

Hydrogen-Transfer and Charge-Transfer in Photochemical and High  
Energy Radiation Induced Reactions. Effects of Thiols.

Final Report

for Period February 1, 1960 - January 31, 1979

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March 1980

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UNDER CONTRACT NO.: DE ACO-76ER03118

(Formerly EY-76-S-02-3118)

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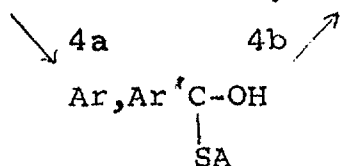
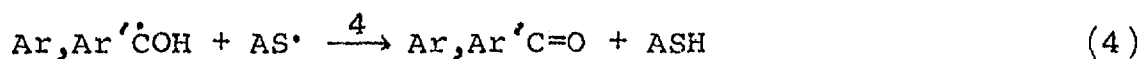
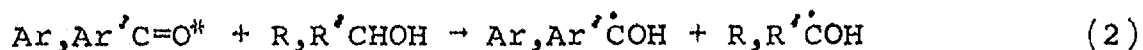
Abstract. Absorption of ultraviolet or visible light, or high energy radiation, may lead to highly reactive free radicals. Work done under this contract showed that thiols affect in very important ways the reactions of these radicals. It was shown that they do so by two reactions: (i) transfer of hydrogen from sulfur of the thiol to a substrate radical, converting the radical to a stable molecule, and the thiol to a reactive thiyl radical; and (ii) transfer of hydrogen from a substrate radical or molecule to thiyl, regenerating thiol. The thiol is thus used repeatedly and a single molecule may affect the consequences of many quanta. Three effects may ensue, depending upon the system irradiated: (i) The substrate radicals may be converted by thiol-thiyl to the original molecules, and protection against radiation damage is afforded. (ii) The radicals may be converted to molecules not identical with the starting materials, and in both cases damage caused by radical combination processes is prevented. (iii) Product yields may be increased where the initial radicals might otherwise regenerate starting materials.

In the course of this work it was shown that rates of reaction of excited species can be correlated with triplet energies and reduction potentials, and with ionization potentials; that amines are very reactive toward excited carbonyl compounds of all types, and that yields of products from these reactions can be increased by thiols, leading to increased efficiency in utilization of light.

Research was started under this contract with study of the effects of thiols on photochemical and  $^{60}\text{Co}$   $\gamma$ -ray induced reactions of organic compounds. It developed into study of the structural features which affect the reactivity of excited aromatic carbonyl compounds and amines, acting as electron and hydrogen atom acceptors and donors respectively. Absorption of light or high energy radiation leads to systems of free radicals, and presence of low concentrations of thiols markedly alters the subsequent courses of their reaction. Mechanisms have been proposed and demonstrated in important instances, describing how rapid transfer of hydrogen atoms from thiol and to thiyl radical, may (i) restore the free radicals to their initial molecular states, negating the effects of absorption of light and inhibiting radiation damage; (ii) lead to different products than would have been formed in the absence of thiol or (iii) increase the efficiency of the photochemical processes. These effects result from the action of low concentrations of thiol, used repeatedly, so that each molecule affects the reactions due to many quanta. This work resulted in 31 scientific publications, which will be referred to in this report by their numbers in the attached list.

We had observed, in work supported by the National Science Foundation, that thiols catalyzed transfer of hydrogen in a simple free radical system. In examining the effect in a photochemical system, the photoreduction of benzophenone by 2-propanol, we were surprised to find efficient inhibition by low concentrations of aromatic thiol (ASH) or disulfide (ASSA), over long periods of irradiation.<sup>1</sup> A single photo-equilibrated level of thiol and disulfide was established from either initial oxidation state, and, if an optically active alcohol was used instead of 2-propanol, it was racemized during the inhibited process, but not during an uninhibited reaction, nor when irradiated with the sulfur compounds alone.<sup>3,4</sup> We proposed

that excited ketone abstracted  $\alpha$ -H from the alcohol in the usual way, forming ketone- and alcohol-derived radicals; the thiol and thiyl radicals returned these to the starting materials, and were themselves not consumed, but converted to their alternate oxidation states, eqs. 1-4. In this way a chain inhibition of a



