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ESR Investigation of C–C Bond Cleavage in Radical Cations

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Removal of an electron from a diamagnetic species often results in weakening of bonding interactions within the resulting radical cation. This process leads to dramatically accelerated rearrangements[1] and fragmentations.[2] The mechanistic details of such activation have been largely unexplored. We present here the first ESR observation of radical cations undergoing C–C bond fragmentation. This study includes kinetic data, activation parameters, and evaluation of the transition state polarization.

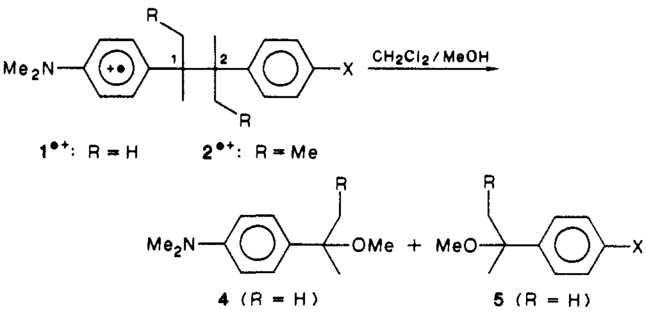
Cleavage of C–C bonds in radical cations has recently attracted considerable attention.[2] Such oxidative fragmentation may provide a useful method of breaking C–C bonds, which are quite strong in neutral molecules. In reports describing such reactions, radical cations have been generated in situ by photoinduced[2b–j] or thermal[2l–n] electron transfer. Under these conditions, the reactive species existed only in low steady-state concentrations, and consequently no kinetic data were available to evaluate the extent of C–C bond activation. Mechanistic details were limited mostly to information gained from product studies.[2] To remedy this situation, we have prepared a series of directly observable radical cations of *N,N*-dimethylaminobicumenes (Scheme I) and studied their reactions.

The radical cations of **1** and **2** (Scheme I) were produced by oxidation of the corresponding bicumenes with tris(4-bromophenyl)aminium hexachloroantimonate (**3**) in CH_2Cl_2–MeOH (5%). All **1**$^{\bullet+}$ and **2**$^{\bullet+}$ gave indistinguishable ESR spectra with the coupling pattern essentially identical with that reported for *N,N*-(dimethylamino)-4-*tert*-butylbenzene.[3] These observations indicate that the unpaired electron in **1**$^{\bullet+}$ and **2**$^{\bullet+}$ is highly localized on the dimethylaminophenyl moiety and that there are no significant interactions between the aromatic rings.

Above 200 K, the ESR signal decayed following first-order kinetics for all radical cations studied except **1g**$^{\bullet+}$ and **1c**$^{\bullet+}$ (Table I). The latter disappeared too rapidly[4] to obtain kinetic data by our technique, even at 160 K. The measured rate constants were independent of concentration of the corresponding neutrals and amount of the oxidant used. Apparently, the products did not interfere with the cleavage of **1**$^{\bullet+}$ since the linear first-order plots were observed for more than 3 half-lives. For **1a**$^{\bullet+}$, which was studied in more detail, the rate constants depended slightly on MeOH concentration. For example, at 240 K the observed $t_{1/2}$ values were 1.9, 2.6, and 3.0 min in solutions containing 5, 11, and 25% (v/v) of methanol. The observed small decreases in the rates of cleavage of **1a**$^{\bullet+}$ in solutions containing increasing amounts of methanol exclude direct nucleophilic participation of this solvent in the fragmentation process.[5]

