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EFFECTS OF MERCAPTANS AND DISULFIDES ON PHOTOCHEMICAL AND HIGH ENERGY RADIATION INDUCED REACTIONS

Progress Report
for Period November 1, 1974--October 31, 1975

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Summary

A. A chain reaction may be formulated at alkaline pH in terms of e^-_{aq} acting as a source of $^-$OH as a reactant, and H· regenerating e^-_{aq}. This may account for radiolytic conversion of CO to formate with high G. ^{60}Co γ-radiolysis of alkaline aqueous acetonitrile and acetamide gave no evidence of a chain; extensive hydrolysis of methyl acetate is now attributed to non radiolytic, normal hydrolysis.

B. 1. Aromatic mercaptans are found to retard photoreduction of a benzophenone by aliphatic amines, largely by hydrogen atom-transfer repair reactions. Aliphatic mercaptans accelerate photoreduction, apparently by affecting the reduction to quenching ratio in the intermediate charge-transfer complex.

2. In photoreduction of a benzophenone by 2,3-butylene glycol at pH 3, the glycol is converted, not to 3-hydroxy-2-butanone, but to 2-butanone, and about 4 molecules of this are formed per molecule of ketone reduced. A short chain appears to be established. Mercaptan appears to accelerate the reduction of the ketone and retard the formation of 2-butanone.

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This report is for the period 1 November 1974 - 31 October 1975.

An article based on work supported by this contract was published during this period: "Free-Radical Coupling, Cleavage and Redox Reactions in ^{60}Co γ-Radiolysis of Aqueous Methyl Acetate. Effects of Additives," T. Bernath, G. H. Parsons, Jr., and S. G. Cohen, J. Am. Chem. Soc., 97, 2413 (1975).

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 abstraction reactions, respectively, eqs. 1-3.

$$A^* + BH_2 \rightarrow AH\cdot + BH\cdot \qquad (1)$$

$$BH\cdot + RSH \rightarrow BH_2 + RS\cdot \qquad (2)$$

$$AH\cdot + RS\cdot \rightarrow A + RSH \qquad (3)$$

Similar processes were demonstrated in ^{60}Co γ-ray irradiated solutions of aqueous organic compounds. These repair reactions interfere with and effectively prevent the radical combination reactions 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, AH_2 and B, 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 to observations of unexpected accelerative effects, in addition to retardation.

Another aspect of our recent work deals with polyfunctional compounds, which may be exemplified by methyl acetate, $CH_3\overset{O}{\overset{\|}{C}}OCH_3$. In γ-radiolysis of this in aqueous solution, e^-_{aq} may react with the carbonyl, leading to $CH_3\dot{C}(O^-)OCH_3$ I^-, $CH_3\dot{C}(OH)OCH_3$ II, and $CH_3\dot{C}O$ IIA, and H· and ·OH may lead to $\cdot CH_2CO_2CH_3$ III, and $CH_3CO_2CH_2\cdot$ IV. This sets up a complex system of free radicals, of which I, II, IIA and IV have donor or reducing properties, and III, and possibly II, have acceptor or oxidizing properties. Their interaction with each other, with the mercaptan-thiyl system, and with ionic redox ions, comprise the subject of the publication this year.

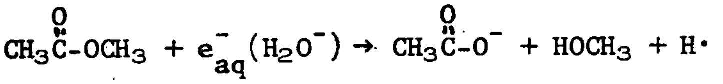
Currently, consideration is being given to the establishment of unusual chain reactions, to the effects of redox reactions, and to acceleration and retardation by mercaptans in photochemical and related ^{60}Co γ-ray induced reactions.

Studies have been carried out along two major lines:

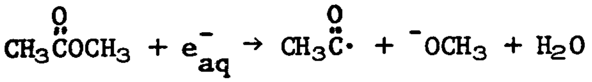
A. ^{60}Co γ irradiation of dilute aqueous solutions of organic compounds.

B. Effects of mercaptans on free radical reactions.

A. In the previous period preliminary experiments by Dr. T. Bernath gave indication that γ-radiolysis of $10^{-2}\underline{M}$ methyl acetate in water, kept at pH in 12 by $Ca(OH)_2$, led to CH_3OH and CH_3COOH with G values in excess of 200, indicating that a chain reaction might have been established. In neutral and slightly acidic pH these hydrolytic products are formed with normally low G values, ~ 2 and 1 respectively. Methanol may be formed by reductive cleavage of methyl acetate, eqs. 4, 5, and by oxidation of radical II, eq. 6,



$$CH_3\overset{O}{\overset{\|}{C}}\text{-}OCH_3 + e^-_{aq}(H_2O^-) \rightarrow CH_3\overset{O}{\overset{\|}{C}}\text{-}O^- + HOCH_3 + H\cdot \qquad (4)$$



$$CH_3\overset{O}{\overset{\|}{C}}OCH_3 + e^-_{aq} \rightarrow CH_3\overset{O}{\overset{\|}{C}}\cdot + {}^-OCH_3 + H_2O \qquad (5)$$

$$CH_3\dot{C}(OH)OCH_3 + H_2O_2 \rightarrow CH_3CO_2H + HOCH_3 + \cdot OH \qquad (6)$$