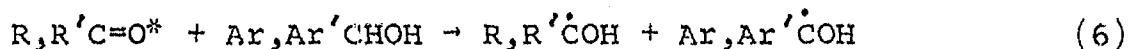
non-chain photochemical reaction was indicated, and the sulfur compounds would be used repeatedly. These reactions provide a chemical mechanism by which one molecule may dissipate the energy introduced by, and the chemical consequences of, the absorption of many quanta. Since high energy radiation also converts organic compounds to free radicals, this mechanism would also be that which leads to protection by thiols against radiation damage. In fact the thiols may completely inhibit the  $^{60}\text{Co}$ - $\gamma$ -ray induced conversion of benzophenone and 2-propanol to benzpinacol and acetone,<sup>3,4</sup> confirming a hydrogen atom transfer mechanism for protection by thiols against radiation damage.

Consideration of the details of these proposals brings one to the core of photochemical and free radical mechanisms: Sulfur compounds are quenchers of excited states (J. B. Guttenplan and S. G. Cohen, *J. Org. Chem.* 38, 2001 (1973)) and part of their inhibiting action may be due to such direct interaction with excited benzophenone rather than to the cyclical free radical process.

The kinetics of the two processes are superficially similar, but naphthalene, a diffusion controlled quencher, was less effective than a thiol in retarding the photoreduction of benzophenone by 2-propanol to benzpinacol.<sup>5</sup> The thiol cannot be acting by quenching since it cannot be more efficient than diffusion control. Its greater efficiency arises since naphthalene must compete with the very rapid reaction of the triplet with a high concentration of alcohol, while the thiol competes effectively with the subsequent free radical reactions.<sup>5</sup> The thiol is less efficient in inhibiting when the reaction is run under alkaline conditions, when ketyl radical ion and thiyl anion are present, indicating that the inhibition involves hydrogen more effectively than electron transfer.<sup>5</sup> Further, naphthalene was without effect on the  $^{60}\text{Co}$   $\gamma$ -ray conversion of benzophenone and 2-propanol to benzpinacol and acetone, demonstrating that excited ketone is not involved in the high energy radiation induced reaction; disulfide offered very effective protection confirming that radiation led to radicals which the sulfur compounds repaired.<sup>7</sup> Finally, flash photolysis experiments showed directly that the sulfur compound may act on the radicals under conditions where it has no effect on the triplet.<sup>12</sup> At low concentration of phenyl disulfide  $10^{-4}$  M, flash photolysis of benzophenone-2-propanol led to undiminished yield of ketyl radical from excited ketone and the alcohol. The ketyl radical disappeared more rapidly in the presence of the sulfur compound than in its absence, presumably via eq. 4, for which a rate constant was estimated,  $> 7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ .

The protection mechanism, eqs. 3 and 4, requires the aliphatic and aromatic ketyl radicals,  $\text{R}, \text{R}'\dot{\text{C}}\text{OH}$  and  $\text{Ar}, \text{Ar}'\dot{\text{C}}\text{OH}$ , to react differently, the former to be reduced by mercaptan, the latter to be oxidized to ketone, while in principle each ketyl might undergo either or both reactions. Observed free radical reactions are always the results of the more rapid processes among several

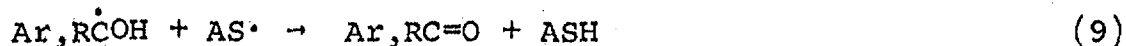
possibilities. Equations 3 and 4 are the more rapid and observed reactions, and, when the starting materials are benzophenone and 2-propanol, they regenerate the starting materials and protection is observed. However the same ketyl radicals may be generated instead from acetone and benzhydrol, eq. 5,6. Thiol and thiyl



convert them via eqs. 3 and 4, to benzophenone and 2-propanol, repair is not observed and the reaction course is changed from that in the absence of sulfur compounds.<sup>19</sup> This change may itself comprise protection as it interferes with possibly harmful radical coupling processes. But true repair results only if regeneration of starting materials results from the most rapid of the possible reactions.

