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## ONE- VS. TWO-ELECTRON OXIDATIONS OF TETRAARYLETHYLENES IN APROTIC SOLVENTS

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### ABSTRACT

The oxidation of dimethylaminophenyl substituted ethylenes and tetra-*p*-anisyl ethylene at a platinum electrode in methylene chloride and acetonitrile solutions was investigated by cyclic and rotating disk electrode voltammetry, potential step chronocoulometry, controlled potential coulometry and e.s.r. spectroscopy. The results show that the oxidations occur by either two one-electron steps or by a single two-electron step depending upon the structure of the molecule. Factors influencing the reaction path are discussed.

### INTRODUCTION

A question of fundamental interest in the electrochemical behavior of organic compounds involves the factors which contribute to stepwise single-electron transfers:



vs. a single two-electron step



In the absence of secondary chemical reactions or slow heterogeneous kinetics, which cause the observed waves to be shifted from their reversible positions, the difference between  $E_1^0$  and  $E_2^0$  is governed by solvation, ion pairing and structural effects [1,2]. In preliminary communications [1,3] we showed that the oxidation of aryl-substituted ethylenes could occur by stepwise one-electron transfers or an apparent single two-electron transfer depending upon solvent and compound. A fuller discussion of this work and a more complete description of the experimental results are given here.

There have been relatively few studies of the electrochemical oxidation of aryl-substituted ethylenes in nonaqueous solvents. Schmidt and Meinert [4] found that 1,2-difluoro-1,1-diphenylethane was formed during the constant current oxidation of 1,1-diphenylethylene in a silver fluoride + acetonitrile

(ACN) solution. The reaction was envisaged as a two-electron oxidation followed by nucleophilic addition to the resulting dication. Mango and Bonner [5] and later Ebersson and Nyberg [6,7] demonstrated that the oxidation of 1,1-diphenylethylene and stilbene in sodium acetate + acetic acid media also resulted in an oxidative addition to the double bond. They assumed the reaction involved an acetate assisted two-electron oxidation of the olefin. In a similar investigation, Inove et al. [8,9] examined the oxidation of stilbene and styrene in methanol. Although the products obtained also suggested oxidative addition to the double bond, the proposed mechanism assumed initial oxidation of methoxide ion to the methoxy free radical, followed by free radical addition to the double bond. O'Connor and Pearl [10] suggested that the oxidation of 3,4-dimethoxypropenyl benzene in ACN occurs by formation of the radical cation followed by coupling and cyclization. Parker and Ebersson [11] have reported a similar coupling reaction of 4,4'-dimethoxystilbene in ACN; the isolated product was analogous to that found for 3,4-dimethoxypropenyl benzene. Schäfer and Steckhan [12] utilized this oxidative dimerization reaction to prepare several phenyl-substituted butanes and butadienes. A somewhat analogous reaction has been reported by Stuart and Ohnesorge [13,14] who found that tetraphenylethylene and tetraanisylethylene (TAE) undergo an oxidative cyclization to the corresponding aryl-substituted phenanthrene. Parker et al. [15] proposed, based on cyclic voltammetric and coulometric data, that TAE in ACN undergoes a direct two-electron oxidation to form the stable dication. We previously contested this mechanism [3].

Related to the research described in this paper are studies of various dimethylamino-substituted ethylenes. Geske and Kuwata [16] conducted a polarographic and electron spin resonance (e.s.r.) investigation of the oxidation of tetra(N,N-dimethylamino)ethylene in ACN and dimethylformamide (DMF). This ethylene was shown to undergo a stepwise oxidation to the cation radical then to the dication. They obtained a well-resolved e.s.r. spectrum of the cation radical and showed that the formation equilibrium constant for the reaction



was about 230. Hünig et al. [17] studied a number of amino-substituted ethylenes. These generally exhibited stepwise oxidations with the formation constants of the radical cations, determined by polarographic measurements, being  $10^3$  to  $10^9$ . Fritsch et al. [18] showed that 1,1-N,N-(dimethylamino)-ethylene is electrolytically oxidized in ACN to a radical cation which rapidly dimerizes and deprotonates to a butadiene, a reaction similar to the previously mentioned coupling reactions. They later described the electrooxidation and e.s.r. of a number of N,N-dimethylamino-substituted ethylenes [19] and found evidence of stepwise one-electron and single two-electron oxidations. The chemical oxidation of tetraamino-substituted ethylenes and the properties of the resulting dications have been reviewed by Wiberg and Buchler [20] and Hoffman [21].

