**PHOTOINDUCED ELECTRON TRANSFER PROCESSES
IN HOMOGENEOUS AND MICROHETEROGENEOUS SOLUTIONS.**

Progress Report

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SUMMARY OF WORK ACCOMPLISHED

APRIL 16, 1989 - SEPTEMBER 1, 1991

The focus of the work described in this report is on single electron transfer reactions of excited states which culminate in the formation of stable or metastable even electron species. For the most part the studies have involved even electron organic substrates which are thus converted photochemically to odd electron species and then at some stage reconvert to even electron products. These reactions generally fall into two rather different categories. In one set of studies we have examined reactions in which the metastable reagents generated by single electron transfer quenching of an excited state undergo novel fragmentation reactions, chiefly involving C-C bond cleavage. These reactions often culminate in novel and potentially useful chemical reactions and frequently have the potential for leading to new chemical products otherwise unaffordable by conventional reaction paths. These studies have focused both on the possibilities for novel net photochemistry as well as the mechanism for these reactions. In a rather different investigation we have also studied reactions in which single electron transfer quenching of an excited state is followed by subsequent reactions which lead reversibly to metastable two electron products which, often stable in themselves, can nonetheless be reacted with each other or with other reagents to regenerate the starting materials with release of energy. The novelty in these reactions is the formation of metastable products which survive on relatively long time scales compared to the typical lifetimes of radical species generated by simple SET processes where an SET back electron transfer process can very rapidly regenerate the starting material. For the sake of clarity this progress report is divided into several sections which highlight different facets of these studies.

I. Photochemical Electron Transfer-Induced Carbon-Carbon Bond Cleavage Reactions.

In 1986, we reported an electron transfer induced fragmentation of amino alcohol and aminoketone donors under irradiation of the electron acceptor thioindigo.⁽¹⁾ We showed in studies supported by DOE 1986-1988 that this is a quite general reaction with stereochemical selectivity, closely related to the two electron Grob fragmentation observed earlier with a number of substrates upon reaction with strong electrophiles.⁽²⁾ During the present project period we have examined several factors involved in the photochemical fragmentation. Most significantly we have evaluated mechanistic aspects in reasonably great detail. We have also greatly expanded the scope of this reaction. These studies provide a linkage between single electron transfer and more conventional two electron organic mechanisms and reactions.

A. Reaction of Amino Alcohols.

The general fragmentation of amino alcohols according to Eq. 1 has been found with a variety of different electron acceptors absorbing light in the near ultraviolet and visible for a wide range of amino alcohols and in a fairly broad range of organic solvents and aqueous surfactant solutions.^(1,3-9)

The rather high degree of diastereomeric selectivity observed with several different amino alcohol-acceptor combinations indicates a general preference for a trans antiperiplanar arrangement

for the amino alcohol during the fragmentation process.⁽⁸⁾ In a number of investigations a strong correlation of reaction efficiency (corrected for quenching) with basicity of the acceptor radical anions suggests that the actual fragmentation involves cooperative reaction between the acceptor anion radical and the donor cation radical in the fragmentation step. Although this reaction has been examined for a wide variety of donor amino alcohols, we have not observed prominent cleavage in most purely aliphatic amino alcohols and generally have not observed cleavage with molecules in which both amine and alcohol functionality are substituents on the same ring.

The cleavage reaction can be initiated by a wide variety of photoexcited electron acceptors. In general when excited singlet acceptors are quenched by the donors, reaction efficiency is low to moderate, depending strongly upon solvent and, as pointed out above, acceptor anion basicity. When the photoexcited acceptor reacts through its excited triplet state, reaction quantum efficiencies are generally much higher, presumably due to the retardation of the energy wasting back electron transfer process. A number of linked amino alcohol donor -- acceptor systems showing relatively high reactivities will be discussed below.

