# Cooperative Electron Transfer Fragmentation Reactions. Amplification of a Photoreaction through A Tandem Chain Fragmentation of Acceptor and Donor Pinacols

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Photofragmentation reactions occurring as a consequence of activation by oxidation or reduction of excited states have been observed for a variety of organic molecules, especially for donors such as amines, pinacols, and substituted diarylethanes.[1–9] In many cases the fragmentation of the ion radical produces a stable (even-electron) product and a redox active radical.[3,4] As a typical example, the cation radicals of electron-rich pinacols such as **1** (KHKH) generate a ketone, K, and the relatively strong reducing ketyl radical, KH• (eq 1).[10–12] In previous studies, we have
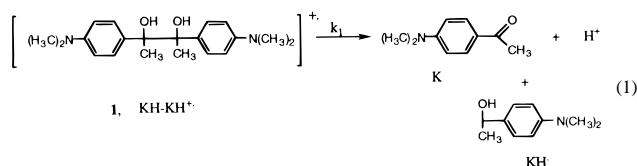
explored subsequent reactions of the photogenerated radicals with reagents such as organic halides.[10–12] In the present investigations, we have synthesized and studied electron-deficient pinacols such as **2** (A_2^{2+}) and find that these undergo parallel fragmentations upon one-electron reduction to generate a stable reduced product (AH^+) and a moderately strong oxidizing radical, $A^{\bullet+}$ (eq 2). Herein we report a cofragmentation which occurs when
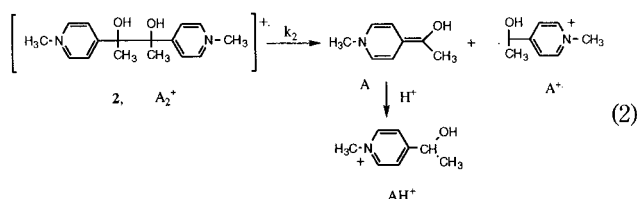
the two substrates are combined such that tandem chain-propagating redox reactions of the two radicals display a remarkable amplification of an initial photoinduced electron-transfer process.

When either KHKH or A_2^{2+} is activated independently by photoinduced electron transfer via quenching of a singlet donor (or acceptor) in acetonitrile, low to moderate efficiencies for

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Table 1. Quantum Yields for Photofragmentation

system[a]	irradiation wavelength[b] (nm)	product detected[c]	$\varphi_{product}$[d]
BAD (5×10^{-4} M) + A_2^{2+} (2×10^{-3} M)	310	AH^+	0.52
KHKH (3×10^{-3} M) + A_2^{2+} (3×10^{-3} M)	326	K, AH^+[g]	9.1
DCA (5×10^{-5} M) + KHKH (3×10^{-3} M)	370	K[f]	0.04
DCA (5×10^{-5} M) + A_2^{2+} (3×10^{-3} M)	370	e,f	0
DCA (5×10^{-5} M) + KHKH (3×10^{-3} M) + A_2^{2+} (3×10^{-3} M)	370	K, AH^+[g]	2.9
DCA (5×10^{-5} M) + BP (2×10^{-1} M) + KHKH (5×10^{-4} M) + A_2^{2+} (5×10^{-4} M)	370	K, AH^+[g]	24
Ru(bpy)$_3^{2+}$ + A_2^{2+}	450	e,f	<0.001
Ru(bpy)$_3^{2+}$ (5×10^{-5} M) + KHKH (2×10^{-3} M)	450	K[f]	0.86
Ru(bpy)$_3^{2+}$ (5×10^{-5} M) + KHKH (2×10^{-3} M) + A_2^{2+} (2×10^{-3} M)	450	K, AH^+[g]	13.8

[a] Acronyms: BAD = bis(*N,N′*-dimethylanisidine); BP = biphenyl; DCA = dicyanoanthracene. [b] The solutions were irradiated with a 250 W high-pressure mercury lamp through a monochromator set at the irradiation wavelength. [c] Product analyzed by UV–vis; product structure determined by ¹H NMR. [d] In a typical experiment, 3×10^{-3} M KHKH and 3×10^{-3} M A_2^{2+} in acetonitrile were irradiated with a 250 W high-pressure mercury lamp through a 0–54 glass filter and a monochromator set at 310 nm at room temperature. The solution was degassed 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. Both Aberchrome 540 and potassium ferrioxlate were used to determine the incident light intensities. The quantum yield for formation of the product was determined at 1–2% conversion of starting material. [e] Product yield was too low to estimate $\varphi_{product}$. [f] Sensitizer decomposition observed. [g] Products K and AH^+ produced in 1:1 ratio as shown in eq 3; they were the only products observed in each case, and the chemical yields are >90%.
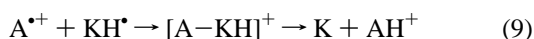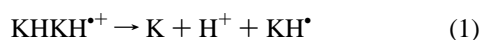
fragmentation are observed, due to the failure of cage escape and/or fragmentation to compete effectively with rapid return electron transfer (Table 1). Previous studies have shown that the rate constant for fragmentation of KHKH•+, k_1, is 1.8×10^5 s⁻¹.[12] We have investigated the rate of fragmentation of $A_2^{\bullet+}$ by laser flash activation (308 nm) of bis(*N,N*-dimethylanisidine) (BAD) in the presence of A_2^{2+} in acetonitrile; the measured rate constant, $k_2 = 1.5 \times 10^5$ s⁻¹, is remarkably close to that of KHKH•+.