In the repair sequence, eqs. 3 and 4, the limiting process is that of eq. 3, abstraction of hydrogen from thiol by the alcohol-derived radical. Thus aromatic thiol is more effective than aliphatic thiol, since its hydrogen is more rapidly abstracted, leading to the more highly stabilized aromatic thiyl. Reaction of eq. 4 is presumably rapid and less critical, involving reactions between two radicals, and the greater stability of the aromatic thiyl may not cause difficulty.

The favored selection of reactions indicated in equations 3 and 4 should not be taken to indicate that two different ketyl radicals are required for the repair mechanism to operate. In a system in which only one species of radical is formed, acetophenone- $\alpha$ -methylbenzyl alcohol, thiol retards and the single species is either reduced by thiol or oxidized by thiyl, eqs. 7-9.<sup>8</sup>



This was demonstrated by the racemization of optically active  $\alpha$ -methylbenzyl alcohol during the thiol-retarded reduction, and by introduction of  $\alpha$ -C-D into regenerated carbinol when the retarded reduction was carried out in the -OD alcohol.<sup>8</sup> However the intermediate radical in this case,  $\text{Ar,R}\dot{\text{C}}\text{OH}$ , with one aromatic group, is more stabilized than when 2-propanol is the reducing agent, the reaction of eq. 8 is less rapid than that of eq. 3, and a higher concentration of thiol is required for equivalent retardation.<sup>8</sup>

This situation is brought to an extreme when the intermediate radical is still more highly stabilized, as in the benzophenone-benzhydrol system, eq. 10, in which a still higher concentration



of thiol is required for efficient retardation.<sup>8,31</sup> In retardation of the reduction by 2-propanol-OD, deuterium was introduced into  $\alpha$ -C, to the extent consistent with the retardation, while none was introduced in retardation of the benzophenone-benzhydrol reaction. All the retardation could be accounted for by quenching of the triplet by the sulfur compound.<sup>31</sup> The benzophenone-ketyl radical is so highly stabilized by resonance that it does not abstract hydrogen from thiol significantly in competition with its dimerization to pinacol.

This is borne out by results of the photoreduction of benzophenone by thiol itself. It is inefficient,  $\phi \sim 0.1$ , and the product is the pinacol. Excited ketone abstracts hydrogen from the thiol, leading to ketyl and thiyl radicals, eq. 11. These largely

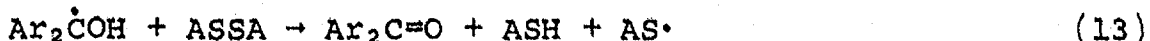


regenerate the starting materials, eq. 4, and impart form pinacol and disulfide, but abstraction by the stabilized ketyl of hydrogen from the high concentration thiol, eq. 12, to form benzhydrol, does not occur significantly in competition with these other reactions.



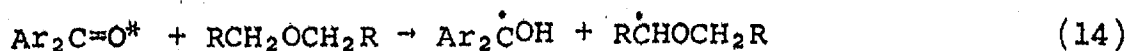
For repair to occur by the hydrogen transfer mechanism the radicals must be sufficiently reactive so that they abstract hydrogen from thiol efficiently in competition with radical-radical reactions. In high energy radiolysis of aqueous solutions highly reactive hydrogen and hydroxyl radicals and solvated electrons are formed, and these can convert organic substrates to free radicals which are sufficiently energetic to react with sulfur compounds.

A significant aspect of the model system which we have studied most, benzophenone-2-propanol, is that the sulfur compounds may be used indefinitely; they are not consumed, and continuously negate the consequences of absorption of radiation. This would result if only disproportionating hydrogen transfers, regenerating the sulfur compounds in their alternate oxidation states, occurred, eqs. 3,4. It arises, however only if combination reactions, consuming the sulfur compounds irreversibly, do not occur. This is the case in the model system since the coupling of ketyl and thiyl, eq. 4a, leads to an unstable monothiohemiketal which decomposes, eq. 4b. Also, coupling of thiyl to disulfide may occur, and this reenters the cycle, being reduced by ketyl radical, eq. 13.<sup>31</sup>

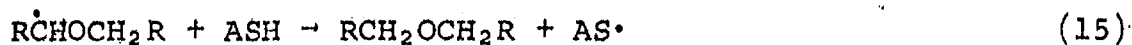


A slight modification however leads to consumption of the sulfur compound.<sup>10,13</sup> If the ketone is reduced by an ether instead of an alcohol, a ketyl and an  $\alpha$ -alkoxyalkyl radical are formed, eq. 14.