Studies of the mechanism of the amino alcohol photofragmentation indicate that the reaction may involve three different sets of intermediates. Excited state quenching involving neutral donors and acceptors produces oppositely charged ion radicals. In nonpolar solvents, such as benzene where $\epsilon < 7$, these are generated as a contact radical ion pair (CRIP). In more polar solvents, a solvent separated radical ion pair (SSRIP) should be more stable and thus formed either by direct electron transfer or by decay of a CRIP. Dissociation of the CRIP to free ions is relatively unlikely in non polar solvents. However, in moderately polar solvents such as acetonitrile the SSRIP can dissociate into free ions and thus in these cases reaction from either set of intermediates is possible. In a number of recent studies it has been found that donor-acceptor excited state electron transfer bypassing the SSRIP can be achieved through use of a cosensitizer.⁽¹⁰⁻¹³⁾ In a typical situation an acceptor is photoexcited (Eq. 2) and then quenched by the cosensitizer (CS), a donor whose cation

radical is relatively stable and whose SSRIP with $A^{\cdot-}$ has a high efficiency (γ) of cage escape to yield free ions (Eq. 3). In a subsequent diffusional process, the cosensitizer cation radical undergoes a ground state SET with D to give the free ions A^- , D^+ with an efficiency, γ (Eq. 4).

We have used this technique with biphenyl as a cosensitizer and several different acceptors to investigate the reactivity of the different intermediates that can be involved in amino alcohol photofragmentation (Scheme 1).

The results of this study may be summarized briefly as follows. For amino alcohols and acceptors with reasonably basic anion radicals, $A^{\cdot-}$, reaction in the CRIP is frequently competitive with back electron transfer for quenching of excited singlets. However for SSRIPs, relatively lower overall reactivity is observed and most of this reactivity is indicated to likely come from free ions formed via cage escape. Biphenyl cosensitization studies indicate that reactivity from free ions is very high, presumably due to the very long lifetime of the cation radical.⁽¹⁴⁾ In this case fragmentation may likely occur with the assistance of the solvent acting as a base. Electrochemical studies have pointed out that cation radical of the amino alcohols will fragment, but we have not yet been able to assess the precise rate of the "unassisted" fragmentation.

Reaction in nonpolar solvents via the CRIP can be observed as mentioned above for several different donor-acceptor combinations. In some, but not all, cases where a moderately efficient reaction is observed, quenching of the acceptor fluorescence is accompanied by appearance of exciplex fluorescence. We have studied a number of aminoalcohol-acceptor combinations which are simultaneously reactive and emissive. It seems very clear from these investigations that the

CRIP and exciplex are the same species as has been suggested in a number of previous investigations. Interestingly we have found that addition of base to solutions of aminoalcohol-

Scheme 1

quenched acceptors results in a quenching of exciplex fluorescence and simultaneously an enhancement of the fragmentation efficiency.^(8, 9) We have also observed very prominent exciplex fluorescence simultaneous with moderately efficient fragmentation in a number of linked aminoalcohol-acceptor molecules. Although most of our studies have focused on vicinal aminoalcohols, we have also examined a number of molecules in which the amine and alcohol functionalities are separated by conjugated or nonconjugated systems. We have found for example that amino alcohols **1** and **3** undergo efficient fragmentation while **2** does not.⁽¹⁵⁾ In both **1** and **3** benzylic separation of the amine and alcohol functionality permits reaction analogous to that observed in vicinal amino alcohols while **2** lacks this possibility. Very recently we have synthesized **4** and are examining the possibility that it fragments with a concurrent skeletal rearrangement analogous to the rearrangement observed with related carbocations. To date we have found **4** quite unreactive with a number of different acceptors although excited state quenching via SET has been indicated in some cases.⁽¹⁶⁾ We are still examining the possibility that this

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reacts with concurrent fragmentation and rearrangement in at least low to moderate efficiency.

B. Reaction of Amino Ketones.

In the case of aminoalcohols, we have shown that moderately efficient and chemically clean reaction occurs in non polar solvents within contact ion-pairs in which both donor cation-radical and acceptor anion-radical play important roles. The acceptor anion radical acts as a base which catalyzes the concerted carbon-carbon bond fragmentation by deprotonation of the donor cation-radicals. This effect, however, was also found to be even more important in the fragmentation of amino-ketone systems.

