



## Results and Discussion

Typical cyclic voltammetric data for TMPE in  $\text{CH}_3\text{CN}$  containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) is shown in Table 1A.

The behavior exactly corresponds to a two-electron transfer:  $E_{\text{pa}} - E_{\text{pc}}$  is 30 mV and  $E_{\text{pa}} - E_{\text{pa}/2}$  is 28.5 mV as compared to the theoretical values<sup>5</sup> of 29.5 mV and 28.2 mV, respectively. Moreover the current function,  $i_{\text{pa}}/\nu^{1/2}c$ , is  $34 \mu\text{A V}^{-1/2} \text{s}^{1/2} \text{mmol}^{-1}$  l, which is about  $2^{3/2}$  times the value found for a known, one-electron oxidation of a similar molecule, 1,1-bis(*p*-N,N-dimethylaminophenyl)-2,2-diphenylethylene (12.5). Voltammetry with an RDE shows a value of  $i_1/c$  of  $19.9 \mu\text{A mmol}^{-1}$  l and a slope of  $E$  vs.  $\log [i/(i_1 - i)]$  of 29.5 mV. Controlled potential coulometry at an electrode maintained at 0.4 V vs. SCE gave an  $n_{\text{app}}$  value of 2.0; the resulting solution showed no e.s.r. signal. Reduction of the electrolyzed solution at -0.2 V (reversal coulometry<sup>6</sup>) also showed  $n_{\text{app}} = 2.0$  and regeneration of the starting material. All of these observations are consistent with the reversible two-electron oxidation of TMPE to a stable dication.

The results for TAE are quite different in  $\text{CH}_3\text{CN}$ -0.1 M TBAP. The cyclic voltammetric results (Table 1B) show  $E_{\text{pa}} - E_{\text{pc}}$  of 50 mV and  $E_{\text{pa}} - E_{\text{pa}/2}$  of 43 mV. This larger splitting cannot be ascribed to irreversibility in the electron transfer reaction, since  $E_{\text{pa}}$  and  $E_{\text{pc}}$  are essentially independent of scan rate  $\nu$ . These results are best explained by two closely spaced, reversible one-electron transfers<sup>7,8</sup>. From the value of  $E_{\text{pa}} - E_{\text{pa}/2}$ , the separation between the  $E^0$  values ( $E_2^0 - E_1^0$ ) of the two-steps can be calculated to be about 7 mV<sup>8</sup>. Voltammetry at the RDE shows  $i_1/c$  of  $19.5 \mu\text{A mmol}^{-1}$  l and a log plot slope of 49 mV. The closeness of the  $i_1/c$  values of TAE and TMPE show that the overall reactions and the diffusion coefficients of both species are essentially the

TABLE I

TYPICAL CYCLIC VOLTAMMETRIC DATA FOR TMPE AND TAE<sup>a</sup>

$\nu/\text{Vs}^{-1}$	$E_{\text{pa}}/\text{V}$ vs. SCE	$E_{\text{pc}}/\text{V}$	$i_{\text{pa}}/\mu\text{A}$	$i_{\text{pc}}/\mu\text{A}$	$i_{\text{pc}}/i_{\text{pa}}$	$i_{\text{pa}}\nu^{-1/2}c^{-1}/\mu\text{A V}^{-1/2}\text{s}^{1/2} \text{l mmol}^{-1}$
<b>A. TMPE, 1.23 mM in <math>\text{CH}_3\text{CN}</math>-0.1 M TBAP</b>						
0.051	0.163	0.131	9.5	9.7	1.0	34
0.102	0.161	0.131	13.4	13.7	1.02	34.5
0.254	0.161	0.131	21.2	21.4	1.01	34.2
0.356	0.16	0.13	26.2	26.9	1.01	35.4
<b>B. TAE, 2.19 mM in <math>\text{CH}_3\text{CN}</math>-0.1 M TBAP</b>						
0.051	0.895	0.845	14.2	14.2	1.00	28.6
0.102	0.895	0.845	20.0	20.3	1.02	28.8
0.254	0.895	0.845	31.6	31.9	1.01	28.6
0.356	0.89	0.84	37	37	1.0	28
2.54	0.90	0.85				
<b>C. TAE, 1.84 mM in <math>\text{CH}_2\text{Cl}_2</math>-0.2 M TBAP</b>						
0.051	0.99	0.85	7.2	7.2	1.0	17.3
0.102	0.99	0.85	10.0	10	1.0	17.2
0.254	0.99	0.85	15.4	16	1.0	16.6
0.356	0.99	0.85	18.2	19	1.1	16.5

<sup>a</sup>The electrode was a platinum disc with an area of  $0.013 \text{ cm}^2$ . The  $iR$  compensation in  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$  was about 200 and 1100 ohms, respectively.