The observed decays are due to C–C bond fragmentation as shown by product studies.[6] Under conditions similar to the kinetic runs, **1a**$^{\bullet+}$ gave **4** (87%) and **5a** (85%) as determined by NMR. The ether **5a** and α-methylstyrene were isolated and identified by comparison with authentic samples. The styrene is a product of decomposition of **5a** and is not observed in reaction mixtures prior to workup. Ether **4**, or products of its decomposition, could not be isolated. This ether was also detected in 67% yield when **1c** was treated with **3**. Similarly **1g**$^{\bullet+}$ produced **4** (57%) and **5g** (62%) in addition to small amounts of as yet unidentified products. The observed products, ethers **4** and **5**, are apparently derived from the nucleophilic attack of methanol on the corresponding cumyl cations. One of these cations is formed directly from the fragmentation of the radical cation. The other must be derived from the radical produced in the same step via one-electron oxidation. The most likely oxidant is another molecule of **1**$^{\bullet+}$ present in the medium. Thus, two molecules of **1**$^{\bullet+}$ disappear per one C–C bond cleaved. This interpretation is consistent with the observed stoichiometry[6] and leads to the conclusion that the observed rates are two times the actual fragmentation rates.

Scheme I



X	H	OMe	NMe$_2$	Br	Ac	CN	NO$_2$
	a	b	c	d	e	f	g

Table I. Kinetic Data for C–C Bond Cleavage in Radical Cations[a,b]

radical cation	$k_{obsd}\cdot10^2$ (s^{-1}) at 253 K	ΔH^* (kcal/mol)	ΔS^* (eu)
1a$^{\bullet+}$	1.4	12.0 ± 0.8	−19 ± 3
1b$^{\bullet+}$	7.9	12.8 ± 0.6	−12 ± 2
1c$^{\bullet+}$	>500[c]		
1d$^{\bullet+}$	1.2	12.3 ± 1.0	−18 ± 3
1e$^{\bullet+}$	0.65	10.3 ± 1.0	−27 ± 3
1b$^{\bullet+}$	0.33	11.8 ± 0.8	−27 ± 2
1g$^{\bullet+}$	0.28[d]		
2a$^{\bullet+}$	96.0[e]	15.3 ± 1.0	2 ± 3

[a] In CH_2Cl_2/MeOH (5% v/v), initial concentration of radical cations was ca. 10^{-4} M. The estimated error of the rate constants is ±15%. [b] The activation parameters were obtained from rate constants measured at different temperatures (at least six measurements) by a least-squares procedure. The reported intervals are at 95% confidence level. Essentially, identical estimates were obtained by a nonlinear fitting procedure (ref 15). [c] Estimated. [d] Nonexponential decays below 245 K. [e] Calculated; k_{obsd} (220 K) = $1.0\cdot10^{-2}$ s^{-1}.

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[4] The reaction of **1c**$^{\bullet+}$ may involve formation and subsequent rapid fragmentation of **1c**$^{2+}$

[5] Similar rates of C–C bond fragmentation were observed in reactions run without methanol.

[6] The product yields are based on amount of added oxidant. Two equivalents of oxidant are needed to completely consume starting materials. Ethers **4** and **5** are thermally unstable. No products with the intact central C–C bond were detected.

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The unambiguous interpretation of the kinetic parameters and substituent effects require that the cleavage process be irreversible under the reaction conditions. This requirement is apparently met[7] for our system as shown in experiments with **2a**$^{\bullet+}$. A sample of single diastereoisomer[8] of **2a** was treated with 1 equiv of **3**. After the reaction was complete, 46% of the starting material was recovered. NMR analysis of this material indicated no detectable isomerization. Also of importance for mechanistic considerations, the observed activation parameters exclude involvement of an electron jump from the nonaminated ring as a kinetically significant step.[9]

The observed activation parameters indicate *significant C–C bond activation upon electron removal*. For comparison, the homolysis[11] of bicumene has $\Delta H^{\ddagger} = 46$ kcal/mol and $\Delta S^{\ddagger} = 14$ eu, and the activation energy is higher than that of **1a**$^{\bullet+}$ by ca. 20 kcal/mol (at 300 K). Although the entropies of activation for reactions in solution are difficult to rationalize,[12] the negative $\Delta S^{\ddagger}$ values for **1**$^{\bullet+}$ indicate that highly ordered solvation of the transition state is probably involved. This conclusion is supported by the activation parameters for **2**$^{\bullet+}$, where steric hindrance to solvation seems to result in higher $\Delta H^{\ddagger}$. Such an interpretation is an apparent contradiction to the results observed for **1a**$^{\bullet+}$ in solutions containing varying amounts of methanol (see above). These results indicated that the ground state is slightly more stabilized than the transition state by increased solvent polarity or hydrogen bonding. The contradiction can be reconciled by assuming that in solvation of the transition state the geometrical constraints are of greater importance than a small change in polarity of the medium.

