$$

$$k_k(>\dot{C}NH-)(>C{=}O) > k_{2b}(>\dot{C}NH-)(RSH) \tag{8}$$

$$k_{2a}(>CHNH-)(RS\cdot) > k_b'(RS\cdot)(>\dot{C}-OH) \tag{9}$$

The inefficient catalysis by thiol of reduction of N-alkyl-anilines, as compared with dialkylamines, is noteworthy. The n electrons of an aniline are delocalized over the benzene ring. This would render them less effective in stabilizing the arylaminoalkyl radical and the transition state for its formation. Thus, the thiyl radical would abstract α-H less rapidly than from dialkylamines, the inequality of eq 9 would be less favorable, and catalysis by thiol would thus be less effective. Very effective quenching of the singlet by anilines[36] might contribute to low thiol catalysis.

Primary Amines. The failure of thiol to catalyze the inefficient reduction of fluorenone by primary amines was unexpected. It cannot be due to the stronger α-C–H bond of primary amines, which might prevent efficient abstraction of α-C–H by thiyl,[37] since thiol catalyzes the reduction of benzophenone by both primary and secondary amines. Absence of this catalysis and low k_{ir} indicate that the efficiency of the reduction is limited by the fraction of the triplet reacting with the primary amine before decay and not by formation and disproportionation of aminyl radicals. To the extent that the triplet may interact with the n electrons, the higher ionization potential,[38] stronger N–H bonds,[39] and less stabilized monoalkylaminyl radical and radical cation, as compared

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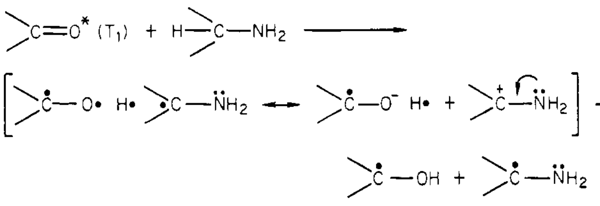
with secondary amines, may lead to some quenching, but not to significant abstraction of H from N and formation of aminyl radicals. Reduction of fluorenone by a primary amine may well proceed via attack on α-H, with abstraction made possibly by polar contributions to stabilization of the transition state and the aminoalkyl radical (eq 4 and 10). This reaction also appears to be



(10)

facilitated by the polar microenvironment of hydroxyethylamine. It is similar to the abstraction of α-H from alcohols[7] by the more reactive n,π^* triplet of benzophenone. Benzophenone appears to abstract α-H from primary amines in this way, since a deuterium kinetic isotope effect has been observed,[21b] but benzophenone also abstracts H from N of primary aliphatic amines. The failure of the fluorenone triplet to abstract from 2-propanol or cyclohexane underlines[1,2] its dependence on the stabilization which α-N provides.

In accordance with this analysis, catalysis by thiol of the reduction of fluorenone by primary amine should occur if aminyl radicals are introduced into the system. A primary amine which has no α-C–H, i.e., *tert*-butylamine, reacts with a benzophenone triplet and forms ketyl and aminyl radicals with unit efficiency. This leads to little net reduction as disproportionation (eq 1 and 6) dominates over ketyl–ketyl coupling.[21b] In the photoreduction of benzophenone by 2-aminobutane *tert*-butylamine in high concentration (5 M) was added, reacted with the triplet, and inhibited the photoreduction.[22] Then, addition of a low concentration of aliphatic thiol negated this inhibition, as the *tert*-butylaminyl radical initiated the catalytic sequence of hydrogen transfers (eq 2).[22] *tert*-Butylamine cannot be used in this way in the fluorenone system because of a medium effect on triplet yield,[15-17] and it is doubtful, in any event, that it would lead to ketyl and aminyl radicals. However, aniline, with high k_{ir} ($>2 \times 10^9$ M^{-1} s^{-1}), forms fluorenone ketyl and aminyl radicals in high yield.[31] At low concentration, aniline essentially completely inhibited reduction by 2-aminobutane by anilino–ketyl disproportionation (Table V, line 2). Reversal of this inhibition by thiol (line 3) indicates that a rapid radical sequence occurs (eq 11–13).

$$>C{=}O^*(T_1) + C_6H_5NH_2 \rightarrow\ >\dot{C}\text{-}OH + C_6H_5NH\cdot \qquad (11)$$

$$C_6H_5NH\cdot + RSH + \rightarrow C_6H_5NH_2 + RS\cdot \qquad (12)$$

$$RS\cdot +\ >CHNH_2 \rightarrow RSH +\ >\dot{C}NH_2 \qquad (13)$$

Anilino radical abstracts H from thiol; thiyl abstracts H from α-C of 2-aminobutane, and overall reduction results. Indeed catalysis of the aniline-inhibited reduction leads to higher efficiency than the direct reduction, φ 0.6 as compared with 0.3. Essentially all the triplet is trapped by aniline, leading to a high yield of anilino radical and then, via the catalytic sequence, to a higher yield of aminoalkyl radical than results from the direct reaction of triplet with 2-aminobutane.