## EXPERIMENTAL

*Chemicals*

The solvents used in this work were acetonitrile (ACN) and methylene chloride (MC). Practical grade ACN, obtained from Matheson, Coleman and Bell, was purified by a modification of a previously described procedure [22]. The MC was Baker Chemical Company or Aldrich Chemical Corporation reagent grade. In general, the solvent could be used as received. However, an acidic impurity appeared in some batches; its removal was effected by a simple fractional distillation from calcium hydride [23].

The supporting electrolyte used in most experiments was polarographic grade tetra-*n*-butylammonium perchlorate (TBAP) obtained from Southwestern Analytical Chemical Company. It was dried in a vacuum oven at 100°C for two days, then stored over anhydrous magnesium perchlorate. The other supporting electrolytes used were lithium perchlorate and sodium perchlorate obtained from G. Frederick Smith Chemical Company. These salts were purified by multiple recrystallizations from water, followed by dehydration in a vacuum oven at 150°C and storage over anhydrous magnesium perchlorate.

*N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) was prepared by neutralization of the dihydrochloride obtained from Eastman Organic Chemical and was sublimed before use. Tetra-*p*-anisylethylene (TAE) was kindly supplied by Dr. E.A. Chandross. Tetrakis(*p*-*N,N*-dimethylaminophenyl)ethylene (OMPE) was prepared by the method of Gatterman [24]. *Cis*- and *trans*-1,2-bis(*p*-*N,N*-dimethylaminophenyl)-1,2-diphenylethylene (sTMPE) was prepared by the method of Buckles and Meinhardt [25]. Although these authors reported only one isomer from the reaction (coupling of *p*-*N,N*-dimethylaminobenzophenone with tin and HCl), we obtained both the *cis* and *trans* forms. The isomers were separated by fractional crystallization from 1:1 benzene/Skelly B, yielding a more soluble *cis*-isomer (m.p. 201.5–205.5°C), and a less soluble *trans*-isomer (m.p. 222–230°C), which produced distinctly different n.m.r. spectra. 1,1-Bis(*p*-*N,N*-dimethylaminophenyl)-2,2-diphenylethylene (uTMPE) was prepared by a modification of the method of Schönberg [26].

Preparation of the previously unreported 1,1,2-tris(*p*-*N,N*-dimethylaminophenyl)-2-phenylethylene (HMPE) was as follows. The diazo compound prepared from 2 g (0.008 mole) *p*-dimethylaminobenzophenone hydrazone was added to a benzene solution of 2.4 g (0.008 mole) 4,4'-bis(dimethylamino)-thiobenzophenone, and the mixture was stirred for two days at room temperature. After the benzene solution was concentrated and chromatographed on an alumina column, eluting with benzene, 3.1 g (77%) of a tan colored episulfide was obtained. The desulfuration of 0.36 g (0.0007 mole) episulfide with 0.53 g (0.002 mole) triphenylphosphine in 25 ml *p*-xylene yielded the ethylene. Two recrystallizations from ethanol resulted in 0.23 g (70%) of the ethylene with m.p. 193–194.5°C; u.v. max (CHCl<sub>3</sub>) 365 nm ( $1.82 \times 10^4$ ); n.m.r. (CDCl<sub>3</sub>), 2.8  $\delta$ , two incompletely resolved singlets (18 H total), 6.5  $\delta$  multiplet (12 H) and 6.9  $\delta$ , singlet (5 H); mass spectrum  $m/e = 461$ ,  $m/2e =$

230.5. Anal.: calcd. for  $C_{32}H_{35}N_3$ : C, 83.26; H, 7.64; N, 9.10. Found: C, 83.49; H, 7.52; N, 8.72.

In general all of the prepared compounds were purified by recrystallizations and chromatography; details of the preparations and characterizations are available [26].

