Photoinduced Electron Transfer Bond Fragmentations

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Introduction

One of the most active areas of investigation in the search for new photochemical reactions over the past two decades has been electron transfer reactions initiated by photoexcitation of either a potential donor or a potential acceptor from the pair A,D which typically shows no interaction in the ground state. When the reaction is carried out in solution with neutral donors and acceptors, the initial product is an ion radical pair ($A^{\bullet-}$, $D^{\bullet+}$), eq 1. The ion radical pair

$$A + D \xrightarrow{h\nu} A^* \text{ (or } D^*) + D \text{ (or A)} \xrightarrow{k_q} A^{\bullet-} + D^{\bullet+} \quad (1)$$
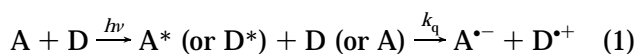
may be formed rapidly and with high efficiency when the quenching process is energetically favorable. Once formed, the ion radical pair typically can decay via return electron transfer (k_{-et}) or undergo cage escape (k_{ce}) or reaction of one or both geminate ion radicals (k_r) as outlined in Figure 1.

Rates of both forward and return electron transfer have been the focus of numerous investigations.[1−8] In many cases, particularly when the reactive excited state is a singlet state, the rate of return electron transfer is fast enough so that only very low efficiencies of reaction are possible unless cage escape or reaction is very rapid. Among the candidates offering good prospects for efficient reaction are A,D combinations where one or both of the ion radicals are indicated to be highly reactive or unstable. Typical examples include donors where oxidation takes place at a heteroatom containing nonbonding electrons such as N, S, or O and acceptors such as organic halides which can readily expel a stable halide ion. Data from mass spectroscopic studies suggest that, in the gas phase, these types of radical cations fragment rapidly.[9] Electrochemical oxidation of these compounds in solution is generally irreversible, once again indicating the instability of these radical cations. For most organic halides, electrochemical reduction is also irreversible.[10] This Account will focus on a rich array of novel and relatively efficient bond fragmentation reactions which have been observed for radical cations of substituted amines and related compounds and the development of an understanding of their

Figure 1. General kinetic scheme for the reactions available to a radical ion pair formed upon electron transfer quenching of an excited donor or acceptor.

mechanisms.[11−22] There have also been several reports in the literature of studies on the fragmentation reactions of radical anions[23−32] which will not be covered in this Account.

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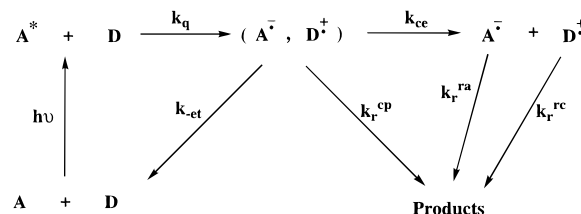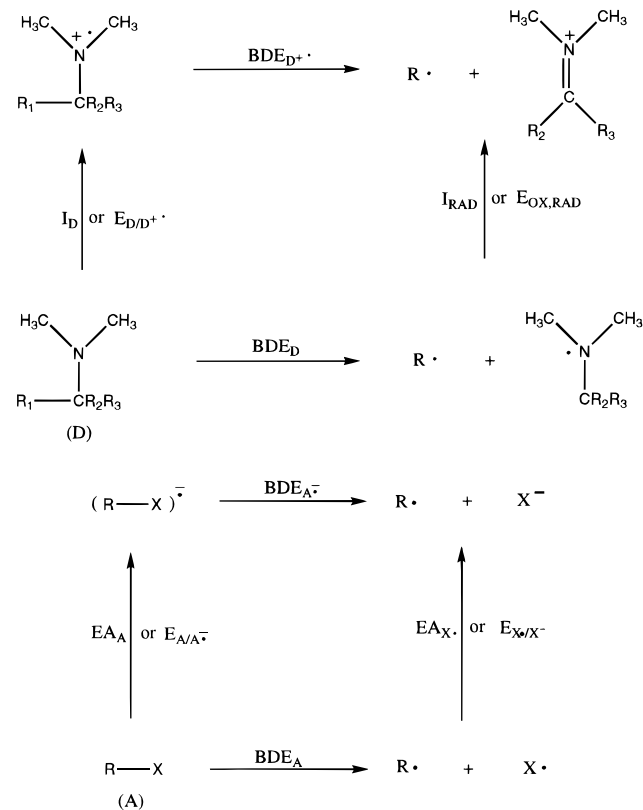
Figure 2. Thermochemical cycle for potential fragmentation reactions of neutral molecules and ion radicals.