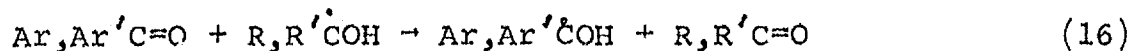




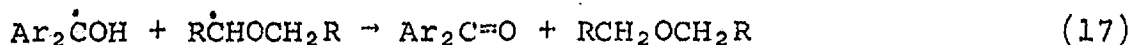
Deuterium labelling and racemization studies show that sulfur compounds repair by regenerating starting materials in the usual way eqs. 4 and 15.



However, while the alcohol derived radical formed in eq. 2 is rapidly oxidized by ground-state ketone, eq. 16, this course is not available in reduction by the ether. The ether-derived radical



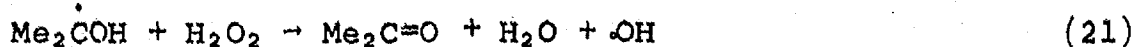
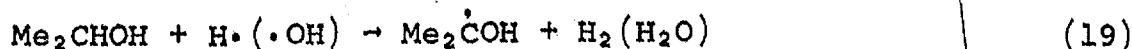
persists and in part disproportionates with ketyl radical, decreasing the quantum yield of reduction, eq. 17. Further, in the



thiol retarded reaction, the thiyl and ether-derived radicals slowly couple to form a stable monothioether, eq. 18. They do this more slowly than the thiyl enters into repair with ketyl, eq. 4, but the thiol is finally consumed and protection ceases.<sup>10,13</sup>

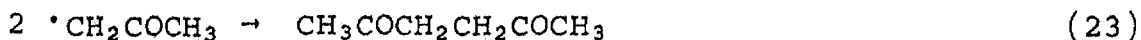


Effects of thiols and other additives on <sup>60</sup>Co γ-radiolysis of dilute aqueous solutions of 2-propanol,<sup>22</sup> acetone,<sup>22</sup> and methyl acetate<sup>28</sup> were also studied. In radiolysis of aqueous 2-propanol, hydrogen atom and hydroxyl abstract α-H from the alcohol, and this radical leads to acetone and to pinacol, eqs. 19-21.



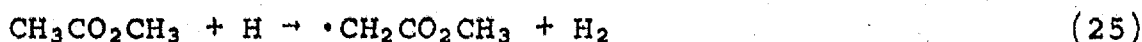
Thiols greatly diminish formation of these products. Introduction of deuterium indicated that thiol converted the intermediate radical back to 2-propanol, by the repair mechanism, eq. 3. The yield of  $H_2$  was not affected, indicating that the initial damage is not prevented, but repair intervenes, by hydrogen transfer, before irreversible damage occurs.<sup>22</sup>

$^{60}Co$   $\gamma$ -radiolysis of aqueous acetone is complex and thiol leads in part to increased damage and in part to protection. Solvated electron adds to acetone, leading to the alcohol-derived radical,  $Me_2\dot{C}OH$ , and this appears to react with acetone, forming 2-propanol and acetyl radical.<sup>16</sup> Acetyl radical leads to 2,5-hexanedione, eqs. 22,23.



