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The Decay Rates of Radical Anions of Polyfluorobenzoic Acids in Water

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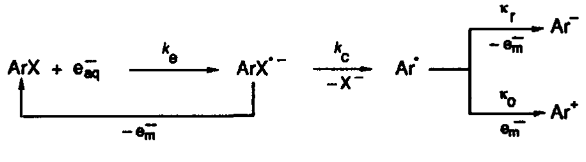
The decay rates ($k_c = 3 \times 10^3$–10^9 s^{-1}) of radical anions of polyfluorobenzoates and the redox potentials of radical anion decay products have been determined by photoelectron injection from mercury into aqueous electrolyte solutions (PIMES).

Haloarene radical anions are of major importance as intermediates in $S_{RN}1$ substitution and reductive dehalogenation reactions.[1–4] However, data on transient radical anions and the radical products of their decay, particularly in protic media, are rather scarce. PIMES can be used to study short-lived electron adducts in any polar liquids,[5,6] which makes this method rather promising as regards the solution of similar problems. Earlier, the potential of this technique was convincingly demonstrated by studying the radical anion decay of monohalobenzoic acids.[6]

Radical anions $ArX^{\cdot -}$ result from the acceptance of solvated electrons arising from photoinjection by the corresponding arene.[6,7] Thereafter some of the radical anions diffuse to the photoelectrode where they are oxidized. Other radical anions decompose to form the aryl radicals $Ar^{\cdot}$ which can be either oxidized or reduced depending on the electrode potential, Scheme 1.



Scheme 1

Within the framework of Scheme 1, for the case of Ar reduction, the measured residual photoinduced charge of electrode Q_∞ is related to the decay rate k_c by eqn. (1),[6]

