

MASTER

Hydrogen-Transfer and Charge-Transfer in
Photochemical Reactions

Progress Report

for Period October 1, 1976--September 31, 1977

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SUMMARY

1. Quantitative studies have been made of effects of sulfur compounds on photoreduction of benzophenone by amines. Aromatic mercaptans and disulfides are converted to photostationary equilibrium concentrations of the two forms, and retard photoreduction very efficiently, to a small extent by light absorption and quenching of triplet ($\sim 10\%$), to a large extent ($\sim 60\%$) by repeated hydrogen transfer reactions, and the remainder by quenching of the charge transfer complex. Aliphatic disulfides are reduced, mercaptans are not oxidized, the two states are not equilibrated, and photoreduction by amines is accelerated by aliphatic mercaptans. The acceleration is attributed to catalysis of proton transfer in the charge-transfer complex. Ratios of rate constants for reduction of amine-derived radicals by mercaptans to oxidation by ketone are obtained.

2. Effects of light absorption, triplet quenching and hydrogen transfer are calculated in retardation by mercaptans of photoreduction by alcohols. In reduction by 2-propanol and acetophenone, more hydrogen transfer is observed than would be calculated, indicating that thiyl radicals, in addition to ketone triplet, abstract hydrogen. In reduction by benzhydrol, retardation is due entirely to light absorption and quenching. Benzophenone ketyl radical is too highly stabilized for hydrogen abstraction to compete with radical demerization. Rate constants for abstraction of hydrogen from aromatic mercaptans by the ketyl radicals are estimated.

3. In photoreduction of fluorenone by substituted dimethylanilines, low quantum yield due to an electron donating substituent is increased by decrease in polarity of solvent, and low quantum yield due to electron withdrawing substituents is increased by increase in polarity of solvent. The results are attributed to effects of substituents and solvent polarity on extent of charge transfer in the charge transfer complex.

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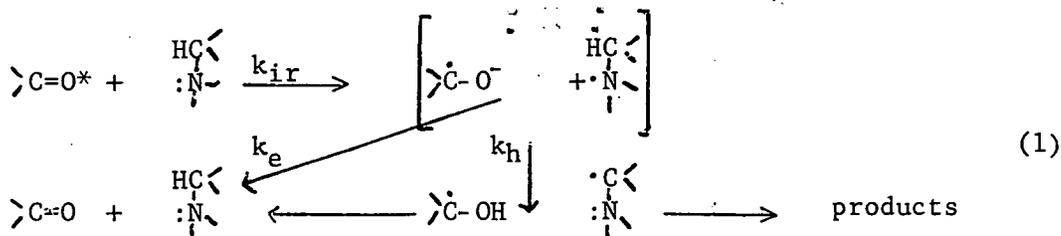
This report is for the period October 1, 1976 - October 1, 1977. An article based on work supported by this contract has been accepted for publication in a forthcoming issue of the Israel Journal of Chemistry on "Chemistry of The Excited State", dedicated to the memory of Professor Gabriel Stein. The article is "Acceleration and Retardation by Mercaptans of Photoreduction by Amines" by Saul G. Cohen, Anita W. Rose and Paul G. Stone.

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 abstraction. 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 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 donors, alcohols, 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 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.

Work has been carried out in this period on: 1. Acceleration and retardation by mercaptans in photoreduction by amines; 2. Reactions of sulfur compounds in retardation of photoreduction by alcohols; 3. Effects of solvent on the partitioning of the charge transfer complex formed from excited carbonyl triplet and amine donors.

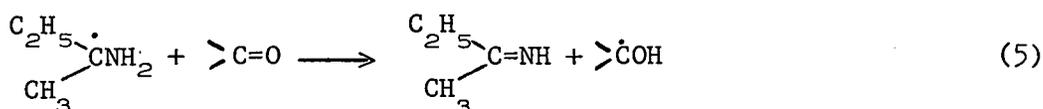
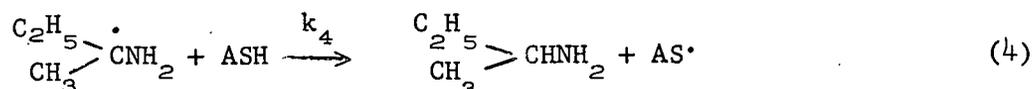
1. Acceleration and Retardation by Mercaptans in Photoreduction by Amines: Reaction of excited carbonyl compounds, and possibly other radical-like acceptor-species, with amino compounds, thioethers and other electron donors appear to proceed via intermediate charge-transfer complexes, CTC. Rate constant of formation of CTC, k_{ir} , is affected by triplet energy and reduction potential of the carbonyl compound, and ionization or oxidation potential of the donor. The quantum yield for formation of final reduction product depends (i) on the fate of the CTC, the ratio of hydrogen transfer and radical formation, k_h , to charge destruction and quenching, k_e , and (ii) on the fate of the radicals, the ratios of their conversion to products to their disproportionation to starting materials, eq. 1.



