Dissociative Electron Transfer between Arene Radical Anions and 1-Iodobutane studied by Pulse Radiolysis

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The second-order rate constants for reactions between an arene radical anion and 1-iodobutane have been obtained over a range of $\log(k/dm^3\ mol^{-1}\ s^{-1})$, from ca. 6 up to the bimolecular diffusion limit; a linear dependence of $\log k$ on E° for the donor radical anion is found and interpreted in a qualitative fashion.

Electron transfer with simultaneous dissociation of a covalent bond is an important step in reactions for which a single electron transfer (s.e.t.) mechanism is proposed.[1] The dissociative electron transfer reaction between aromatic radical anions and alkyl halides is a simple model for s.e.t. reactions and its kinetics have been examined in some detail.[2—4] Reactions with $k < 10^6\ dm^3\ mol^{-1}\ s^{-1}$ were followed by a voltammetric technique. The value of $\log k$ for the reaction with a given alkyl halide was considered to depend in a quadratic manner on the reduction potential (E_D°) of the radical anion donor, in conformity with the theory of Marcus for non-dissociative electron transfer reactions.

We have applied pulse radiolysis techniques to follow reactions of 1-iodobutane with arene radical anions where $k > 10^6\ mol^{-1}\ s^{-1}$. Our results are collected in Table 1. Figure 1 illustrates the variation of $\log k$ with E_D°, combining these values with those of Saveant[3] obtained by voltammetry. There is a good linear correlation between the two variables over more than seven orders of magnitude (of k) and until the diffusion limit for fast reactions is reached. Values of E_D° are obtained from the averaged literature data,[3—5] brought to the same scale (V vs. standard calomel electrode) by noting identical compounds in individual lists.

Electrochemical studies have indicated that the electron-

Table 1. Rate constants for reaction between arene radical anions and 1-iodobutane at 20 °C.

Radical anion from:	$-E_D^\circ$/V vs. s.c.e.	log (k/dm³ mol⁻¹ s⁻¹) in DMF	log (k/dm³ mol⁻¹ s⁻¹) in NMP
Collidine	2.8[a]		9.54
α-Methylstyrene	2.54[b]	9.80	9.75
Biphenyl	2.56[c]	9.49	9.42
Styrene	2.35[b]		9.48
trans-Stilbene	2.17[c]	7.82	7.82
Pyrene	2.04[c]		6.59
Anthracene	1.92[c]	6.29[d]	6.20

[a] Taken from ref. 8. [b] From ref. 9. [c] From ref. 5. [d] Ref. 3 gives log (k/dm³ mol⁻¹ s⁻¹) = 5.95.
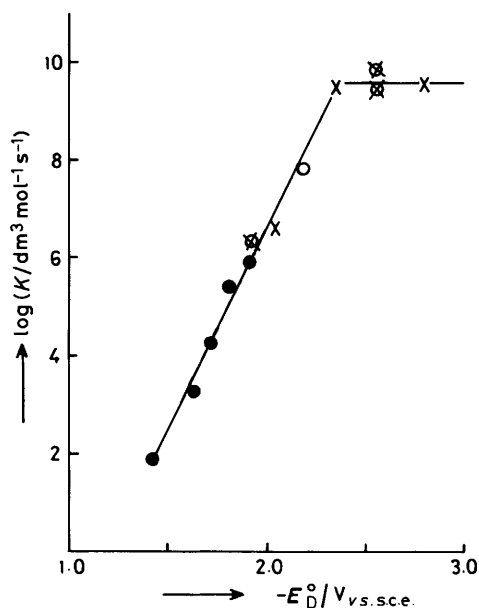
Figure 1. Depence of the rate constant (k) for the reaction between arene radical anions and 1-iodobutane on the redox potential (E_D°) for the arene/radical anion couple; (●) experimental points from ref. 3, (○) experimental points in dimethylformamide, (×) experimental points in N-methylpyrrolidine; all at 20 °C. Gradient of slope is $0.49F/2.3RT$, horizontal line has $k_{diff} = 4.0 \times 10^9$ dm³ mol⁻¹ s⁻¹.

transfer step is of the outer-sphere type and follows equation (1). Our rate measurements cannot rule out a type of inner-sphere nucleophilic substitution [equation (2)]. However the good linear relationship does not support the nucleophilic substitution process where, over the range of substrates studied, steric effects would be expected to lead to a scatter of experimental points.