Additional support for the importance of entropy factors is the observation that the differences in rate constants for **1a–g**$^{\bullet+}$ are due largely to $\Delta\Delta S^{\ddagger}$. The substituent effect on the reaction rate is, however, rather small. This effect ($\log k_{\mathrm{rel}}$) correlates well ($r = 0.998$) with σ^{+} values[13a] yielding ρ^{+} of -0.8. This value indicates a small but significant positive charge formation on carbon 2 (Scheme I). There is no correlation ($r < 0.68$) with $\sigma^{\bullet}$ values of Arnold[13b,c] or Creary.[13d] Lack of such correlation excludes formation of an unpolarized radical center on carbon 2. However, the observed ρ^{+} is consistent with a polarized radical center,[14] and, in accordance with this observation, the transition state for C–C bond cleavage in **1**$^{\bullet+}$ can be described in valence-bond terms as an interacting radical–cation pair ($\mathrm{ArC}^{\bullet}\cdots{}^{+}\mathrm{CAr}' \leftrightarrow \mathrm{ArC}^{+}\cdots{}^{\bullet}\mathrm{CAr}'$).

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[7] Recombination of the radical and cation faster than rotation of fragments and slower than oxidation of radical would not be detected.

[8] Diastereochemically pure **2a** of as yet unconfirmed stereochemistry was used. As little as 3% of the other diastereoisomer would have been easily detected. Meso and dl diastereoisomers of the parent hydrocarbon have essentially identical heats of formation (Kratt, G.; Beckhaus, H.-D.; Lindner, H. J.; Ruchardt, C. *Chem. Ber* **1983**, *116*, 3235).

[9] For example, the oxidation potentials of 4-(*N*,*N*-dimethylamino)toluene and 4-methoxytoluene differ by almost 1 V.[10] The activation energy for such a jump would be at least 23 kcal/mol, much larger than that observed for **1b**$^{\bullet+}$ (16.5 kcal/mol at 300 K).

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Are Triplet Exciplexes Involved in [2 + 2] Photocycloaddition of Cyclic Enones to Alkenes?

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In his seminal 1964 paper on photocycloaddition of cyclic enones to alkenes, Corey[1] suggested that the reaction proceeds by interaction of an enone excited state (subsequently identified as a triplet state)[2] with the alkene to give initially an "oriented π-complex"[1] (or exciplex)[3] which leads to a 1,4-biradical and ultimately cyclization and disproportionation products. De Mayo[4] later recognized that any of these intermediates could in principle revert to enone and alkene ground states. In the interim, enone–alkene photocycloaddition (or photoannelation) has become arguably the most frequently utilized photochemical reaction by synthetic organic chemists.[5]

Corey[1] invoked a polar π-complex, with alkene as electron donor and enone as acceptor, to rationalize the regiochemistry in photocycloadditions to cyclohexenone and "relative rate factors" determined from yields of photoadducts of cyclohexenone to alkenes formed under competitive conditions. However, photoproduct yields in multistep processes depend on overall quantum efficiencies (QE) and not on the rate of a single specific step, as demonstrated many years ago by Wagner for the Norrish type II reaction of aromatic ketones.[6] Thus, Corey's data[1] and similar findings[7] in fact provide no insight into alkene reactivity or the nature of the initial intermediate(s) formed from enone triplets and alkenes. In addition, the charge distribution assigned to Corey's exciplex assumed a reactive enone n,π^* triplet state,[1] although the reactive state is known to be a π,π^* state,[8] which for most enones is the lowest triplet.[9] Nonetheless, the exciplex hypothesis has enjoyed general acceptance for nearly 25 years,[5] although Eaton suggested[10] that this mechanism was not entirely satisfactory in rationalizing all available data.[11] We now present kinetic data which is clearly inconsistent with the Corey–de Mayo exciplex hypothesis.

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