6398 *J. Am. Chem. Soc.* **1995,** *117,* 6398–6399

Photoinduced Electron Transfer Double Fragmentation: An Oxygen-Mediated Radical Chain Process in the Cofragmentation of Aminopinacol Donors with Organic Halides

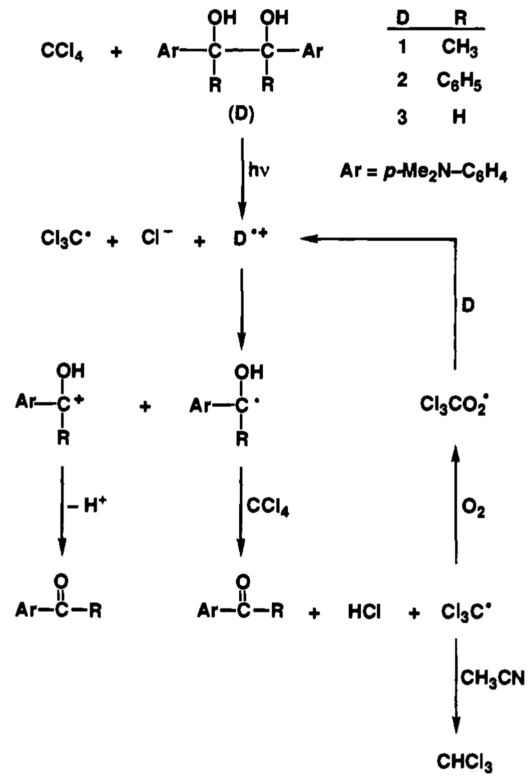
Liaohai Chen, Mohammad S. Farahat, Hong Gan,
Samir Farid,*[,1] and David G. Whitten*

Department of Chemistry, University of Rochester
Rochester, New York 14627

Received March 16, 1995

Investigations of photoinduced electron transfer reactions have led to the finding of several ion–radical fragmentation reactions in which relatively strong covalent bonds in the neutral (or starting molecule) rapidly cleave in the one-electron redox product.[2] Among oxidized donors that undergo relatively rapid bond-breaking reactions are 1,2-diarylethanes, pinacols, diamines, and amino alcohols.[3–8] One-electron reduction of acceptors such as ethers, esters, and organic halides can also result in bond cleavage;[9–14] the cleavage of organic halides is particularly interesting since electrochemical studies as well as thermochemical calculations indicate that the carbon halide bond can have a negative bond energy in certain reduced halides and that the cleavage process must be extremely rapid.[12–14] The efficiency of these reactions is determined by the relative rates of back electron transfer ($k_{-\mathrm{et}}$), fragmentation (k_f), and separation of the ion–radical pair (k_{sep}). While some examples of fast bond cleavage of ion radical systems have been reported and high quantum efficiencies have been obtained, the quantum yield of fragmentation reactions is generally low due to the fast back electron transfer ($k_{-\mathrm{et}}$), which can be in the range of $\sim 10^9$–10^{11} s^{-1} when singlet excited state quenching is involved. One strategy for increasing the efficiency of net fragmentation reactions is to use both a fragmentable donor and a fragmentable acceptor in a potential cofragmentation process.[15] In this way even a slowly fragmenting redox intermediate can form product with high efficiency if the rapid fragmentation of its cointermediate can avert return electron transfer. In the present paper we report an investigation in which excited states of amino pinacols **1**–**3** are reacted with the halides CCl$_4$, benzyl bromide, and *p*-cyanobenzyl bromide. Interesting results from this study include the finding that low-to-moderate quantum efficiencies for reaction are observed when the reactions are carried out under degassed conditions, indicating that the halide radical anions must survive long enough within the initial ion pair formed in the quenching step to undergo considerable return electron transfer.[16] More strikingly, we find that for certain pinacol–halide combinations reaction in aerated solutions leads to much higher efficiencies, which can be attributed to a chain reaction involving oxygen capture of a primary radical product.

Scheme 1. Possible Reaction Pathways for Amino Pinacols with CCl$_4$ in Acetonitrile



Pinacols **1**–**3** were prepared as previously described.[17] Carbon tetrachloride and benzyl bromide were purified by distillation while *p*-cyanobenzyl bromide was purified by recrystallization from hexane. The fluorescence of the three pinacols was found to be quenched by the three halides at or near diffusion-controlled rates in acetonitrile. Irradiation of the pinacols in the presence of the halides was found to lead to spectral changes consistent with oxidative cleavage of the central C–C bond to form the corresponding carbonyl products[17] (Scheme 1). A study of the reaction of **1** with carbon tetrachloride in degassed deuterated acetonitrile by ^{1}H-NMR showed *p*-(*N*,*N*-dimethylamino)acetophenone as the only detectable proton-bearing product. When the reaction in degassed deuterated acetonitrile was monitored by ^{13}C-NMR using ^{13}C-labeled carbon tetrachloride, the only product detected was deuteriochloroform. However, when the same irradiation was carried out in aerated solution, the only peak detected by ^{13}C-NMR was a singlet at 134.5 ppm, which we assign to an oxygenated species, presumably CCl$_3$O$_2$H.[18] Quantum yields for the fragmentations as measured by disappearance of pinacol are given in Table 1. In all cases the reaction in degassed

---

(1) Research Laboratories, Eastman Kodak Company, Rochester, NY 14650-2109.

