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THE ELECTROCHEMICAL OXIDATION OF BENZIDINE

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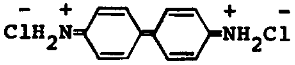
Numerous papers have appeared in the literature describing the electrochemical oxidation of aromatic amines such as aniline, phenylene diamines and substituted benzidines[1-10]. However, none has dealt with the oxidation of benzidine itself. In the course of our studies in mechanistic electro-organic chemistry, we investigated the oxidization of benzidine and wish to propose a mechanism for this oxidation which is based on polarographic as well as product analysis data.

Polarographic data was obtained on a solution of benzidine hydrochloride in 50% aqueous ethanol buffered with 0.2M NaH_2PO_4, 0.2M Na_2HPO_4. The pH was adjusted using concentrated hydrochloric acid. At pH ≤ 2, the oxidation of benzidine was found to be reversible as indicated from cyclic voltammetry on a stationary graphite disc (Figure 1). Two peaks were observed (anodic and cathodic) which were separated by 60 mv., and the height of the peaks varied linearly with the square root of the sweep rate[11].

At pH $\geq$ 3 the oxidation of benzidine hydrochloride became irreversible and the peak potential shifted to a more positive value, (Figure 2).



(I)

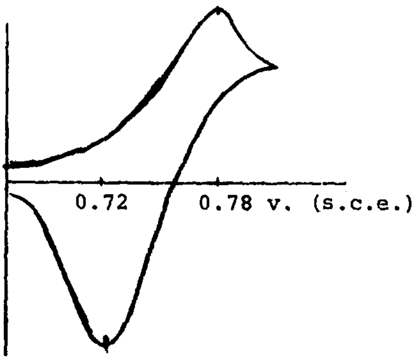


Fig. 1 - Cyclic voltammetry of benzidine hydrochloride in 50% aqueous ethanol buffered with 0.2M Na_2HPO_4, 0.2M NaH_2PO_4 pH = 0.7 sweep rate = 10 sec/inch

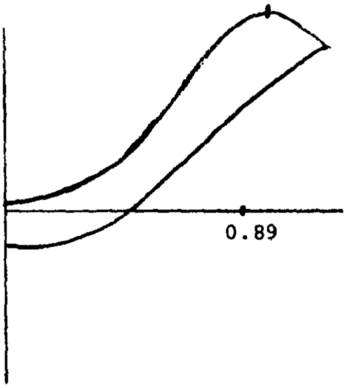
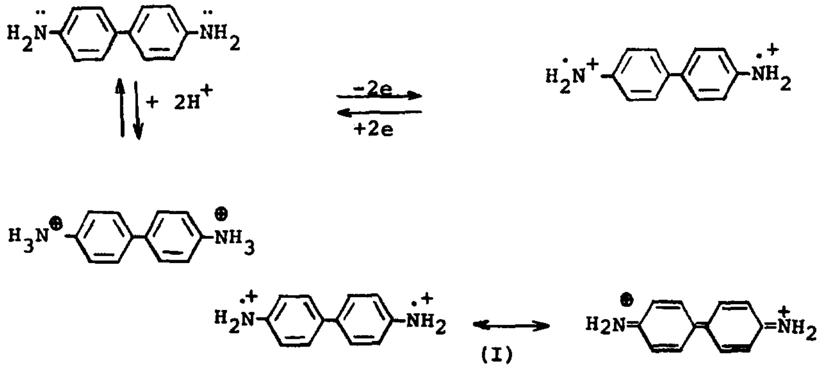


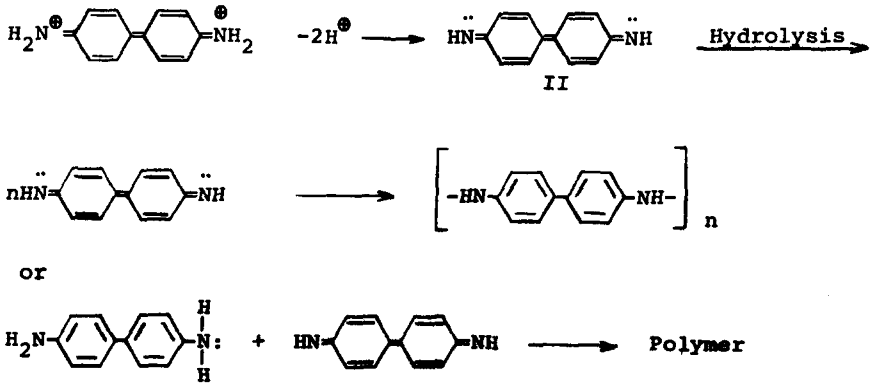
Fig. 2 - Cyclic voltammetry of benzidine hydrochloride in same solution as described under Fig 1 pH = 3 sweep rate = 10 sec/inch

Controlled potential electrolysis (1.1 v., s.c.e.), of a solution of 3.0 g. benzidine hydrochloride in 500 ml. 0.7 N HCl at a platinum electrode in an undivided cell afforded a reddish-yellow precipitate (50%) which was identified as the salt (I) from a comparison with an authentic sample[9].
The perchlorate salt of (I) is prepared in 98% yield from the oxidation of benzidine with MnO_2 in perchloric acid[12]. Its U.V. spectrum in ethanol showed the following absorbtions: λ_{max}^{EtOH} = 285, 413, 426, 446, 662 mu. The salt obtained from the electrochemical oxidation of benzidine exhibited the following U.V. absorbtions: λ_{max}^{EtOH} = 284, 410, 425, 445, 662 mu.

The electrochemical oxidation of benzidine to the corresponding salt (I), may be interpreted in terms of the mechanism proposed by Adams and coworkers[7] for the oxidation of N,N-dimethylaniline:



According to the above mechanism, at pH $\lesssim 2$, compound (I) is stable and can undergo reduction to give back starting material. However, at pH $\gtrsim 3$, a side reaction takes place as depicted below:



Compound II, if formed, is too reactive and would be expected to hydrolyze or condense with itself or benzidine to give a polymeric product. This is supported by the observation that the salt (I) was quite stable in concentrated acid solution but appeared to decompose in solutions which were neutral or slightly acidic.

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