Unimolecular Cleavage of C–C Bonds in Radical Anions of Nitroaromatic Derivatives

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The sterically congested radical anions of nitro substituted 1,2-diphenylethane derivatives undergo irreversible, unimolecular C–C bond scission with activation parameters indicative of significant C–C bond activation relative to the neutral molecules.

A common reaction of radical anions is fragmentation into a radical and anion.[1] Scission of carbon–halogen, carbon–oxygen, and carbon–sulphur bonds in such processes is often characterized by a much faster rate than that for the corresponding homolytic or heterolytic cleavage.[1] This suggests that one-electron reduction may be a general method for activation of bonds in otherwise unreactive species.

Reductive cleavage of C–C bonds is widely used on a preparative scale,[2] but the mechanism of such scission has received little attention. Most mechanistic studies published so far invoke a dianion as the fragmenting species.[2—4] The extent of C–C bond activation by one-electron reduction has remained largely unexplored.

We report here the first examples of e.s.r. observation of radical anions undergoing facile, unimolecular C–C bond scission and the determination of their activation parameters for cleavage. Our investigation employed derivatives of 1-(4-nitrophenyl)-2-phenyl-1,1,2,2-tetra-alkylethanes (**1**) and (**2**).

All the compounds under study are sterically congested.[5] This crowding weakens the central C–C bond, counterbalancing the usual high stability of radical anions of nitroaromatic derivatives. Additionally, the conformation of these compounds is such that the scissile bond can overlap with the π-systems of both aromatic rings, as evidenced by *X*-ray and n.m.r. analysis.† The orbital overlap allows for resonance stabilization in the transition state and is believed to be essential for the fragmentation to occur.[1]

The radical ions were generated by chemical reduction with lithium 2,4,6-tri-t-butylnitrobenzenide or the K^+ or Na^+ salts of *N*,*N*-dimethylaminonaphthalenide.[6] E.s.r. spectra in dimethyl sulphoxide (DMSO) solution showed a 27-peak pattern with coupling constants $a_N = 10.15 \pm 0.05$, $a_{H_o} = 3.30 \pm 0.05$, and $a_{H_m} = 1.10 \pm 0.05$ G (G = 10^{-4} T) for all compounds. The spectra are consistent with a high degree of spin localization on the *p*-nitrophenyl moiety. The decay of the signal at various temperatures was used to obtain kinetic data.

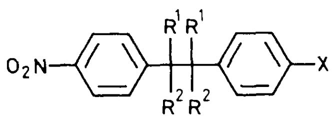
All anions decayed‡ at room temperature with conveniently measurable rates. First order kinetics were observed in all cases, regardless of the counterion and solvent use [DMSO, dimethylformamide (DMF), tetrahydrofuran (THF)]. This is in contrast to C–C bond fragmentation reported by Walsh,[4] where the kinetic order was strongly dependent on counterion. The observed rate constant for decay in DMSO at 20 °C for Li^+ ($\mathbf{1a}^{\cdot-}$) was $k_{1a} = 6.5 \times 10^{-4}\ s^{-1}$ and the measured activation parameters were $\Delta H^{\ddagger} = 22.4(8)$ kcal mol^{-1}, $\Delta S^{\ddagger} = 3(3)$ cal mol^{-1} K^{-1} (cal = 4.184 J). The electron withdrawing substituent in ($\mathbf{1b}^{\cdot-}$) accelerated the rate of cleavage substantially [$k_{1b} = 2.3 \times 10^{-2}\ s^{-1}$, $\Delta H^{\ddagger} = 17(1)$ kcal mol^{-1}, $\Delta S^{\ddagger} = -8(4)$ cal mol^{-1} K^{-1}], indicating a significant charge transfer across the scissile bond in the transition state. The radical anions of slightly less strained[5] (**2a**) and (**2b**) disappeared at slower rates [$k_{2a} = 8.9 \times 10^{-5}\ s^{-1}$, $\Delta H^{\ddagger} = 25.2(6)$ kcal mol^{-1}, $\Delta S^{\ddagger} = 9(2)$ cal mol^{-1} K^{-1}; $k_{2b} = 2.9 \times 10^{-4}\ s^{-1}$, $\Delta H^{\ddagger} = 22(1)$ kcal mol^{-1}, $\Delta S^{\ddagger} = 1(4)$ cal mol^{-1} K^{-1}].

