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THE ELECTROCHEMICAL REDUCTIVE CARBOXYLATION OF BENZALANILINE IN MOLTEN TETRAETHYL AMMONIUM p-TOLUENESULFONATE

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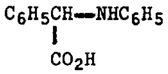
The electrochemistry of molten inorganic salt systems has been extensively studied[1,2] Several reports have appeared of the electrochemical oxidation of organic compounds to CO_2 in high temperature fuel cells. In contrast, molten quaternary ammonium salts have received little attention except in terms of physical measurements[4,6] or electrochemical studies of inorganic substances.[7,8] Molten quaternary ammonium salts are one-component solvent-supporting electrolyte systems of relatively high conductivity with the capability of dissolving both organic and inorganic substances. Their melting points usually lie in the range 50-250°C. Moreover, there exists a wide choice of aprotic as well as protogenic salts. Thus, thermally stable quaternary ammonium salts are well suited for moderate to high temperature electro-organic synthesis. To our knowledge, only a single preliminary report[9] has appeared on the electrochemistry of polycyclic aromatic hydrocarbons in molten tetrabutylammonium nitrate at 150°C.

We have found that molten tetraethylammonium p-toluenesulfonate (Et_4p-TS) is an excellent medium for electrochemical reduction reactions. The melt exhibits no noticeable decomposition over several days at temperatures between 125 and 185°C. The conductivity at 140° is 1×10^{-2} ohm^{-1} cm^{-1} and the solubility of a variety of organic substrates is high. The salt is hygroscopic and must be handled accordingly but it is easily purified by crystallization from acetone and its high solubility in water allows convenient separation from organic reaction products. A clean silver wire dipping into the melt saturated with silver p-toluenesulfonate (Agp-TS) provides a stable reference electrode for electrochemical studies.

Current-voltage curves for molten Et_4Np-TS at a Hg cathode are shown in Figure 1. At Hg, the useful potential range is from 0.0 to -2.5v. *vs.* Ag/Ag^+, while at Pt the apparent range is from ca. +4.0 to -2.5v. The large positive range is the result of a passivation effect in the oxidation of the melt which also occurs at graphite, so this salt does not appear useful for anodic reactions. As expected, saturating the melt with CO_2 exerts almost no effect on the current-voltage curve on Hg because CO_2 is reduced at more cathodic potentials in aprotic media ($E_{1/2}$ = -2.24v. in DMSO).[15] Addition of benzalaniline (1), however, markedly shifts the curve to more anodic potentials and 1 is reduced at about -1.7 V *vs.* Ag/Ag^+ (Fig. 1).

$C_6H_5CH = NC_6H_5$

1



$C_6H_5\underset{\displaystyle CO_2H}{\underset{|}{CH}}-NHC_6H_5$

2

The electrode process occurring at -1.5v is due an impurity, probably benzaldehyde, in the benzalaniline. The Tafel plot[10] for the reduction of 1 in Et_4Np-TS saturated with CO_2 at 140°C has a slope of 204 mV/decade in the linear region which corresponds to $\alpha n=0.40$. The mechanism of reduction probably involves the transfer of one electron to 1 in the rate determining step of the electrode process. A controlled potential electrolysis of 1 at -2.0 V in Et_4Np-TS saturated with CO_2 at 140° was carried out at a stirred Hg pool cathode.[11] The catholyte was then poured into cold water and extracted with $HCCl_3$ to give d,l-α-phenyl-phenylglycine[12] 2, m.p. 178-180°C formed with a current efficiency of 60%. The electrochemical synthesis of α-amino-acids by reductive carboxylation has not been reported previously, although Wawzonek and co-workers[13] have described the cathodic carboxylation of trans-stilbene in DMF.[14]

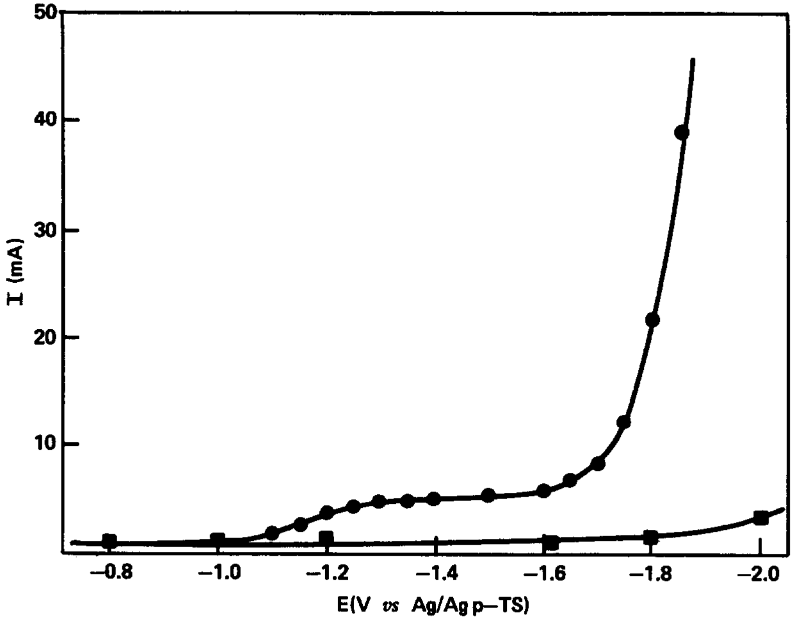


FIGURE 1. CURRENT–VOLTAGE CURVES FOR MOLTEN Et_4N p–TS AT 140°C AT A STIRRED Hg POOL CATHODE; ■–MOLTEN Et_4N p–TS UNDER N_2; ●–MOLTEN Et_4N p–TS SATURATED WITH CO_2, CONTAINING 0.2 MOLAL BENZALANILINE.

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11) A Wenking 61RS Potentiostat was employed. A 3-compartment glass electrolysis cell with fritted glass diaphragms was used and the reference compartment was separated by a very fine frit. The anode was a large Pt gauze.

12) A. McKenzie and S. C. Bate, *J. Chem. Soc.*, **107**, 1681 (1915); the I. R. spectrum and elemental analysis were consistent with the designated structure.

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14) We have also found that carboxylation of benzalaniline in DMF solution containing $(n\text{-Bu})_4NClO_4$ gives **2** in comparable yield.

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