(2) For recent reviews, see, for example: (a) Albini, A.; Sulpizio, A. In *Photoinduced Electron Transfer*; Fox, M. A.; Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part C, p 88. (b) Kochi, J. K. *Acta Chem. Scand.* **1990**, *44*, 409. (c) Saeva, F. D. *Top. Curr. Chem.* **1990**, *156*, 59. (d) Whitten, D. G.; Chesta, C.; Ci, X.; Kellett, M. A.; Yam, V. W. In *Photochemical Processes in Organized Molecular Systems*; Honda, K., Ed.; Elsevier Science Publishers, B. V.: Amsterdam, 1991.

(3) Kellett, M. A.; Whitten, D. G. *Res. Chem. Intermed.*, in press.

(4) Whitten, D. G.; Kellett, M. A.; Leon, J. W.; Gan, H. *Proceedings of the 9th International Conference on Photochemical Conversion and Solar Energy;* International Academic Publishers: Beijing, 1992.

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

(6) Saeva, F. D.; Breslin, D. J.; Luss, H. R. *J. Am. Chem. Soc.* **1991**, *113*, 5333.

(7) Tanner, D.; Chen, J. J.; Chen, L.; Luelo, C. *J. Am. Chem. Soc.* **1991**, *113*, 8074.

(8) Arnold, B. R.; Scaiano, J. C.; McGimpsey, W. G. *J. Am. Chem. Soc.* **1992**, *114*, 9978.

(9) Maslak, P.; Kula, J.; Chateauneuf, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 2304.

(10) Simon, J. D.; Peter, K. S. *Organometallics* **1983**, *2*, 1867.

(11) Ohashi, M.; Otani, S.; Kyushin, S. *Chem. Lett.* **1991**, 631.

(12) Mautner, M. M.-N.; Neta, P.; Norris, R. K.; Wilson, K. *J. Phys. Chem.* **1986**, *90*, 168.

(13) Neta, P.; Behar, D. *J. Am. Chem. Soc.* **1981**, *103*, 103.

(14) (a) Andrieux, C. P.; Gorande, A. L.; Saveant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 6892. (b) Saveant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 10595.

(15) Maslak, P.; Chapman, W. H. *J. Org. Chem.* **1990**, *55*, 6334.

(16) The results obtained in this study, together with a more detailed examination of electron transfer photoreactions involving CCl$_4$, suggest that the electron transfer process is not dissociative: M. S. Farahat, L. Chen, S. Farid, and D. G. Whitten, to be published.

(17) Gan, H.; Leinhos, U.; Gould, I. R.; Whitten, D. G. *J. Phys. Chem.* **1995**, *99*, 3566.

(18) Substitution of H by an oxygen function usually results in downfield shifts of 35–60 ppm for C. Due to the relative stability of CCl$_3$O$_2$H[22] it is reasonable to assign the peak at 134.5 to CCl$_3$O$_2$H.

0002-7863/95/1517-6398$09.00/0

Table 1. Quantum Yields for Pinacol Fragmentation with Organic Halides

pinacol	conditns[a]	*p*-cyanobenzyl bromide	benzyl bromide	carbon tetrachloride
1	aerated	3.7–3.9	1.1–1.5	8.2–10.1
	degassed	0.22	0.14	0.42–0.55
2	aerated	0.87–1.1	0.45–0.52	2.7–2.8
	degassed	0.038	0.041	0.11
3	aerated	0.98	0.56	1.1
	degassed	0.094		0.24

[a] In a typical experiment, 2.0×10^{-3} M **1** and 0.78 M carbon tetrachloride in acetonitrile (in which case, 98% of the pinacol fluorescence was quenched) was irradiated with a 250 W high-pressure mercury lamp through a 0-54 glass filter and a 334 nm interference filter at room temperature. Degassed solutions were prepared by six cycles of freeze–pump–thaw degassing and sealed under high vacuum (ca. 1×10^{-5} Torr). The reaction was monitored by the appearance of the ketone product absorption at 340 nm. The quantum yeild for pinacol fragmentation was assumed to be half of the quantum yield for formation of ketone, which was determined at 1% conversion of the starting material.

solution leads to quantum yields substantially lower than unity even under conditions under which excited state quenching is complete.[16]