Acetic acid may be formed in eqs. 4 and 6, and by oxidation of radical IIA and IV, as by radical III, eqs. 7, 8.

$$CH_3\dot{C}{=}O + \cdot CH_2CO_2CH_3 + H_2O \rightarrow CH_3CO_2H + CH_3CO_2CH_3 \qquad (7)$$

$$CH_3CO_2CH_2\cdot + \cdot CH_2CO_2CH_3 + H_2O \rightarrow CH_3CO_2H + CH_2{=}O + CH_3CO_2CH_3 \qquad (8)$$

The possibility of establishing a chain reaction under alkaline conditions lies in a propagating sequence of eqs. 4 and 9.

$$H\cdot + {}^{-}OH \rightarrow e^{-}_{aq}(H_2O^{-}) \qquad (9)$$

This was rendered plausible by a related, reported, chain reaction, the conversion at alkaline pH of CO to formate with very high G (J. J. Weiss, Rad. Res. Suppl., 4, 141 (1964)). This may be formulated analogously, eq. 10, 9

$$CO + e^{-}_{aq} \rightarrow HCO_2^{-} + H\cdot \qquad (10)$$

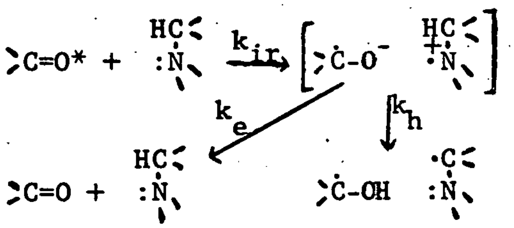
However careful study by Dr. Goyal of the methyl acetate system indicated that this compound is very easily hydrolyzed at pH 12, and in the time scale of preparation and irradiation of the solutions all the acetic acid and methanol could be accounted for by normal hydrolysis, while the ester is quite stable at pH 7 and lower.

The possibility of e^{-}_{aq} being a source of ^{-}OH and H· in a hydrolytic process was examined with a substrate which would be more stable to alkaline hydrolysis, acetamide. ^{60}Co irradiation of 10^{-2} M CH_3CONH_2 at pH 12.2 at 5×10^{18} eV ml^{-1} and 10×10^{18} eV ml^{-1} led to disappearance of 49×10^{16} and 78×10^{16} molecules of CH_3CONH_2, G values of 9.8 and 7.8 respectively. These values are slightly high, but do not give evidence for an extensive chain.

Similarly, acetonitrile, in which the nitrile group might be an analogue of CO and lead to an amide, gave no evidence of a chain hydration on irradiation in dilute alkaline aqueous solution. Irradiation of 9.5×10^{-3} M CH_3CN, pH 12.4, 5.0×10^{18} eV ml^{-1}, led to disappearance of 24×10^{16} molecules ml^{-1}, $G(-CH_3CN) = 4.7$. Irradiation of 9.5×10^{-3} M CH_3CN, pH 6.1, 6.7×10^{18} eV ml^{-1} led to disappearance of 26×10^{16} molecules ml^{-1}, $G(-CH_3CN) = 3.9$. Acetaldehyde was found and e^{-}_{aq} may be important in reacting with CH_3CN, but a chain was not established.

This leaves unresolved the question of whether the chain reaction occurs in radiolysis of CO in aqueous medium, as reported. Carbon monoxide can react thermally with hydroxide ion, ^{-}OH, to form formate, the reverse of its formation in acid catalyzed dehydration of formic acid, but possibly not sufficiently rapidly to account for its reported conversion to formate in radiolysis. Carbon monoxide also reacts with hydroxyl radical, ·OH, forming CO_2 and H·. Thus it might react with e^{-}_{aq}, H_2O^{-}, to form formate and H· and establish a chain.

B. 1. Reaction of excited carbonyl compounds, and possibly other radical like acceptor species, with amino compounds appears to proceed via charge transfer complexes. The rates 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, eq. 11



(11)

Mercaptans might be expected to retard such reactions by hydrogen transfer repair processes analogous to those in related systems of oxygen compounds, eqs. 2, 3. We find that aromatic mercaptans and disulfides do inhibit the photoreduction of benzophenone by 2-butylamine in benzene, but less efficiently than they do the photoreduction by 2-propanol. Higher concentrations of sulfur compound must be used for equivalent retardation than in the alcohol system, and part of the inhibition may be due to direct interaction between excited ketone and sulfur compound. Deuterium introduction and racemization indicate that part, but not all, of the retardation arises from the expected hydrogen transfer repair processes. This may indicate that transfer of H· from the amine derived radical to ground state ketone, eq. 12, is faster than from the alcohol derived radical in the related reduction by alcohols.

$$>C=O + H_2N-\dot{C}< \rightarrow >\dot{C}-OH + HN=C< \qquad (12)$$

Aromatic mercaptans are more efficient in inhibiting photoreduction of benzophenone by triethylamine in t-butyl alcohol than in inhibiting the photoreduction by 2-butylamine. This may indicate that the radical derived from the tertiary amine reduces ground state ketone less rapidly, and is more efficiently reduced by mercaptan, eq. 13, 14