Under conditions similar to those in the kinetic runs, the products collected after four or five half-lives at room temperature were derived from cleavage of the central C–C bond and accounted for 80—90% of the mass balance. The identity of the products was dependent on the work-up procedure. In general, quenching with oxygen gave tertiary *p*-nitrobenzyl alcohols and X-substituted styrenes, while treatment of the reaction mixtures with deoxygenated methanol yielded corresponding benzylic hydrocarbons. In addition to 'half-molecule' products, small amounts of radical coupling products derived from unsubstituted (X = H) radicals were also observed. Although the isolated products are consistent with the expected formation of the benzylic anions and radicals, the redox processes§ in the reaction mixture and work-up make unambiguous assignment of the product origins difficult.

The reversibility of the cleavage process was probed with ($\mathbf{2a}^{\cdot-}$) and ($\mathbf{2b}^{\cdot-}$). The radical anions of the nitro compounds derived from the *meso* and (±) hydrocarbons were allowed to react (in separate experiments) for three half-lives. The reaction was quenched with $MeOH/H_2O$ and the unreacted (**2a**) and (**2b**) were recovered and examined by n.m.r. spectroscopy. No isomerization (<1%) was detected in either case. We conclude that within the usual limits of such a test the fragmentation reaction is irreversible.

The measured activation parameters allow us to exclude an electron jump to the non-nitrated ring as a kinetically significant step in the cleavage. The difference in reduction potential[7] between *p*-nitrotoluene and *p*-cyanotoluene corresponds to *ca.* 27 kcal mol^{-1}, while the observed $\Delta G^{\ddagger}$ for ($\mathbf{1b}^{\cdot-}$) is only 19.5 kcal mol^{-1} (at 300 K). Such an exclusion is important for unambiguous interpretation of substituent effects and other mechanistic aspects.

The observed activation parameters indicate significant bond activation upon one-electron reduction. For comparison, the homolytic cleavage[5] of the parent hydrocarbon of (**1**) has $\Delta H^{\ddagger} = 42$ kcal mol^{-1}, $\Delta S^{\ddagger} = 26$ cal mol^{-1} K^{-1} and activation energy $\Delta G^{\ddagger} = 34$ kcal mol^{-1}, higher than that for ($\mathbf{1a}^{\cdot-}$) by *ca.* 13 kcal mol^{-1} (300 K). A similar trend is observed for (**2a**), where the hydrocarbon analogue[5] has $\Delta G^{\ddagger} = 31$ kcal



(**1a**) X = H, $R^1 = R^2 = Et$
(**1b**) X = CN, $R^1 = R^2 = Et$
(**2a**) X = H, $R^1 = Me$, $R^2 = Pr^i$ (*meso*)
(**2b**) X = H, $R^1 = Me$, $R^2 = Pr^i$ (±)

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† Details of these studies will be published elsewhere. Compare also ref. 5.

‡ The quoted kinetic data are for the Li^+ salts at 20 °C. The estimated errors of rate constants are ±15%. The standard deviations of the least significant digit for the activation parameters are in parentheses.

§ These processes include single electron-transfer between the radicals, anions, and radical anions as well as reaction with O_2.

mol^{-1} for homolytic cleavage, while (**2a**$^{-\cdot}$) fragments with $\Delta G^{\ddagger}$ = 22 kcal mol^{-1}. Interestingly, the entropies of activation for scission of radical anions are much smaller than those for homolytic cleavage.[5] This fact can be attributed to incomplete release of strain in the transition state for cleavage of the radical anions or to loss of degrees of freedom due to solvent rearrangement associated with fragmentation. It should be noted that the reductive activation of C–C bonds for cleavage is expected to be larger in compounds which are poorer electron acceptors than nitroaromatics.

The reported facile fragmentation of C–C bonds in radical anions provides us with a convenient experimental system to probe the reductive activation of C–C bonds in more detail.

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