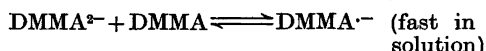


# Reactions of Aromatic Anion Radicals and Dianions. VI. The Contribution of Homogeneous Electron Transfer Reactions to Electrochemically Irreversible Electrode Processes

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The voltammetric reduction of 3,8-dimethyl-2-methoxyazocine (DMMA) was studied in THF, DMF, and acetonitrile in the presence of  $\text{Bu}_4\text{NBF}_4$  and  $\text{Me}_4\text{NBF}_4$ . When the counter ion was  $\text{Me}_4\text{N}^+$ , the reduction was observed to be a quasi-reversible process in DMF providing that proton donors were excluded. In DMF and THF, both containing traces of water, or in dry acetonitrile, the very basic  $\text{DMMA}^{2-}$  was rapidly protonated. In the presence of  $\text{Bu}_4\text{N}^+$ , the reduction of DMMA is best described by the following equations:

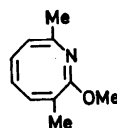


Simulated cyclic voltammograms for this mechanism were nearly identical to the experimental voltammograms. It was concluded that the reason for the slow electron transfer to DMMA at the electrode is due to an electrolyte effect rather than to the activation energy necessary to bring DMMA from the tub conformation into a planar or near planar transition state for electron transfer.

The electrochemically irreversible reduction of cyclooctatetraene (COT) to the anion radical has been related to the activation energy necessary to flatten the tub conformation of COT into a planar transition state.<sup>1</sup> Characteristic of such irreversible electrochemical processes are cyclic voltammograms in which the re-

duction peak for the substrate and the corresponding oxidation peak for the ion radical are separated by more than the theoretical amount for a one electron process, 57 mV.<sup>2</sup> The peak separation for the  $\text{COT}-\text{COT}^{\cdot-}$  couple in DMF containing  $\text{Bu}_4\text{NBF}_4$  is of the order of 200 mV at room temperature.<sup>3</sup> A much larger peak separation and hence a much slower electron transfer has been reported for a related compound, 3,8-dimethyl-2-methoxyazocine (1, DMMA). A peak separation of about 800 mV and a heterogeneous rate constant for electron transfer of  $10^{-6}$  cm/s were reported.<sup>4</sup>

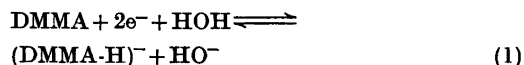
Here we report the results of a voltammetric study of the reduction of DMMA which show that the data previously reported<sup>4</sup> were obtained under conditions where the DMMA anions were rapidly protonated and are thus irrelevant to the discussion of electron transfer kinetics.



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The cyclic voltammogram of DMMA in carefully purified THF containing  $\text{Bu}_4\text{NBF}_4$  (0.2 M) was essentially the same as that previously reported<sup>4</sup> and consisted of a broad two electron reduction peak and a corresponding oxidation

peak on the reverse scan, the peak to peak separation being about 1 V. When the last traces of water or other proton donors were removed by adding activated alumina to the cell,<sup>5,6</sup> the voltammogram was characteristic for a quasi-reversible redox reaction with a peak separation of about 300 mV. Thus, the voltammogram recorded in the absence of alumina and that previously reported<sup>4</sup> were due to the electron transfer protonation reaction (1).



The rate of electron transfer between organic molecules and an electrode in aprotic media has been shown to be greater in the presence of tetramethylammonium ion than when larger supporting electrolyte cations are used.<sup>3,6a,7</sup> The voltammogram for the reduction of DMMA in DMF in the presence of  $\text{Me}_4\text{NBF}_4$  is illustrated in Fig. 1. The 2e redox couple shows a peak separation of 80 mV. The two electron reduction peak could not be resolved into consecutive 1e steps by cooling to  $-60^\circ\text{C}$  or by heating the voltammetric solution. Consequently, it appears that  $E^\circ$  for reaction (2) is at more negative potential than that for (3)

