Photoinduced electron transfer double fragmentation: an oxygen-mediated radical chain process in the co-fragmentation of substituted pinacol donors with carbon tetrachloride

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Abstract

Investigations of photoinduced electron transfer processes have led to the observation of several ion radical fragmentation reactions in which strong covalent bonds in the neutral (or starting) molecules rapidly cleave in the one-electron redox products. Donors that undergo rapid bond breaking reactions on one-electron oxidation include 1,2-diarylethanes, pinacols, diamines and aminoalcohols. One-electron reduction of acceptors, such as ethers, esters and organic halides, can also result in bond cleavage. The efficiency of these reactions is determined by the competition between back electron transfer (k_{-et}), fragmentation (k_r) and separation of the ion radical pair (k_{sep}). The quantum yields are generally low since this competition is dominated by back electron transfer ($k_{-et} \approx 10^9$–10^{11} s^{-1}). One strategy to increase the fragmentation efficiency is to utilize very rapid co-fragmentations of both donor and acceptor thus allowing return electron transfer to be minimized. Cleavage reactions of organic halides are potentially useful in this regard because electrochemical studies and thermochemical calculations suggest that, for certain reduced halides, the electron transfer is dissociative. In this paper, we report the excited state reactivity of several amino- and methoxy- substituted pinacols with the halogenated acceptor carbon tetrachloride. Low to moderate quantum efficiencies (approximately 0.04–0.6) are observed for these reactions when irradiations are carried out under degassed conditions. However, for some pinacols, irradiation in the presence of O_2 results in significantly larger quantum yields (approximately 1–10) suggesting a chain mechanism. Data from nuclear magnetic resonance (NMR), electron spin resonance (ESR) and time- resolved absorption spectroscopy suggest that the primary halide radical formed from dissociation is captured by O_2 to give a peroxyl radical which then propagates the chain reaction.

Keywords: Photoinduced electron transfer; Co-fragmentation; Radical chain process; Pinacol; Carbon tetrachloride

1. Introduction

A major challenge in photochemistry is to find reactions of radical ions or radical ion pairs, generated through photoinduced electron transfer, which can compete with and offer useful alternatives to return electron transfer [1]. Since return electron transfer from singlet radical ion pairs may occur on time scales as rapid as subnanoseconds, any competitive process must occur on a comparable time scale unless the return electron transfer is circumvented by techniques such as co-sensitization or by enhanced and efficient cage escape. In this paper, we report the co-fragmentation of the aromatic pinacols 1–7 (Fig. 1) with organic halides. Studies of these reactions were initially of interest because of the possibility that both the pinacol donor and halide acceptor would fragment following single electron transfer redox reactions to give rad-

ical ions [2]. In previous investigations [3], it has been found that pinacol cation radicals fragment rather slowly; however, the fragmentation of organic halides on one-electron reduction is expected to be very fast and some studies have suggested [4,5] that the electron transfer process itself may be dissociative. Thus we were attracted by the possibility that photochemical co-fragmentation might occur with high efficiency. Interesting results from this study include the finding that low to moderate quantum efficiencies of 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. However, and perhaps more strikingly, the reaction of certain pinacol–halide combinations in aerated solutions can lead to very high efficiencies of reaction forming, among
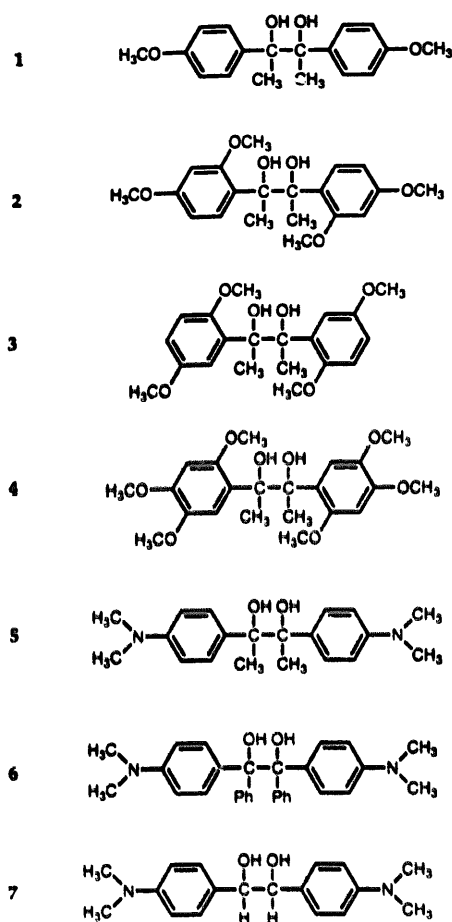
Fig. 1. Structures of the pinacols 1–7.

other products, strong acids, which can be attributed to a chain reaction involving oxygen capture of a primary radical product.

