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The Role of the Leaving Group in the Dissociation of Radical Anions of 9-(Aryloxymethyl)anthracenes

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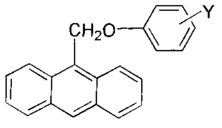
The formation and subsequent dissociation of radical anions ($RX^{-\bullet}$) are important processes in connection with the $S_{RN}1$ mechanism.[1] The dissociation reaction is accompanied by the redistribution of electron density to the forming fragments. Considering the electron apportionment, two distinct modes such as a homolysis (to give $R^- + X^\bullet$) and a heterolysis (to give $R^\bullet + X^-$) are possible,[2] but a homolysis route is a rare event in organic radical anions containing a carbon−heteroatom bond (e.g., carbon−halogen and carbon−phenoxy). Maslak and Guthrie[2b] have shown that the substituent on the phenoxy ring influences the lifetime of the radical anion of *p*-nitrobenzyl phenyl ether. No attempt has been made to determine the absolute rate for dissociation of arylmethyl phenyl ether radical anions.

In this communication the kinetics for dissociation of the radical anions of substituted 9-(phenoxymethyl)anthracenes (**1a**−**f**)[3] have been determined by using the pulse radiolysis technique. The kinetic data show a significant influence of substituent on the dissociation of the radical anion.



(**1**)

a (Y = H), **b** (Y = *p*-MeO), **c** (Y = *p*-Me)
d (Y = *p*-Et), **e** (Y = *p*-F), **f** (Y = *m*-F)

1-Methyl-2-pyrrolidinone (NMP) solutions of **1a**−**f** held in Suprasil quartz cells were irradiated with an 8-ns pulse of 28 MeV electrons at room temperature and the transient absorption spectra were recorded at various times after the pulse.[4] In all cases the spectrum observed immediately after the pulse had an absorption maximum at around 710 nm and was assigned to the corresponding anthracene radical anions. All these spectra changed with time to result in a 430-nm peak, which was identical with those of **1a**−**f**. This absorption was assigned to the (9-anthryl)methyl radical by comparison with the spectrum observed by the pulse radiolysis of 9-(chloromethyl)anthracene.[5] On the basis of these observations, the sequence of events in the reductive cleavage reaction of 9-(phenoxymethyl)anthracene ($AnCH_2OPh$) can be depicted as shown in Scheme 1. That is, the reaction involves two successive distinct steps, addition of an electron to give the corresponding anthracene radical anion and then dissociation of the C−O bond to form the (9-anthryl)methyl radical ($AnCH_2^\bullet$) and phenoxide ion (PhO^-). The rate of the latter process was determined by monitoring the rate of decay of the 710-nm absorption and the rate of the concomitant buildup of the 430-nm absorption. The rates were found to be first-order and independent of the solute concentration (1−10 mM). The kinetic data gathered in Table 1 show the variation of the rate constant (k_Y/s^{-1}) with the substituent. A Hammett plot of $\log(k_Y/k_H)$ with the σ values of the substituents results in an excellent correlation (Figure 1)[6] and gives the reaction constant (ρ) of 1.62. The value of ρ indicates that the substituent electronic effect is important in the dissociation reaction.

Table 1. Rate Constants for Dissociation of the Radical Anions of **1a**−**f**

Y	k/s^{-1}
p-MeO	4.1×10^5
p-Me	5.8×10^5
p-Et	6.3×10^5
H	1.1×10^6
p-F	1.4×10^6
m-F	3.8×10^6

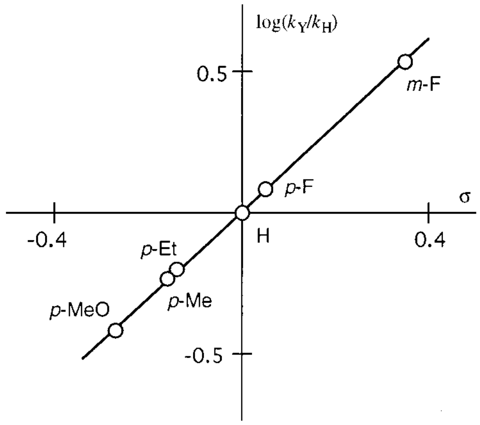


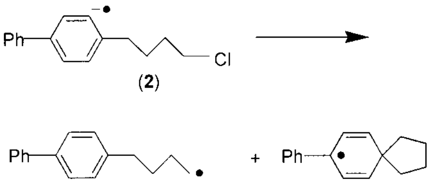
Figure 1. Hammett plot of $\log(k_Y/k_H)$ versus σ for the dissociation reaction of the radical anions of **1a**−**f** in 1-methyl-2-pyrrolidone.

Scheme 1

$$AnCH_2OAr \xrightarrow{e^-} {}^{-\bullet}AnCH_2OAr$$

$$\longrightarrow AnCH_2^\bullet + ArO^-$$

Scheme 2



(**2**)

(**3**) (**4**)

We previously reported that, as shown in Scheme 2, the radical anion of 1-(*p*-biphenylyl)-4-chlorobutane (**2**, $\lambda_{max} = 410$ nm), generated by the reaction with the solvated electron, reacts unimolecularly to give a mixture of the dissociative ET and S_N2

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[1] (a) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734. (b) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413. (c) Bowmann, W. R. *Chem. Soc. Rev.* **1988**, *17*, 283. (d) Saveant, J.-M. *Tetrahedron* **1994**, *50*, 10117.