Thiol markedly increases the formation of 2-propanol, as it did in the acetone-benzhydrol photochemical system.<sup>19</sup> The efficient abstraction of hydrogen from thiol, eq. 3, the reaction which leads to protection of 2-propanol, increases the damage to acetone. On the other hand thiol completely prevents the dimerization to 2,5-hexanedione, eq. 23, reducing acetyl radical to acetone. This is an important repair process, preventing radical coupling, or macromolecule cross-linking in biological systems.<sup>22</sup>

Radiolysis of aqueous methyl acetate is even more complex.<sup>28</sup> Abstraction of H from  $CH_3$  of the alkoxy and acyl moieties by OH and H lead to  $CH_3CO_2CH_2\cdot$  and  $\cdot CH_2CO_2CH_3$ , eqs. 24 and 25, which may be repaired by thiol. Addition of  $e_{aq}^-$  and  $H^+$



lead to  $\text{CH}_3\dot{\text{C}}(\text{O}^-)\text{OCH}_3$  and  $\text{CH}_3\dot{\text{C}}(\text{OH})\text{OCH}_3$ , which may be repaired by thiyl, and cleave to  $\text{CH}_3\dot{\text{C}}\text{O}$ . Five coupling products of these radicals are found; their formation was prevented by thiol and thiyl which offered very substantial protection by hydrogen transfer reactions. Acetic acid was also formed in high yield, by oxidation and not by a hydrolytic mechanism. Thiol also prevented this. However thiol led to acetaldehyde, instead, a product not formed in the absence of thiol. Reduction of  $\text{CH}_3\dot{\text{C}}(\text{OH})\text{OCH}_3$  by thiol may lead to acetaldehyde, and oxidation of it by  $\text{H}_2\text{O}_2$  or other species may be responsible for much of the acetic acid. H and OH are indicated to abstract H as indicated in eqs. 24 and 25, with H reacting as a nucleophilic radical at the site which may support a negative charge in the transition state, and OH as an electrophilic radical, acting at the site which may support a positive charge. The resulting radicals then have oxidizing and reducing properties, respectively, and a variety of disproportionations may occur.<sup>28</sup> Such radical redox reactions were observed in the disproportionation of substituted diarylketyl radicals and radical anions.<sup>26</sup>

Results of these studies of the effects of thiols on photochemical and radiation induced reactions were presented at chemical and photobiological<sup>6</sup> meetings, at a meeting sponsored by the International Atomic Energy Agency,<sup>11</sup> and at a meeting on organo-sulfur chemistry,<sup>14</sup> and reviews were written.<sup>11,14</sup>

We have also carried out purely photochemical studies in excited carbonyl-donor systems. We have considered three fundamental problems in these studies, (i) the rates of reaction of the excited triplets with the donor molecules; (ii) the yields of radicals from these reactions; and (iii) the final yields of products or the quantum yields of photoreduction of the carbonyl compounds.