2. Experimental details

Pinacols 1–7 were prepared as previously described [3] by the samarium-mediated reductive coupling of the corresponding ketones. Carbon tetrachloride (Aldrich HPLC grade) was used without further purification. Fluorescence from each of the pinacols was found to be quenched by carbon tetrachloride at or near diffusion-controlled rates in acetonitrile. Irradiation of the pinacols (250 W high pressure Hg lamp, 334 nm interference filter) in the presence of CCl_4 was found to lead to spectral changes consistent with oxidative cleavage of the central C–C bond to form the corresponding carbonyl products. The carbonyl products were verified using UV–visible and nuclear magnetic resonance (NMR) spectroscopy.

Laser flash photolysis experiments were carried out using an excimer (Lambda Physik Lextra 50, XeCl, 308 nm) pumped dye laser (Lambda Physik LPD 3002, 7 ns pulse width) as the excitation source. Transient absorptions were monitored at right angles to excitation with a conventional xenon lamp, monochromator, photomultiplier tube arrangement. The signal from the photomultiplier tube was recorded and digitized with a Tektronix TDS 620 digitizing oscilloscope and then passed to a microcomputer for storage and analysis. The excitation beam energy was typically attenuated to less than 2–3 mJ per pulse, and appropriate long pass filters were placed on either side of the sample to prevent analyzing light photolysis.

3. Results and discussion

As indicated above, our initial interest was in the use of organic halides as acceptors. Previous studies have suggested that electron transfer to organic halides may be dissociative, i.e. rather than forming discrete ion radicals (Eq. (1)), electron transfer proceeds to give fragmentation products directly (Eq. (2))

$$D^* + R-X \longrightarrow D^{•+}, R-X^{•-} \tag{1}$$

$$D^* + R-X \longrightarrow D^{•+} + R^• + X^- \tag{2}$$

We felt that an investigation of the reaction using pinacol donors might be especially useful to determine whether reaction via Eq. (2) occurs, since these pinacols undergo slow fragmentation in clean reactions which can be readily monitored by transient spectroscopy and product analysis. The pinacols may participate in photoinduced electron transfer reactions either by direct excitation to the fluorescent singlet state in the presence of non-absorbing acceptors (Eqs. (1) and (2)) or by reaction with photoexcited acceptors (Eq. (3))

$$D + A^* \longrightarrow D^{•+}, A^{•-} \tag{3}$$

We have examined independently the fragmentation of pinacols 1–7 using reaction (3) and acceptors such as 9,10-dicyanoanthracene (DCA) or N-methylquinolinium cation (NMQ^+). Table 1 lists the fragmentation rate constants measured for several of these pinacols by laser flash transient spectroscopy. In general, the technique of co- sensitization

Table 1
Measured kinetic parameters for pinacols in CH_3CN

Pinacol	$K_{SV}(CCl_4)$ [a] (M^{-1})	τ_f [b] (ns)	k_{BP} [c] $(10^6 s^{-1})$
1	90.3	4.6	>10
2	8.21		7.0
3	52.3		4.5
4	31.6		2.5
5	52.4	2.6	0.18 [d]
6	57.1	1.5	0.04 [d]
7	53.3	2.1	<0.005 [d]