The above results for photoreaction of the pinacols with halide acceptors in degassed solution can be described by the reactions shown in Scheme 1. The lower than unit quantum efficiencies are ascribed to competition between fragmentation of the acceptor anion and return electron transfer, since the pinacols have been previously shown to fragment at rates which would not compete with return electron transfer from a singlet ion–radical pair.[17] Evidence that return electron transfer limits the quantum efficiency is also provided by picosecond laser transient absorption spectroscopy studies of pinacols **1** and **2** with carbon tetrachloride and benzyl bromide.[16] For these studies argon deoxygenated solutions of pinacol and halide were irradiated in a flow cell at high concentrations of halide (2.6 M) to allow laser excitation at 355 nm. Under these conditions direct excitation is followed by a fast generation of a transient at 480 nm assigned to the pinacol cation which shows decay patterns dependent upon the pinacol–halide combination used. For both **1** and **2** with benzyl bromide and for **2** with carbon tetrachloride a rapid decay of the majority of the transient signal on a time scale of 100–200 ps was observed followed by a plateau of extremely slow decay which matched the rate of unassisted pinacol fragmentation previously observed. For **1** and carbon tetrachloride no fast decay could be observed after the initial buildup of the transients, within the 50 ps time resolution of the instrument.

Further support for the mechanism for cofragmentation in degassed solution was provided by spin-trapping experiments with the 2-methyl-2-nitrosopropane dimer (MNP) in irradiated samples of **1** with carbon tetrachloride in acetonitrile. A single radical was trapped which gave spectra and hyperfine coupling constants in agreement with the reported values for the adduct of $^\bullet CCl_3$ with MNP.[19] In contrast, irradiation of the same solution under aerated conditions showed only an enhanced signal in the region where a weak absorption is observed in blank solutions of MNP (an MNP decomposition product); however, this coincides with the reported signal for the MNP trapped $CCl_3O_2^\bullet$ radical.[19]

As indicated in Table 1, the photoreaction of pinacols **1** and **2** with *p*-cyanobenzyl bromide and carbon tetrachloride in aerated solutions gives pinacol disappearance quantum efficiencies much higher than unity, suggesting that a chain reaction may be operative. Since it is unlikely that the ambient oxygen concentrations will affect either the quenching or initial fragmentation processes outlined in Scheme 1, the most reasonable source of the chain process must be in subsequent reactions of the radicals generated in the fragmentation step. For $^\bullet CCl_3$, reaction with oxygen is well established (with rate constants on the order of 10^9 M^{-1} s^{-1})[20] and it has also been demonstrated that the resultant radical, $CCl_3O_2^\bullet$, is a strong oxidant which should be capable of oxidizing ground state pinacol as indicated in Scheme 1.[20–24] The ^{13}C-NMR results described above are also in accord with oxygen trapping of the radical formed by cleavage of carbon tetrachloride. The quantum yield in aerated solution was suppressed from 10 to 0.6 for **1**–CCl_4 by addition of the radical scavenger 2,6-di-*tert*-butyl-4-methylphenol.

The chain reaction proposed in Scheme 1 is reasonable on the basis of both experimental evidence and energetic considerations. The difference between the nonchain process and the chain reaction is attributed to the difference in reactivity between $^\bullet CCl_3$ and $CCl_3O_2^\bullet$ in that the former is not sufficiently reactive to efficiently oxidize ground state pinacol while the latter should easily do so.[25] It is likely that a similar mechanism is involved with the benzyl halide acceptors. The chain process is interesting in that it produces not only oxidized pinacol but also acid with high efficiency. The production of acid can be readily detected in aerated solutions; however, the current system is not an ideal photo acid generating one since the pinacols and their oxidative cleavage products are weakly basic substituted anilines. However, the reactions observed in this study should be fairly general and the use of nonbasic donors should permit similar chain processes to occur resulting in highly efficient acid and free radical generation via cofragmentation.

Acknowledgment. We are grateful to the Department of Energy (Grant No. DE-FG02-86ER13504) for support of this research. We are also grateful to the Center for Photoinduced Charge Transfer for use of the laser spectroscopic facilities. We are also indebted to Professor K. Ingold for helpful suggestions.

JA950867A

---

(19) Symons, M. C. R. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2205.

(20) Neta, P.; Brault, D. *J. Phys. Chem.* **1984**, *88*, 2857.

(21) Neta, P.; Huie, R. E.; Maruthamutha, P.; Steenken, S. *J. Phys. Chem.* **1989**, *93*, 7654.

(22) Shen, X.; Lind, J.; Eriksen, T. E. *J. Phys. Chem.* **1989**, *93*, 553.

(23) Burk, R. F.; Lane, J. M.; Patel, K. *J. Clin.Invest.* **1984**, *74*, 1996.

(24) Russell, J. J.; Seetala, J. A.; Gutman, D.; Danis, F.; Caralp, F.; Lightfoot, P. D.; Lesclaux, R.; Melius, C. F.; Senkan, S. M. *J. Phys. Chem.* **1990**, *94*, 3277.

(25) The redox potential for $Cl_3CO_2^\bullet$ was estimated from kinetics to be higher than 1 V vs NHE (Huie, R.; Neta, P. *Int. J. Chem. Kinet.* **1986**, *18*, 1185). The pinacols have peak potentials for oxidation at 0.7 V vs SCE.[17]