The photofragmentation reaction of amino-ketone **5** in the presence of dicyanoanthracene (DCA) was carried out in benzene (~1% water) which afforded three primary products in high overall chemical yields (90%) with the indicated stoichiometry (Eq. 5) and a modest quantum

efficiency ($\Phi = 0.038$).^(17, 18) A mechanism for the overall conversion described in Equation 5 is given in Scheme 2. Thus anion assisted cation radical fragmentation is proposed for this reaction.⁽¹⁸⁾ While the unassisted cleavage of cation radical $5^{+\bullet}$ could also yield the same products, thermochemical cycle estimation of the carbon-carbon bond energy in $5^{+\bullet}$ of about 30 kcal/mole suggests that the acceptor anion radical assisted path is more probable. This is supported with experiments in polar solvents. Unlike the electron transfer induced fragmentation of aminoalcohols which occur in a wide range of solvents, the present reaction proceeds poorly in polar solvents, such as acetonitrile or methanol. Both the quantum yield and the chemical yield are decreased. Thus in the present case, the reaction appears governed both by the generation of reactive partners as a contact ion pair or exciplex and also by the absence of appreciable solvent stabilization of the potential nucleophile and substrate.

The same fragmentation has also been observed with other related donor-acceptor combinations (**5**/Ti; **6** or **7**/DCA), suggesting that this reaction path could be fairly general for photogenerated contact ion-radical pair in non polar solvents.

Scheme 2

C. Carbon-Carbon Bond Cleavage in 1,2-Diamines.

The photoinduced electron transfer fragmentation of 1,2-diamines has been investigated and a reasonable understanding of the factors important in this reaction has been achieved. This study was undertaken to investigate the generality of the carbon-carbon bond cleavage reaction that was previously observed in the photoinduced electron transfer processes of 1,2-aminoalcohols and aminoketones with various excited electron acceptors.^(1, 3-7, 17, 18) It is seen that this same reactivity is present for the diamines and in many cases the diamine is more reactive than analogous aminoalcohols. The influence of solvent polarity, electron acceptor structure, diamine donor structure, and the photochemical method employed has been determined and related to the relative reactivity of the diamines as compared with the aminoalcohols.

The acceptor-dependence of aminoalcohols as compared to ditertiary amines was observed by the study of styrene derived amine donors.⁽¹⁹⁾ The two compounds which were compared were the diamine **8**, 1,2-dimorpholino-1-phenyl ethane, and the analogous aminoalcohol **9**, 1-phenyl-2-morpholinoethanol. Studies of the photolysis of solutions of **8** and **9** with a variety of acceptors

and in several different solvents demonstrated that the relative reactivities of the two donor substrates can be reversed by the manipulation of acceptor anion-radical basicity and by the polarity of the solvent. With acceptor molecules that have relatively basic anion radicals, such as thioindigo

(TI) or β -lapachone (β -lap), the aminoalcohol was found to be the more reactive by a factor of as much as 2:1, due to the deprotonation assistance on the aminoalcohol fragmentation. However, with relatively non-basic acceptors, dicyano-(DCA) and tetracyanoanthracene (TCA), the diamine is more reactive by as much as 33:1 for TCA, due to its ability to undergo fragmentation through an unassisted manifold with the lone pair on nitrogen. These subtle mechanistic differences are outlined in Scheme 3 and 4 which demonstrate the deprotonation assistance for the aminoalcohol and the unassisted diamine fragmentation pathways. The same trends were observed when the solvent polarity was varied. When a non-polar solvent, such as benzene, was used (with a "reactive" acceptor" (TI)), the aminoalcohol is more reactive, but in a polar solvent (acetonitrile), the radical ion pair formed by electron transfer is rapidly solvent separated which hinders the deprotonation of the aminoalcohol and thus the diamine is more reactive by a factor of 3.5:1 for TI in acetonitrile.

The meso and d,l isomers of the diprimary amine **10** were independently synthesized⁽²⁰⁻²⁴⁾ and their reactivity investigated in studies analogous to those used with the styrene diamine and aminoalcohol.⁽²⁵⁾