and that the product of the electrode reaction is  $\text{DMMA}^{2-}$ . That the reduction is a direct 2e process was



further demonstrated by the sweep rate dependence of the reduction peak potential. A plot of the peak separation as function of the logarithm of the voltage sweep rate was linear at sweep rates higher than  $100 \text{ mV s}^{-1}$  with a slope of 65 mV/decade. The peak potential shift for an irreversible electron transfer reaction is  $30/\alpha n_\alpha \text{ mV/decade}$ ,<sup>8</sup> *i.e.* the peak potential separation for an irreversible reduction coupled to an irreversible oxidation increases  $60/\alpha n_\alpha \text{ mV/decade}$  at  $25^\circ\text{C}$ . From the symmetry of the observed cyclic voltammogram we conclude, that  $\alpha$  must be close to 0.5, and  $n_\alpha$  must then be 2, *i.e.* it is a direct two electron reduction. The mechanism of the reduction under these conditions can be described as DMMA diffusing to and  $\text{DMMA}^{2-}$  diffusing from the electrode without the intermediate formation of  $\text{DMMA}^{\cdot-}$  (4). Under comparable

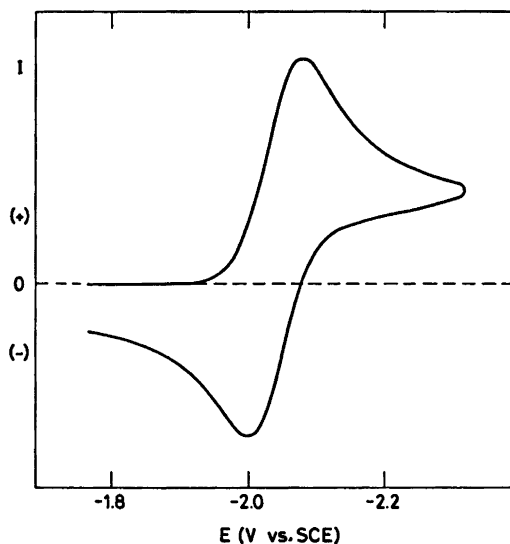


Fig. 1. Cyclic voltammogram of DMMA in DMF containing  $\text{Bu}_4\text{NBF}_4$  (0.2 M) and  $\text{Me}_4\text{NBF}_4$  (saturated). Voltage sweep rate  $240 \text{ mV/s}$ .

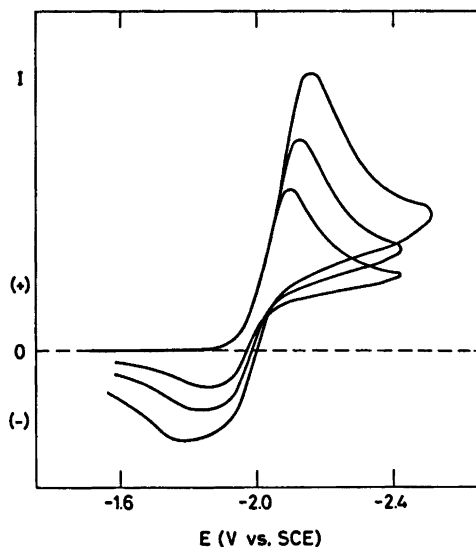


Fig. 2. Cyclic voltammograms of DMMA in DMF containing  $\text{Bu}_4\text{NBF}_4$  (0.2 M). Voltage sweep rate for voltammograms of increasing currents; 153, 310 and  $620 \text{ mV/s}$ .

