

Hydrogen-Transfer and Charge-Transfer in
Photochemical and Radiation Induced Reactions

Progress Report
for Period November 1, 1975--October 31, 1976

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Abstract

1. The relative importance of light absorption, quenching of triplet, and hydrogen transfer repair has been examined in retardation by mercaptans of photoreduction of aromatic ketones by alcohols. In the reduction of benzophenone by 2-propanol, retardation is efficient and, after correction for the first two effects, is due entirely to hydrogen-transfer repair, as indicated by deuterium labelling. In reduction of acetophenone by α -methylbenzyl alcohol, repair by hydrogen transfer is also operative. In reduction of benzophenone by benzhydrol, retardation is less efficient and is due to quenching, as the ketyl radical does not abstract hydrogen from mercaptan rapidly in competition with coupling. Deuterium isotope effects are discussed in terms of competitive reactions.

2. Photoreduction of benzophenone by 2-butylamine and by triethylamine is retarded by aromatic mercaptans and disulfides. Of the retardation not due to light absorption and triplet quenching by the sulfur compounds, half is due to hydrogen-transfer repair, as indicated by racemization and deuterium labelling. The remainder is attributed to quenching by the sulfur compound of the charge-transfer-complex intermediate. Photoreduction by primary and secondary amines, but not by tertiary amines, is accelerated by aliphatic mercaptans. The acceleration is attributed to catalysis of hydrogen transfer by the mercaptan in the charge-transfer complex. The effect is large in hydrocarbon solvent, less in polar organic solvents and absent in water.

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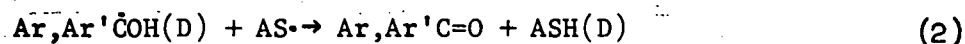
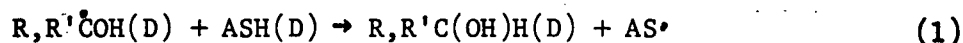
An article based on work supported by this contract was published during this period: "Acceleration by Aliphatic Mercaptan in the Photoexcited Carbonyl-Amine Redox System," S.G. Cohen, A.W. Rose and P.G. Stone, Tetrahedron Letters, 3101 (1976).

Introduction: The program was initiated by our observation that mercaptans and disulfides retard and inhibit the photoreduction of benzophenone by 2-propanol. We demonstrated that this was largely due to a repair mechanism, that radicals were formed in the photochemical process by hydrogen abstraction, in the presence as well as in the absence of sulfur compound, and that mercaptan and thiyl radical restore the substrate derived radicals to their original molecular states by rapid hydrogen donation and abstractions. Similar processes were demonstrated in ⁶⁰Co γ-ray irradiated solutions of aqueous organic compounds. These repair reactions interfere with and effectively prevent the radical combinations which may be the normal course of photochemical and radiation induced damage. We showed that the "repair" reactions are catalyzed disproportionations which normally do not compete favorably with the damaging radical combination reactions. The "repair" reactions may lead to the alternate disproportionation products, changing the composition from the original, but preventing coupling and cross-linking. The sulfur compounds are regenerated in their alternate valence states in these repair reactions and may be used repeatedly in chain inhibition of non-chain processes

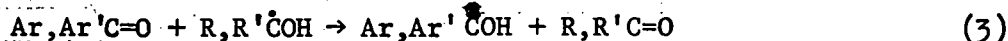
These investigations began with study of oxygen containing substrates, alcohols, ketones, and ethers, for which the prior literature in photochemistry and radiation chemistry was helpful. Much of our more recent work has been with amino compounds, and has led to innovative quantitative contributions to quenching and reaction via charge-transfer complexes. Study of effects of mercaptans on photoreduction by amines is leading in some cases to observations of unexpected accelerative effects, in others, to retardation. This leads to study of the properties of excited charge-transfer complexes and the means for affecting their reactions. These studies will be extended to reactions initiated by absorption of visible light.

1. A detailed analysis has been made of the relative importance, under varying circumstances, of the several ways by which mercaptans and disulfides may retard photochemical reactions- by competition for the absorption of light, by quenching, and by the hydrogen transfer mechanism.

a. In photoreduction of benzophenone by 2-propanol, the rate was halved by 0.001 M of an aromatic mercaptan, 2-mercaptomesitylene, and an aliphatic mercaptan was much less effective. The aromatic mercaptan was more effective in 2-propanol-OD than in the absence of deuterium. After correction for absorption of light, and for direct quenching of the ketone triplet based on quenching constants determined from the effect on phosphorescence, the remaining retardation is attributed to the hydrogen transfer mechanism. This was confirmed quantitatively by introduction of the appropriate amount of deuterium during retardation in deuterio systems. The retardation involves reduction of the 2-propanol-derived radical by mercaptan, the step which introduces deuterium, eq. 1, and oxidation of the ketone derived radical by thiyl, radical, eq. 2.