A thermodynamic/thermochemical analysis of potential bond fragmentation processes for the ion radicals mentioned above provides a ready basis for understanding the overall reactivity. Thus, as shown in Figure 2 donors such as amines and acceptors such as halides are characterized by large differences in the ionization potentials of the neutral molecules and potential fragment radicals. The thermochemical cycles developed by Arnold and co-workers,[21,22] Dinnocenzo,[33] and Wayner and co-workers[34,35] show that the bond dissociation energies (BDE) in the radical ion may be much lower than those in the parent neutral molecule, and thus fragmentation (in some cases highly selective) is not a surprising consequence of the photoredox process.

Early examples of irreversible redox reactions of substituted amines due to reactions of this sort include the use of reagents such as triethanolamine as sacrificial scavengers in photoinduced electron transfer reactions involving "stable" ion radicals as initial products.[36] Simple tertiary amines have been found to undergo moderately rapid deprotonation upon one-electron oxidation, presumably due to the relatively high acidity of the protons in these cation radicals.[37] We thought that C–C bond breakage might be an alternative to deprotonation, especially when additional activating factors could be incorporated, as in amino alcohols.

1,2-Disubstituted Ethanes

A. General Considerations.
The scheme shown in Figure 1 describes the reaction as carried out under

steady state conditions where there are very low concentrations of all intermediates. Several factors must be taken into consideration with respect to this scheme when the detailed mechanisms of fragmentation reactions are discussed. (1) All of the compounds studied as donors have oxidation potentials around 1 V vs SCE, similar to those of other amine donors such as *N,N*-dimethylaniline. (2) For photoexcited acceptors, reaction frequently occurs through the excited singlet state, initially forming a singlet radical ion pair, and the rate constant for back electron transfer (k_{-et}) within these singlet ion pairs is typically on the order of 10^9–10^{11} s^{-1}.[38] Unless k_r is very large, most reaction will occur after cage escape and the quantum yield of product formation will be limited to the quantum yield of cage escape[39]. (3) For oppositely charged ion radical pairs, the rate constant for cage escape (k_{ce})[40] ranges from ca. 10^9 s^{-1} in acetonitrile to much lower values in nonpolar solvents such as benzene. (4) If positively charged acceptors are used with neutral donors, k_{ce} should increase, and indeed in many cases much higher yields of free ions are obtained.[41,42] (5) Similarly, if triplet acceptors are used, k_{-et} is reduced, by even as much as 10^3 s^{-1}, so that again higher yields of reaction (cage escape followed by fragmentation) can occur.[43]

B. Measurement of Unassisted Bond Fragmentation Rate Constants. Most of the original work in this area relied on calculation (or estimation) of the bond fragmentation rate constants from steady state measurements of the quantum yields of product formation. These studies provided information on the effects of acceptor structure, solvent, external additives, and isotopes.

Recently, we and others have been developing methods where the fragmentation of the donor radical cations can be followed directly via time-resolved absorption spectroscopy. The donor radical cation is generally produced using the technique of cosensitization as illustrated by the equations below:

$$DCA^* \ [(NMQ^+)^*] + C \rightarrow DCA^{\bullet -} \ (NMQ^\bullet) + C^{\bullet +} \quad (2)$$

$$C^{\bullet +} + D \rightarrow C + D^{\bullet +} \quad (3)$$
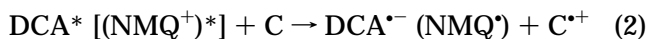
Excitation of either 9,10-dicyanoanthracene (DCA)[44] or *N*-methylquinoline (NMQ$^+$)[45] results in formation of the singlet excited state. The singlet excited acceptor is then diffusionally quenched by a high oxidation potential electron donor (cosensitizer, C) such as *m*-xylene (in the case of NMQ$^+$) or biphenyl (in the case of DCA) leading to production of the *m*-xylene or biphenyl radical cation in good yield, both of which are powerful oxidizing agents, eq 2. It is this radical cation, C$^{\bullet +}$, that then oxidizes the donor substrate, D

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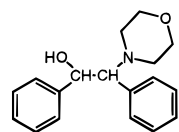(43) Leon, J. W.; Whitten, D. G. *J. Am. Chem. Soc.* **1993**, *115*, 8038.