In contrast to the moderate to low efficiencies observed when either **1** or **2** is independently activated by single electron transfer, by using nonfragmenting donors or acceptors, irradiation of degassed acetonitrile solutions containing **1** (3×10^{-3} M) and **2** (3×10^{-3} M) at 310 nm (where only **1** is excited) yields efficient and stoichiometric fragmentation of both pinacols according to eq 3.[13] The quantum yield for formation of either photoproduct
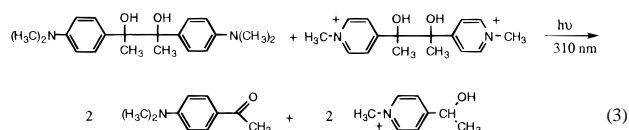
(K or AH^+) measured in this case is 9 ± 1. (No reaction occurs in the absence of light). The greater than unit quantum efficiency observed when the two pinacols are reacted together clearly suggests a chain process initiated by a single-electron-transfer quenching of **1*** by **2**. We estimate the oxidation potential of

KH$^{\bullet}$ to be ca. -1 V (vs SCE) from previous studies[15] and the reduction potential of A$^{\bullet+}$ to be >1.3 V (vs SCE).[14,16] The oxidation potential of **1** is $\sim$0.7 V (vs SCE), and the reduction potential of **2** is -0.7 V (vs SCE). Given this propensity of the radicals generated by fragmentation of **1** and **2** to be strong reductants and oxidants, respectively, the mechanism outlined by eqs 1, 2, and 4–9 is proposed. The key chain-carrying steps in this process are the reactions of the radical intermediates in oxidizing and reducing the substrates **1** and **2** in eqs 7 and 8.[14] Possible chain termination steps include eqs 9–11. Equation 9

$$\text{KHKH} \rightarrow \text{KHKH*} \tag{4}$$

$$\text{KHKH*} + \text{A}_2{}^{2+} \rightarrow \text{KHKH}^{\bullet+} + \text{A}_2{}^{\bullet+} \tag{5}$$

$$\text{KHKH}^{\bullet+} \rightarrow \text{K} + \text{H}^+ + \text{KH}^{\bullet} \tag{1}$$

$$\text{A}_2{}^{\bullet+} \rightarrow \text{A} + \text{A}^{\bullet+} \tag{2}$$

$$\text{A} + \text{H}^+ \rightarrow \text{AH}^+ \tag{6}$$

$$\text{KH}^{\bullet} + \text{A}_2{}^{2+} \rightarrow \text{K} + \text{H}^+ + \text{A}_2{}^{\bullet+} \tag{7}$$

$$\text{A}^{\bullet+} + \text{KHKH} \rightarrow \text{A} + \text{KHKH}^{\bullet+} \tag{8}$$

$$\text{A}^{\bullet+} + \text{KH}^{\bullet} \rightarrow [\text{A}-\text{KH}]^+ \rightarrow \text{K} + \text{AH}^+ \tag{9}$$

$$2\text{A}^{\bullet+} \rightarrow \text{A}_2{}^{\bullet+} \tag{10}$$

$$2\text{KH}^{\bullet} \rightarrow \text{KHKH} \tag{11}$$

appears reasonable since independent attempts to synthesize the "mixed" donor–acceptor pinacol, A–KH$^+$, result in the isolation of products AH$^+$ and K. From a kinetic analysis based on the above equations, when the reaction is carried out with [KHKH] $\gg$ [A$_2{}^{2+}$] under the condition such that eq 11 should be the predominant termination step, the quantum yield is given by eq 12 where f is the fraction of initial quenching events leading to

$$\varphi_{\text{product}} = f + \left(\frac{4k_7{}^2 f}{I_0 A k_9}\right)^{1/2} [\text{A}_2{}^{2+}] \tag{12}$$

the formation of intermediate KHKH$^{\bullet+}$ and A$_2{}^{\bullet+}$, A is the absorbance, and k_7 and k_9 are the rate constants for eqs 7 and 9. This predicts that the quantum yields will increase with an increase of [A$_2{}^{2+}$] and also with a decrease of light intensity, which has been experimentally verified.