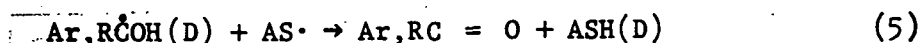
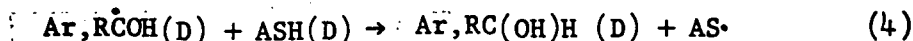
The limiting step in this retardation cycle is that of eq. 1, oxidation of the mercaptan by one of the radicals. Thus the aromatic mercaptan is more effective than the aliphatic, as it leads to the more stable thiyl radical and is more easily oxidized. The alcohol derived radical dominates in this oxidation- reduction since it is less stabilized than the aromatic ketyl radical and more reactive. This limiting step, eq. 1, must occur in competition with other possible reactions of the reactive alcohol derived radical, if it is to be operative and effective. In the system studied, the major competitive reaction is oxidation of the alcohol derived radical by ground-state ketone, which normally leads to a maximum quantum yield of two for the photoreduction, eq. 3.



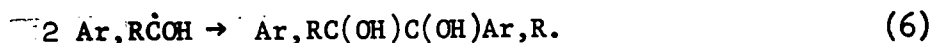
The observed overall deuterium kinetic isotope effect, more favorable retardation in the deuterio system, indicates that the normal isotope effect is somewhat larger in the oxygen to oxygen transfer, eq. 3, than in the sulfur to carbon transfer, eq. 1. This may be attributed to the higher polarizability of sulfur.

b. In photoreduction of acetophenone by α -methylbenzyl alcohol, retardation was less effective, the rate being halved by 0.005 diphenyl disulfide. Deuterium was introduced during the retardation, indicating that the one arylalkylketyl radical

formed in this reaction may be reduced by mercaptan and oxidized by thiyl radical, eqs. 4,5. In this case



retardation was less efficient in the deuterio than in the hydrogen system. The retardation depends on competition between reduction of the ketyl radical by mercaptan and coupling of the ketyl radicals to form the pinacol, eq. 6. The latter reaction



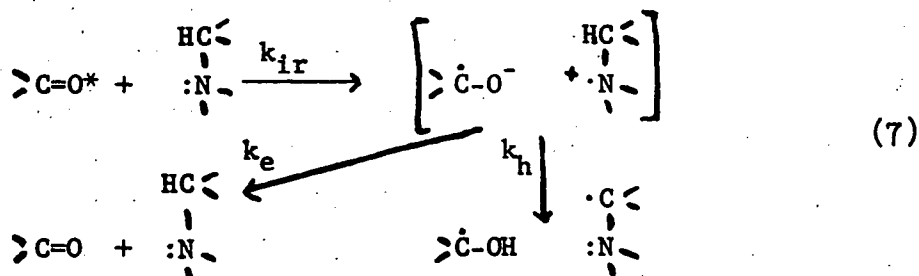
involves no isotope effect, while the reduction, eq. 4, does.

c. The rate of photoreduction of benzophenone by benzhydrol was halved by 0.01 M 2-mercaptomesitylene, no deuterium was incorporated into benzhydrol during the retardation, and the sulfur compound showed equal retarding effectiveness in deuterio and protio systems. The retardation was due entirely to quenching of triplet by the mercaptan. Retardation by the hydrogen transfer mechanism would require oxidation and reduction of benzophenone ketyl radical by thiyl radical and mercaptan respectively. This is possible in principal, and related reactions occur in the acetophenone- α -methylbenzyl alcohol system, above. The limiting step in the cycle would in this case be oxidation of the mercaptan by the benzophenone ketyl radical in competition with dimerization of the ketyl radicals to the pinacol. The rate of the oxidation process is decreased by the high stabilization of this ketyl radical, so that it does not compete effectively with the dimerization. In the event, as one wishes to study the retardation, mercaptan concentration is increased, and the retardation results from quenching of the triplet.

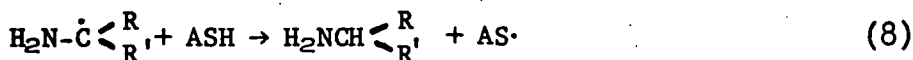
This work is being written up for publication.