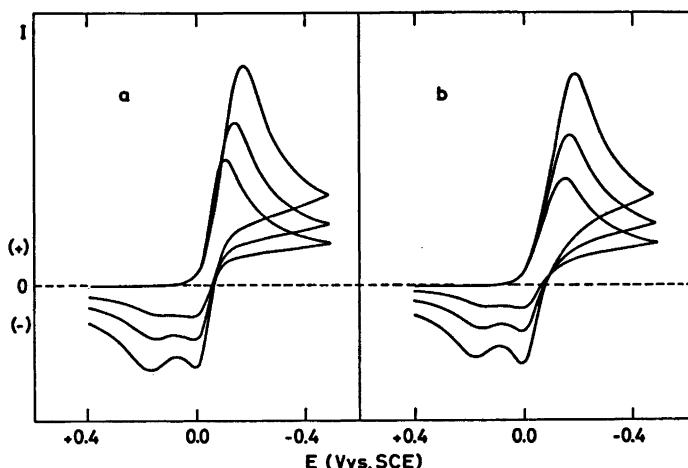
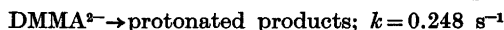
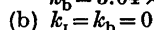
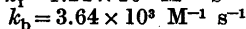
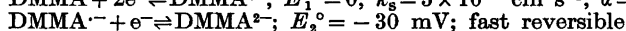
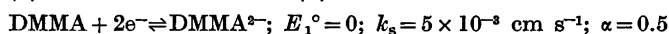


Fig. 3. Simulated cyclic voltammograms for the reduction of DMMA assuming that  $\text{DMMA} + \text{DMMA}^{2-} \rightleftharpoons 2\text{DMMA}^{\cdot-}$

(a) is fast in solution and (b) is slow in solution. The simulated mechanism is:

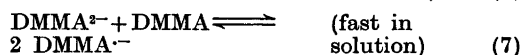


Sweep rates 620, 310 and 155  $\text{mV s}^{-1}$ ; temperature  $+11^\circ \text{C}$ . These values are calculated assuming that all diffusion coefficients are equal to  $9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ .

conditions, COT is reduced in two consecutive steps with a  $\Delta E^0$  of about 250 mV. A further contrast between COT and DMMA is the relative stability of the corresponding dianions. COT shows two reversible 1e reductions leading to  $\text{COT}^{2-}$  in acetonitrile<sup>3,8</sup> even at very low voltage sweep rates. On the other hand, no reverse current was observed during cyclic voltammetry of DMMA at voltage sweep rates up to 1 v/s. We therefore conclude that  $\text{DMMA}^{2-}$  is so basic that it is rapidly protonated by acetonitrile.

When  $\text{Bu}_4\text{N}^+$  instead of  $\text{Me}_4\text{N}^+$  was the counter ion, the mechanism of the reduction of DMMA in DMF is far more complicated than (4). The cyclic voltammograms (Fig. 2) show that the reduction peak is sharp while the oxidation gives rise to two broad overlapping peaks. The initial part of the reduction peak is independent of the voltage sweep rate, i.e. the current is determined *only* by the potential and *not* by the sweep rate. Voltammograms such as those in Fig. 2 have previ-

ously been reported<sup>1,3</sup> for COT and have been attributed<sup>1</sup> to the slow electron transfer to COT due to the activation energy for ring flattening. If the latter were the case, homogeneous electron transfer would also be slow since the same forces must be overcome. The expected cyclic voltammograms, calculated by digital simulation,<sup>9</sup> for such a case are shown in Fig. 3b. The significant differences between the observed (Fig. 2) and the calculated (Fig. 3b) voltammograms are the initial slopes of the reduction curves and the widths of the reduction peaks. The form of the experimental voltammograms (Fig. 2) are very closely reproduced by simulation (Fig. 3a) for the following reaction scheme (5–7). While the heterogeneous electron



transfer (5) to DMMA is slow due to the presence of the bulky  $\text{Bu}_4\text{N}^+$  ions, the homogeneous electron transfer to DMMA from the dianion (7) is not inhibited to the same degree. Therefore, the primary cause of the slowness of (5) cannot be the activation energy for bringing DMMA from the tub conformation into a planar or near planar transition state for electron transfer, as was previously proposed for DMMA<sup>4</sup> and originally for COT.<sup>1</sup> Although the experimental (Fig. 2) and calculated (Fig. 3a) voltammograms are nearly identical in shape, schemes other than (5–7) may possibly also fit the data.

More detailed studies of the voltammetric reduction of COT, DMMA, and related systems will appear later.

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