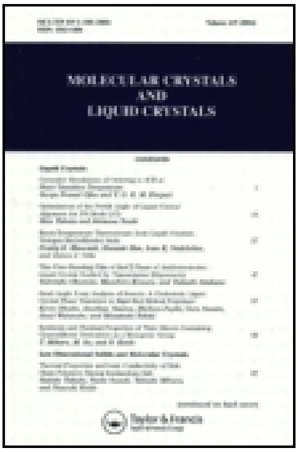

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CARBON-CARBON BOND CLEAVAGE IN PHOTOGENERATED RADICAL ANIONS.

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Abstract Electron acceptors yielding highly labile radical anions have been designed based on thermodynamic considerations. The radical anions of these acceptors were produced by an electron transfer from excited states of aromatic amines. The radical anions undergo rapid C-C bond scission with rates in the 10^6 - 10^{10} s^{-1} range. These are the first examples of C-C bond cleavage in photogenerated radical anions. The observed rates indicate that the activation energies for cleavage are only slightly higher than the free energies of the reactions, even for near-thermoneutral reactions.

Keywords: Carbon-Carbon bond cleavage, photogenerated radical anions, photoinduced electron transfer, self-destinctive acceptors

INTRODUCTION

Mesolytic cleavages, *i.e.*, unimolecular fragmentations of radical ions to radicals and ions, are tremendously accelerated in comparison to the corresponding homolytic processes.[2-6] During our investigation of carbon-carbon bond scissions in various radical ions, we have found that the acceleration has thermodynamic origins, and that most of the thermodynamic advantage is expressed in the lowering of the activation energy for cleavage.[6ef] Facile C-C bond fragmentations were observed in radical cations[1-3] (*catiomesolysis*) as well as radical anions[5,6] (*aniomesolysis*).

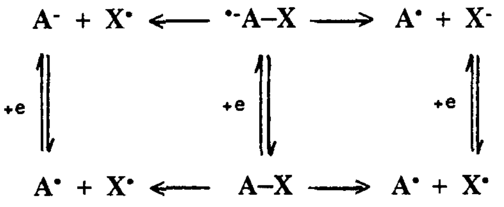
The radical ions are conveniently generated by photoinduced electron transfer between appropriately selected donors and acceptors.[2,7] The rapid mesolysis of one of the radical ions produced in such a way may serve as a synthetic method for generation of radical or ion intermediates, or as a mechanistic probe for the photoinduced charge-transfer processes. In the context of the latter, the C-C bond cleavage was shown to be a convenient "molecular clock" for investigation of back-electron-transfer,[6b] ion pairing[6h] and other relevant reactions involved in photoinduced electron transfer.

Until now, the examples of C-C bond scission in photogenerated radical ions were limited to radical cations.[3] Although there are many known examples of reductive cleavage of C-C bonds,[5] they are all limited to thermally generated radical anions, most commonly involving metal reductions. The radical anions, in principle, could be as reactive as radical cations,[6] and therefore the C-C bond scission should be also accessible in photochemical systems. In such systems the C-C cleavage reactions have to compete with back-electron transfer processes. Thus, the cleavage is expected to be photoefficient only for rapidly fragmenting radical anions. Here, we describe the design of electron acceptors which yield labile radical anions, and present first examples of C-C bond cleavage in photogenerated radical anions.

DESIGN OF SELF-DESTRUCTIVE ELECTRON ACCEPTORS

As we have shown recently,[6] mesolytic cleavages have very small "intrinsic" kinetic barriers,[7] *i.e.*, the activation energy for cleavage is only slightly larger than the thermodynamic barrier for the reaction. It is sufficient, therefore, to design systems with small or negative free-energy change accompanying the cleavage. A photochemically efficient system requires that the activation energy for cleavage of the radical ion be small (preferably $\leq$ 10 kcal/mol), and thus, the change in the free energy for the radical ion fragmentation should be in the same range.