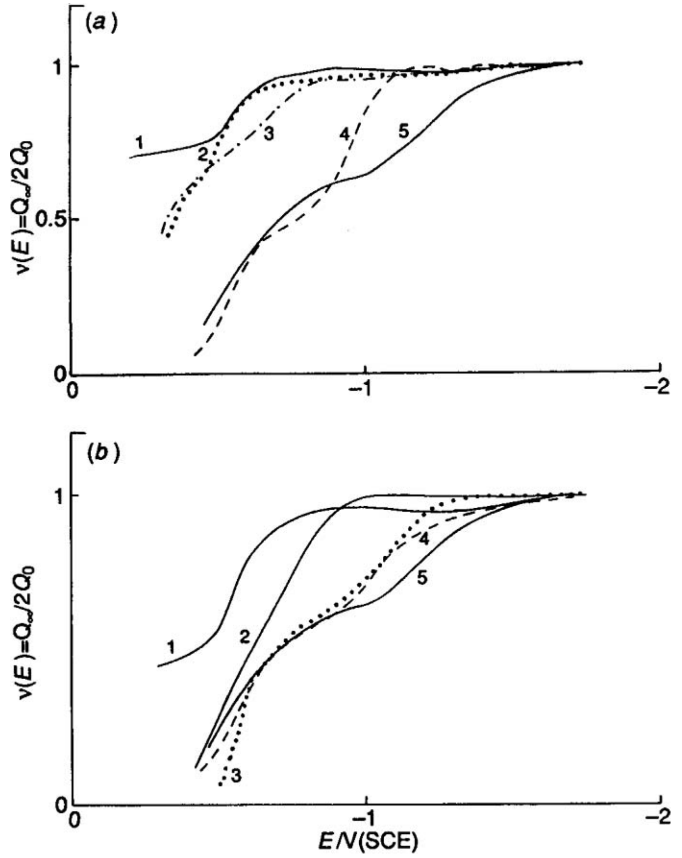


Fig. 1 Photopolarograms $\nu(E) = Q_\infty(E)/2Q_0(E)$ of fluorinated benzoates (normalized to maximum). (*a*) 1: $C_6F_5CO_2^-$; 2: 2,3,5,6-F_4-$C_6HCO_2^-$; 3: 3,4,5-F_3-$C_6H_2CO_2^-$; 4: 2,4,6-F_3-$C_6H_2CO_2^-$; 5: 4-F-$C_6H_4CO_2^-$; (*b*) 1: 2,3-F_2-$C_6H_3CO_2^-$; 2: 3,4-F_2-$C_6H_3CO_2^-$; 3: 2,4-F_2-$C_6H_3CO_2^-$; 4: 2,6-F_2-$C_6H_3CO_2^-$; 5: 4-F-$C_6H_4CO_2^-$

$$\frac{Q_{\text{lim}}}{2Q_0} = 1 - \exp(-x_1/l_a); \quad Q_{\text{lim}} = Q_\infty(N_a)|_{N_a \to \infty} \qquad (1)$$

where Q_0 is the full photoinjected charge, x_1 is the mean distance between e_{aq}^- and the photoelectrode plane, $l_a = (D_a/k_c)^{1/2}$, D_a is the radical anion diffusion coefficient and N_a is the acceptor concentration. The parameters Q_0 and x_1 are estimated from the measurements using acceptors whose radical anions have a short lifetime, *e.g.* N_2O ($k_c \geqslant 5 \times 10^9$ s^{-1}).[8]

A pulsed-laser photoelectrochemical set-up[6,8] was used, which contained a three-electrode cell with a replaceable fixed-mercury electrode. Measurements were performed for a 0.5 mol dm^{-3} KCl (+KOH) aqueous solution, pH = 13.4.

In order to use eqn. (1) one should initially obtain the photopolarograms $\nu(E) = Q_\infty(E)/2Q_0(E)$ for all substances and determine the range of electrode potentials (E) for which the radical anion decay products are reduced [which corresponds to the climb of $\nu(E)$ to the plateau]. According to the $\nu(E)$ dependence, Fig. 1(*a*, *b*), the characteristic potential of the climb to the plateau ($E_{0.9}$) is dependent on both the number of fluorine atoms and their position in the aromatic ring. The potentials chosen as corresponding to the level 0.9 of the maximum value of ν are listed in Table 1.

The concentration dependences $Q_\infty(N_a)$ were measured at the potential $E = -1.6$ V corresponding to the rise to the plateau in the photopolarograms of all fluorobenzoates. The diffusion coefficient for all radical anions was assumed to be equal to the value for toluene, $D_a = 8 \times 10^{-6}$ cm^2 s^{-1}.[9] The decay rates k_c are summarized in Table 1.

Assuming that the radical anion decay is caused by cleavage across the C–F bond, the regularities observed can be analysed using the concepts available concerning the mechanism of this process.[1,10–13] Decay of the π-electron radical anions *via* a planar transient complex is forbidden since the initial electronic state exhibits π-symmetry and the final one shows σ-symmetry.[10] The prohibition is, however, lifted by an out-of-plane deviation of the C–F bonds bringing about the mixing of the ground Π-, and dissociative Σ*-, terms of the radical anion. The contribution of the Σ*-state and, hence, the decay rate, increases with decreasing difference between the energies of the Π- and Σ*-states and increasing unpaired electron density on the carbon coupled with the fluorine atom.[12,13]

Table 1 The decay rates of the radical anions (k_c) and the potentials $E_{0.9}$ of the decay products