10 meso

10 d,l

The fragmentation reaction of these compounds could be followed by monitoring the formation of benzaldehyde in the NMR of irradiated samples of the two isomers with thioindigo as the electron acceptor in benzene- d_6 . Direct comparison of the reactivity of the two isomers was followed by monitoring the UV-vis bleaching of the different acceptors with extended periods of

irradiation. In the case of thioindigo, the two isomers react at essentially the same rate with the only difference reflecting a slight difference in their TI fluorescence quenching constants. The relative reactivities were found to be nearly the same regardless of the solvent (either benzene or acetonitrile). With β -lapachone as the acceptor, the reactivities were again very similar with a slight favoring of the meso isomer by a factor of 1.1 times that of d,l. For the cyanoaromatic acceptors, (DCA and TCA), the fluorescence quenching follows the same trends as noted for thioindigo. The d,l isomer was the better quencher in both cases with a 1.2:1 ratio for DCA and a 1.3:1 ratio for TCA. In the cases of TI and β -lap in benzene solution, the bleaching of the acceptor was seen to coincide with the growing in of the reduced acceptor which absorbs at higher energy (shorter wavelengths). However for the DCA and TCA in benzene, bleaching is the only observable reaction, which probably reflects either the nonabsorbing nature of DCAH_2 or its insolubility. Even more interesting differences were noted with TCA in acetonitrile. Irradiation of a degassed yellow solution of TCA and either isomer of **10** in acetonitrile caused a dramatic color change to occur with a resulting deep blue solution; the decrease of the TCA absorbance was concurrent with the appearance of a large amount of structured absorbance throughout the long wavelength visible spectra. The intensity of the blue color increased with continued irradiation until all of the original TCA absorbance was bleached. When the sealed tube was exposed to oxygen the blue color disappeared rapidly with the reappearance of the original yellow color which corresponded to a complete regeneration of the initial TCA absorbance. This blue color was found to correspond to the formation of the anion radical of tetracyanoanthracene stabilized in degassed acetonitrile solution.⁽²⁶⁾ The formation of the anion radical was verified by EPR and a bulk electrolysis of a degassed TCA solution in an electrochemical cell with a transparent platinum mesh electrode. The UV-vis absorption spectrum obtained by this electrochemical method was identical to that observed for the photochemical process and both of these spectra were in agreement with one obtained by an

Scheme 3 . General Mechanism of Diamine Fragmentation

Scheme 4. General Scheme for Aminoalcohol Fragmentation

independent laser flash photolysis study of TCA with a toluene donor.⁽²⁷⁾ Chemical analysis of the oxidation of **10** under these conditions shows that the net reaction is given by Eq. 6.

Subsequent studies were performed to compare several diamine substrates and an analogous aminoalcohol in a variety of different photochemical systems. The manipulation of solvent and the use of cosensitization permitted us to determine the extent of reaction from each of the three distinct radical ion pair intermediates formed from the photoinduced electron transfer step. These three intermediate sets are the contact radical ion pair (CRIP), the solvent separated ion pair (SSRIP), and the free ions (FI) as described in the previous section (see Eq 2, 3 and 4 and Scheme 1).

The meso isomer of diamine **10** was compared to its tetramethyl ditertiary amine derivative **11** and the previously studied aminoalcohol **12**, using the solvents and cosensitization methods mentioned above.⁽¹⁴⁾ The results are summarized in Table 1.

The results in Table 1 are in accord with the trends seen in the previous experiments, in which the diamines tend to be more reactive with the cyanoaromatic acceptors and in polar solvents where

Table 1. Quantum Yields of Acceptor Change (Corrected to 100% Quenching)

Donor/Acceptor	Solvent w/ or w/o cosensitizer			
	Benzene	Acetonitrile	Acetonitrile:H ₂ O (95:5)	Acetonitrile / Biphenyl
10 / DCA	0.011	0.129	0.77	0.43
10 / TCA	0.10	1.09	0.98	0.38
11 / DCA	0.006	0.068	0.22	0.45
11 / TCA	0.37	0.40	0.20	0.36
12 / DCA	0.010	-----	0.003	0.46
12 / TCA	0.014	0.035	0.04	0.29

the deprotonation assistance to the aminoalcohol is greatly hindered. On the other hand, the cosensitization experiments produced some new and interesting observations. Under the cosensitization conditions back electron transfer should be much slower from the kinetically free ions produced in relatively low steady state concentration, thus the fragmentation reaction should be more favorable due to the longer lifetime of the reactive intermediate diamine cation radical. Therefore it can be hypothesized that the donors should all react with a similar quantum yield, since the calculated bond dissociation energies for the cation radicals are all on the same order of magnitude, and this quantum yield should be limited only by the yield of free ions from the cosensitized electron transfer process. For TCA, the yield of free ions has been shown to be $\phi_{\text{fi}} = 0.24$, and using the mechanistic scheme (Scheme 3, 4 and Eq. 6) and the fact that TCA anion radical is formed as a stable product, we anticipate a quantum yield of TCA reduction to be in the range 0.4 to 0.5 for this cosensitized process. The actual values fall a little short of this range but the quantum yields are very similar for both diamines and the aminoalcohol. For DCA the reported free ion yield is 0.75 to 0.83 and since the DCA is reduced to DCAH₂, there is one DCA is