[a] Stern–Volmer quenching constant.
[b] Fluorescence lifetimes in CH_3CN.
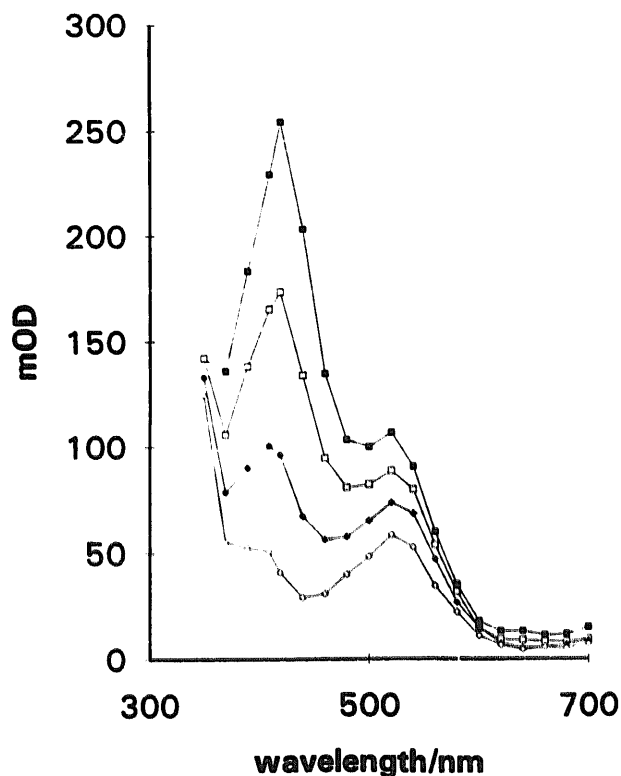[d] Rate constants for bond fragmentation.
[d] Ref. [3].

Fig. 2. Time-resolved difierence absorption spectra after 340 nm excitation of an Ar-saturated acetonitrile solution containing N-methylquinolinium hexafluorophosphate $(OD_{340}=0.6)$, 0.5 M m-xylene and 10^{-3} M pinacol 4. The spectra correspond to the following times after the pulse: ■, 300 ns; □, 500 ns; ◇, 900 ns; ◆, 2.4 μs.

was used to produce the pinacol radical cations, according to the following equations

$$NMQ^+(DCA)^* + C \longrightarrow NMQ^\cdot(DCA^-) + C^{\cdot+} \qquad (4)$$

$$C^{\cdot+} + P \longrightarrow C + P^{\cdot+} \qquad (5)$$

Excitation of either DCA or NMQ^+ results in the formation of the singlet excited state. The singlet excited acceptor is then diffusionally quenched by a high oxidation potential electron donor (co-sensitizer, C), such as m-xylene (in the case of NMQ^+) or biphenyl (in the case of DCA), leading to the production of the m-xylene or biphenyl radical cation in good yield, both of which are powerful oxidizing agents. It is this radical cation, $C^{\cdot+}$, which oxidizes the pinacol substrate P (Eq. (5)). Exciation of samples of NMQ^+/m-xylene (0.5 M) in the presence of pinacols 2, 4 and 5 (at approximately 10^{-3} M) results in similar transient absorption spectra. The initial spectra, having absorption maxima at 420 nm, are attributed to the radical cations of the pinacols [3]. The final spectra consist of a number of overlapping absorptions primarily from the N-methylquinolyl radical and presumably the ketyl radicals formed from bond fragmentation. The spectrum of 5 (Fig. 2) is similar to that of the p-toluidine radical cation prepared in the same manner and to the reported spectrum of the radical cation of N,N-dimethylaniline. The observed first-order rate constants for the pinacol radical cat-

ions are independent of the excitation energy and the concentration of the pinacol. The formation of the radical cation of pinacol 4 was also followed via time-resolved absorption spectroscopy using the DCA/biphenyl co-sensitization system. On excitation of an argon- saturated sample containing DCA ($OD_{410}=0.6$), biphenyl (0.2 M), N-methoxy-4-phenylpyridinium tetrafluoroborate (5 mM) and pinacol 4 (0.1–1 mM), a new absorption appears concomitant with the decay of the biphenyl radical cation [6]. This new transient species has a difference absorption spectrum identical with that discussed above and is observed to decay via first-order kinetics with a rate constant identical, within experimental error, to that measured using the NMQ^+/m-xylene co-sensitization system. We have also measured directly the bond fragmentation rate constants using this same co-sensitization procedure in our laboratory and have found that these rate constants for the pinacols are of the same order of magnitude as those observed for a series of 1,2- disubstituted aminoalcohols, but at least an order of magnitude slower than those observed for a series of 1,2-aromatic diamines [7].

All of the pinacols exhibit fluorescence at approximately 340 nm, which is quenched on addition of carbon tetrachloride. By monitoring the reduction in the fluorescence intensity as a function of the CCl_4 concentration, Stern–Volmer quenching constants were calculated for the pinacols 1–7 (Table 1). The fluorescence lifetimes for several of the pinacols have been measured via the technique of single photon counting and are also presented in Table 1.