The free-energy for mesolysis ($\Delta G(^{\bullet -}AX)$) can be estimated from a simple thermodynamic cycle (Scheme 1).[6e,9] In the case of radical anions wherein the extra electron was added to an antibonding orbital in the neutral precursor, it can be shown that the free energy of mesolysis is smaller than the free energy of homolysis ($\Delta G(AX)$) by the difference (ΔE) in the reduction potentials between the radical anion precursor (E_{AX}) and one of the radicals produced ($E_{X\cdot}$ or $E_{A\cdot}$, whichever is easier to reduce).[6e]



$$\Delta G(^{\bullet-}AX) = \Delta G(AX) - \Delta E$$

where $\Delta E = E_{A\cdot} - E_{AX}$ or

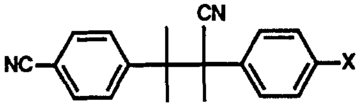
$$\Delta E = E_{X\cdot} - E_{AX}$$

Scheme 1.

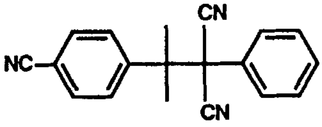
$\Delta G(AX)$ can be approximated by the activation energy for homolysis of the substrates, which can be obtained experimentally for compounds with relatively weak C-C bonds[10] (see below). The required reversible redox potentials for the radical anion precursors and the $A^\bullet/A^-$ or $X^\bullet/X^-$ couples can be measured quite accurately by a modified cyclic voltammetry method (CV)[11] or by a second-harmonic ac voltammetry (SHAC) technique.[12] Thus, radical anion precursors with desired free energies for cleavage can be easily designed.

Analysis of Scheme 1 indicates that if the cleavage reaction is to have a small (or negative) $\Delta G(^{\bullet-}AX)$, the radical anion precursors must have a weak bond (homolytically) and a high reduction potential. On the other hand, the anion produced (A^- or X^-) must be as stable as possible. Taking into account that the radical anion has to be accessible by photoinduced ET, the largest driving force (smallest or most negative $\Delta G(^{\bullet-}A{-}X)$) can be found in systems where the unpaired electron is delocalized on one side of the scissile bond (for example, on an A moiety), while the most stable anion fragment is formed from the other "half" of the molecule (in this example, X^-).

Using these guidelines, we have prepared a series of p-cyanobicumenes **1** - **4** as radical anion precursors and estimated their free energies for mesolysis. The bicumenes were prepared by radical coupling of the corresponding benzylic derivatives. The homolytic cleavage of **1** - **4** was carried out in decalin in the presence of excess thiophenol as radical scavenger. The homolysis reactions were very clean. Only the corresponding benzylic fragments and phenyl disulfide were obtained as products. Under these conditions the cleavage is presumed to be irreversible,[10] and the measured activation parameters can be used as an estimate of the free energy of homolysis of the central C-C bond in these compounds.[10] The obtained data are collected in Table 1.



1: X = H
2: X = OMe
3: X = CF_3



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The redox potentials of the precursors and the corresponding fragments were obtained by CV.[11] The α-cyanobenzylic anions under consideration were quite stable and their oxidation potentials were obtained without difficulty.[12] Based on the measured redox potentials and homolysis energies, the mesolytic free energies of radical anions of **1** - **4** were estimated and are summarized in Table 1.

CLEAVAGE OF C-C BONDS IN PHOTOGENERATED RADICAL IONS

Aromatic amines are commonly used as electron donors in photochemical reactions.[13] Most often, the amines are used as quenchers of excited states of other molecules.[13] Examples where amine excited states serve as electron donors to ground state molecules are more limited.[14] The *N,N*-dimethyl derivatives of aniline used in our study are known to have fluorescent singlet excited states with nanosecond lifetimes.[7b,13,14] The energies of the singlets are high, in the 3.8 eV range. The singlet excited states efficiently intersystem cross to the triplet states. The triplet excited states have lifetimes in the microsecond range and energies on the order of 3.0 eV. Both excited states are, therefore, good electron donors.[7b,13,14] Additionally, irradiation of the very electron rich amines, *N,N,N',N'*-tetramethyl derivatives of benzidine (TMB) and p-phenylenediamine (TMPD) may lead to electron ejection.[7b,13,14]

Table 1. Carbon-carbon bond cleavage in photogenerated radical anions.