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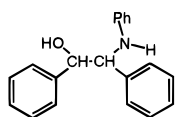
(eq 3). For these donor−acceptor combinations the return electron transfer is far into the Marcus inverted region (highly exothermic) and thus is expected and observed[44] to be somewhat slow such that cage escape is the dominant path and yields of $C^{\bullet+}$ are high. In addition, when NMQ^+ is used as the sensitizer, the initial electron transfer results in the formation of a neutral ($NMQ^{\bullet}$) and a positively charged ($C^{\bullet+}$) species, rather than two oppositely charged species, which also enhances the cage escape yield. We have assumed that the bond fragmentation rate constant, k_{BF}, is equal to the observed rate constant for decay of the radical cation. This assumption is valid under experimental conditions where the concentration of radical cation formed is very low (less than ca. 5×10^{-7} M) to eliminate contributions from second-order recombinations to the rate constant and the rate of fragmentation is slow relative to return electron transfer. Table 1 presents values of k_{BF} for a series of amino alcohol and diamine donors measured in this manner. Table 3 presents values of k_{BF} for a series of pinacol donors measured in the same fashion and discussed later in the text.
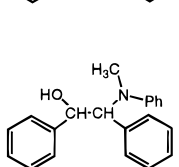
C. Specific Examples. 1. Amino Alcohols.
Some of the first photofragmentation reactions studied in our laboratory and others involved amino alcohols as donors.[46−52] The initially formed radical cations selectively fragment at the C−C bond between the amine and alcohol functions to yield a ketone and an α-amino radical (Figure 3). The close relationship between these reactions and the Grob fragmentation[53−55] of even-electron species has been noted earlier.[51,52] The rate constants for unassisted bond fragmentation have been measured for a number of these compounds (Table 1, structures **1−4**) and, while
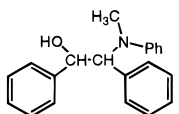
Table 1. Rate Constants for Bond Fragmentation (k_{BF}) of Amino Alcohol and Diamine Radical Cations[a]

structure	k_{BF}/ (10^6 s^{-1})	structure	k_{BF}/ (10^6 s^{-1})	structure	k_{BF}/ (10^6 s^{-1})
1	0.29	4	1.4	7	2200
2	0.43	5	5.7	8	3400
3	0.26	6	140		

[a] These values were obtained via laser flash photolysis utilizing the NMQ^+/m-xylene cosensitization method.

to the system. If the hydrogen of the alcohol group is replaced by deuterium, a primary isotope effect on Φ_H/Φ_D is observed. This ratio increases from 1.3 to 4 as the basicity of the acceptor radical anion decreases.[50] Thus, the mechanism is consistent with base-assisted deprotonation of the radical cation concommitant with C−C bond cleavage. This explains the observation that the quantum yields of product increase as the polarity of the solvent decreases and are dependent upon the specific structure of the acceptor. In the less polar solvents, the primary species formed is a contact radical ion pair (CRIP) in which the anion radical partner may act as a base and deprotonate the radical cation, thus accelerating fragmentation and enabling this process to compete with return electron transfer. We have observed that the lifetime of the radical cation decreases linearly with increasing concentration of an added base such as pyridine. Schanze et al.[48] have suggested that deprotonation of the amino alcohol radical cation is the rate determining step in these reactions.