#### *Apparatus*

Most voltammetric experiments were performed on an instrument similar to that described by Anson and Payne [27], equipped with positive feedback for  $iR$ -compensation. The compensation was adjusted as follows: a potential step was applied to the cell, the compensation increased until damped oscillations were observed in the current-time curve, and then the compensation reduced until a smooth curve was obtained. Controlled potential coulometric experiments utilized a Wenking-type potentiostat equipped with a Krohn-Hite DCA-10 amplifier. The current-time curve was displayed on a Varian Model G-14 strip chart recorder; current integration was accomplished using the digital readout system described by Bard and Solon [28].

Vacuum cells and vacuum line preparation techniques [29] were employed for all experiments. The working electrode for most of the transient experiments was a platinum disk electrode of geometric area  $0.013 \text{ cm}^2$ . The electrode was fabricated by sealing a platinum wire in a 6 mm soft glass tube, then grinding both platinum and glass to a planar surface using carborundum grinding powders on a glass plate. Contact with the platinum wire was made with mercury and a copper wire. Small scratches left in the platinum by the grinding process were removed by polishing with a Superior H.R. water soluble red rouge. The electrode was then oxidized with nitric acid, reduced with acidic ferrous ammonium sulfate solution, and cycled in the supporting electrolyte solution. The working electrode for the coulometric experiments was a platinum gauze electrode; this same gauze was used as the counter electrode in all other experiments. The counter electrode for coulometry was a platinum spiral placed in an 8 mm fritted glass tube. The fritted counter electrode compartment usually was filled with an aqueous potassium nitrate agar salt bridge for additional separation. An aqueous saturated calomel electrode (SCE) with a 3% agar + 1 *M* potassium nitrate salt bridge terminated with a fine porosity frit was used as the reference electrode.

In e.s.r. examination of a coulometric solution, a sample was removed into an evacuated 3 mm Pyrex tube attached to the electrochemical cell. The sample was frozen in liquid nitrogen, and the tube was sealed and removed with a torch. After the sample thawed, the e.s.r. experiments were carried out on Varian Models V-4502 or E-4 spectrometers.

#### RESULTS

The tetraarylethylenes studied are shown in Fig. 1. Experiments were also conducted on a model compound whose electrochemical behavior has been