N-Methylaniline behaves similarly to aniline in inhibiting photoreduction by 2-aminobutane and effecting catalysis by thiol (Table V). This indicates that low catalysis by thiol of the photoreduction by *N*-methylaniline, itself (Table III) is not due to inefficiency in abstraction of H from thiol by the more stable secondary anilino radical but to less efficient abstraction of α-H from the *N*-alkylaniline than from purely aliphatic amines.

The small increase in quantum yield, from <0.02 to 0.07, on addition of benzenethiol to fluorenone–aniline in the absence of a reducing amine (Table V, lines 1 and 6) is similar to that observed in the benzophenone–*tert*-butylamine–pentanethiol system.[22] This indicates that, after abstraction of H from S by an aminyl radical, the thiyl–ketyl disproportionation is less efficient than aminyl–ketyl disproportionation in competing with coupling of ketyl radicals to pinacol. Catalysis by benzenethiol of the aniline-inhibited reduction by 2-aminobutane (lines 7–9) is less effective at lower concentration of the aliphatic amine and at higher concentrations of thiol, consistent with the proposed mechanism. The effect of concentration of aliphatic amine on the catalysis is also seen in the *N*-methylaniline–1-pentanethiol system.

Catalysis by benzenethiol is less effective than that by 1-pentanethiol. The outcome of the competing radical reactions in such systems is, of course, sensitive to structure. Hydrogen is abstracted more rapidly from aromatic than from aliphatic thiol, and the aromatic thiyl radical is a less effective abstracter of α-H from amines and alcohols. The transfer of H from α-C to thiyl is critical to catalysis and will be more favorable with aliphatic thiyl, while transfer from S–H to α-C is inhibitory and will be more favorable with aromatic thiol. This accounts for the lower catalytic effect of aromatic thiol and the decrease at higher concentrations which was not observed at the concentrations of aliphatic thiol used. Indeed, in benzophenone–amine systems aromatic thiols led to inhibition and catalysis was observed only by aliphatic thiol.[40] Benzophenone abstracts H from α-C and N of amines, and aromatic thiol may transfer H rapidly to the α-aminoalkyl radical, leading to net inhibition. In the fluorenone system, the aniline inhibition leads initially only to N-centered radicals and then to thiyl radicals, and any subsequent net abstraction of H from α-H is observed as catalysis. Analogous structural effects are also observed in the photoreduction of benzophenone by alcohols. The α-hydroxyalkyl radical is less stabilized and more reactive than the α-aminoalkyl radical. Thus, the alcohol-derived radical abstracts H from S more effectively in the critical inhibition step, and thiyl abstracts H from α-C of alcohols less rapidly in the critical catalytic step, in competition with the other competing processes. In these systems, then, both aliphatic and aromatic thiols lead to inhibition, with the aromatic thiols being the more effective inhibitors. Only in the benzophenone–benzhydrol system, with the easily abstracted benzhydrol α-H and the highly stabilized diphenylketyl radical, was catalysis by thiol observed, in a *tert*-butylamine-inhibited reduction.[22b]

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Registry No. Fluorenone, 486-25-9; 2-$C_4H_9NH_2$, 13952-84-6; $(C_2H_5)_3N$, 121-44-8; $(C_2H_5)_2NCH_2CH_2OH$, 100-37-8; $(HOCH_2CH_2)_3N$, 102-71-6; $H_2NCH_2CH_2N(C_2H_2)_2$, 100-36-7; $H_2NCH_2CH_2N(CH_3)_2$, 108-00-9; $(2\text{-}C_3H_7)_2NH$, 108-18-9; $(3\text{-}C_3H_7)_2NH$, 142-84-7; 2-$C_4H_9NHCH_3$, 7713-69-1; $HOCH_2CH_2NHC_2H_5$, 110-73-6; $CH_3NH(CH_2)_4NHCH_3$, 16011-97-5; $C_6H_5NHCH_3$, 100-61-8; $C_6H_5NHCH(CH_3)_2$, 768-52-5; $HOCH_2CH_2NH_2$, 141-43-5; 1-$C_5H_{11}NH_2$, 110-58-7; C_6H_5SH, 108-98-5; $C_6H_5NH_2$, 62-53-3; PSH, 110-66-7.

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