Kinetic Evidence for Direct Electron Transfer between Tris(4-bromophenyl)ammoniumyl and the Acetate Anion in Acetonitrile Solution

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The reaction between tris(4-bromophenyl)ammoniumyl, electrogenerated from the parent amine, and the acetate anion has been studied in acetonitrile solution using rotating disc voltammetry and shown to involve a direct electron transfer reaction, resulting in an EC′ mechanism, in contrast to a previously reported suggestion that acylation of the radical cation was the dominant reaction pathway under these conditions.

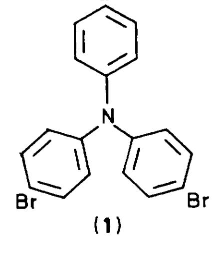
The uses of the cation radical ($\mathbf{1}^{+\cdot}$) of tris(4-bromophenylamine)(**1**) for diverse homogeneous oxidations are well known.[1,2] The cation radical ($\mathbf{1}^{+\cdot}$) has been shown to oxidise carboxylate anions[2,3] and Steckhan[3] proposed an electron transfer reaction (1). This was strongly disputed by Eberson[4] who, for the case R = Me, considered acyloxylation of the aryl groups to be the reaction mode and showed, *via* product analysis, that the reaction carried out homogeneously produced the 2-acetoxy compound [reaction (2)]. When this reaction was initiated *via* electrochemical oxidation of (**1**) the process seemed to proceed *via* an ECE type pathway[4] in contrast to the EC′ scheme required by Steckhan's proposal. The observations of Steckhan and Eberson are contradictory although a significant difference may be that Eberson[4] used the complex $(MeCO_2)_2H^-$ rather than acetate anions.

$$RCO_2^- \rightarrow R^\cdot + CO_2 + e^- \qquad (1)$$

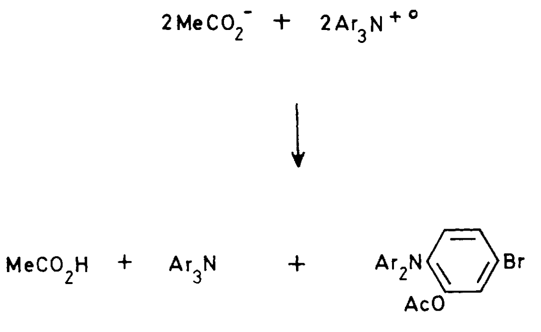
We have re-investigated the mechanism of the reaction between acetate and ($\mathbf{1}^{+\cdot}$) using rotating disc voltammetry. Experiments were conducted in dried, distilled acetonitrile. Tetrabutylammonium perchlorate (recrystallised) served as background electrolyte (0.1 mol dm^{-3}). Tetrabutylammonium acetate (>95%) and (**1**) (>98%) were used as received from Aldrich. Acetic acid was AnalaR grade. All measurements were made at a rotating platinum disc electrode (diameter *ca.* 7 mm) supplied, along with a supporting motor, motor-controller, and potentiostat, by Oxford Electrodes. Solutions were outgassed with dry argon prior to use.

The cation radical ($\mathbf{1}^{+\cdot}$) was generated electrochemically from (**1**) and the transport-limited current *vs.* rotation speed behaviour analysed. Figure 1 shows a plot of the transport-limited current as a function of the square root of the disc rotation speed (ω/Hz) for various ratios of acetate:acetic acid obtained by adding different amounts of acetic acid and tetrabutylammonium acetate to a 2.4×10^{-3} M solution of (**1**) in acetonitrile. In the absence of acetate 'Levich' type behaviour characteristic of a simple one electron oxidation [of (**1**) to ($\mathbf{1}^{+\cdot}$)] is seen.[5] A diffusion coefficient of (**1**) of 1.9×10^{-5} cm^2 s^{-1} was deduced.

Addition of acetate to (**1**) produces behaviour typical of an EC′ process[6] in which currents larger than expected for a



(**1**)



(2)