2. Diamines. The observed rate constants for fragmentation of these compounds are in general higher than those for the aminoalcohols ($10^6−10^8$ s^{-1}) as shown in Table 1 for structures **5−8**, as well as

1

2 erythro

3 threo

4

5

6 trans Ph, R=CH$_3$

7 cis Ph, R=H

8 trans Ph, R=H

the fragmentations are relatively slow ($10^4−10^6$ s^{-1}), they are found to be accelerated upon addition of base

other values reported in the literature.[56−58] Thermochemical calculations indicate that the BDE of a diamine radical cation is lower than that for an amino alcohol radical cation, and thus the fragmentation rate constants may be expected to be higher.[59] The mechanism appears to operate via an unassisted pathway which explains why the yields of product formation increase as the solvent polarity increases.[60] From the scheme shown in Figure 1, the rate of cage escape (k_{ce}) should increase with solvent polarity, and hence the yield of free ions should increase while the efficiency of return electron transfer decreases. Under these

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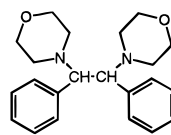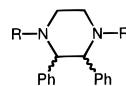(55) Gleiter, R.; Stohrer, W.-D.; Hoffman, R. *Helv. Chim. Acta* **1972**, *55*, 893.

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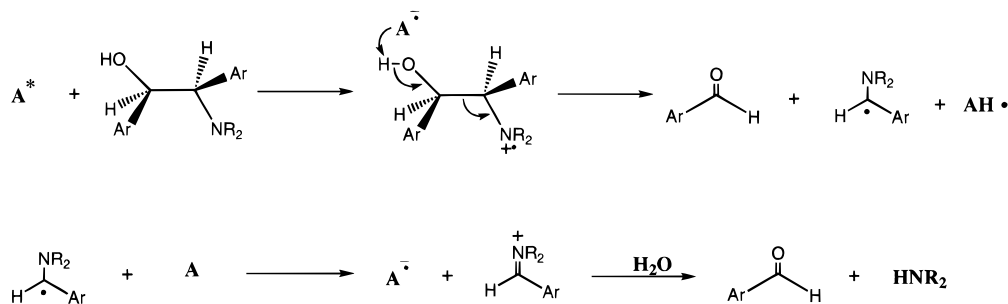
Figure 3. General mechanism for cleavage of an amino alcohol radical cation to yield ketone products.
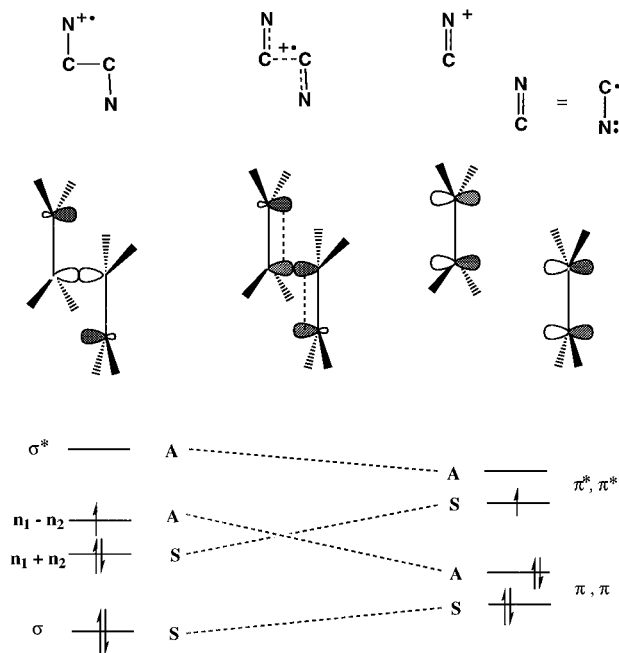

Figure 4. Correlation diagram and orbital alignments for the low-energy bond fragmentation of a diamine radical cation.

conditions the geminate radical ion pair is more rapidly solvated, thus separating these species and enhancing cage escape, consequently reducing return electron transfer.

Studies of the fragmentation rate constants as a function of temperature in general show a very small enthalpy of activation and a relatively large negative entropy of activation.[61] One explanation for the negative ΔS may be the π bonding developing in the transition state (Figure 4); the cation fragmentation leads to two new π systems, the neutral radical, which is analogous to a reduced iminium ion, and an iminium ion. Fragmentation of the parent neutral diamine would be expected to be much more unfavorable from an energetic point of view but would likely involve a positive entropy of activation since no net π bonding would result in the transition state.