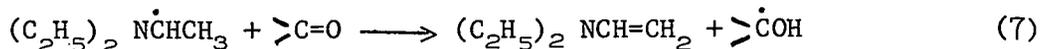
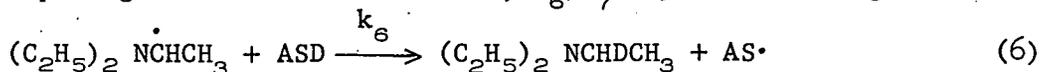
Mercaptans might be expected to retard such reactions by repeated hydrogen-transfer processes, analogous to those in retardation of photoreduction by alcohols, eqs. 2, 3.



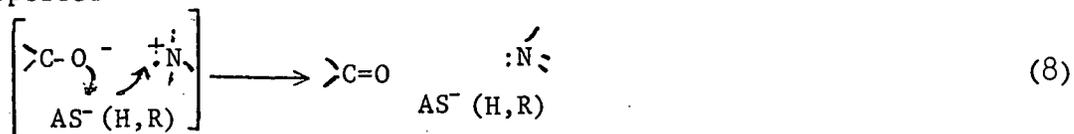
Aromatic mercaptans and disulfides retard photoreduction of benzophenone by amines and are equilibrated to 62% thiyl as mercaptan in the process. Racemization of sec-butylamine during retarded photoreduction indicated that about half the retardation, after correction for masking and quenching, was due to the hydrogen-transfer mechanism. From the rates of racemization and photoreduction and the concentrations of mercaptan and ketone, the ratio of rate constants of the competing reactions, reduction of amine-derived radical by mercaptan and oxidation of it by ketone is calculated $k_4/k_5 = 30$.



This is an order of magnitude lower than for the corresponding reactions in retardation of photoreduction by 2-propanol. The low value is attributed to the low reactivity of the amine-derived radical in abstracting hydrogen from mercaptan. Introduction of deuterium into triethylamine in retarded reduction by this amine in *t*-butyl alcohol-OD also indicated that about half the corrected retardation was due to the hydrogen-transfer mechanism. The ratio of the rate constants of the competing reactions was obtained, $k_6/k_7 = 310$. This high value

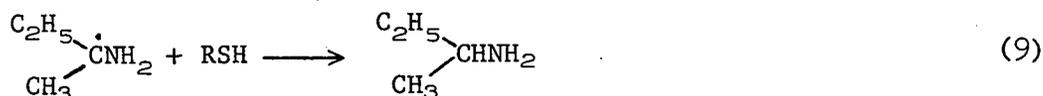


is attributed to the low value of k_7 , for a reaction involving breaking of a C-H bond. The remainder of the efficient retardation by the aromatic mercaptan, equivalent in importance to hydrogen transfer is attributed to quenching by back electron transfer by mercaptan or mercaptide within the CTC eq. 8. This is supported

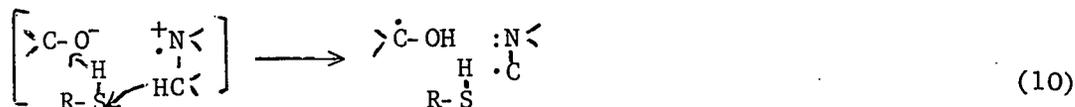


by our observation that aromatic thioethers, ASR, phenyl ethyl sulfide and diphenyl sulfide retard photoreduction by amines and not that by alcohols.

