ACCELERATION BY ALIPHATIC MERCAPTAN IN THE
PHOTOEXCITED CARBONYL-AMINE REDOX SYSTEM
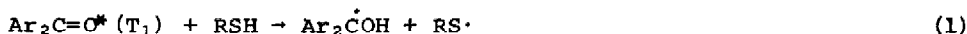
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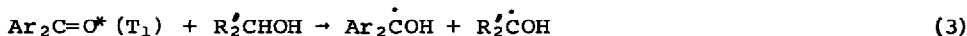Department of Chemistry, Brandeis University, Waltham, Mass. 02154

Summary. Low concentration of aliphatic mercaptan increases the quantum
yield of photoreduction of benzophenone by 2-butylamine, nearly to the
theoretical maximum value. It is proposed that the effect arises from
catalysis by mercaptan of transfer of hydrogen from the amine radical
cation to the ketyl radical anion in the charge-transfer complex.

Mercaptans are efficient quenchers and inefficient reducing agents of pho-
toexcited benzophenone[1] and acetophenone.[2] The quenching may involve charge-
transfer largely or hydrogen transfer facilitated by charge-transfer, and if
hydrogen transfer should occur[3] disproportionation and little net reduction,
resulting in quenching, follow[4] eqs. 1,2.

$$Ar_2C=O^* \ (T_1) + RSH \rightarrow Ar_2\overset{.}{C}OH + RS\cdot \tag{1}$$

$$Ar_2\overset{.}{C}OH + RS\cdot \rightarrow Ar_2C=O(So) + RSH \tag{2}$$

Alcohols and amines[5] are effective photoreducing agents for benzophenone.
Mercaptans strongly retard the photoreduction by alcohols and the photooxida-
tion of the alcohols, and they protect against radiation damage;[4] they may do
so via hydrogen transfer reactions,[4,5] which, may, but need not,[7] convert
photochemically and radiolytically produced radicals to starting materials,
eqs. 3,4,2.

$$Ar_2C=O^* \ (T_1) + R_2'CHOH \rightarrow Ar_2\overset{.}{C}OH + R_2'\overset{.}{C}OH \tag{3}$$

$$R_2'\overset{.}{C}OH + RSH \rightarrow R_2'CHOH + RS\cdot \tag{4}$$

We now find unexpected acceleration by an aliphatic mercaptan of photo-
reduction of benzophenone by 2-butylamine. Solutions of benzophenone and 2-
butylamine, without additive and with varying concentration of sulfur compound,
were degassed by freeze-thaw cycles, closed under argon and irradiated simul-
taneously in 1 cm Pyrex tubes by a G.E. H85 U.V. lamp on a turntable. Rates
of reduction were obtained from the decrease in absorption at 344 nm or at
1660 cm^{-1} with time of irradiation. Some results are summarized in the Table.

Table I.   Effects of Sulfur Compounds on Photoreduction of 0.14 $\underline{M}$ Benzo-
phenone by 1.3 $\underline{M}$ 2-Butylamine

| Additive	$\underline{M}$	Solvent	R_s/R_o [a]
1-Pentanethiol	0.021	Benzene	1.54
n-Propyl disulfide[b]	0.022	Benzene	~ 1
1-Pentanethiol	0.019	Acetonitrile	1.37
1-Pentanethiol	0.021	t-Butyl Alcohol	1.23
1-Pentanethiol	0.019	Cyclohexane	1.51
1-Pentanethiol	0.00002	Benzene	1.0
1-Pentanethiol	0.00023	Benzene	1.1
1-Pentanethiol	0.0023	Benzene	1.3
1-Pentanethiol	0.023	Benzene	1.5
1-Pentanethiol	0.17	Benzene	1.2
2-Mercaptomesitylene	0.0001	Benzene	0.65
2-Mercaptomesitylene	0.001	Benzene	0.59
2-Mercaptomesitylene	0.01	Benzene	<0.01

[a]   Ratio of rates of photoreduction in the presence of the indicated con-
centration of thiol, R_s, to that in absence of thiol, R_o.

[b]   Initial rate is unaffected by the disulfide; subsequent acceleration
may be due to formation of mercaptan.

An aliphatic mercaptan accelerates photoreduction by the amine, while an
aromatic mercaptan, as in reduction by alcohols,[8] retards very efficiently.
Acceleration by the aliphatic mercaptan was confirmed in quantum yield measure-
ments by ferrioxalate actinometry in a Bausch and Lomb Monochromator.   Quantum
yields for photoreduction of 0.13 $\underline{M}$ benzophenone by 1.3 $\underline{M}$ 2-butylamine in ben-
zene, without and with added 0.022 $\underline{M}$ 1-pentanethiol were φ_o = 1.17 and
φ_s = 1.82, φ_s/φ_o = 1.56.   For similar solutions of the components in tert-butyl
alcohol, with and without added 0.013 $\underline{M}$ pentanethiol, quantum yields were
obtained, φ_o = 1.26, φ_s = 1.60, φ_s/φ_o = 1.27.   Accelerations were similar on
the turntable and on the monochromator.   Reduction products in absence and

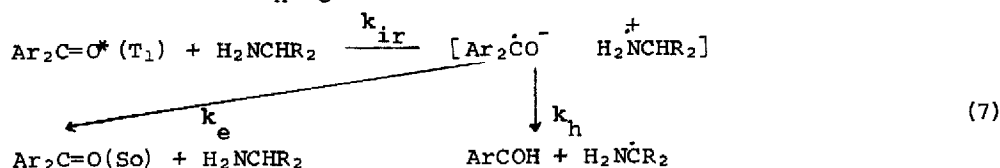presence of mercaptan were identical, benzopinacol.