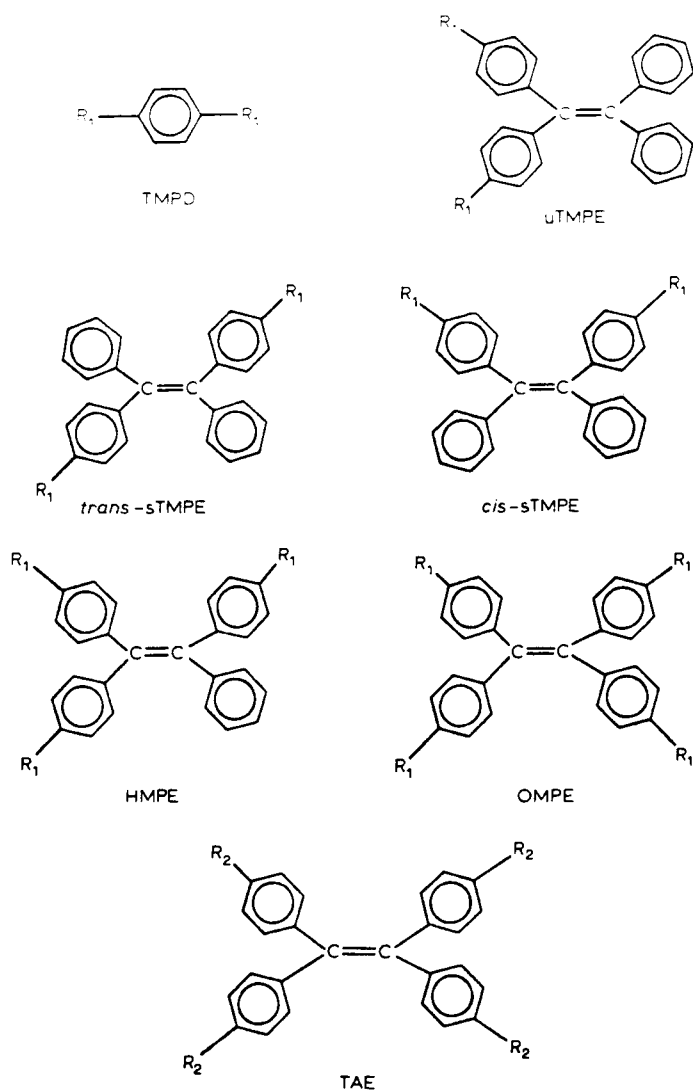


Fig. 1. Compounds in this study;  $R_1 = N(CH_3)_2$ ,  $R_2 = OCH_3$ .

well characterized: *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD). Dvořák et al. [30] have shown that the oxidation of TMPD in ACN occurs by a stepwise process involving two, well-separated, one-electron steps. The first step is a reversible oxidation of TMPD to a stable cation radical; this oxidation will serve as a model for a one-electron oxidation in the following discussions.

The aryl-substituted ethylenes can be classified as belonging to one of the following groups: (a) two well-separated one-electron processes, (b) two

poorly separated, unresolved, one-electron processes, or (c) direct two-electron processes, or at least two one-electron processes in which the second occurs more readily than the first, depending on their behavior during oxidation.

*Cyclic and rotating disk electrode voltammetry in methylene chloride*

The cyclic voltammetric behavior of the compounds of interest in MC solution is summarized in Table 1. Representative voltammograms are given in Fig. 2 and detailed tables of data at varying scan rates are given in ref. 26. Of the tetraarylethylenes considered, only uTMPE shows two well-separated waves, each corresponding (by comparison to TMPD) to one-electron oxidations. The current function for the first wave is slightly smaller than that for TMPD because of the smaller diffusion coefficient of uTMPE. The second oxidation wave for uTMPE is irreversible. The current function for the second wave, when measured from the decaying current of the first wave (Fig. 2a) is about 10% larger than that of the first wave. The peak width,  $E_{pa} - E_{pa/2}$ , is 50 mV. These parameters correspond more closely to a reversible one-electron charge transfer followed by a fast chemical reaction than to those expected for a slow charge transfer step. Thus uTMPE belongs to group (a) and involves a reversible oxidation to a fairly stable radical cation at the first wave and reversible oxidation to a dication which undergoes a rapid decomposition reaction at the second wave.

The cyclic voltammetry of TAE (Fig. 2b) clearly demonstrates the presence of two closely spaced waves. Because of the poor separation of the two waves, the data in Table 1 reflect only the peak currents and peak potentials of the composite wave. The current function of 16.9 for this composite wave, compared to the one-electron value of about 13 and the two-electron value of 31 to 34 (see below) for these compounds, is consistent with a mechanism involving two closely spaced one-electron waves [31] [group (b) behavior]. A comparison of the wave with theoretical ones for stepwise electron transfer yields a mechanism in which TAE is oxidized to a stable radical cation and then to a stable dication, with the  $E^0$  of the second step about 90 mV more positive than that of the first.

The other substituted ethylenes, sTMPE, OMPE, and HMPE, which involve at least one dimethylaminophenyl group on both ethylenic carbons, all show very similar behavior and a single oxidation wave (Fig. 2c). The peak potential separations,  $E_{pa} - E_{pc}$ , are 30 to 40 mV and the current function is about  $(2)^{3/2}$  times that of uTMPE. These results are consistent with single reversible two-electron oxidations to stable dications, i.e., group (c) behavior. Although the results at the 1 mM concentration level show reasonably constant current functions and  $i_{pc}/i_{pa}$  ratios with scan rate, at lower concentrations a distinct decrease in current function and increase in  $i_{pc}/i_{pa}$  with scan rate is observed (Table 2). These results are best explained by weak adsorption of the dication, since the cyclic voltammetric curves generally agree with the theoretical treatment of this mechanism by Shain and Wopschall [32] and Laviron [33]. This