consumed for each electron transfer event and thus the limiting quantum yield of acceptor change should be in the same 0.75 to 0.83 range. Again from Table 1 it is noted that the quantum yields are all very similar but lower than the limiting value. Although the reason for the yields being somewhat less than the limiting values has not yet been established, it is still interesting to note that reactivity differences between the donors are pretty much eliminated by using cosensitization and that the probability of fragmentation is high once the free ions are reached for all of the donors studied.

Concurrent with the studies of the stereoisomers of diamine **10**, some aliphatic di-primary amines **13** and **14** were examined for their reactivity with the different electron acceptors.⁽²⁵⁾

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14

The quenching of thioindigo fluorescence was determined and **14** was found to be the better quencher by a factor of 1.1 times. However, both **13** and **14** were found to be about 3 times better quenchers than the diamine **10** isomers. In a comparison photolysis study, the diamine **14** was found to bleach the thioindigo absorbance at a rate two times greater than diamine **13**, but both were 15 times less reactive than either of the isomers of **10**. When the triplet acceptor B-lap was used, **14** was still favored but the reactivities were 10 times greater than with TI. Product analysis for these amines has yet to be completed and thus it would be fortuitous to claim that the bleaching of the acceptors is concurrent with a fragmentation of these diamines, **13** and **14**.

Preliminary studies have been performed to further understand the role of biphenyl in these systems by studying the reactivity of the diamines when sensitized by interaction with the

TCA/Biphenyl exciplex in benzene. Quantum yield determinations for the bleaching of TCA by photolysis of solutions of TCA and the diamines with and without biphenyl showed a reproducible trend in which biphenyl exciplex "consensitization" caused a decrease in the observed quantum yield. This is opposite to the effect seen for biphenyl in acetonitrile, where consensitization provides the free radical ion pairs and higher quantum yields for bleaching and product formation. The quantum yield observed for the reaction from the TCA/Biphenyl exciplex in benzene was about 60% of that observed for direct quenching by both the diamines, **10** and **11**. This decrease is postulated to be caused by an increase in decay pathways out of the TCA/Biphenyl exciplex, either through non-radiative processes or possibly back electron transfer from biphenyl to TCA. The quantum yields from this study were the product of a bit of mathematical manipulation to extrapolate to a point where all of the TCA monomer fluorescence is quenched by biphenyl and where all of the TCA/biphenyl exciplex fluorescence is quenched by the donor diamine. However this decrease in quantum yield initially appears to be relatively constant for two different concentrations of donor used.

D. Singlet Oxygen Mediated Fragmentations.

As the foregoing discussion has pointed out, a variety of amine and oxygen-containing donors undergo effective two-electron redox reactions when activated via single electron transfer quenching of excited acceptors absorbing at fairly low energies in the visible or near UV. Among the potential acceptors which might be anticipated to initiate these reactions is excited singlet oxygen, which is easily generated with several long-wavelength absorbing dyes as sensitizers. Amines have long been known to quench singlet oxygen.⁽²⁸⁻³⁰⁾ It has been suggested that this quenching proceeds by electron-transfer from the electron-rich substrate (amine donor) to the singlet oxygen to give a cation radical-superoxide ion pair or charge transfer complex.⁽³¹⁻³⁴⁾ However in most cases the steps following electron transfer have not been clearly delineated.⁽³⁵⁻³⁸⁾ In many cases, it has been observed the quenching of singlet oxygen by an amine (and most other

donors) results in no net chemistry.⁽²⁸⁾ It is assumed this is due to rapid back-electron transfer. We have found in several cases with fragmentable amine donor that quenching of singlet oxygen is accompanied by moderately efficient reactions of the resulting ion pair.