Acceleration by the mercaptan appears to be present at 2×10^{-4} $\underline{M}$ mercaptan (Table I). The effect increases with concentration and then decreases at some concentration greater than 0.02 $\underline{M}$ mercaptan. The maximum quantum yield is 2, possible only when all triplets lead to hydrogen abstraction, and all amine derived radicals reduce a ground state ketone, eq. 5.

$$Ar_2C=O(So) + R',R''\overset{\cdot}{C}NH_2 \rightarrow Ar_2\overset{\cdot}{C}OH + R',R''C=NH \tag{5}$$
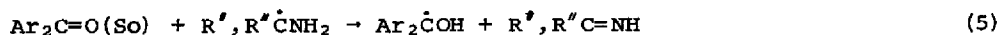
The 54% increase due to 0.022 $\underline{M}$ mercaptan in benzene is large, increasing φ from 1.17 to 1.82, nearly to the maximum. The accelerating effect of mercaptan appears to be less in the single experiment in the more polar solvent acetonitrile, and still less in the hydroxylic solvent tert-butyl alcohol. With values of quenching constant for mercaptan[1] and amine[9] equal to 1.7×10^7 $\underline{M}^{-1}$ sec^{-1} and 2.5×10^8 $\underline{M}^{-1}$ sec^{-1} respectively, the decrease in rate at 0.17 $\underline{M}$ mercaptan, 1.3 $\underline{M}$ amine, cannot be due to quenching of triplet by mercaptan and is attributed to increasing importance of the hydrogen transfer retarding reactions, eqs. 2,6.

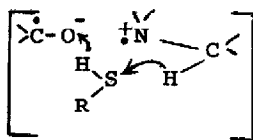$$R'R''\overset{\cdot}{C}NH_2 + RSH \rightarrow R',R''CHNH_2 + RS\cdot \tag{6}$$
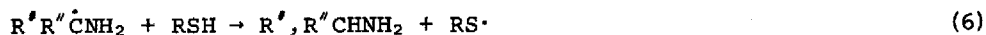
At the lower concentrations of mercaptan all reaction of excited ketone starts normally with the amine. Reactions of excited benzophenone with amines differ from those with alcohols in proceeding with very high rate constant, $> 10^8$ $\underline{M}^{-1}$ sec^{-1}. This is reflected in high rates of quenching of phosphorescence by amines[9] and low sensitivity to physical quenchers.[10] However the reactions do not proceed with maximum quantum yield, and may be less efficient than in reduction by alcohols.[11] Since reduction of ground state ketone, eq. 5, appeared efficient, we concluded that amines act rapidly as both quenchers and reducing agents. A mechanism was proposed, involving initial rapid formation of a charge-transfer complex, CTC, k_{ir}, followed either by hydrogen transfer and radical formation, k_h, or by spin-inversion and quenching k_e. The latter would account for the loss of efficiency, and quantum yields would depend largely on the k_h/k_e ratio.[6,5] On the basis of this mechanism we

$$Ar_2C=O^*(T_1) + H_2NCHR_2 \xrightarrow{k_{ir}} [Ar_2\overset{\cdot}{C}O^- \quad H_2\overset{+}{N}CHR_2]$$

$$\swarrow k_e \qquad\qquad \downarrow k_h \tag{7}$$

$$Ar_2C=O(So) + H_2NCHR_2 \qquad ArCOH + H_2N\overset{\cdot}{C}R_2$$
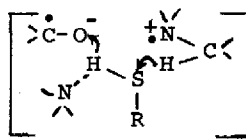
propose that hydrogen transfer within the CTC, k_h, is assisted relative to k_e, by aliphatic mercaptan, and this increases the quantum yield, Formula I. This

might be assisted by amine at high concentration of amine, Formula II.

In photoreduction of benzophenone by 2-butylamine, at concentrations above 0.02 $\underline{M}$ amine, photoreduction became more rapid than predicted from low concentration data.[12] We proposed that a second molecule of amine assists in transfer of hydrogen in the CTC, increasing quantum yield, in a process analogous to that of Formula I, and that the hydrogen transfer may also be assisted by a hydroxylic solvent, and this may be further assisted by amine, in a process analogous to that of Formula II. Such catalysis by mercaptan and amine of oxidation of amines may be important in the intramolecular circumstances of biological oxidations. The aromatic mercaptan acts only as a very effective retarder, Table 1, and the details of this process are being studied further.

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