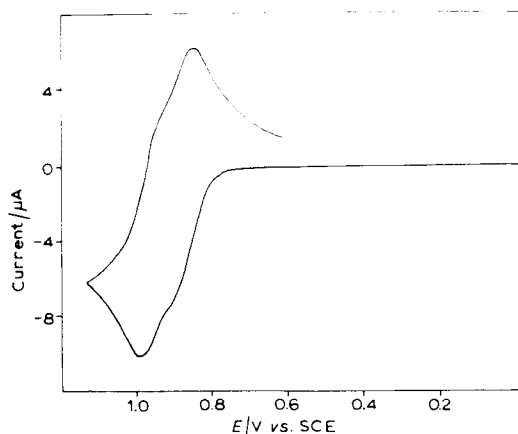


Fig.1. Cyclic voltammogram of 1.84 mM TAE in 0.2 M TBAP-CH<sub>2</sub>Cl<sub>2</sub>.

same. Note, however, that the cyclic voltammetric  $i_p/\nu^{1/2}c$  value for TAE is considerably smaller than that for TMPE, as predicted for stepwise reversible one-electron transfers as opposed to a single two-electron transfer<sup>7</sup>. Controlled potential coulometric oxidation of TAE at 1.2 V vs. SCE gave  $n_{app}$  of about 2.1, with some suggestion of slow reaction of the dication with some solution species. A sample drawn during the electrolysis and examined by e.s.r. showed an intense singlet produced by the TAE cation radical; the hyperfine splittings are probably smeared out because of rapid exchange between the cation radical and both parent and dication.

Even stronger evidence of a stepwise oxidation of TAE is provided by electrochemistry in CH<sub>2</sub>Cl<sub>2</sub>, in which cation radicals are more stable<sup>9</sup>. Cyclic voltammetry in this case clearly shows the splitting of the oxidation wave (Fig.1) and the data (Table 1C) are consistent with a reversible stepwise reaction with separation of  $E^0$  values greater than 90 mV. Note also that the value of  $i_{pa}/\nu^{1/2}c$  is much closer to that of a one-electron reaction, as expected for stepwise reactions separated by this amount (see reference 7, Fig.2B). Coulometry of TAE in CH<sub>2</sub>Cl<sub>2</sub> at 1.2 V vs. SCE gave  $n_{app} = 2.1$ . Oxidation at 0.95 V however gave  $n_{app} = 0.86$ ; examination of this solution by e.s.r. showed a spectrum with some hyperfine structure. Well-resolved spectra were obtained by use of methanesulfonic acid in CH<sub>2</sub>Cl<sub>2</sub><sup>2</sup>.

The results of these studies suggest that the oxidation of TAE occurs via reversible, stepwise one-electron transfers. Other oxidations, of which TMPE is typical, do produce results which suggest direct two-electron transfer, although more detailed kinetic studies are required to elucidate the nature of the electron-transfer processes. Because the separation between waves is quite large with aromatic hydrocarbons, oxidations of these at the first anodic wave occur by one-electron transfers.

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*References*

- 1 V.D. Parker, K. Nyberg and L. Ebersson, *J. Electroanal. Chem.*, 22 (1969) 150.
- 2 J.A. Valenzuela and A.J. Bard, *J. Phys. Chem.*, 72 (1968) 286.
- 3 E.R. Brown, D.E. Smith and G.L. Booman, *Anal. Chem.*, 40 (1968) 1411.
- 4 See e.g. J.L. Sadler and A.J. Bard, *J. Am. Chem. Soc.*, 90 (1968) 1979 and references contained therein.
- 5 R.S. Nicholson and I. Shain, *Anal. Chem.*, 36 (1964) 706 and references contained therein.
- 6 A.J. Bard and S.V. Tatwawadi, *J. Phys. Chem.*, 68 (1964) 2676.
- 7 D.S. Polcyn and I. Shain, *Anal. Chem.*, 38 (1966) 370.
- 8 R.L. Myers and I. Shain, *Anal. Chem.*, 41 (1969) 980.
- 9 J. Phelps, K.S.V. Santhanam and A.J. Bard, *J. Am. Chem. Soc.*, 89 (1967) 1752.

*J. Electroanal. Chem.*, 25 (1970) App.2-5