Initial investigation with aminoalcohols as potential substrates showed that irradiation of the singlet oxygen sensitizer Rose Bengal or the organic soluble Rose Bengal derivative⁽³⁹⁾ results in two-electron oxidation of the aminoalcohol according to Eq. 7.⁽⁶⁾

A reasonable mechanism is shown in Scheme 5. This mechanism is supported by a variety of experimental studies, including product analysis, singlet oxygen quenching, and singlet oxygen luminescence quenching. This reaction has been observed for amino alcohols such as **12**, **15** as well as the biological active methyl ephedrine **16**.

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1, 2 Amino ketones, such as **6** and **7** yield additional possibilities for novel reaction with singlet oxygen. Following the quenching of singlet oxygen by the aminoketone, the resulting cation radical-superoxide ion pair has three options: back-electron transfer, reaction or cage

Scheme 5. Singlet Oxygen Induced Amino-Alcohol Fragmentation

escape.⁽¹⁷⁾ In the case of reaction, the newly formed superoxide anion could exhibit two major reaction pathways with the amino ketone cation: the superoxide can act as a base--removing a proton, or it can add nucleophilically to the ketone moiety. Both the nucleophilic and basic properties of superoxide have been well described.⁽⁴⁰⁾ When amino ketone is allowed to react with singlet oxygen, several products are detected (Eq. 8).

Product distribution supports a mechanism similar to that of the reaction with amino alcohols, with an important difference, in that the superoxide reacting as a nucleophile leads to the acid and amide (Scheme 6). Scheme 7 outlines a plausible mechanism whereby the benzyl derivative may be produced by the basic action of superoxide. These mechanisms are also supported by results of ¹⁸O₂ labelling experiments.

As reported earlier, 1,2 diamines have been shown to fragment after photo-induced electron transfer with acceptors such as thioindigo, β-lapachone, and dicyanoanthracene (section 1C). Diamines **8** and **17** have been observed to undergo a fragmentation reaction with singlet oxygen. The major product of this reaction is benzaldehyde.⁽⁴¹⁾ This reaction is presumed to take place by a mechanism similar to that of other photo-induced electron transfer fragmentations (Scheme 3), i.e., the excited acceptor (in this case singlet oxygen) oxidizes one of the amines; the diamine can then fragment with the assistance of the lone pair of electrons on the other amine moiety.

Scheme 7. Mechanism of Aminoketone Oxidation.

17

Direct quenching of the IR luminescence of singlet oxygen has been measured for aminoalcohol **12** and aminoketone **6**.⁽⁴²⁾ The rates are $6.5 \times 10^6 \text{ m}^{-1} \text{ s}^{-1}$ and $1.28 \times 10^6 \text{ m}^{-1} \text{ s}^{-1}$ respectively. These quenching rates correlate with the respective oxidation potentials of the molecules, the aminoalcohol's oxidation potential being lower than the aminoketone's. Oxidation potentials also are indicated to limit the respective quantum efficiencies of the reactions; e.g. the oxidation potential of diamines is less than or equal to that of aminoalcohols and aminoalcohol's oxidation potentials are less than those of the aminoketones. The quantum efficiency of diamine fragmentation is greater than or equal to that of the aminoalcohols and the aminoalcohols are more efficient than the aminoketones. (The quantum efficiencies of these reactions range from approximately 0.008 to 0.02, respectively.) The reactions of aminoalcohols, aminoketones, and diamines have all been studied using non polar benzene as a solvent. However, the aminoalcohol fragmentation and the aminoketone reaction have also been observed in polar solvents, such as acetonitrile and methanol. Rose Bengal and an organic soluble Rose Bengal derivative were used to sensitize singlet oxygen in the majority of the studies. Palladium tetraphenyl porphyrin (PdTPP) was also used to sensitize singlet oxygen and gave the same products as the Rose Bengal sensitized reaction in all cases. Interestingly, in the absence of oxygen, photo-excited PdTPP can act as a electron acceptor being first reduced to the chlorin and then the isobacteriochlorin while facilitating the cleavage of amino alcohol **12**.