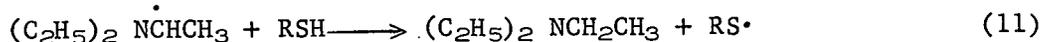
On the other hand, aliphatic mercaptans accelerate photoreduction by amines, while they retard photoreduction by alcohols. Acceleration is observed at 10^{-2} - 10^{-4} M aliphatic mercaptan and may raise quantum yields nearly to the theoretical maximum value of 2. Mercaptan and disulfide are not rapidly equilibrated and net reduction of disulfide is observed. At high concentration, >0.1 M 1-pentanethiol, acceleration decreased, and on the basis that this arises from the hydrogen transfer reaction, eq. 9,



The ratio of rate constants for the competitive reactions may be calculated, $k_9/k_5 \approx 0.2$, leading to the ratio of rate constants for abstraction of hydrogen by this radical from aromatic and aliphatic mercaptans, $k_4/k_9 = 125$. The accelerating effect is diminished by polarity of solvent, and absent in water. The acceleration is attributed to catalysis of proton transfer in the CTC, eq. 10, a process analogous to catalysis by amine.

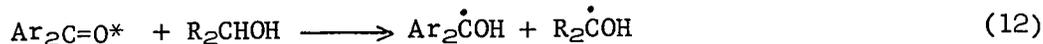


Aliphatic mercaptan did not accelerate photoreduction by a tertiary amine. Some retardation was observed, which may be attributed to the hydrogen transfer reaction eq. 11. The ratio of rate constants for the competitive



reactions may be calculated, $k_{11}/k_7 \approx 0.9$, leading to the ratio of rate constants for abstraction of hydrogen by this radical from aromatic and aliphatic mercaptans, $k_8/k_{11} \geq 350$. This greater sensitivity as compared with the primary amine-derived radical indicates a lower reactivity of the tertiary amine-derived radical; and the lower sensitivity in the alcohol system indicates a greater reactivity of the alcohol-derived radical. The attached preprint comprises a more detailed description of this work.

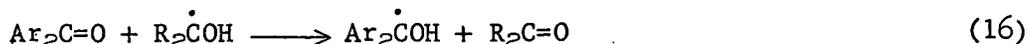
2. Reactions of Sulfur Compounds in Retardation of Photoreduction by Alcohols.
The cyclic hydrogen transfer mechanism of retardation may be indicated in eqs. 12 - 14. Conversion of initially



present mercaptan or disulfide to a photostationary equilibrium concentration of the two, racemization of optically active reducing alcohol, and introduction of carbon-bound deuterium, eq. 15, support this mechanism.



Aromatic mercaptans and disulfides are now known to be efficient quenchers for excited carbonyls, and contributions to the retardation of light absorption, quenching, and hydrogen transfer may be calculated. The limiting process in the latter mechanism is the oxidation of the mercaptan by the alcohol-derived radical, and this must compete with oxidation of this radical by ground-state ketone, eq. 16. In

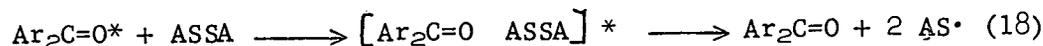


photoreduction of 0.5 M benzophenone in 2-propanol, the rate was halved by 0.003 M mesityl thiol group, present 70% as mercaptan, the remainder as disulfide. The sulfur compounds would absorb 2% of the light and the sulfur compounds would quench 8% of the triplet. The remainder, 80% of the retardation, would be due to the hydrogen transfer mechanism.

A similar calculation may be applied to the racemization of 2-octanol in the retarded reduction of 0.03 M ketone, on the basis that k_{12} is similar to that for 2-propanol. At 0.03 M initial concentration of 2-mercaptomesitylene, the sulfur compounds absorbed 25% of the light and quenched 65% of the triplet, and the reduction was essentially completely inhibited. The calculated rate of abstraction of hydrogen by the triplet would, over the period of irradiation lead to a decrease in rotation of 0.26°. The observed decrease was 0.72°. It appears that quenching of the ketone by the sulfur compounds initiates processes which racemize the alcohol. Similarly, a study of deuterium labelling indicated introduction of excess deuterium. Photoreduction of 0.2 M benzophenone by 1 M 2-propanol-OD in benzene was decreased in rate, by 0.002 M 2-mercaptomesitylene, from 3.4 to 0.6 $\times 10^{-5}$ M sec⁻¹. Masking, 3%, and quenching, 45%, would reduce the rate to 1.8 $\times 10^{-5}$ M sec⁻¹ and the remainder of the reduction, by hydrogen transfer, would introduce C-D at a rate of 0.6 $\times 10^{-5}$ M sec⁻¹. The observed rate was 0.9 $\times 10^{-5}$ M sec⁻¹.