TABLE 1  
Summary of cyclic voltammetric and rotating disk electrode data <sup>a</sup>

Compound <sup>b</sup>	Concn./mM	C.v	RDE <sup>f</sup>							
			$E_{pa}/V$ (vs. SCE)	$E_{pc}/V$ (vs. SCE)	$i_{pa}v^{-1/2}c^{-1}/\mu\text{As}^{1/2}V^{-1/2}\text{mM}^{-1}$	$i_{pc}/i_{pa}$	$E_{1/2}/V$ (vs. SCE)	Log plot <sup>c</sup> slope/mV	$i_L\omega^{1/2}c^{1/2}/\mu\text{As}^{-1/2}\text{mM}^{-1}$	$1/f$ (Group)
TMPD	3.69		0.21	0.14	14.9	1.10				
uTMPE <sup>c</sup>	1.71		0.61	0.55	12.9	1.02	0.568	58	0.87	a
TAE	1.84		0.99	0.85	16.9	1.04	0.911	<sup>g</sup>	1.52	a
sTMPE <sup>d</sup>	1.65		0.44	0.41	33.8	1.05	0.440	34	2.06	b
OMPE	1.03		0.18	0.14	31.1	1.02	0.158	36	1.81	c
HMPE	1.32		0.32	0.28	31.0	1.02	0.321	36	1.94	c

<sup>a</sup> The solution was 0.2 M TBAP in methylene chloride and the working electrode was a Pt disk, geometric area 0.013 cm<sup>2</sup>. Average results for scan rates,  $v$ , between 0.05 and 1 V s<sup>-1</sup>.

<sup>b</sup> See Fig. 1.

<sup>c</sup> For second wave,  $E_{pa} = 0.88$  V vs. SCE,  $i_{pa}(2)/i_{pa}(1) = 1.1$ .  $E_{1/2} = 0.85$  V vs. SCE, log plot slope  $-1 = 5.0$  mV and  $i_L/\omega^{1/2}c^{1/2} = 1.64$ .

<sup>d</sup> *Cis* and *trans* forms show virtually identical electrochemical properties.

<sup>e</sup> Reciprocal of slope of  $\log(i/i_L - i)$  vs.  $E$ .

<sup>f</sup> Rotation rate,  $\omega$ , 1000 rpm.

<sup>g</sup> Nonlinear, see text.