	$\Delta G(AX)^a$	$E_{X\cdot}{}^b$	ΔE^c	$\Delta G(^{\bullet-}AX)^d$	$k_f{}^e$	$\Delta G^{\ddagger}(^{\bullet-}AX)^f$	Φ^g
	(kcal/mol)	V	(kcal/mol)		(s^{-1})	(kcal/mol)	
1	39.7	-0.81	35.9	3.8	$9.1 \cdot 10^6$	7.5	0.052
2	38.7	-0.93	33.2	5.5	$8.5 \cdot 10^5$	8.7	0.019
3	40.0	-0.52	42.7	-2.7	$2.0 \cdot 10^8$	5.5	0.068
4	33.8	+0.22	59.7	-26.0	$5.0 \cdot 10^9$	3.7	0.370

(a) Activation energies for homolysis at 300 K, assumed to be equal to the free energy change of homolysis. (b) Oxidation potentials of the corresponding α-cyanobenzyl anions, in 0.1 M Et_4NClO_4 in DMSO *vs* SCE. (c) The difference (in kcal/mol) between the oxidation potential of the α–cyanobenzyl anion ($E_{X\cdot}$) and the reduction potential of the acceptor (E_{AX} = -2.37 V *vs.* SCE for all acceptors). (d) Estimated free energy of mesolysis (kcal/mol). (e) The rate of C-C bond scission in the radical anions. (f) Estimated activation energy for mesolytic scission. (g) The quantum yield for disappearance of **1** - **4** (0.0015 M) with TMB (0.003 M) measured at 305 ± 5 nm.

The nitrile acceptors of our study are predicted by Weller's equation[15] to quench both the singlet and triplet excited states in a diffusion-limited process. In fact, all compounds quenched the fluorescence of TMB in CH_3CN with diffusion-controlled rates ($1.2 \pm 0.4 \cdot 10^{10}$ M^{-1} s^{-1}). Irradiation of the amines above 300 nm in the presence of **1** - **4** led to very efficient reactions. The cyanobicumenes were consumed within minutes, and products characteristic of the cleavage of the central C-C bond were recovered in high yields (see below). The bicumenes, **1** - **4**, did not absorb light below 300 nm, and remained unchanged if the samples were irradiated without amine present. The reaction was quenched by p-dicyanobenzene (see below). Irradiation of acetophenone, a triplet sensitizer, in the presence of **1** - **4** gave no reaction, excluding an energy transfer process as a mode of C-C bond scission.

The products of the reaction were consistent with radical anion cleavage. For example, in the case of TMB, the amine was recovered unchanged and **1** yielded α-methylbenzyl nitrile (68% yield), α-methyl-p-cyanostyrene (78%) and bis-p-cyanobicumene (7%). Similar fragments were produced in high yields from **2** and **3**. In the case of **4**, only the styrene fragment was recovered quantitatively. The fate of α-cyanobenzyl nitrile was not determined. TMPD and **1** gave similar products, although in this case the secondary reaction between the TMPD and α-methylbenzyl nitrile led to quantitative alkylation of the amine.[16] The styrene was produced in 45% yield, while the radical coupling product, bis-p-cyanobicumene, was formed in 40% yield. In addition small amounts (3%) of p-cyanocumene were detected. Other amines tried, *N,N*-dimethylated aniline (DMA), anisidine (DMAN), and 1-naphthyl amine (DMN) gave similar products, although the ratios of products were amine dependent. All reactions were very efficient. Only minutes of irradiation were required to completely consume the starting materials.

