

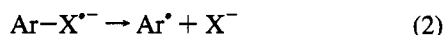
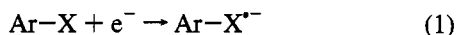
## $\sigma$ -Radical Anion as a Key Intermediate in the Dissociation Reaction of Aryl Halide Radical Anions

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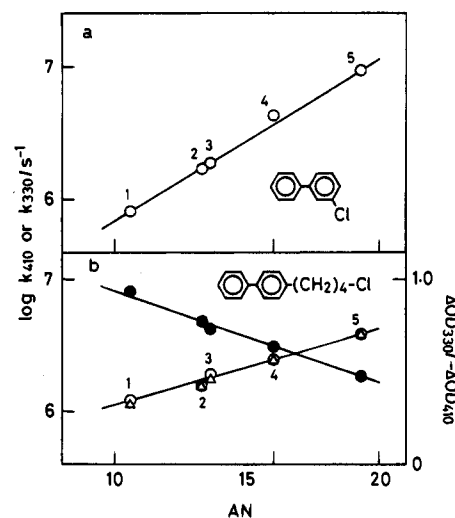
The dissociative electron capture of aryl halides involves two successive and distinct steps: the injection of one electron forming the radical anion and then the dissociation of a carbon–halogen (C–X) bond to form a  $\sigma$ -aryl radical and a halide ion (reactions 1 and 2).



Mechanistic and kinetic information for these reactions is provided from electrochemical<sup>1</sup> and pulse radiolysis<sup>2</sup> studies. For reaction 2 an intramolecular electron-transfer (ET) mechanism has been proposed where the unpaired electron, first located in the  $\pi^*$  orbital of the aromatic moiety, is transferred, with concerted breaking, into the C–X  $\sigma^*$  orbital<sup>1b</sup> or the halogen atom.<sup>2b,c</sup> On the other hand, a quantum mechanical study has shown that the rate-determining step of reaction 2 is the breaking of the C–X bond in the  $\sigma$  radical anion with the localization of the negative charge at an *ipso* carbon atom.<sup>3</sup>

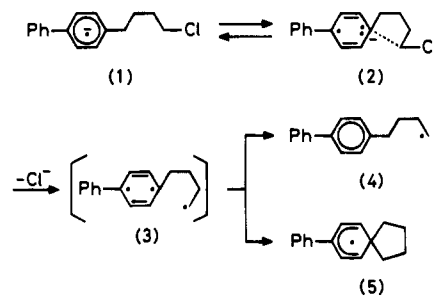
We have previously found that the radical anions of 1-aryl- $\omega$ -haloalkanes [ $\text{Ar}(\text{CH}_2)_n\text{X}$ ;  $\text{Ar} = p\text{-C}_6\text{H}_5\text{C}_6\text{H}_4$  ( $\text{BP}_{\text{X}-n}$ ) and  $\text{C}_6\text{H}_5\text{CO}$  ( $\text{BZ}_{\text{X}-n}$ )] undergo intramolecular reactions in which dissociative ET and  $\text{S}_{\text{N}}2$  products are competitively formed (see, for example, Scheme 1). The yield of a cyclic radical decreases with an increase in the reaction rate depending upon the donor ability of the radical anion, the leaving ability of the halogen, and the polarity of the solvent.<sup>4</sup> In the same manner, the dissociation reaction of  $\text{ArX}^{\cdot-}$  was found to be sensitive to the polarity of the solvent.<sup>5</sup> The present study provides the first experimental evidence for the presence of the  $\sigma$  radical anion as a key intermediate in reaction 2.

Figure 1 illustrates the variation with an acceptor number (AN)<sup>6a</sup> (a measure of the electrophilic properties of the solvent) in the decay rate constants ( $\log k_{410}$ ,  $\text{s}^{-1}$ ) of the radical anions ( $\lambda_{\text{max}} = 410 \text{ nm}$ ) of  $m\text{-C}_6\text{H}_5\text{C}_6\text{H}_4\text{Cl}$  and  $\text{BP}_{\text{Cl}-4}$  (1) and the formation rate constant ( $\log k_{330}$ ,  $\text{s}^{-1}$ ) of a spirocyclic radical (5;  $\lambda_{\text{max}} = 300 \text{ nm}$ ; Scheme 1) generated by an  $\text{S}_{\text{N}}2$  reaction. It



**Figure 1.** Variation in the decay rate constants ( $\log k_{410}$ ) of the radical anions of *m*-chlorobiphenyl (a) and  $\text{BP}_{\text{Cl}-4}$  (b) (O) with the acceptor number (AN) of the solvent. The formation rate constant ( $\log k_{330}$ ) of a spirocyclic radical ( $\Delta$ ; see Scheme 1) and its yield ( $\bullet$ ;  $\Delta\text{OD}_{330}/\Delta\text{OD}_{410}$ ): 1, hexamethylphosphoric triamide; 2, *N*-methyl-2-pyrrolidone; 3, *N,N*-dimethylacetamide; 4, *N,N*-dimethylformamide; 5, dimethyl sulfoxide.