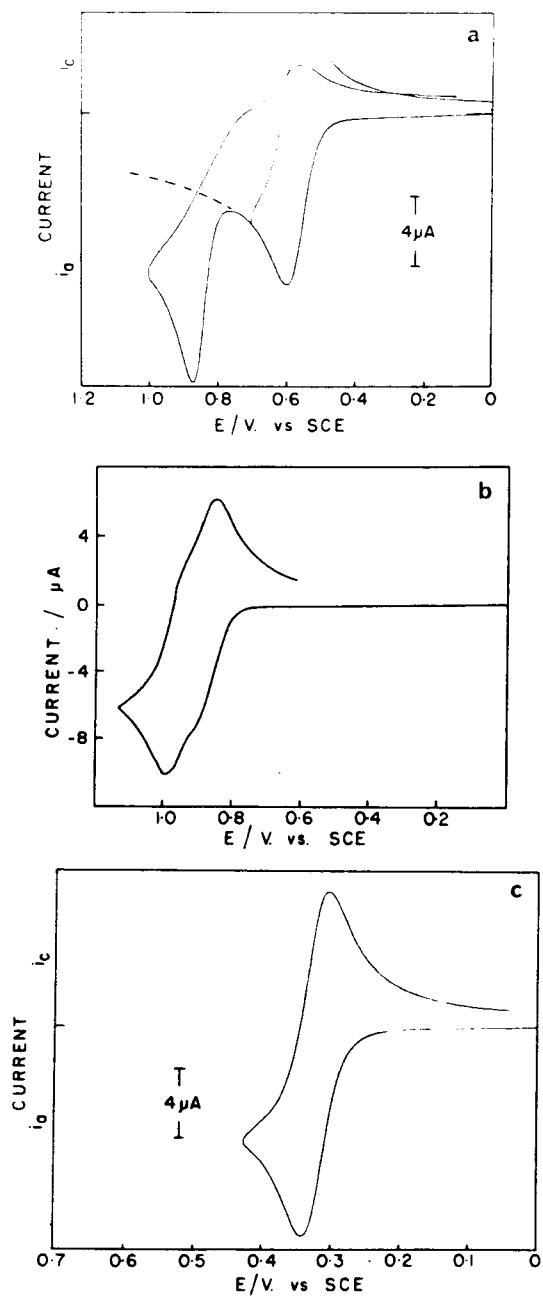


Fig. 2. Cyclic voltammetric oxidation of (a) uTMPE, (b) TAE and (c) HMPE in 0.2 M TBAP + methylene chloride at platinum electrode.



TABLE 2

Cyclic voltammetric data for 1,1,2-tris(*p*-N,N-dimethylaminophenyl)-2-phenylethylene (HMPE)<sup>a</sup>

Scan rate/V s <sup>-1</sup>	$E_{pa}/V$ (vs. SCE)	$E_{pc}/V$ (vs. SCE)	$i_{pa}/\mu A$	$i_{pc}/\mu A$	$i_{pc}/i_{pa}$	$i_{pa}t^{-1/2}c^{-1}/\mu A s^{1/2}V^{-1/2}mM^{-1}$
<i>(A) Oxidation of HMPE</i>						
Concentration: 1.32 mM						
0.051	0.31	0.27 <sub>5</sub>	9.4	9.6	1.02	31.5
0.102	0.31	0.27 <sub>5</sub>	13.3	13.4	1.01	31.8
0.152	0.31	0.27 <sub>5</sub>	16.2	16.5	1.02	31.6
0.203	0.31	0.27 <sub>5</sub>	18.9	19.5	1.03	31.8
0.254	0.31	0.27	21.2	21.5	1.01	31.8
0.304	0.32	0.27 <sub>5</sub>	22	22.5	1.02	31
0.406	0.32	0.27	25	26	1.04	30
0.508	0.32	0.27	28	28.5	1.02	30
0.762	0.32	0.27	34	35	1.01	30
1.016	0.32	0.27	39	40	1.01	30
Concentration: 0.41 mM						
0.051	0.30 <sub>5</sub>	0.28	2.82	3.0	1.1	30.4
0.102	0.30 <sub>5</sub>	0.28	4.00	4.4	1.1	30.8
0.152	0.31	0.27 <sub>5</sub>	5.02	5.5	1.1	30.4
0.203	0.31	0.27 <sub>5</sub>	5.50	6.0	1.1	29.8
0.254	0.31	0.27	6.05	6.7	1.1	29.4
0.304	0.31 <sub>5</sub>	0.27	6.6 <sub>5</sub>	7.3	1.1	29.5
0.356	0.32	0.26	6.9	7.8	1.1	29
0.406	0.32	0.26	7.4	8.4	1.1	29
0.457	0.32	0.26	7.8	8.9	1.1	28
0.508	0.32	0.26	8.2	9.6	1.2	28
0.762	0.32	0.26	10.0	12.0	1.2	28
Concentration: 0.10 mM						
0.051	0.32 <sub>5</sub>	0.29	0.61	0.64	1.1	27
0.102	0.32 <sub>5</sub>	0.29	0.86	0.93	1.1	27
0.152	0.32 <sub>5</sub>	0.28 <sub>5</sub>	1.04	1.16	1.11	27
0.203	0.32 <sub>5</sub>	0.28 <sub>5</sub>	1.20	1.40	1.17	27
0.254	0.32 <sub>5</sub>	0.29	1.35	1.55	1.15	27
0.304	0.32 <sub>5</sub>	0.28 <sub>5</sub>	1.47	1.75	1.19	27
0.356	0.32 <sub>5</sub>	0.28	1.52	1.19	1.25	25
0.406	0.32 <sub>5</sub>	0.28	1.64	2.0	1.2	26
0.457	0.32 <sub>5</sub>	0.28	1.74	2.2	1.3	26
0.508	0.32 <sub>5</sub>	0.28	1.84	2.3	1.3	26
0.762	0.32 <sub>5</sub>	0.28	2.18	3.0	1.4	25
1.016	0.32 <sub>5</sub>	0.27 <sub>5</sub>	2.44	3.5 <sub>5</sub>	1.5	25
<i>(B) Reduction of HMPE solution totally oxidized at +0.6 V vs. SCE</i>						
Concentration: 0.97 mM						
			$i_{pa}/i_{pc}$	$i_{pc}v^{-1/2}c^{-1}/\mu A s^{1/2}V^{-1/2}mM^{-1}$		
0.051	0.340	0.300	5.36	5.40	0.99	24.6
0.102	0.340	0.300	7.52	7.68	0.98	25.0
0.152	0.340	0.300	9.20	9.36	0.98	24.8
0.203	0.340	0.300	10.7	10.9	0.98	24.8
0.254	0.34	0.30	13.2	13.7	0.97	25.6
0.304	0.34	0.30	14.1	14.2	0.99	24.4
0.406	0.34	0.30	15.0	15.2	0.98	24.6