II. Reversible Electron Transfer Reactions.

Photoinduced electron transfer reactions have been proposed to be a potentially useful process in terms of energy storage and energy conversion.⁽⁴³⁻⁴⁹⁾ Although a large number of photoinduced electron transfer reactions have been investigated, examples of recyclable systems which store light energy based on solution charge transfer chemistry are quite rare.⁽⁵⁰⁻⁵²⁾ Photooxidation of tertiary amines by excited electron acceptors is generally indicated to occur by a sequence of electron transfer, proton transfer and electron transfer.⁽⁵³⁻⁵⁹⁾ Recently we have shown that the photooxidation of triethylamine by β -lapachone yielded a semiquinone radical and an enamine which could store about 10 to 15 kcal/mole.⁽⁵⁹⁾ The possible thermal reversion has been discussed. However, due to the instability and reactivity of the products formed in this reaction, it is very difficult to obtain efficient reversibility or recycling. The reversibility of the particular photochemical system depends largely on the reactivity and thermal stability of the "primary intermediates" or metastable products. Energetically, these products are quite reactive and generally lead to the formation of thermodynamically more stable secondary products. In principle, the energy rich "primary intermediates" could be accumulated if the secondary reactions are effectively eliminated under carefully controlled conditions. By utilizing this strategy, we have designed a system in which the "primary intermediates" have been effectively stabilized. furthermore, the thermal reversion of the intermediates to regenerate the starting materials is achieved.

Photooxidation of tertiary amines by excited state electron acceptors can lead to the formation of various intermediates and products.^(3, 19, 54-59) Among them, iminium ions have been proposed in several cases to be the precursor of the final isolable products.^(3, 54-59) Even though many iminium ion compounds have been shown to be stable molecules and have been synthesized

independently,⁽⁶⁰⁾ the direct detection and isolation of iminium ions from photoinduced electron-transfer reactions is generally not realized, due to reactivity of iminium ions toward nucleophiles present under the experimental conditions. In our study, we found that the reactivity of iminium ion intermediates in the photochemical reaction can be effectively controlled by steric substitutions.

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In the presence of water (0.1%), irradiation of a 1:1 mixture of AQ and **22** (ca 5×10^{-3} M) in acetonitrile leads to the formation of two major products in good chemical yield (>90% by NMR analysis or >80% in terms of isolated **24**).⁽⁶¹⁾ These products were readily characterized by proton NMR and determined to be dealkylated amine and the hydroxymethyl adduct of AQ, 9-hydroxy-9-(hydroxymethyl)anthrone (**24**) (Scheme. 8). The reaction proceeds smoothly in several other solvents (acetone, benzene, and methylene chloride) but only very slowly in methanol (due to the interaction of intermediates with the solvent); an identical reaction is observed between AQ and **23**. As a reactive intermediate, iminium ions are trapped by water and hydrolyzed to secondary amines and formaldehyde; which further reacts with 9,10-anthrahydroquinone anion via a dark reaction to afford **24** as the final product. The overall reaction according to Scheme 8 thus consists of a photochemical stage ($\Phi = 0.25$ to 0.46 for the disappearance of AQ) resulting in formation of AQH₂ (or AQH⁻, its conjugate base) and a dark process in which **24** is generated.

In contrast to the above reaction, when 9,10-anthraquinone was irradiated with amine **21** (1:1, ca 5×10^{-3} M) in wet solvent (benzene-d₆ or acetonitrile-d₃), **25** was the only product formed (Scheme 9).

Scheme 8

a: See Reference 63

Scheme 9

Adduct **24**, as in the case of **22** or **23**, was not detected. The same results were obtained when the reaction was carried out in dry benzene. When the irradiated sample was heated at 95°C or opened to air, no obvious change can be observed. Therefore, the adduct **25** is not only stable thermally, but also stable to the air.

In contrast, if 9,10-anthraquinone and amine **22** or **23** are photolyzed in rigorously dry degassed benzene solution, rather different results are obtained. Other than **24** and demethylated amine (a trace of water, which was consumed completely after the irradiation, is responsible for the formation of these products), metastable products are also observed which are found to be thermally unstable and sensitive to air. About 40% recovery of 9,10-anthraquinone ($\lambda_{\text{max}} = 326$

nm) was detected upon two hours heating at 95°C of an irradiated sample (followed by UV, AQ: $1 \times 10^{-3}\text{M}$; **23**: $1 \times 10^{-2}\text{M}$; with 50% conversion) . No recovery, however, is observed when 0.1% water is present in the reaction solution. Experimental evidence showed that **24** is thermally stable at the temperature (95°C), therefore, 9,10-anthraquinone recovery must come from other products or reactive intermediates.