The fragmentation of the cyclic diamines **6**−**8** has been studied by steady state photochemical methods,[62] and the fragmentation of the radical cation of **6** has been successfully followed by time-resolved absorption spectroscopy (Table 1). The rate constants for these diamines are the highest that we have observed in our laboratory and show a very interesting trend with

respect to molecular conformation. While diamine **6**, the di-N-methylated compound, fragments with a rate constant of 1.4×10^8 s^{-1}, compounds **7** and **8**, the parent H-substituted compounds, fragment with rate constants 20−40 times higher.[63] It seems likely that the reason for this striking difference is the result of preferred conformations of these molecules. In the lowest energy conformation of diamine **6**, the N-methyl groups will probably prefer the equatorial positions, thus forcing the nitrogen lone pairs to be perpendicular to the orbitals of the breaking bond. This contention is supported by MM3 calculations which find that the structure with the N-methyl groups equatorial is approximately 9 kcal/mol lower in energy than the structure having axial N-methyl groups. Alternatively, in diamines **7** and **8**, the nitrogen lone pairs may be preferentially in the equatorial positions and can align favorably[55] with the cleaving bond (Figure 5).

The reactions of the linked acceptor−diamine donor dyads **9** and **10** provide interesting mechanistic information on these reactions.[43] The fragmentation of these compounds should be kinetically simpler than the intermolecular fragmentations outlined in Figure 1 since cage escape is no longer a competing process.
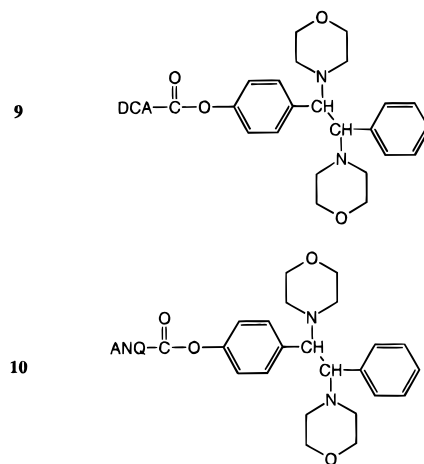
Thus, the fragmentation efficiency should directly reflect the competition between return electron transfer (k_{-et}) and bond fragmentation (k_{BF}). Excitation of **9** results in the formation of the 9,10-dicyanoanthracene excited singlet state as the electron acceptor. Very low fragmentation yields (<0.01) are observed for this compound as a result of return

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(63) While the rate constant for bond fragmentation of diamine **6** can be monitored in a picosecond transient absorption experiment, the rates of fragmentation for diamines **7** and **8** are within the time resolution of our instrumentation. Thus, we have calculated the rate constants for fragmentation of diamines **7** and **8** from steady state quantum yield data.
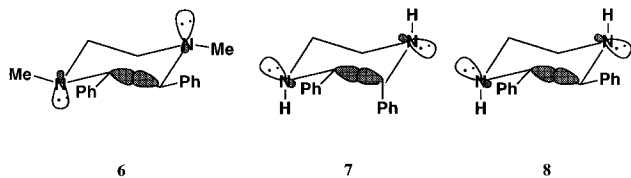
Figure 5. Orbital alignments that affect the fragmentation efficincy for the cyclic diamines.

electron transfer effectively competing with bond fragmentation. Alternatively, excitation of **10** results in the formation of the anthraquinone excited triplet state as the electron acceptor, which therefore makes return electron transfer "forbidden". In fact, very good yields of fragmentation (0.33−0.78, depending upon the solvent) are observed for this compound.

3. "Remote" Amino Alcohols. As an extension of the studies on the amino alcohols, we have also investigated the reactivity of the amino alcohols **11**−**13** having benzylic separation of their functionalities.[52]
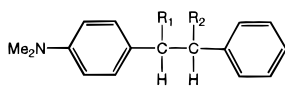
11	R_1 = H,	R_2 = OH
12	R_1 = OH,	R_2 = OH
13	R_1 = OH,	R_2 = H

Compounds **11** and **12** undergo clean and moderately efficient fragmentation at the C−C bond after electron transfer to a suitable acceptor, while **13** is found to simply undergo oxidation of the alcohol to a ketone without C−C bond fragmentation. Similarly, the symmetrically substituted **14** undergoes clean and efficient C−C bond fragmentation to form two ketones. This result also suggests that bond fragmentation after photoinduced electron transfer may also be a general reaction for 1,2-diols (pinacols).[64,65] Recent studies of these compounds are discussed in detail below.