2. Reaction of excited carbonyl compounds, and possibly other radical like acceptor species, with amino compounds, thioethers, and other donors appears to proceed via charge transfer complexes. The rate constants of formation of the complexes, k_{ir} , are affected by the triplet energy and reduction potential of the carbonyl compound, and the ionization potential of the amine. The quantum yields of reduction depend on the fate of the charge-transfer complex, the ratio of hydrogen transfer and radical formation, k_h , to charge destruction

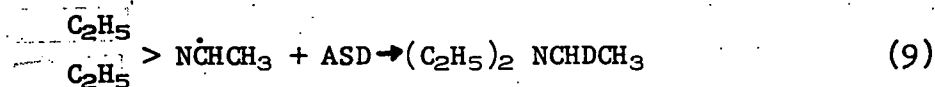
and quenching, k_e . This is indicated for photoreduction by an amine in eq. 7.



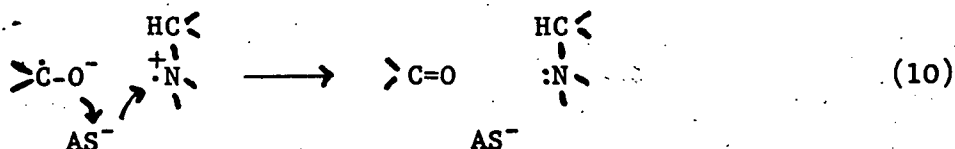
Mercaptans might be expected to retard such reactions by hydrogen transfer repair processes analogous to those in related systems of oxygen compounds, eqs. 1,2. We find that aromatic mercaptans and disulfides do inhibit the photoreduction of benzophenone by 2-butylamine in benzene. After corrections due to absorption of light and direct quenching, the order of effectiveness in retarding by hydrogen transfer and other mechanisms is p-chlorophenylthiol > phenylthiol > 2-mercaptomesitylene. Study of the retarded reduction with optically active amine led to racemization, and the extent of racemization indicated that only half of the corrected retardation was due to reduction of the amine derived radical by mercaptan, eq. 8.



b. This was examined further in retardation by 2-mercaptomesitylene of photoreduction of benzophenone by triethylamine in tert-butyl alcohol and tert-butyl alcohol-OD. The retardation was efficient and study of introduction of deuterium into the amine in a retarded reduction in the deuterated solvent indicated again that about half the



retardation is due to the hydrogen transfer process eq. 9. We suggest that the remainder of the retardation may be due to a reaction of the mercaptan, or mercaptide ion in the presence of amine, with the charge transfer complex, increasing quenching, k_e , relative to hydrogen transfer, k_h eq. 10.

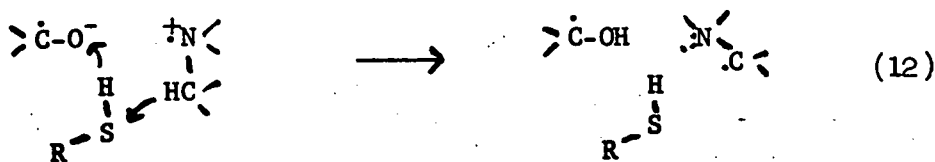


c. This idea is supported by results of study of reduction in the presence of phenylethyl sulfide. Photoreduction of benzophenone by 2-butylamine in benzene

is retarded by this thioether, while reduction by 2-propanol, which does not proceed via a charge transfer complex is unaffected. This aromatic thioether may interact with a charge transfer complex in an analogous fashion, eq. 11, and have no effect on direct abstraction of hydrogen from the alcohol



d. Substantial acceleration of photoreduction of benzophenone by 2-butylamine was caused by low concentration, $\sim 0.01 \text{ M}$, aliphatic mercaptan, raising the quantum yield to 1.8, nearly to the maximum theoretical value of 2. The acceleration was strongest in cyclohexane and benzene, weaker in acetonitrile and tert-butyl alcohol, and absent in water at pH 12. Reduction by a secondary amine, diisopropylamine was also accelerated by aliphatic mercaptan, while that by triethylamine was not accelerated. Some results are summarized in the table. We suggest that the acceleration is due to an interaction of the aliphatic mercaptan with the charge-transfer complex which, in contrast with that of the aromatic mercaptan, increases hydrogen-transfer, k_h , relative to quenching, k_e , eq. 12.



e. This work is being extended to study of possible acceleration by mercaptan and amine of photoreduction by a thioether.