The initial reaction rates may be measured by the effects of

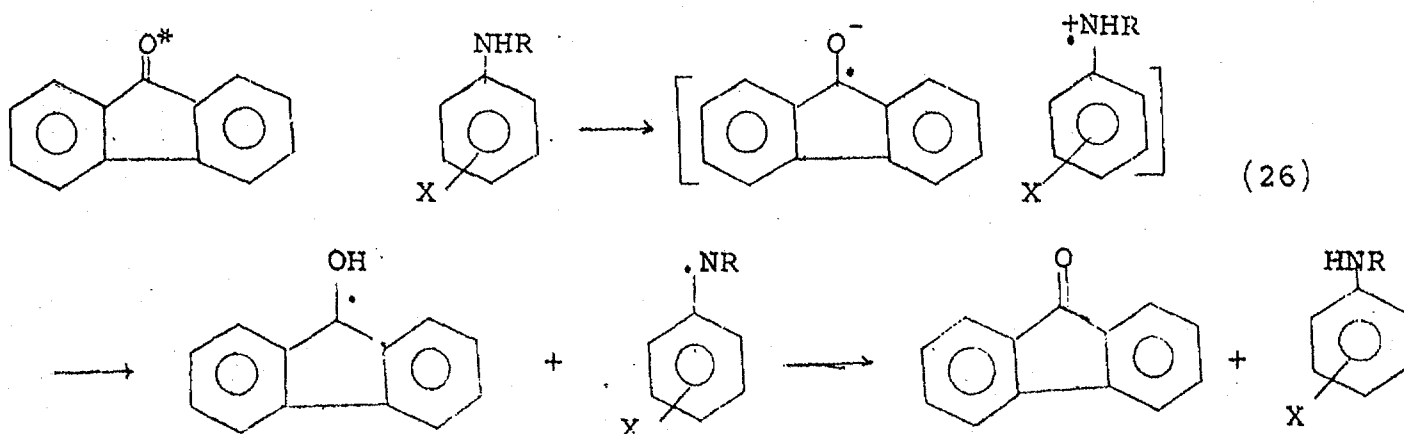
diffusion controlled physical quenchers on the rates of reduction, by the effects of the donors on phosphorescence quantum yields where these may be observed, and by the effects of the donors on triplet lifetimes in flash photolysis studies. Results determined in the different ways have been supportive of each other. We have sought correlation of these rates with physical properties of the reactants. We have found<sup>23</sup> that the log of the rate constants of reaction of benzophenone triplet with a variety of donors is linear with their ionization potential -- and these donors include primary, secondary and tertiary aliphatic amines, aliphatic thiols and thioethers, olefins, ethers and alcohols. Rate constants varied over three orders of magnitude,  $10^6$ - $10^9$   $\text{M}^{-1} \text{s}^{-1}$ , and ionization potentials from 10 to 7.5 eV. Aromatic donors also showed a linear relationship with  $\log k_{ir}$ , but lower rate constant for a given ionization potential and a higher dependence on ionization potential. Donors were aromatic amines, phosphine, ether, and hydrocarbons. Rate constants were  $10^4$ - $10^9$   $\text{M}^{-1} \text{s}^{-1}$ , and ionization potentials 9-7 eV.<sup>24</sup> In a study<sup>24</sup> of fluorenone-donor systems a single linear relationship was found between  $\log k_{ir}$  and ionization potential of aromatic and aliphatic donors, -- anilines, aliphatic amines and a thioether. Great variation in  $k_{ir}$  was observed,  $10^4$ - $10^{10}$   $\text{M}^{-1} \text{s}^{-1}$ , and a somewhat higher dependence on ionization potential, indicating greater dependency on charge development in the quenching transition states.

In a study in which a single donor, triethylamine, and a variety of carbonyl compounds were examined, a linear relationship was found between  $\log k_{ir}$  and the reduction potentials of the excited triplets, the latter indicated by  $(-{}^3\Delta E_{O,O} - E(A^-/A))$ , the triplet energy and the reduction potential of the ground state respectively. This relationship was independent of configuration of the excited state -  $n, \pi^*$ ,  $\pi\pi^*$  and charge-transfer. Thus the relationship of eq. 26, equivalent to a linear free energy relationship, was proposed, and appears to have some general

and predictive validity.

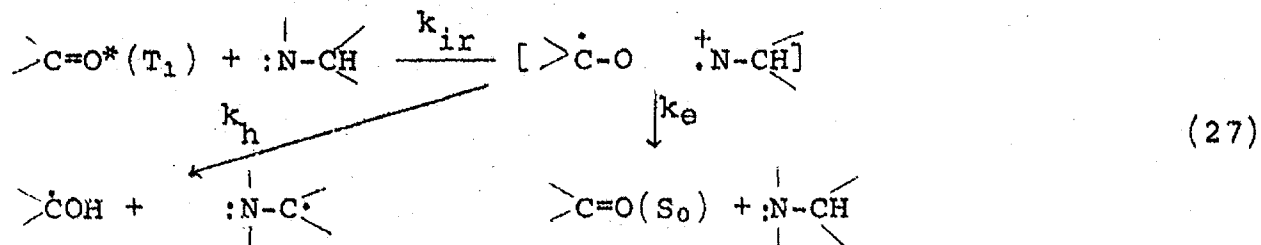
$$\log k_{ir} \sim \text{I.P.D} - {}^3\Delta E_{0,0} - E(A^-/A) + C \quad (26)$$