<sup>a</sup> The solution was 0.2 M TBAP in CH<sub>2</sub>Cl<sub>2</sub>. The working electrode was platinum disk with geometric area 0.013 cm<sup>2</sup>.

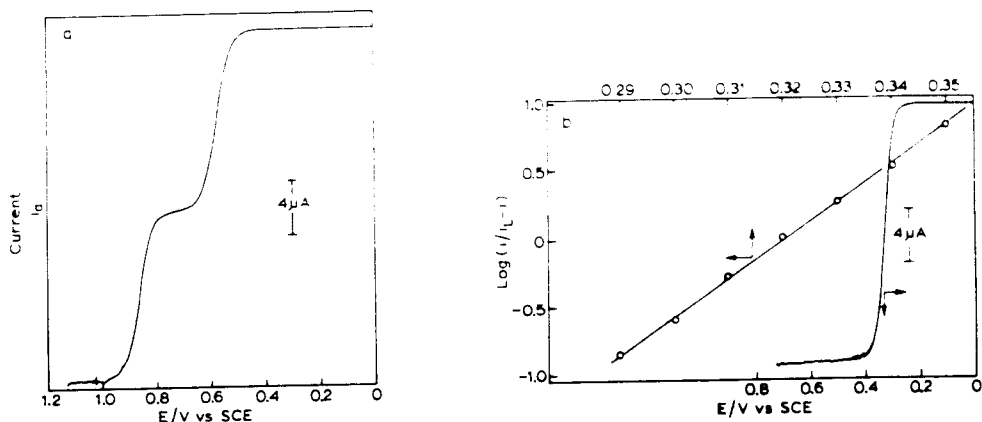


Fig. 3. Rotating disk voltammetry of (a) uTMPE and (b) HMPE in 0.2 M TBAP + methylene chloride. Also shown in (b) is logarithmic analysis of HMPE wave.

adsorption was studied in more detail by double potential step chronocoulometry.

Typical voltammograms at the rotating disk electrode (RDE) are shown in Fig. 3; the data are summarized in Table 1. The results generally confirm those of cyclic voltammetry; the deviation of the slope for the group (c) compounds from the expected theoretical value of 29 mV probably reflects some uncompensated  $iR$ -drop. The log plot for TAE was curved, as expected for a voltammogram of two unresolved waves. The experimental points could be fit very well (Fig. 4), using the polarographic treatment of Müller [34] and Brdička [35] assuming two reversible electron transfers with an equilibrium constant of the reaction



of 55, with  $E^0$ 's for the first and second steps of 0.86 and 0.96 V vs. SCE, respectively.