An entirely different result was obtained in retardation by 0.01 M 2-mercaptomesitylene of photoreduction of 0.2 M benzophenone by 1 M benzhydrol in t-butyl alcohol-OD. No deuterium was introduced. Masking would reduce the rate by 12%, quenching by 48%, to 46% of the unretarded rate. The observed retardation was 47%, and none was due to the hydrogen transfer mechanism. Benzophenone ketyl radical was present, but is too highly stabilized to abstract hydrogen from the mercaptan in competition with its coupling to benzpinacol. On the basis of the observed retarded rate of photoreduction and the rate constant for ketyl dimerization, the concentration of ketyl may be calculated, 4 $\times 10^{-7}$ M. If the absence of C-D indicates that the hydrogen abstraction is <1% as fast as dimerization, the rate constant for abstraction of hydrogen by benzophenone ketyl from 2-mercaptomesitylene is estimated, <60 M⁻¹ sec⁻¹. In a photoreduction in 2-propanol the concentration of 2-hydroxy-2-propyl radical must be quite low, <10⁻⁸ M, since it is oxidized by ketone and does not appear in coupling products. From the rate of deuteration in a reduction retarded by 0.0015 M 2-mercaptomesitylene, the rate constant for this hydrogen abstraction, eq. 15, is calculated to be >6 $\times 10^5$ M⁻¹ sec⁻¹, 10⁴ greater than that for abstraction by benzophenone ketyl radical.

The excess racemization and deuterium introduction that appear to result from quenching of the triplet by the sulfur compounds indicate that thiyl radicals are formed and abstract hydrogen, eqs. 17 - 19.



Formation of thiyl radicals, eqs. 17, 18, may be inefficient, and they may largely oxidize ketyl, eq. 14, but reactions 19, 13 and 15 appear to occur also. Thiyl would also abstract from benzhydrol, but reduction back to benzhydrol; eq. 20, is too slow to compete with coupling,



Further studies have been carried out on the benzophenone-benzhydrol-mesityl thiyl system. The disulfide was not decomposed when irradiated with the ketone alone. Irradiation of the ketone and the mercaptan led to the disulfide, initial quantum yield $\phi=0.1$, and to benzpinacol, eq. 17, but to no benzhydrol, confirming the absence of eq. 20 at an observed rate. Irradiation of benzophenone-benzhydrol-disulfide led to reduction of disulfide via eqs. 18 and 19 and possibly also by reduction by ketyl, eq. 21.



The disulfide was also reduced when irradiated with benzhydrol in benzene in the absence of benzophenone, $\phi=0.06$. Excited disulfide, and/or thiyl radicals from excited disulfide, abstract hydrogen from the hydrol. Abstraction of hydrogen from alcohol by thiyl radical is demonstrated as a likely cause of excess racemization and introduction of deuterium. Addition of benzophenone to such a system increased reduction of disulfide, apparently via formation of benzophenone ketyl, followed by eq. 21.

3. Partitioning of the CTC: A critical property of light induced reactions is the proportion of the excitation energy which leads to useful chemical reaction as compared with that which does not. In our systems, conditions can usually be established such that the excited donor-acceptor interaction occurs with high efficiency. Loss may result by quenching within the CTC, k_e , eq. 1, by formation of free radical cations and anions which may disproportionate, and by formation of free radicals which may also disproportionate. Free radical cations and anions need not disproportionate and might interact with greater or lesser probability of proton transfer and radical formation than do the partially formed pair in the CTC. The factors that lead to disproportionation of charged or uncharged radical species are not clear.

To explore factors which may affect effective use of light we are studying effects of solvent in photoreduction of fluorenone by substituted N,N-dimethylanilines. Strong electron attracting and electron donating substituents lead to low quantum yields, $\phi = 0-0.3$, while those with zero or small negative values of σ^+ lead to higher quantum yields, $\phi = 0.6 - 0.7$. Insufficient electron

transfer may lead to quenching without much hydrogen, transfer and too much electron transfer may be a property of stabilized charged species which also lead to disproportionation. Values of k_{ir} for formation of the CTC's rise with increasing electron availability and approach diffusion control.

In reduction by p-ethoxydimethylaniline, for which there may be excessive charge separation in the CTC, change from benzene to cyclohexane increased ϕ_{lim} from 0.38 to 0.48, with no change in k_{ir} . On the other hand, addition of acetonitrile decreased ϕ_{lim} , 0.4 M of the more polar solvent leading to a 30%, and 1.5 M to a 70% decrease.