3. Work has been started on ^{60}Co γ -radiolysis of dilute aqueous N-methylacetamide, $\text{CH}_3\text{CONHCH}_3$, as a model for related proteinaceous material. The nature of the cleavage and coupling products is being studied.

Table 1
Effects of aliphatic mercaptans on photoreduction
of 0.14 M benzophenone by amines.

Amine	Mercaptan	<u>M</u>	Solvent	R_s/R_o^a
2-BuNH ₂ ^b	n-C ₅ H ₁₁ SH	0.00002	C ₆ H ₆	1.0
2-BuNH ₂	n-C ₅ H ₁₁ SH	0.00023	C ₆ H ₆	1.2
2-BuNH ₂	n-C ₅ H ₁₁ SH	0.0023	C ₆ H ₆	1.4
2-BuNH ₂	n-C ₅ H ₁₁ SH	0.021	C ₆ H ₆	1.54
2-BuNH ₂	n-C ₅ H ₁₁ SH	0.17	C ₆ H ₆	1.2
2-BuNH ₂	n-C ₅ H ₁₁ SH	0.019	c-C ₆ H ₁₂	1.51
2-BuNH ₂	n-C ₅ H ₁₁ SH	0.019	CH ₃ CN	1.37
2-BuNH ₂	n-C ₅ H ₁₁ SH	0.021	t-C ₄ H ₉ OH ^c	1.23
2-BuNH ₂	HOCH ₂ CH ₂ SH	0.03	C ₆ H ₆	1.3
2-BuNH ₂ ^d	HOCH ₂ CH ₂ SH	0.03	H ₂ O pH ₁₂	0.9
HOCH ₂ CH ₂ NH ₂	n-C ₅ H ₁₁ SH	0.026	CH ₃ CN	1.0
(2-Pr) ₂ NH ^e	n-C ₅ H ₁₁ SH	0.016	C ₆ H ₆	2.3
(2-Pr) ₂ NH	n-C ₅ H ₁₁ SH	0.16	C ₆ H ₆	2.6
(2-Pr) ₂ NH	n-C ₅ H ₁₁ SH	0.62	C ₆ H ₆	2.2
Et ₃ N ^f	n-C ₅ H ₁₁ SH	0.0122	CH ₃ CN	1.0
Et ₃ N	n-C ₅ H ₁₁ SH	0.122	CH ₃ CN	0.6
Et ₂ NCH ₂ CH ₂ OH ^g	n-C ₅ H ₁₁ SH	0.010	CH ₃ CN	1.0
Et ₂ tNCH ₂ CH ₂ OH	n-C ₅ H ₁₁ SH	0.10	CH ₃ CN	0.80

- a. Ratio of rates of photoreduction in the presence of the indicated concentration of thiol, R_s , to that in the absence of thiol, R_o .
- b. Concentration of 2-butylamine was 1.3 M, R_o corresponds to $\phi = 1.17$.
- c. R_o corresponds to $\phi = 1.26$, 1.3 M 2-butylamine in tert-butyl alcohol.
- d. 0.047 M 4-Benzylbenzoate, 0.56 M 2-butylamine.
- e. 0.52 M Diisopropyl amine; R_o corresponds to $\phi = 0.48$. In a similar experiment with 2.0 M diisopropylamine 0.16 n-pentyl mercaptan, $R_s/R_o = 2.4$.
- f. 0.10 M Triethylamine; R_o corresponds to $\phi = 1.10$.
- g. 0.47 M N,N-Diethylethanolamine; R_o corresponds to $\phi = 1.3$

Participating in the work during the period of this report were Professor S.G. Cohen, Principal Investigator, Dr. Paul G. Stone, Ph.D., Columbia University, and Dr. Herbert Rose, Ph.D., Northeastern University. Dr. Rose was on the project in the period May 1 - September 30, 1976.

The principal investigator has devoted 20% of his effort to the project and expects to continue to do so.