In an extension of this, reaction of excited fluorenone with a series of thirteen p-substituted dimethylanilines led to a linear relationship between  $\log k_{ir}$  and  $\sigma, \sigma^+$  and  $\sigma^-$ , with rate constants varying  $10^7$ - $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . Remarkably, the quantum yields for photoreduction of the ketone were low with both high and low rate constants, (p-OEt and p-CN compounds) and highest at intermediate values,  $\phi \sim 0.6$  for the unsubstituted compound. The reason for this is not clear; both insufficient and excessive charge development may lead to return to the ground state.<sup>25</sup> However primary yields of free radicals should be determined. In a related study, reaction of excited fluorenone with meta- and para-substituted anilines and mono-N-alkyl anilines led to linear relationships between  $\log k_{ir}$  and  $\sigma^+, \sigma^-$  values. Only quenching was observed with no net photoreduction of the ketone.<sup>27</sup> We conclude that an important charge-transfer interaction is involved, that H is transferred from N, and that the ketyl and aminyl radicals disproportionate to regenerate the starting materials, eq. 26.



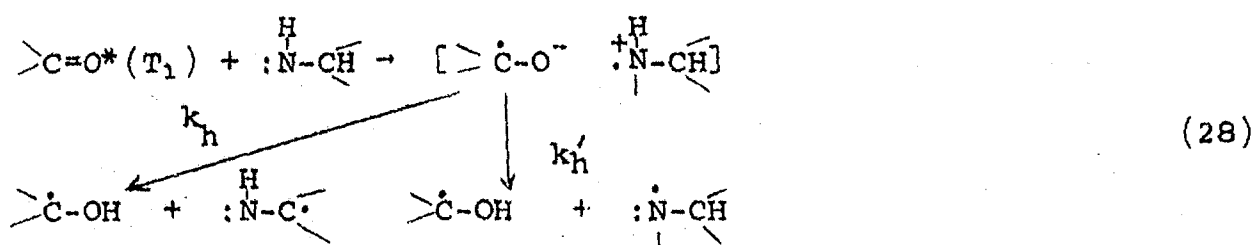
Early in this program we became interested in the failure of p-aminobenzophenone to be photoreduced by alcohols. We found that this could be accomplished efficiently if the amino group was protonated by making the solution acidic.<sup>9</sup> Similarly, dimethylaminobenzophenone was not reduced by alcohol, but was photoreduced by acidified alcohol, and methylation to the trimethylammonium compound also led to a fully reactive ketone.<sup>9,15,26</sup> Coordination of the n-electrons of the aromatic amino group, removing their conjugation with the carbonyl, sufficed to allow such ketones to be photoreduced by alcohols. However this is not necessary to effect their photoreduction. We have found that tertiary amines are very effective photoreducing agents, and p-aminobenzophenone is photoreduced by triethylamine, preferably in a non-polar solvent.<sup>18</sup> Study of photoreduction of benzophenone by tertiary amines was hindered by formation of light absorbing transients which acted as quenchers and led to low quantum yields. This problem is not found in reduction in aqueous solutions where such transients are not formed.<sup>17</sup> However ketones which have unreactive triplets in polar solvents can not be studied in this way.

Photoreduction by amines is characterized by high rate constants, effectiveness with ketones which are not photoreduced by alcohols, and less than theoretical quantum yields of final redox products. These properties were rationalized in terms of initial rapid charge-transfer interaction,  $k_{ir}$ , followed either by hydrogen transfer and radical formation,  $k_h$ , or by return to the ground state,  $k_e$ , the latter two processes both facilitated by the initial charge-transfer, eq. 27.

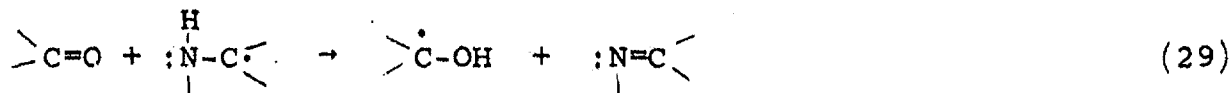


In the course of study of the effects of thiols on such processes we found that aromatic thiols inhibited them, as expected.<sup>30</sup> Racemization of optically active amine and introduction of deuterium supported hydrogen transfer repair reactions analogous to those in inhibition of photoreduction by alcohols, eqs. 3,4. However, unexpectedly, we found that aliphatic thiols accelerated photoreduction by primary and secondary amines. The increase in quantum yield can be very substantial and it was initially attributed to thiol participating in the partitioning of the charge-transfer complex as a third component, increasing the  $k_h/k_e$  ratio.<sup>29,30</sup>