For p-cyanodimethylaniline, for which charge development in the CTC may be insufficient in benzene, 1 M or 2 M acetonitrile raised ϕ_{lim} by 50%, from 0.17 to 0.26, but 8 M acetonitrile led to a lower value, $\phi_{lim} = 0.13$. This may be due to lower triplet yield. Values of k_{ir} were unchanged by presence of 1 M or 2 M acetonitrile.

The results of these solvent studies support the proposal, above, as to the need for sufficient, but not excessive charge development in the CTC for efficient chemical reaction, since we are observing effects on formation of final products. They might also arise from effects of solvent on combination and disproportionation of free ionic and radical species which may have been formed initially in different, higher efficiency. Flash photolysis studies will be informative as to this.

Another problem must be noted. Effects of concentration of reducing agent were very similar for these dimethylanilines, and led to a narrow range of values of k_d/k_{ir} , from 3×10^{-4} M for the p-ethoxy compound to 2×10^{-3} M for the p-cyano. Since values of k_{ir} range widely, from 8×10^9 M⁻¹ sec⁻¹ to 5×10^6 M⁻¹ sec⁻¹ for these two compounds, values of k_d appear to vary, 2×10^6 sec⁻¹ and 1×10^4 sec⁻¹ for reductions by the p-ethoxy and p-cyanodimethylanilines respectively. Values of k_d should be independent of the reducing agent and not parallel values of k_{ir} . The standard kinetic analysis may not be appropriate and additional factors may have to be taken into account. One such factor may be the presence of ground-state complexes, formed to a greater degree the lower the ionization potential of the donor.

Participating in the work during the period of this report were Professor Saul G. Cohen, Principal Investigator, Dr. Paul G. Stone, Ph.D., Columbia, October 1, 1976 - April 30, 1977, Dr. Anne Ehret, Ph.D., U.C.L.A., June 1, 1977 - Dr. Herbert Rose, Ph.D., Northeastern, September 1, 1977 - , Dr. Frederick Pepper, Ph.D., Brandeis University, April 1, 1977 - August 31, 1977.

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 articles, published or currently in press.

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.
14. "Action of Mercaptans and Disulfides in Free Radical, Photochemical, and High Energy Radiation Induced Reactions" in "Organosulfur Chemistry," M. J. Janssen, Editor, Interscience-Wiley, New York 1967, pp. 33-56, S. G. Cohen.
15. "Photoreduction of p-Dimethylaminobenzophenone. Effect of Acid," J. Amer. Chem. Soc., 89, 5409 (1967), S. G. Cohen and M. N. Siddiqui.
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).
21. "Effects of Quenchers on Photoreduction of p-Benzoylbenzenesulfonic Acid in Aqueous 2-Propanol," by Saul G. Cohen and G. Caird Ramsay, J. Amer. Chem. Soc., 93, 1166 (1971).
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).
24. "Triplet Energies, Reduction Potentials and Ionization Potentials in Carbonyl-Donor Partial Charge-Transfer Interactions, II," by Joseph B. Guttenplan and Saul G. Cohen, Tetrahedron Letters, 2163 (1972).
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.
26. "Effects of Substituents on Combination and Disproportionation of Diarylketyl Radicals and Radical Anions," J. Amer. Chem. Soc., 96, 5124 (1974), S. G. Cohen, G. C. Ramsay, N. M. Stein, and S. Y. Weinstein.
27. "Quenching of Photoexcited Fluorenone by Meta- and Para-Substituted Anilines and Mono-N-substituted Anilines. Some Linear Free-Energy Relationships," J. Amer. Chem. Soc., 96, 6643 (1974), G. H. Parsons, Jr., L. T. Mendelson and S. G. Cohen.
28. "Free-Radical Coupling, Cleavage, and Redox Reactions in ⁶⁰Co 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.
29. "Acceleration by Aliphatic Mercaptans in the Photoexcited Carbonyl-Amine Redox System" Tetrahedron Letters, 3101 (1976).
30. "Acceleration and Retardation by Mercaptans of Photoreduction by Amines", by Saul G. Cohen, Anita W. Rose and Paul G. Stone, in press. Israel Journal of Chemistry, in "Chemistry of the Excited State".

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