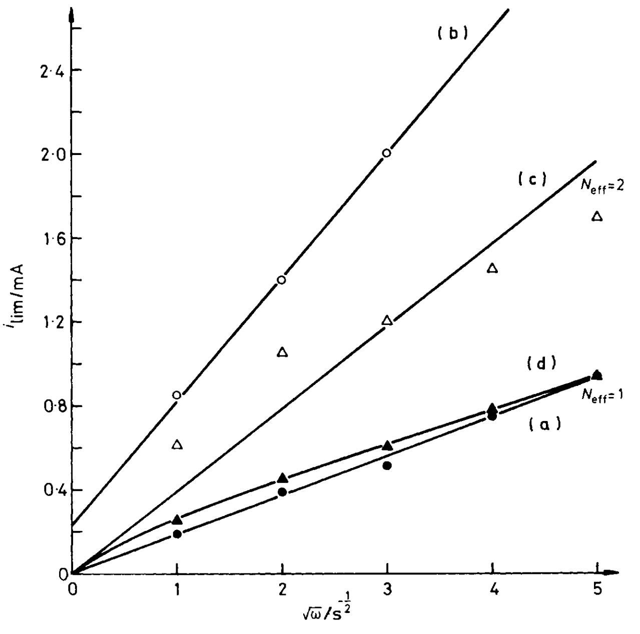


Figure 1. Transport-limited current *vs.* the square root of the disc rotation speed for a 2.4×10^{-3} mol dm^{-3} solution of (**1**), containing (a) no added $MeCO_2^-$ or $MeCO_2H$; (b) 2.3×10^{-2} mol dm^{-3} $MeCO_2^-$; (c) 2.3×10^{-2} mol dm^{-3} $MeCO_2^-$ and 2.65×10^{-2} mol dm^{-3} $MeCO_2H$; (d) 2.3×10^{-2} mol dm^{-3} $MeCO_2^-$ and 2.65×10^{-1} mol dm^{-3} $MeCO_2H$.

simple one-electron process occur and the 'effective' number of electrons, N_{eff}, transferred increases as the rotation speed is lowered. We show elsewhere[7] that these data *quantitatively* analyse as an EC′ mechanism of the 'pre-equilibrium' type [reactions (3)—(5)].[7,8]

$$Ar_3N - e^- \rightarrow Ar_3N^{+\cdot} \qquad (3)$$

$$Ar_3N^{+\cdot} + MeCO_2^- \rightleftharpoons Ar_3N + MeCO_2^{\cdot} \qquad (4)$$

$$MeCO_2^{\cdot} \rightarrow Me^{\cdot} + CO_2 \qquad (5)$$

The addition of increasing amounts of acetic acid to the solution of acetate + (**1**) results in a progressive lowering of the current and at a concentration of acetic acid of 1.59 mol dm^{-3} the behaviour was again that of a simple one-electron process. This suggests, given the known reaction (6),

$$MeCO_2^- + MeCO_2H \rightleftharpoons (MeCO_2)_2H^- \qquad (6)$$

that whereas the acetate anion can undergo electron transfer with ($1^{+\cdot}$) on the rotating disc timescale, the dimeric species cannot. The latter must evidently react slowly but homogeneously with the radical cation, presumably forming the products observed by Eberson. For intermediate concentrations of acetic acid the equilibrium is balanced so that some of the dimer can dissociate and thus react *via* the acetate anion: an ECC′ process. Under these conditions the current–rotation speed data in Figure 1 are not dissimilar from that of an ECE process,[9] namely an approximate transition in N_{eff} from one to two as the rotation speed is reduced. This then resembles Eberson's observations.

The equilibrium constant for reaction (6) is given by equation (7). Analogous equilibrium constants for many other carboxylic acids have all been found to lie within the range[10] 10^3—10^4 mol dm^{-3}. Eberson's experiments used 10^{-3} mol dm^{-3} of the dimer. Calculation suggests, assuming K in the above range, that the 'ECE' behaviour in Figure 1 might have been expected in his electrochemical experiments. Why his product analysis of the homogeneously conducted reaction showed acetoxylation as the main reaction pathway may be rationalised in terms of reactions (8)—(11), in which the first two reactions are reversible and $MeCO_2^-$ may, or may not, be derived from the dimer. It is apparent that acetoxylation will occur with high levels of (1^+); electron transfer products will be formed with low concentrations. In Eberson's homogeneous experiments the concentration is much higher than when (1^+) is generated electrochemically. The apparent contradictions in the literature may thus be reconciled.

$$K = [(MeCO_2)_2H^-]/[MeCO_2^-][MeCO_2H] \qquad (7)$$

$$Ar_3N^{+\cdot} + MeCO_2^- \rightleftharpoons Ar_2NAr^{\cdot}(H)OAc \qquad (8)$$

$$Ar_3N^{+\cdot} + MeCO_2^- \rightleftharpoons Ar_3N + MeCO_2^{\cdot} \qquad (9)$$

$$Ar_2NAr^{\cdot}(H)OAc + Ar_3N^{+\cdot} \rightarrow Ar_2NArOAc + H^+ + Ar_3N \qquad (10)$$

$$MeCO_2^{\cdot} \rightarrow Me^{\cdot} + CO_2 \qquad (11)$$

We conclude that simple electron transfer between tris(4-bromo-phenyl)ammoniumyl and acetate may indeed occur.

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