Inspection of the proposed mechanism suggests that virtually any process generating either radical KH$^{\bullet}$ or A$^{\bullet+}$ in the presence of **1** and **2** should result in efficient reaction, provided the radicals are not scavenged by new reactions. Accordingly, we find that irradiation of the potential acceptor 9,10-dicyanoanthracene (DCA) (5×10^{-5} M) in the presence of **1** and **2** (each 3×10^{-3} M) with light (370 nm) not absorbed by either pinacol leads to a reaction efficiency of 2.9 (Table 1). In contrast, irradiation of DCA in acetonitrile in the presence of **1** leads to much lower efficiencies due to the low cage escape yield (and relatively low value of k_1) while essentially no reaction occurs when DCA is

irradiated in acetonitrile in the presence of the acceptor pinacol **2**. While irradiation of DCA–**1** in degassed acetonitrile results in decomposition of the DCA, there is no observable decomposition of the sensitizer when the mixture of **1**, **2**, and DCA is irradiated. Even higher quantum yields are obtained when a mixture of the two pinacols in acetonitrile is irradiated using Ru-(bipy)$_3{}^{2+}$ as the light-absorbing "sensitizer" (450 nm). Here again, very low efficiencies for reaction (Table 1) are observed when Ru(bipy)$_3{}^{2+}$ is irradiated independently in the presence of **1** or **2**, even though both pinacols quench the excited state of Ru(bipy)$_3{}^{2+}$ at rates close to diffusion-controlled. The foregoing results are reasonable in that the initial products of single-electron-transfer quenching of the excited sensitizers, DCA$^{\bullet-}$, Ru(bipy)$_3{}^{1+}$, and Ru(bipy)$_3{}^{3+}$, are anticipated to reduce **2** or oxidize **1**, respectively, and thus initiate the chain process.

An estimation of the "chain length" or amplification that occurs as a result of the subsequent steps may be obtained from a "cosensitization" study using the system DCA–biphenyl (BP)[17] as the initiation vehicle. Here, quenching of DCA^{1*} by BP results in the formation of DCA$^{-\bullet}$ and BP$^{\bullet+}$ with an efficiency (in acetonitrile) of 0.6; since both of these ion radicals should be reactive toward the substrates **1** and **2**, a net efficiency of "initiation" of 1.2 is anticipated.[17] The measured quantum efficiency under these conditions is 24, the highest value measured thus far. This indicates a net chain length of 20 for each ion radical initiator or an *amplification factor* of 40 over the photochemical quantum efficiency of "initial" products.

The results obtained in this study offer an interesting comparison to those obtained in an earlier investigation of the photoreaction of **1** and related donor pinacols with CCl$_4$.[10,11] In these studies we found that, in the absence of oxygen, simple cofragmentation was observed with quantum yields significantly below unity. In contrast, with oxygen present relatively high quantum efficiencies, indicative of a chain reaction, were observed. In this case the CCl$_3{}^{\bullet}$ radical produced by fragmentation of the acceptor is evidently not sufficiently reactive to oxidize the pinacol; however, interception of CCl$_3{}^{\bullet}$ by oxygen to form CCl$_3$O$_2{}^{\bullet}$ provides a sufficiently strong oxidant to promote a chain process.[18] In the present case we find that oxygen reduces the efficiency of the double fragmentation (and changes the net products formed), most likely by reacting with the radicals A$^{\bullet+}$ and KH$^{\bullet}$ to produce the corresponding ketones.

The present results may provide a general method of producing highly efficient photoreactions initiated by electron-transfer quenching of excited states.[20] For example, since the essential feature of both substrates in the present study is the redox-mediated release of redox reactive radicals, the construction of a variety of substrates having suitable redox potentials and general structures, H–K–P–H and A–P'$^{2+}$, could result in a reaction of comparable efficiency but with quite different (and potentially useful) products. Longer chain lengths should be attainable for reactions occurring in microheterogeneous media or under different concentration or flux regimes or initiation procedures.

(13) A ^{1}H NMR study of complete consumption of an equimolar mixture of **1** and **2** leading to the formation of K and AH$^+$ without any other products detected demonstrates greater than 95% conversion via eq 3. Similar conversion is also observed when the reaction is initiated by sensitization. For quantitative analysis, the new CH$_3$ signals of AH$^+$ and K at 2.48 and 1.50 ppm were monitored and the same results were verified by aromatic signals.

(14) An alternate to reaction 8 which would also propagate net reaction 3 would be an H-atom-abstraction-mediated fragmentation:

$$\text{A}^{\bullet+} + \text{H}-\text{K}-\text{K}-\text{H} \rightarrow \text{AH}^+ + \text{K} + \text{KH}^{\bullet}$$
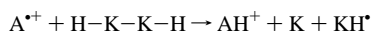
Although this reaction cannot be rigorously excluded at this time, we think it is unlikely since the use of 2-propanol as a solvent does not suppress the photoreaction.

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(16) A$^{\bullet+}$ oxidizes tris(2,2′-bipyridine)ruthenium(II)$^{2+}$ (Ru(bipy)$_3{}^{2+}$) to Ru-(bipy)$_3{}^{3+}$.

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(18) Another example of a chain process initiated by photoinduced electron transfer followed by a complex sequence including proposed deprotonation of a cation radical and its subsequent oxidation, coupled with decarboxylation of an anion radical, has been reported.[19]

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(20) Of course, the reactions need not be photoinitiated since they represent effectively the coupling of electrochemical "ece" reactions in which the "reactive products" of a reduction and oxidation can undergo a cross reaction with the starting material. Thus, electrochemical or other chemical initiation (an oxidizing or reducing free radical) should readily trigger this type of reaction.