To better analyze these reactions, TMB was used as the excited state donor. As mentioned above, the reaction is catalytic in this case. Additionally, both excited states of this amine are well characterized.[14] Thus, the singlet TMB* has a lifetime of 11 ns in CH_3CN, and its quantum yield for intersystem crossing to the triplet is 0.63. The triplet has a 5 μs lifetime in the same solvent. As expected from such a system, the quantum yield for disappearance of **1** should be concentration dependent.[14] At low concentrations of **1**, only TMB^3 is quenched yielding triplet ion pairs ($TMB^{\bullet+}$ $\mathbf{1}^{\bullet-}$). The fragmentation of $\mathbf{1}^{\bullet-}$, or ion separation (see below), competes with back-electron transfer. Since the electron transfer is spin-forbidden, the overall reaction should be relatively efficient. At higher concentration of **1**, more excited state molecules of TMB are quenched, but an increasing fraction of them is in the singlet state. This fraction gives singlet ion pairs, within which the back-electron transfer shoud be more efficient. The overall efficiency of the photoreaction, therefore, should not increase linearly with increasing concentration of **1**.

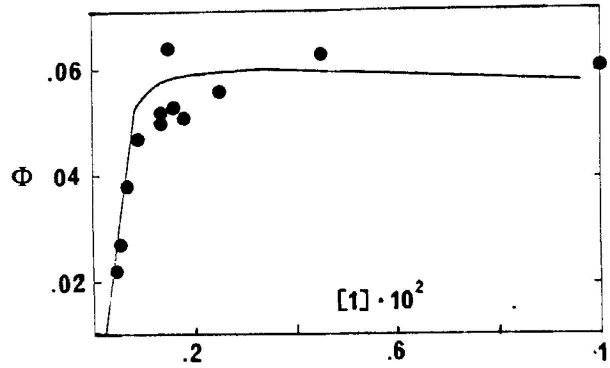

Figure 1. The quantum yield for disappearance of **1** as a function of the concentration of **1**. The mixture of TMB (0.003 M) and **1** was irradiated at 305 ± 5 nm. The line represents a fit of the data using the lifetimes and quantum yields for the triplet and singlet states of TMB.

These predictions are confirmed by experiments. The quantum yield for disappearance of **1** is a function of concentration of **1**, as shown in Fig. 1. The line drawn corresponds to a fit of the experimental data to the theoretical prediction discussed above, using the stated lifetimes of the triplet and singlet states.[14] The efficiency of cleavage within the triplet manifold is *ca.* 8 times larger than in the singlet manifold. As shown below, this efficiency is mostly determined by the relative rates of ion separation and back-electron transfer.

The reactions are efficiently quenched by p-dicyanobenzene (DCB). The quenching is due to two processes. The first one involves direct quenching of excited states of the amine. The second process corresponds to electron transfer from the radical anion of our acceptor (**1** - **4**) to DCB, which should be diffusion limited. The quenching of the amine by DCB can be investigated independently; therefore, the drop in the quantum yield for disappearance of **1** - **4** in the presence of DCB due to the first process can be easily estimated and corrected for. Plotting the corrected quantum yields for disappearance of the substrate as a function of DCB concentration provides estimates of the rate of cleavage of the radical anions. Such data are shown in Fig. 2. Both **1**$^{\bullet-}$ and **2**$^{\bullet-}$ are intercepted by DCB, indicating that under these conditions the electron transfer to DCB has a rate comparable to the rate of cleavage (Table 1). On the other hand, no effect of DCB on the corrected quantum yield for disappearance of **3** and **4** was observed. This result implies that both these radical anions cleave too rapidly to be intercepted by DCB, *i.e.*, their rate of cleavage should be at least five times faster than that determined for **1**$^{\bullet-}$.

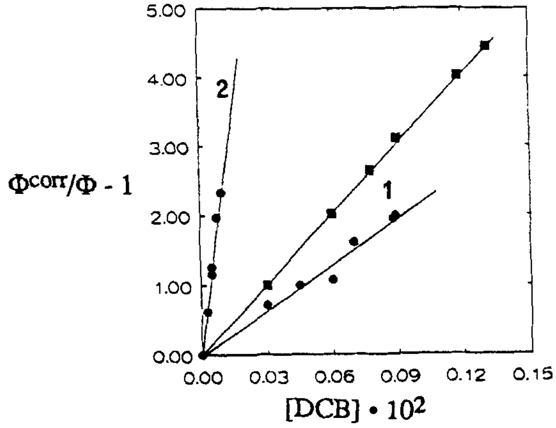

Figure 2. The ratio of the quantum yield measured without DCB (Φ^{corr}) to the quantum yield measured in the presence of various concentrations of DCB (the corrections account for the amine's excited states quenching by DCB). The circles correspond to experiments with TMB, the squares to experiments with TMPD. The slopes of the lines drawn are equal to k_d/k_f, where k_d is the diffusion-limited rate of electron transfer from the bicumene radical anions to DCB, and k_f is the rate of radical anion fragmentation.