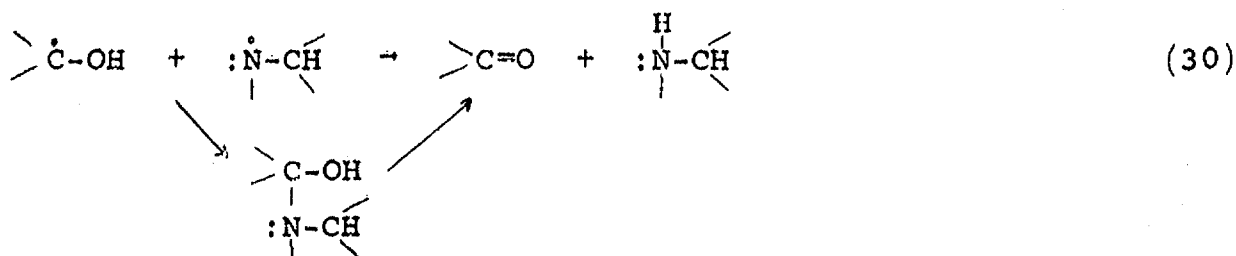
However in studies carried out after the termination of this contract, supported in part by the National Science Foundation, we have found that the mechanism both for the photoreduction, eq. 21, and for the acceleration, must be modified. Laser-flash photolysis experiments now show that ketyl radicals are formed with essentially unit quantum yield in reaction of benzophenone with the common primary, secondary and tertiary aliphatic amines. The failure to achieve perfect quantum efficiency in the yield of final reduction products can not be attributed to quenching, and the  $k_e$  process, eq. 27, does not generally occur. Therefore the thiol can not increase quantum yields by affecting the  $k_h/k_e$  process. Further experiments support the view that, in photoreduction by primary and secondary amines, H is abstracted in part from  $\alpha$ -C and in part from N, leading to ketyl radicals and to  $\alpha$ -aminoalkyl radicals,  $k_h$ , and to alkylaminyl radicals  $k_h'$ , eq. 28.  $\alpha$ -Aminoalkyl radicals are



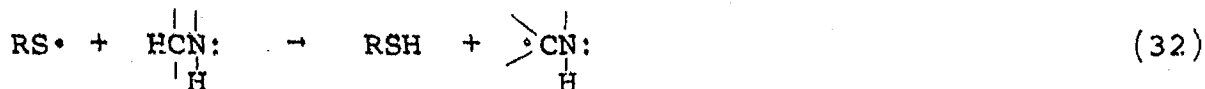
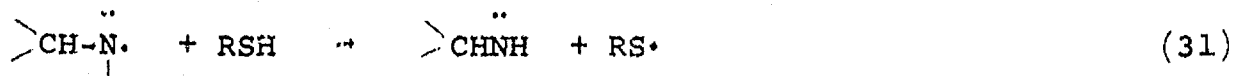
oxidized by ground-state ketone, eq. 29, as in reduction by alcohols, eq. 16, but alkylaminyl radicals react with ketyl to



regenerate starting materials, eq. 30, as do thiyl radicals, eq. 4, and thus cause loss of quantum efficiency.



We now propose that aliphatic thiols increase quantum yields for photoreduction by primary and secondary amines by a sequence of hydrogen transfer reactions which convert alkylaminyl to aminoalkyl radicals, preventing the light wasting process of eq. 30. The aminyl radical abstracts H from thiol, eq. 31, and thiyl radical abstracts H from  $\alpha$ -C of the amine, eq. 32.



Thus, at the start of our study we found that rapid transfer of H from thiol and to thiyl radical efficiently inhibited certain photochemical reactions, and provided a mechanism for protection against damage by high energy radiation. Now we find that closely related rapid hydrogen atom transfer reactions from and to sulfur may increase the quantum yields of photochemical reactions and prevent the wasteful conversion of radiant to thermal energy.



Publications issued on work done with support of Contract DE-AC02-76ER03118 (formerly EY-76-S-02-3118) Saul G. Cohen, Principal Investigator.

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