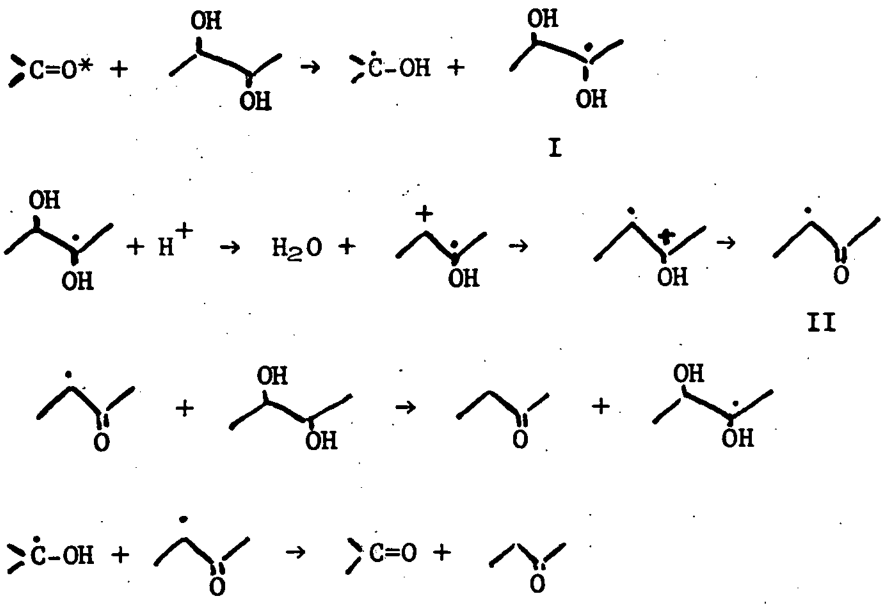
$$>C=O + R_2N-\dot{C}H-CH_3 \rightarrow >\dot{C}-OH + R_2NCH=CH_2 \qquad (13)$$

$$R_2N\dot{C}HCH_3 + ASH \rightarrow R_2NCH_2CH_3 + AS\cdot \qquad (14)$$

The effect of aliphatic mercaptans is quite different in photoreduction by amines than by alcohols. n-Propyl and n-pentyl mercaptans <u>increase</u> the rate of photoreduction of benzophenone by 2-butylamine in benzene and in acetonitrile by ~ 50%.

The mercaptans themselves are very feeble photoreducing agents. Since the rates, or quantum yields, are determined largely by the relative amounts of hydrogen transfer and quenching in the charge-transfer complex, eq. 11, it appears that mercaptan present in low concentration, $\sim 10^{-2}$ $\underline{M}$, may react with the complex and catalyze the hydrogen transfer.

B. 2. In extending the study of effects of mercaptans on radical reactions to polyfunctional systems, we are examining the photo-oxidation of 2,3-butylene glycol by a benzophenone in aqueous systems. Such reactions are related to those of the hydroxyl radical from Fenton's reagent or from radiolysis of water. The mercaptan corresponds to the reducing species, Fe^{+2} in Fenton's reagent, e^{-}_{aq} in radiolysis. Preliminary results indicate that photoreduction of the ketone by the glycol is less efficient at pH 3 than at pH 7, and less efficient than by 2-propanol. At pH 3 $\sim$ 4 x as much 2-butanone is formed as ketone is reduced giving preliminary evidence of a chain reaction. This may be formulated:



(15)

(16)

(17)

(18)

Aryl ketone and glycol derived radicals may be formed in the initiation process, eq. 15; the glycol derived radical I, with donor properties, may be converted by acid to the alkanone derived radical, with acceptor properties, II, eq. 16; radical II may abstract hydrogen from glycol, establishing the chain. Termination may be by coupling reactions and by regeneration of aryl ketone by oxidation of aryl ketyl by alkanone derived radical, eq. 18. Addition of mercaptan appears to increase reduction of the arylketone and decrease the formation of 2-butanone. It may do this by reducing the alkanone derived II to 2-butanone, decreasing the chain length, and decreasing reoxidation of aryl ketone derived radical.

Participating in the work during the period of this report were Professor S. G. Cohen, Principal Investigator, Dr. G. C. Goyal, Ph.D., University of Calgary, Dr. Paul Stone, Ph.D., Columbia University and Mr. Herbert Estreicher, undergraduate, Brandeis University. Dr. Goyal worked during the period October 1974 - May 1975, and left for personal reasons. Dr. Stone joined the project in April 1975. Dr. Bernath left in October 1974, and presented a talk based on work supported by this contract at the I.U.P.A.C. meeting in Jerusalem, July 1975.

The principal investigator has devoted 15% 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.

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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 Phenyldisulfide," 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 ^{60}Co 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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28. "Free-Radical Coupling, Cleavage, and Redox Reactions in ^{60}Co γ Radiolysis of Aqueous Methyl Acetate. Effects of Additives," J. Amer. Chem. Soc., 97, 2413 (1975), T. Bernath, G. H. Parsons, Jr., and S. G. Cohen.