The measured rate of mesolysis for **1**$^{\bullet-}$ and **2**$^{\bullet-}$ are well below the rate of ion separation in acetonitrile[17] ($5 \cdot 10^8$ s^{-1}). Thus, the measured quantum yields for these compounds (Table 1) reflect mainly a competition between the back-electron transfer and the ion separation.[17] In the case of **1**$^{\bullet-}$, the reencounters of the separated ions are quite minimal due to the rapid rate of fragmentation. The reencounters are more likely in the case of **2**$^{\bullet-}$, and this is reflected in the lower quantum yield measured for disappearance of **2**. The quantum yield for disappearance of **3** was similar to that for

1, although the rate of fragmentation of $\mathbf{3}^{\bullet-}$ is at least 5 times faster than that of $\mathbf{1}^{\bullet-}$. These results require that the rate of cleavage of $\mathbf{3}^{\bullet-}$ be similar to the rate of ion separation in this solvent. Assuming that the rates of back-electron transfer are the same for all radical anions, the rate of mesolysis of $\mathbf{3}^{\bullet-}$ can be estimated to be $2{\bullet}10^8$ s^{-1}; indeed, very close to the rate of ion separation.[17] Again, using the back-electron transfer rate as a reference, the cleavage of $\mathbf{4}^{\bullet-}$ can be estimated to be $5{\bullet}10^9$ s^{-1}.

CONCLUSIONS

The results of the investigation of the first examples of C-C bond cleavage in photogenerated radical anions are summarized in Table 1. The design of acceptors based on thermodynamic considerations has proven very successful. All prepared bicumene radical anions cleaved rapidly, leading to photoreactions with high overall efficiencies. The quantum yields for TMB were in the 0.02 - 0.37 range, and even higher for other amines studied, reaching 0.85 in the case of DMAN or DMA.[19]

The measured rates of cleavage confirmed our earlier conclusion, that the "intrinsic" barriers in mesolytic reactions are quite low.[6] This observation is valid even for near-thermoneutral reactions, although the "intrinsic" barrier increases systematically for reactions with increasing driving forces, implying a curvature of the $\Delta G^{\ddagger} = f(\Delta G)$ function. This trend is especially pronounced in the case of $\mathbf{4}^{\bullet-}$. The cleavage of this radical anion is highly exergonic, but the rate of cleavage is "only" $5{\bullet}10^9$ s^{-1}. Possibly, the slow mesolysis of this radical anion indicates the presence of an inverted-region in mesolytic cleavages of single bonds.

The prepared self-destructive acceptors are convenient molecular clocks for probing electron-transfer reactions and ion-pairing phenomena in photoinduced charge-transfer processes. They are stable under a variety of conditions, do not absorb light above 300 nm and can be easily modified to provide radical anions with lifetimes in the 10^5 - 10^{10} s^{-1} range. Application of these compounds for exploration of the photochemistry of aromatic amines and other donors is in progress.

EXPERIMENTAL SECTION

The synthesis of acceptors **1** - **4**, and detailed product studies will be described elsewhere.[19] All studies were carried out in deoxygenated CH_3CN solutions under argon. The argon was purified by passing through an oxygen-removal catalyst and a drying agent. The typical concentration of the amines was 0.0020 - 0.0040 M; the quantum yields for disappearance were independent of amine concentration. All amines were recrystallized before use. The DMN was used as received. The quantum yields were measured as described previously[6d] at 305 ± 5 nm. The preparative irradiations were performed through a pyrex filter using a 450 W mercury Hanovia lamp.

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