The thermal reversal of the photoreaction can also be followed by ^1H NMR of both 9,10-anthraquinone and amine (**22** or **23**). In a typical experiment, 20 minutes irradiation of 9,10-anthraquinone ($1.7 \times 10^{-2}\text{M}$) and **23** ($2.8 \times 10^{-2}\text{M}$) solution (in freeze-pump-thaw degassed dry benzene- d_6 , internal standard, benzene) leads to 85% conversion of AQ and 61% conversion of **23** and gives very clean formation of the metastable intermediate which was easily detected due to its characteristic proton signals. This intermediate is stable at room temperature, yet, upon opening the sample to the air, it disappeared immediately with the concurrent recovery of AQ. If the irradiated sample is heated in a water bath (95°C), the recovery of both AQ (up to 55%) and **23** (up to 30%) are observed with the decrease of the metastable intermediate on the same time scale. Further irradiation of above sample yields the same metastable product which again thermally reverts to the starting materials. Similarly, with amine **22** analogous results are obtained.

Because we are unable to detect any radical signal in an ESR experiment, it is not likely that the metastable compound is a radical species, although we cannot rule it out completely. It is also not likely to be the addition product **26** since such an adduct should be both thermally stable and insensitive to air, as was found for compound **25**. 9,10-Anthrahydroquinone can be oxidized quantitatively by oxygen to 9,10-anthraquinone⁽⁶²⁾ which suggests that the intermediate which is generated in the photoreaction of AQ and **22** or **23** may be an ion pair of 9,10-anthrahydroquinone anion AQH^- and the iminium ion. Steric hindrance of the tetramethyl-substituted iminium ion has prevented it from reacting with the larger size nucleophile, the 9,10-anthrahydroquinone anion. Only small sized nucleophiles, such as water can attack the hindered iminium ion to give the stable

products. In the case of amine **21**, the iminium ion intermediate is not sterically hindered. It reacts effectively with nucleophiles. While the radical coupling mechanism cannot be ruled out for the formation of **24** (Scheme 9), it could, however, be prohibited in the case of amine **22** and **23** due to the unfavorable steric interaction within the radical pair. The reverse reaction could follow the pathways 6 and 7 as shown in Scheme 8. Electron transfer from AQH^- to the iminium ion, which requires about 25-30 kcal/mole,⁽⁶³⁾ could be induced thermally to generate a radical pair (pathway 6). Hydrogen atom transfer from the semiquinone radical to the amine radical within the pair will lead to the regeneration of starting materials (pathway 7).

Further support of the ion pair intermediate comes from the solvent effect. When the reaction of AQ and **23** was performed in dry acetonitrile, AQH_2 has been observed to be a stable product. Neither of the dark reactions (one leads to the formation of **24** which require the presence of water, and the one leads to the regeneration of the starting materials) occur. In polar solvent (acetonitrile) the ion pair converts to free ions which are effectively unreactive in the reverse process due to the relatively high activation energy involved.

This study shows that utilization of photoinduced electron transfer reactions in a simple organic system as a light harvesting and storage process is possibly a reversible process. By utilizing the thermochemical cycle calculation and the redox potentials of the corresponding substances, the enthalpy of the reaction to produce the ion pair intermediate is estimated to be around 9 kcal/mole (Scheme 9).⁽⁶³⁾ While relatively little energy is "stored" in the present case, the finding that the products can survive on a relatively long time scale by the driving of a net two electron redox process suggests this type of process could be useful for several applications.

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63. The estimate of the energy of radical pair, (3) in Scheme 8, uses BDE (H_2) = 104 kcal/mole, BDE (amine) = 84 kcal/mole, and BDE (AQH_2) = 86 kcal/mole, and the heat of hydrogenation of AQ equals -34 kcal/mole. Energy of the ion pair, (4) in Scheme 8, is estimated by using above value and the reduction potential of iminium ion (~ 1.0 eV vs SCE)⁶⁴ and oxidation potential of hydroquinone⁶⁵ or phenolate⁶⁶ (~ 0 eV vs SCE).
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