No.	Substance	k_c/s^{-1}	$E_{0.9}$/V (SCE)
1	2-F-$C_6H_4CO_2^-$	$(1 \pm 0.7) \times 10^4$	—
2	3-F-$C_6H_4CO_2^-$	$\leqslant 3 \times 10^3$	—
3	4-F-$C_6H_4CO_2^-$	$(3.3 \pm 1) \times 10^5$ $(2.3 \pm 0.5) \times 10^5$ [6] $(6 \pm 1) \times 10^5$ [7]	−1.22
4	2,3-F_2-$C_6H_3CO_2^-$	$(1.3 \pm 0.5) \times 10^7$	−0.55
5	2,4-F_2-$C_6H_3CO_2^-$	$(1.2 \pm 0.5) \times 10^7$	−1.08
6	2,5-F_2-$C_6H_3CO_2^-$	$(1.4 \pm 0.5) \times 10^5$	—
7	2,6-F_2-$C_6H_3CO_2^-$	$(1.3 \pm 0.5) \times 10^6$	−1.08
8	3,4-F_2-$C_6H_3CO_2^-$	$(4 \pm 1.5) \times 10^7$	−0.78
9	2,4,6-F_3-$C_6H_2CO_2^-$	$(6 \pm 2.5) \times 10^7$	−0.98
10	3,4,5-F_2-$C_6H_2CO_2^-$	$(2 \pm 1) \times 10^8$	−0.66
11	4-H-$C_6F_4CO_2^-$	$(2.7 \pm 1.5) \times 10^7$	−0.55
12	4-H-$C_6F_4CO_2^-$	$(2.5 \pm 1.5) \times 10^8$	−0.55
13	$C_6F_5CO_2^-$	$\leqslant 10^9$	−0.55

The data given in Table 1 show that, despite the increased strength of the C–F bond observed on accumulation of fluorine atoms,[14] the radical anion lifetime substantially decreases rather than increases. Such an alternation of k_c indicates that the above factors characterizing the interaction between the Π- and Σ*-states are of major importance for radical anion decay varying in the direction of easier C–F cleavage. The variation of k_c in the series of isomeric compounds (4-F > 2-F > 3-F; 2,4-F_2 > 2,6-F_2 > 2,5-F_2) indicates that the easiness of C–F bond cleavage with change in C–F bond position relative to the carboxylate group varies in the order *meta* < *ortho* < *para*, corresponding to the electron density distribution expected for the Π-state of benzoate radical anions.[15] However, it is readily seen that the mutual disposition of the fluorine atoms has a greater effect on the k_c value than their position relative to the carboxylate group. In this case, the radical anion stability drastically decreases with the fluorine atoms occupying the neighbouring sites; this is confirmed by the ratios between the k_c values: 2,5-F_2 < 2,3-F_2; 2,4-F_2 < 3,4-F_2 and 2,4,6-F_3 < 3,4,5-F_3. In a qualitative fashion this effect can be explained by the mutual electrostatic repulsion of the neighbouring fluorine atoms which surely needs a more rigorous theoretical rationalization.

Although there is a fair similarity between the photopolarograms $\nu(E)$ and the usual polarographic waves, these can be interpreted in a somewhat different way. For Scheme 1 ($N_a \to \infty$), the relative height of $\nu(E)$ is determined by the competition between the electrode reaction rates of oxidation (κ_0) and reduction (κ_r) of the radical anion decay products.[5,6] In this case the anode potential range ($\kappa_0 \gg \kappa_r$) corresponds to $\nu = 0$, and the climb to the plateau in the cathode range ($\kappa_0 \ll \kappa_r$) corresponds to $\nu = 2$. The final registration time can give a pre-wave with $\nu = 1$.[5]

Note that the shape of curves $\nu(E)$ generally corresponds to the dependence of the easiness of radical anion fragmentation on the mutual disposition of the fluorine atoms and carboxylate group discussed above. The variation in $E_{0.9}$ observed for the series of substances under study could actually characterize the dependence of the capability of Ar˙ to be reduced on the number and location of fluorine atoms, since the E^* potential at which $\kappa_0 = \kappa_r$ is related to the standard redox potential E_0 as $E^* + E_0 = \text{const}$.[5] However, we believe that a detailed discussion of photopolarograms is so far untimely since the nature of the decay products participating in the electrode reaction is not clear. In particular, the formation of organomercury compounds cannot be ruled out.[16]

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