4. Cofragmentation: Pinacols with Carbon Tetrachloride. The electron transfer reaction between pinacol donors and carbon tetrachloride[66] attracted our attention initially because of the possibility that both the pinacol donor and halide acceptor should fragment following the single electron transfer. There have been several reports[67,68] of halide ion loss upon reduction of an alkyl or aryl halide to support this contention. Furthermore, some studies have suggested that the halide anion radical has a negative bond dissociation energy and that the electron transfer process itself is dissociative.[25,69] .

If the electron transfer to the halide acceptor is in fact dissociative, then the quantum yield of bond fragmentation should approach unity regardless of the starting pinacol since there will be no competition from back electron transfer, assuming that the two decay

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Table 2. Quantum Yields (Φ) for Ketone Formation from Irradiation of the Substituted Pinacols in the Presence of Carbon Tetrachloride and Oxidation Potentials (E_{ox}) of the Pinacols in CH_3CN.

pinacol	$\Phi_{\text{air saturated}}$	Φ_{degassed}	E_{ox}/(V vs NHE)
14	8.2	0.4	0.8
15	0.1	0.1	1.5
16	0.7	0.7	1.3
17	0.3	0.5	1.0
18	1.5	0.6	0.9

Table 3. Rate Constants for Bond Fragmentation (k_{BF}) of Substituted Pinacol Radical Cations[a]

pinacol	k_{BF}/ (10^6 s^{-1})	pinacol	k_{BF}/ (10^6 s^{-1})	pincol	k_{BF}/ (10^6 s^{-1})
14	0.18	**17**	4.5	**20**	
15	>10	**18**	2.5		
16	7.5	**19**			

[a] These values were obtained via laser flash photolysis utilizing the NMQ^+/m-xylene cosensitization method.

pathways available to the radical cation are return electron transfer and fragmentation. However, if the acceptor anion radical exists with a finite lifetime, then there is the possibility of return electron transfer and the quantum yields for product formation should be less than 1. Low to moderate quantum yields for formation of the corresponding acetophenones are observed for irradiation (ca. 300 nm) of samples containing pinacols **14**−**18** in the presence of 0.8 M
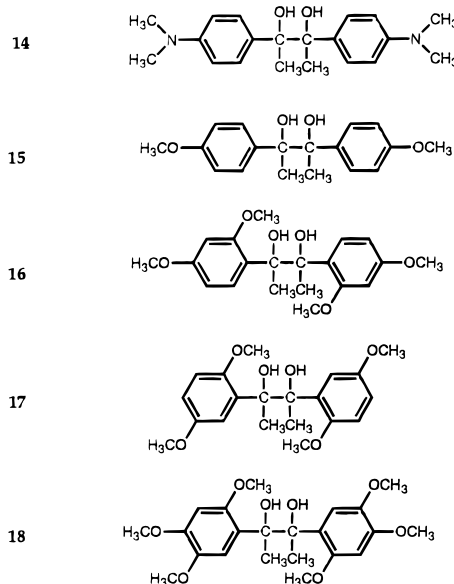
CCl_4 under degassed conditions. However, for pinacols **14** and **18**, irradiation in the presence of CCl_4 (0.8 M) and O_2 results in quantum yields larger than 1, suggesting a chain reaction (Table 2). This mechanism is evidently not operative for pinacols **15**−**17** because the yields for air-saturated samples containing these compounds are less than or equal to the degassed yield. The bond fragmentation rate constants (k_{BF}), listed in Table 3, are in the order predicted based on the stability of the corresponding radical cation.

