Stabilisation of Organic Cation-radicals; a Novel Anodic Synthesis of Cation-radical Salts

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Summary Cation-radicals prepared in trifluoroacetic acid show greatly enhanced stability; stable salts can be prepared simply by electrolysis in the presence of an equivalent amount of a suitable counter ion and then evaporation of the solvent.

STABLE cation-radical salts are usually prepared by oxidation of aromatic compounds.[1] Ions prepared in strong acids such as concentrated sulphuric acid for e.s.r. studies are generally not isolable from these media. The anodic preparation in aprotic media such as acetonitrile is only applicable to very stable cation-radicals since only the most stable ions show more than transient existance in polar solvents. The isolation of stable salts is possible only in large excess of supporting electrolyte. We report a superior method of preparation of stable solutions of cation-radicals and isolation of the salts.

Although pure trifluoroacetic acid has low conductivity,[2] it is possible to conduct electrolyses in this medium without using a supporting electrolyte. In a representative case, thianthrene (0·10 mmol) was subjected to constant current (10·0 mA) electrolysis in trifluoroacetic acid (50 ml) for 16·1 min (1·0 F mol^{-1}). The resulting solution of thianthrenium trifluoroacetate showed no signs of decomposition even after standing for 3 weeks. Evaporation of the solvent from this solution left the purple thianthrenium trifluoroacetate which was not stable at room temperature but apparently reacted with residual water left in the flask. This difficulty can be avoided by complete evaporation at low temperatures. When a counter ion other than trifluoroacetate is desirable, equivalent amounts of substrate and an

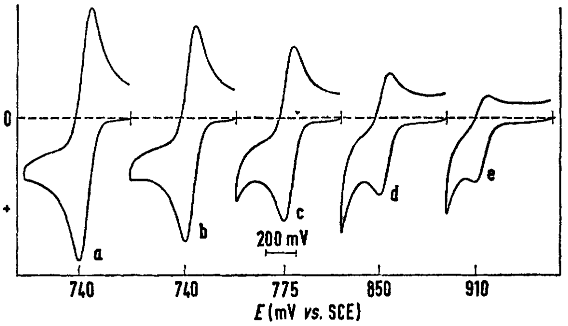

FIGURE. *Cyclic voltammetry at a platinum electrode for the oxidation of thianthrene in trifluoroacetic acid containing* $\text{Bu}^n{}_4\text{NBF}_4$. *Percent added water;* a = 0, b = 9·1, c = 23, d = 37 *and* e = 50. *Voltage sweep rate* = 150 mVs^{-1}.

acid stronger than trifluoroacetic can be electrolysed in trifluoroacetic acid. For example, electrolysis of thianthrene in the presence of perchloric acid results in the formation of thianthrenium perchlorate.

The high reactivity of cation-radicals towards water is well known. Thianthrenium ion reacts rapidly with water at low concentrations in acetonitrile.[3-5] The extraordinary stability of cation-radicals in aqueous trifluoroacetic acid is illustrated by the cyclic voltammetric behaviour of thianthrene in trifluoroacetic acid containing varying amounts of water (Figure). In reagent grade trifluoroacetic acid,† thianthrene shows a reversible cyclic voltammogram with the ratio of cathodic to anodic peak currents being equal to 1·0 (Figure a). Addition of water (1·0 ml) to this solution (10 ml) had practically no effect on the reversibility of the voltammogram (Figure b). Addition of more water (3·0 ml) gave a solution still showing a reversible redox couple (Figure c). The ratio of cathodic to anodic peak currents was slightly less than 1·0 when the solution contained 37% water (Figure d). Appreciable stability of the cation-radical on the voltammetric time scale was still observed when the solution contained 50% water (Figure e). The decrease in oxidation peak current in going from Figure a to e is due to dilution. The stability of thianthrenium ion in aqueous trifluoroacetic acid is remarkable when one considers the fact that reaction is observed in acetonitrile on the voltammetric time scale at water concentrations as low as 10 mM.[5]

Cation-radicals much less stable than thianthrenium ion can be prepared in trifluoroacetic acid. The cation-radical of 9,10-di-*p*-anisylanthracene is so unstable in acetonitrile that the cyclic voltammogram in carefully purified acetonitrile shows only a small reduction peak for the ion.[6] In trifluoroacetic acid the cation-radical appears to be stable indefinitely. However, the deep blue colour of the radical-ion fades immediately on dilution with acetonitrile. The cation-radical trifluoroacetate can be isolated by removal of the solvent and shows appreciable stability at low temperature. The general lack of knowledge about the reaction pathways of cation-radicals has recently been pointed out.[4] Even the mechanism of the apparently simple reaction, hydroxylation of thianthrenium ion, remains unsettled.[3-5] This work increases the number of accessible ions and reactions which can be used to study cation-radical chemistry.

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† Trifluoroacetic acid from Schuchardt, Munich, containing less than 0·5% water was used without further purification.

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