$$Ar^{\cdot-} + BuI \longrightarrow Ar + Bu^{\cdot} + I^- \quad (1)$$

$$Ar^{\cdot-} + BuI \longrightarrow [Ar\text{--}Bu]^{\cdot} + I^- \quad (2)$$
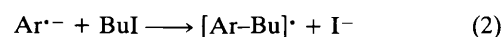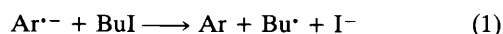
In our work, the same rate constants, within experimental error, were obtained in both dimethylformamide (DMF) and N-methylpyrrolidone (NMP). There is sufficient overlap between the rate window available here with that available through voltammetric techniques for the reaction using anthracene radical anion to be followed by both techniques. The rate constants found agree within experimental error.
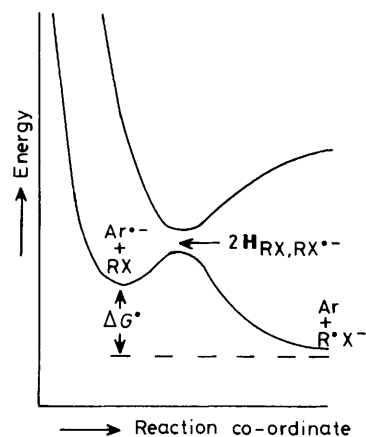
Figure 2. Reaction co-ordinate diagram for the process $Ar^{\cdot-} + BuI \rightarrow Ar + Bu^{\cdot} + I^-$.

The arene radical anion was generated by irradiation of solutions containing the arene (0.01—0.025 mol dm⁻³) with 100 or 200 ns, ca. 25 Gy pulses of 2.5 MeV electrons from a Van de Graaf accelerator. The pseudo-first-order decay of the radical anion by reaction with an excess of 1-iodobutane was followed through the change in optical absorption. A second-order rate constant for the electron transfer process was obtained from a series of experiments using at least four different concentrations of 1-iodobutane. The temperature dependence of k was investigated but is not reported here.

Classical Marcus theory assumes that electron transfer is dominated by solvent vibrations (v ca. 1 cm⁻¹)[6] with perturbation from ligand vibrations in the substrate. The dissociative electron transfer here is dominated by bond cleavage, i.e. strong ligand vibrations (for the C–I bond v ≈ 600 cm⁻¹).[2,3] Although there is evidence[7] that non-dissociative electron-transfer reactions follow a parabolic dependence in certain circumstances, the data reported here for dissociative electron transfer between arene radical anions and 1-iodobutane clearly are not in accordance with such a dependence. A reassessment of the theoretical description for this dissociative electron transfer is necessary in view of the lack of experimental evidence for a quadratic dependence between log k and E_D°.

From a consideration of the intersection of the Morse curve for the C–X bond of the halide and the dissociative curve of the $RX^{\cdot-}$ species, Saveant[2] has shown, subject to certain approximations, that an analytical solution can be found for $\Delta G^\ddagger$ versus ΔG° [equation (3), where $\Delta G^\ddagger$ is the free energy of activation of the reaction and $\Delta G_0^\ddagger = D_{RX}/4 + \lambda_0/4$, D_{RX} being the RX bond dissociation energy and λ_0 the Marcus solvent reorganisation energy]. This analytical solution predicts a quadratic dependence of log k on E_D° that is not observed experimentally.

$$\Delta G^\ddagger = \Delta G_0^\ddagger (1 + \Delta G^\circ/4\Delta G_0^\ddagger)^2 \quad (3)$$

It is necessary to extend this view to take in orbital interactions at the transition state. Whereas there is only weak interaction across the van der Waals distance between the aromatic π* orbital of the donor and the halide, RX, there is likely to be strong interaction between the σ and σ* orbitals of the elongated R–X bond since these have the same symmetry about the line joining the two atoms.

The true value of $\Delta G^\ddagger$ is therefore lower than that calculated from the point of intersection of the Morse curve and the dissociative curve, as above. The lowering of the

energy barrier at the transition state due to this effect is given by $H_{RX,RX^{\cdot-}}$, the electronic matrix element between RX and $RX^{\cdot-}$ (see Figure 2), where $H_{RX,RX^{\cdot-}} = <\psi_{RX}|H|\psi_{RX^{\cdot-}}>$, and H is the Hamiltonian operator. The contribution of the donor to the free energy of the reactants and products is independent of the RX bond length. The effect of varying E_D° is, therefore, to raise or lower the reactant curve relative to that of the products leading to a decrease in the R–X bond length at the transition state as E_D° becomes more negative. Since $H_{RX,RX^{\cdot-}}$ is expected to be a strong function of the R–X bond length, $\Delta G^\ddagger$ will decrease more rapidly than quadratically with respect to ΔG°, thus rationalising our observed linear relationship of log k with E_D°.

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