Results of the studies supported by this contract have led to the following published articles:

1. "Chain Inhibition of a Non-Chain Reaction," Proceedings of the Chemical Society (London), p. 301, 1961, S. G. Cohen, S. Orman and D. Laufer.
2. "Catalysis of Light Initiated Decarbonylation of Aldehydes," Tetrahedron Letters, 2, 43-49 (1962), S. G. Cohen, J. D. Berman and S. Orman.
3. "Mercaptans and Disulfides as Inhibitors of Non-Chain Radiation Induced Reactions," J. Amer. Chem. Soc., 84, 1061 (1962), S. G. Cohen, S. Orman and D. Laufer.
4. "Mercaptans and Disulfides as Inhibitors of Non-Chain Photochemical and Radiation Induced Reactions," J. Amer. Chem. Soc., 84, 3905 (1962), S. G. Cohen, S. Orman and D. Laufer.
5. "Inhibition and Quenching of the Light-Induced Reductions of Benzophenone to Benzpinacol and to Benzhydrol," J. Amer. Chem. Soc., 85, 1642 (1963), S. G. Cohen and W. V. Sherman.
6. "Comments on Mechanisms of Damage by Radiation and Their Inhibition," Radiation Research, Supplement 3, 1963 (pp. 270-279). Implications of Organic Peroxides in Radiobiology, Academic Press, New York, N.Y.
7. "Hydrogen Transfer and Energy Transfer in the γ -Radiolysis of Benzophenone-2-Propanol. Effects of Naphthalene and Phenyl Disulfide," J. Amer. Chem. Soc., 86, 2390 (1964), S. G. Cohen and W. V. Sherman.
8. "Inhibition of Light-Induced Reactions by Mercaptans and Disulfides. Benzophenone-Benzhydrol and Acetophenone- α -Methylbenzyl Alcohol," J. Amer. Chem. Soc., 86, 3060 (1964), S. G. Cohen, D. Laufer and W. V. Sherman.
9. "Photoreduction of Aminobenzophenones," J. Amer. Chem. Soc., 86, 5047 (1964), S. G. Cohen and M. N. Siddiqui.
10. "Photoreduction of Benzophenone by an Ether. Effect of Mercaptan," Tetrahedron Letters, No. 10, pp. 579-583, 1965, S. G. Cohen and S. Aktipis.
11. "Action of Mercaptans and Disulfides in Hydrogen Atom Exchange Reactions," in Exchange Reactions, International Atomic Energy Agency, Vienna, 1965, pp. 279-299, S. G. Cohen.
12. "Flash Photolysis of Benzophenone in 2-Propanol. Effect of Phenyl disulfide," J. Phys. Chem., 70, 178 (1966), S. G. Cohen and W. V. Sherman.
13. "Photoreduction of Benzophenone in Methyl 2-Octyl Ether. Effects of Mercaptan, Disulfide and Oxygen," J. Amer. Chem. Soc., 88, 3587 (1966), S. G. Cohen and S. Aktipis.
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16. "Photoreduction of p-Benzoylphenyltrimethylammonium Salts," J. Amer. Chem. Soc., 89, 5845 (1967), S. G. Cohen, R. Thomas, and M. N. Siddiqui.

17. "Effect of Water on Photoreduction of Aromatic Ketones by Tertiary Amines," J. Amer. Chem. Soc., 90, 521 (1968), S. G. Cohen, H. M. Chao and N. Stein.
18. "Photoreduction of Aminobenzophenones in Nonpolar Media. Effects of Tertiary Amines," J. Phys. Chem., 72, 3782 (1968), S. G. Cohen and J. I. Cohen.
19. "Effect of Mercaptan on Photoreduction of Acetone. Non-Repair Hydrogen Transfer Reactions," Photochemistry and Photobiology, 10, 45 (1969), S. G. Cohen, S. Aktipis, and H. Rubenstein.
20. "Effects of Polar Substituents on Photoreduction and Quenching of Fluorenone by Dimethylanilines," by Saul G. Cohen and George Parsons, J. Amer. Chem. Soc., 92, 7603 (1970).
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22. "Repair and Damage by Mercaptans in ⁶⁰Co γ-Ray Irradiation of Organic Compounds in Aqueous Solution," by Saul G. Cohen and F. L. Lam, Radiation Research, 45, 462 (1971).
23. "Triplet Energies, Reduction Potentials and Ionization Potentials in Carbonyl-Donor Partial Charge-Transfer Interactions, I," by Joseph B. Guttenplan and Saul G. Cohen, J. Amer. Chem. Soc., 94, 9040 (1972).
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25. "Effects of Polar Substituents on Photoreduction and Quenching of Aromatic Ketones by Amines. Fluorenone and Substituted Dimethylanilines," J. Amer. Chem. Soc., 96, 2948 (1974), G. H. Parsons, Jr. and S. G. Cohen.
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29. "Acceleration by Aliphatic Mercaptans in the Photoexcited Carbonyl-Amine Redox System" Tetrahedron Letters, 3101 (1976).