### Scheme 1



is apparent that the rate constants increase with increasing AN, namely, solvent polarity. A good correlation was also found using the Reichardt–Dimroth polarity parameter,  $E_{\text{T}}(30)$ .<sup>6b</sup> The positive slope for the rate constants was also obtained for  $p\text{-CH}_3\text{-COC}_6\text{H}_4\text{Cl}$  and  $\text{BZ}_{\text{Cl}-4}$ , as shown in Figure 2. The same dependence of solvent effects on the reaction rates, observed in both the aryl chloride and intramolecular systems, suggests the presence of a common mechanism as the rate-determining step. The positive slope for the reaction rates indicates, on the basis of the Hughes–Ingold rules,<sup>7</sup> that *the negative charge is more localized in the transition state subjected to intense solvation than in the initial state of the radical anion.*

The yield of 5 ( $\lambda_{\text{max}} = 330 \text{ nm}$ ) from 1 ( $\lambda_{\text{max}} = 410 \text{ nm}$ ) indicated as the ratio  $\Delta\text{OD}_{330}/\Delta\text{OD}_{410}$  decreases with increasing reaction rate (Figure 1b).<sup>8</sup> However, the two rate constants ( $k_{410}$  and  $k_{330}$ ) measured in each solvent are in good agreement within experimental error. It is, therefore, clear that the dissociative ET and  $\text{S}_{\text{N}}2$  reactions are governed by the same activation–driving force–free energy relationship. The recent observation indicated that the yield of a cyclic radical ( $\text{S}_{\text{N}}2$  product in  $\text{BZ}_{\text{Br}-n}$ ) is mainly controlled by the spatial distribution of the radical pair (distance and angle) initially formed.<sup>4d</sup> These results provide clear evidence for the presence of the  $\sigma$  radical anion (2) as illustrated in Scheme 1. If an electron transfer

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(8) A value of  $\Delta\text{OD}_{330}/\Delta\text{OD}_{410}$  was obtained as a ratio of the intensity of the 330 nm band formed with the intensity of the 410 nm band decayed. Total yield of the formation of 4 and 5 should be equal to the initial amount of 1 (see Scheme 1).

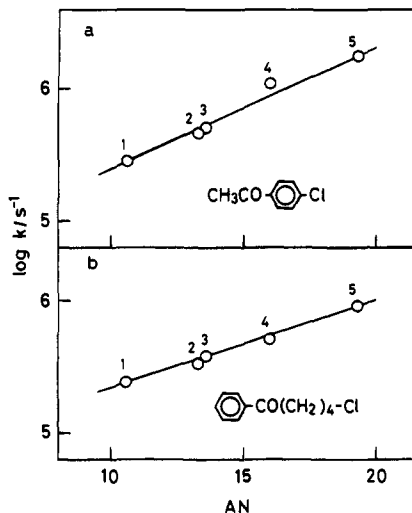
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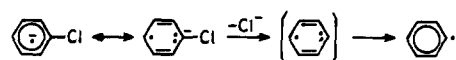


**Figure 2.** Variation in the decay rate constants ( $\log k$ ) of the radical anions of *p*-chloroacetophenone (a) and BZCl-4 (b) with the acceptor number of the solvent: 1, hexamethylphosphoric triamide; 2, *N*-methyl-2-pyrrolidone; 3, *N,N*-dimethylacetamide; 4, *N,N*-dimethylformamide; 5, dimethyl sulfoxide.

takes place from a  $\pi^*$  radical anion, a new bond is not formed because a terminal carbon radical (4) does not react with the aromatic moiety.

The rate constants for the dissociation of  $\text{ArCl}^{\bullet-}$  increase with the solvent polarity in the same manner as that of the intramolecular reactions (Scheme 1). The negative charge should therefore be localized at the carbon atom adjacent to the halogen through the dissociation process of  $\text{ArCl}^{\bullet-}$ . The

### Scheme 2



following mechanism thus emerges from these results. As the C-X bond is stretched, the negative charge that was diffused over the aromatic moiety builds up at the carbon atom adjacent to the halogen, the covalent electron pair is carried away in the 2p atomic orbital of the halogen, and the unpaired electron remains in the  $\sigma$  HOMO orbital of the aryl radical. That is, the dissociation reaction proceeds via the transition state with a localization of the negative charge at the carbon atom adjacent to the halogen.

The proposed mechanism is supported by the following results. The dissociation rate of  $\text{ArX}^{\bullet-}$  varies considerably with the nature of the halogen ( $\text{I} > \text{Br} > \text{Cl}$ ) and its position relative to another noncleavable substituent ( $o > p > m$ ).<sup>1,2</sup> These trends were rationalized by the differences in C-X bond dissociation energies and by the spin-density distribution at the various ring positions of the radical anions. In addition, the dissociation rate is dependent on the nature of the aromatic residue. A comparison of the cleavage rates observed for the cyano, acetyl, and nitro derivatives shows an order of reactivity of  $\text{CN} > \text{CH}_3\text{CO} > \text{NO}_2$ .<sup>1,2</sup> This order reflects the electron affinity of the substituent. The nitro group has a greater electron affinity and thus presents a higher barrier to dehalogenation.

In summary, we have shown that the rate constants for dissociation of  $\text{ArX}^{\bullet-}$ , as well as the rate constants for the intramolecular reactions, increase with the solvent polarity. These results provide clear evidence for the presence of the  $\sigma$  radical anion as a key intermediate in the radical anion reactions.

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