On the basis of our experimental observations, we propose a reaction mechanism as outlined in Figure 6. The initially formed pinacol excited state is quenched via electron transfer to ultimately form the pinacol radical cation and a trichloromethyl radical.
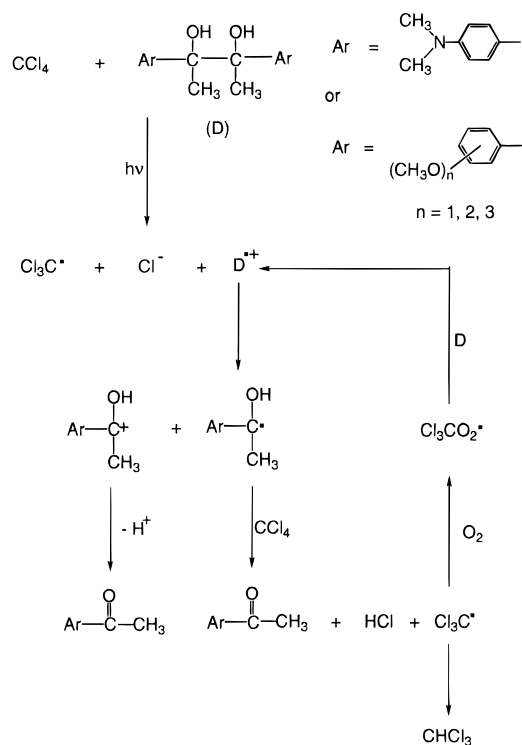
Figure 6. Suggested mechanism for the oxygen-mediated chain reaction involved in the substituted pinacol donor/carbon tetrachloride cofragmentation.

Table 4. Rate Constants for Quenching of the Ketyl Radicals (k) of the Parent Pinacols by Carbon Tetrachloride[a]

parent pinacol	$k/(10^6 \text{ M}^{-1} \text{ s}^{-1})$	parent pinacol	$k/(10^6 \text{ M}^{-1} \text{ s}^{-1})$
14	7.4	**17**	12
15	5.4	18	6.8

[a] These values were obtained by pulse radiolysis in methanol.

The trichloromethyl radical will be trapped by oxygen to form the (trichloromethyl)peroxyl radical, a relatively strong oxidizing agent ($E_{red} > 1$ V vs NHE).[70] This species then oxidizes another pinacol molecule, thus propagating the chain reaction. It seems reasonable that the chain reaction only proceeds in the presence of pinacols **14** and **18** since only their oxidation potentials are below the reduction potential for $CCl_3O_2{}^\bullet$.

We have measured the rate constant for reduction of CCl_4 by several of the ketyl radicals corresponding to a parent pinacol via pulse radiolysis in methanol. These values are presented in Table 4. Radiolysis of methanol results in ionization of the solvent and the

(70) Brault, D.; Neta, P. *J. Phys. Chem.* **1984**, *88*, 2857.
(71) *tert*-Butyl alcohol (0.4 M) was also added to the samples to trap the initially formed organic radicals (e.g., $\bullet CH_2OH$ and $CH_3O\bullet$).

formation of solvated electrons.[71] The ketyl radicals are formed by electron attachment to a precusor ketone to yield a radical anion which is rapidly protonated. It is interesting that the rate constants for reduction of CCl_4 by the ketyl radicals do not appear to be correlated with the estimated oxidation potentials of the radicals. Our data indicate that the reduction of CCl_4 by the ketyl radicals is not a simple electron transfer reaction but is probably more like an "inner sphere" electron transfer or a chlorine atom abstraction. Our data also indicate that formation of H^+ is an essential part of the driving force for the reaction. Results from additional experiments that corroborate these data are, first, the radical anion of dicyanoanthracene, which should be at least as powerful a reducing agent as the ketyl radicals,[20] does not react with CCl_4 under our experimental conditions ($k < 10^3$ M^{-1} s^{-1}) and, second, irradiation of compounds **19** and **20**, where H^+ formation is not possible, in the
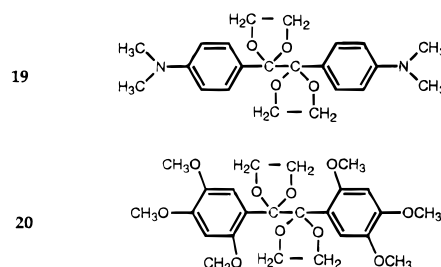
presence of CCl_4 does not yield the corresponding ketone products but rather a mixture including products from condensation of the ketyl and CCl_4.

Summary

In summary, the fragmentation of relatively strong C–C bonds in neutral organic molecules can become a facile process after photoinduced electron transfer. The yields of these processes are enhanced by using techniques such as cosensitization or cofragmentation or through formation of radical ion pairs via triplet excited state precursors. The data collected here show that the values for the rate constants for unassisted fragmentation span 4 orders of magnitude and are controlled to a large extent by orbital alignment in the radical cation.