Irradiation of pinacols 1–7 (approximately 2×10^{-3} M) in degassed benzene or acetonitrile solutions in the presence of CCl_4 (approximately 0.8 M) leads to the production of products derived from the fragmentation of both donor and acceptor (Fig. 3). The quantum efficiencies measured for low (1%) conversion of the starting material (Table 2) for the reaction are substantially lower than unity in each case and vary with the solvent even under conditions in which quenching of the pinacol excited singlet (as indicated by fluorescence quenching, Table 2) is nearly complete. The formation of the ketone product was followed by UV–visible absorption spectroscopy and the incident light intensity in these experiments was measured using both potassium ferrioxalate and Aberchrome actinometers.

The lower than unity quantum yields for the degassed samples are attributed to the competition between fragmentation of the acceptor anion and return electron transfer, since the measured rate constants for bond fragmentation (Table 1) are several orders of magnitude slower than the rate constant typical for return electron transfer from a singlet ion radical pair (approximately 10^9–10^{11} s^{-1}) [4]. It should be noted that Klassen and Ross [8] have observed the transient absorption spectrum of CCl_4^- ($\lambda_{max} = 370$ nm) in 3-methylpentane at 95 K. At this temperature, this species decays over 1 ms. At room temperature, this decay will be greatly enhanced, but, in our experiments, it may only be necessary for $CCl_4^{\cdot-}$ to live for tens of picoseconds in order to partici-
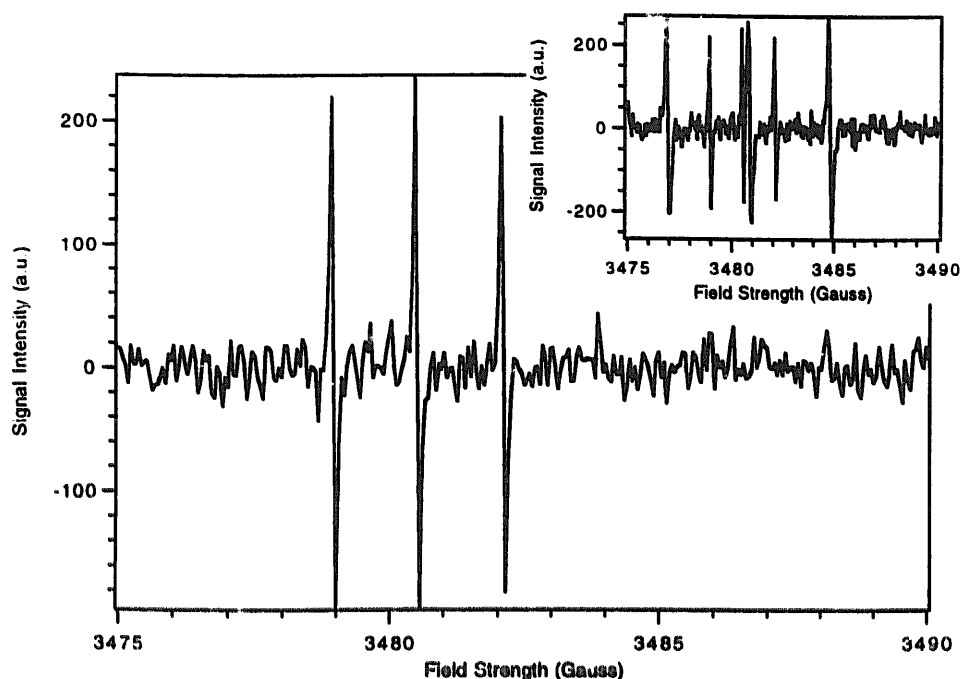
Fig. 3. Proposed reaction scheme for the pinacols 1–7.

pate in back electron transfer with its geminate radical cation partner.

Further support for the proposed mechanism is provided by data from both NMR and electron spin resonance (ESR) experiments. The only product observed by ^{1}H NMR after irradiation of pinacol **5** in the presence of CCl$_4$ (5 M) in deuterated acetonitrile is aceto-(p-N,N-dimethylamino)-phenone. Irradiation of pinacol **5** in the presence of ^{13}C-labeled carbon tetrachloride in degassed, deuterated acetonitrile results in deuterochloroform being the only product detectable by ^{13}C NMR. When a similar sample is irradiated in air-saturated deuteroacetonitrile, a new signal at 134.5 ppm is observed corresponding to CCl$_3$O$_2$H.