[2] (a) Maslak, P.; Guthrie, D. R. *J. Am. Chem. Soc.* **1986**, *108*, 2628. (b) Maslak, P.; Guthrie, D. R. *J. Am. Chem. Soc.* **1986**, *108*, 2637. (c) Guthrie, R. D.; Shi, B. *J. Am. Chem. Soc.* **1990**, *112*, 3135. (d) Maslak, P.; Vallombroso, T. M.; Chapman, W. H., Jr.; Narvaez, J. N. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 73.

[3] (a) The ethers **1a**−**f** were synthesized according to the literature procedure.[3b] (b) Tamura, Y,; Yamamoto, G.; Oki, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1781.

[4] The apparatus for the pulse radiolysis experiments was described in a previous paper.[6b]

[5] (a) The reductive cleavage of 9-(chloromethyl)anthracene occurs via a concerted electron transfer−bond breaking mechanism.[9b] (b) Andrieux, C. P.; Le Gorande, A.; Saveant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 6892.

[6] (a) Such a correlation is observed for radical anions of arylhalide[6b] and 1-benzoyl-ω-haloalkanes.[6c] (b) Saveant, J.-M. *Tetrahedron* **1994**, *50*, 10117. (c) Kimura, N.; Takamuku, S. *J. Am. Chem. Soc.* **1994**, *116*, 4087.

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type products such as 1-(*p*-biphenylyl)-4-butyl radical (**3**, $\lambda_{max} \ll 300$ nm) and 8-phenylspiro[4.5]-6,8-decadienyl radical (**4**, $\lambda_{max} = 330$ nm).[7] It was found that the rate constants (k_{410} and k_{330}, s^{-1}) determined from the decay of the 410-nm absorption and the concomitant buildup of the 330-nm absorption have the same value, irrespective of the product ratio, and increase linearly with an increase in the polarity of the solvent. The results led to the conclusion that the formation processes of **3** and **4** involve a common rate-determining step (i.e., concerted electron-transfer and bond-dissociation process), and hence the radical anion, at first of the π-type would acquire σ-character (i.e., carbanion-like) at the transition state.[8] If the electron transfer takes place from a π^* radical anion, **4** is not formed because a terminal carbon radical (i.e., **3**) does not react with the aromatic moiety.

Similarly, the dissociation rate of the radical anion was found to be dependent on the nature of the solvent. Empirical parameters of solvent polarity are as useful as the empirically derived Hammett constants used in the prediction of substituent effects in chemical reactions. Two empirical parameters introduced by Gutmann[9] are the donor number (DN) and the acceptor number (AN), which reflect the nucleophilic and electrophilic properties of the solvent. Since the reactant and product in the present reaction are anions, the parameter of interest is AN. Figure 2 illustrates the variation of the dissociation rate constant (log k_H) with AN. It is apparent that the dissociation rate increases with increasing AN, namely, solvent polarity. This trend is similar to that found for the intramolecular reaction (Scheme 2). A similar dependence of solvent influence on the reaction rates suggests the presence of a common mechanism as the rate-determining step. The positive slope for the reaction rate indicates that, on the basis of the Hughes−Ingold rules for solvent effects,[10] the negative charge is more localized in the transition state subjected to intense solvation than in the initial state of the radical anion.

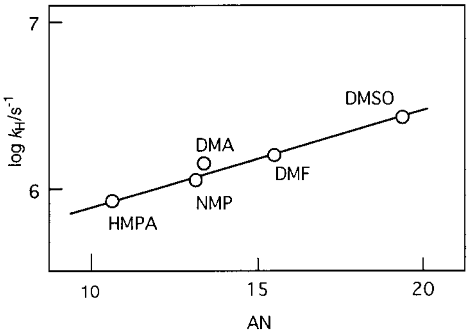

Figure 2. Variation of the dissociation rate constant (log k_H, s^{-1}) of the radical anion of **1a** with the acceptor number (AN) of the solvents: hexamethylphosphoric triamide (HMPA), NMP, dimethylacetamide (DMA), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO).

The results of solvent and substituent effects suggest the participation of a polarized configuration in the reaction.[11] The dissociation mechanism of the radical anion of 9-(phenoxymethyl)anthracene is considered to be the same as that described for the intramolecular reaction in Scheme 2.

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[7] (a) Kigawa, H.; Takamuku, S.; Toki, S.; Kimura, N.; Takeda, S.; Tsumori, K.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 5176. (b) Kimura, N.; Takamuku, S. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1662.

[8] (a) Similarly, a quantum mechanical study led to the conclusion of a substantial σ character of the radical anion in the dissociation reaction.[8b] (b) Moreno, M.; Gallard, I.; Bertian, J. *J. Chem. Soc., Perkin Trans. 2* **1989**, 2017.

[9] Gutmann, V. *Electrochim. Acta* **1976**, *21*, 66.

[10] Ingold, C. K. *Structure and Mechanism in Organic Chemistry*; Cornell University Press: New York, 1969.

[11] (a) In analogy with the solvent effect, the heterolytic dissociation is very much dependent on the electrophilic assistance by the counterion.[11b] (b) Casado, F.; Pisano, L.; Farriol, M.; Gallardo, I.; Marquet, J.; Melloni, G. *J. Org. Chem.* **2000**, *65*, 322 and references therein.