The irradiation of pinacol **5** in the presence of CCl$_4$ in degassed acetonitrile has also been followed via ESR spectroscopy using the spin trapping agent 2-methyl-2-nitrosopropane (MNP) [9]. Under these conditions, a single radical is trapped whose spectrum and hyperfine coupling constants are consistent with the reported values [10] for the adduct of 'CCl$_3$ with MNP (Fig. 4). Irradiation of MNP alone in air-saturated CH$_3$CN results in a signal corresponding to a known decomposition product of MNP [10]. If a sample containing

pinacol **5** and CCl$_4$ is irradiated and the ESR spectrum recorded under identical experimental conditions, a similar spectrum is observed; however, the signal intensity is nearly doubled. It has been reported in the literature [10] that the CCl$_3$O$_2$' adduct of MNP has a nearly identical spectrum to that of the decomposition product. Therefore even though the results in air-saturated solution are not unambiguous, it is not unreasonable to assume that these data are qualitatively consistent with the formation of CCl$_3$O$_2$' in these systems.

The proposed reaction mechanism shown in Fig. 3 includes oxygen trapping of the initially formed trichloromethyl radical to yield the trichloromethylperoxyl radical, CCl$_3$O$_2$' ($E_{red} > 1$ V vs. NHE) [11]. This species then oxidizes another pinacol molecule, thus propagating the chain reaction. Results of measurements of the oxidation peak potentials by cyclic voltammetry are reported in Table 2. It seems reasonable that the chain reaction only proceeds in the presence of pinacols 4–7 since their oxidation potentials (Table 2) are below the reduction potential for CCl$_3$O$_2$'.

Preliminary results from pulse radiolysis experiments [12] suggest that the ketyl radicals of 2,5-dimethoxy- and 2,4,5-trimethoxy-acetophenone react with CCl$_4$, presumably according to the following reaction

$$\underset{\text{Ar-C-R}}{\overset{\text{OH}}{|}} + CCl_4 \longrightarrow \underset{\text{Ar-C-R}}{\overset{O}{\parallel}} + \text{'CCl}_3 + HCl \qquad (6)$$

Pulse radiolysis of methanol solutions (Ar saturated, 0.5 M tert-butyl alcohol) containing either of these ketones results in transient absorptions (λ_{max} near 500 nm for both compounds) assigned to the ketyl radicals. These species decay over 20–30 μs. The addition of CCl$_4$ to the samples enhances the decay and values of 3×10^6 M^{-1} s^{-1} and 7×10^6 M^{-1} s^{-1} for the bimolecular quenching rate constants were calculated for the 2,5-dimethoxy- and 2,4,5-trimethoxy-acetophenone ketyl radicals by CCl$_4$ respectively. Interestingly, we did not observe quenching of the DCA radical anion by CCl$_4$ at concentrations of CCl$_4$ up to 1 M. DCA'$^-$ is a relatively good reducing agent ($E_{red} = -0.91$ vs. SCE for DCA) [6] and should have similar or better reducing power than

Table 2
Observed oxidation potentials for the pinacols and quantum yields of bond fragmentation

Pinacol	$\Phi_{\text{air saturated}}$	Φ_{degassed}	E_{ox}[a] (V vs. NHE)
1	0.04	0.08	1.49
2	0.66	0.69	1.27
3	0.27	0.51	1.24
4	1.53	0.56	0.99
5	8.20	0.42	0.81
6	2.75	0.11	0.95 [b]
7	1.06	0.24	0.95 [b]

[a] Oxidation peak potentials in CH$_3$CN containing tetra-n-butylammonium chloride.
[b] Ref. [3].

Fig. 4. ESR spectrum observed for a solution containing MNP, pinacol 5 and CCl₄ in CH₃CN immediately after photolysis ($\lambda_{exc} > 300$ nm). The inset is the spectrum observed for the same solution, but several minutes after irradiation; the new peaks are due to MNP decomposition.

the ketyl radicals. This allows us to estimate an upper limit for the bimolecular quenching rate constant of DCA^{*-} by CCl_4 as less than $10^3 \, M^{-1} \, s^{-1}$. If this reaction were a simple electron transfer process, we would have expected the ketyl radicals and DCA^{*-} to react with CCl_4 with bimolecular rate constants of the same order of magnitude. However, the difference between the rate constants is nearly a factor of 10^4 and thus it is likely that single electron transfer is not the controlling factor on the rate at which this reaction proceeds.

In summary, the co-fragmentation process reported here provides for a relatively efficient and potentially useful photoinduced electron transfer process particularly since it appears to be a novel method for the photochemical generation of acid.

Acknowledgements

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