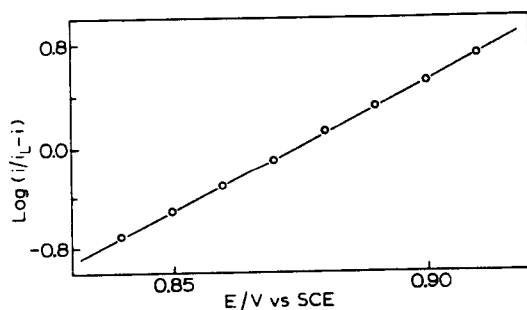


Fig. 4. Logarithmic analysis of the current-potential curve resulting from the oxidation of TAE in methylene chloride at a platinum RDE. The points represent experimental data and the line represents the theoretical curve for  $K = 55$ .

TABLE 3  
Potential step chronoamperometry and chronocoulometry data summary <sup>a, b</sup>

Compound	$E_1/V$ (vs. SCE)	$E_2/V$ (vs. SCE)	$it^{-1/2}$ slope/ $\mu A s^{1/2}$	$nK^c/\mu A$ $s^{1/2} mM^{-1}$	$K^c/\mu A$ $s^{1/2} mM^{-1}$	$Qt^{1/2}$ slope/ $\mu C s^{-1/2}$	$nK^c/c/$ $\mu C s^{-1/2} mM^{-1}$	$K^c/c/$ $\mu C s^{-1/2} mM^{-1}$	$K^c/K^d$
TMPD									
3.69 mM	-0.1	0.5				21.8	5.90	5.90	
uTMPE									
1.71 mM	0.0	0.7	4.06 <sup>e</sup>	2.38	2.38	7.65 <sup>f</sup>	4.48	4.48	1.88
	0.0	1.0	8.00	4.68	2.34	15.6	9.10	9.10	1.95
OMPE									
1.03 mM	-0.2	0.6	4.74	4.60	2.30				
HMPE									
0.97 mM	0.0	0.6				8.12	8.36	4.18	
trans-sTMPE									
1.59 mM	0.0	0.8	7.25	4.56	2.28				
cis-sTMPE									
2.18 mM	0.0	0.7	9.43	4.33	2.11	18.1	8.30	4.15	1.97

<sup>a</sup> The solution was 0.2 M TBAP in  $CH_2Cl_2$ .

<sup>b</sup> The working electrode was a platinum disk of geometric area 0.013  $cm^2$ .

<sup>c</sup> These parameters are defined as  $K = FAD^{1/2}/\pi^{1/2}n$  and  $K^c = 2FAD^{1/2}/\pi^{1/2}n$ .

<sup>d</sup> This parameter has a theoretical value of 2.

<sup>e</sup> Ratio of slopes = 1.97.

<sup>f</sup> Ratio of slopes = 2.03.

Potential step chronoamperometry and chronocoulometry in methylene chloride

Potential step measurements were undertaken to obtain still more confirmatory evidence about the reaction steps, to probe for adsorption of reactants and products, and especially to determine the effectiveness of resistance compensation in MC. The results were evaluated from  $i$  vs.  $t^{-1/2}$  and  $Q$  vs.  $t^{1/2}$  plots, and the electrode diffusion current constants  $K$  and  $K'$ , defined in (6) and (7) were determined. Typical experimental results are given in Table 3 and Fig. 5. The constancy of the

$$it^{1/2}/c_R = FAD^{1/2}/\pi^{1/2} = nK \quad (6)$$

$$(Q - Q_{dl})/t^{1/2} c_R = 2FAD^{1/2}/\pi^{1/2} = nK' \quad (7)$$

$K$  and  $K'$  values for the different compounds with the  $n$ -value assumed from the voltammetric studies confirms these values and demonstrates that these compounds have similar diffusion coefficients. Note also that the ratio  $K'/K$  is close to the theoretically expected value of 2. For uTMPE the ratio of slopes for steps to potentials on the second wave (1.0 V) compared to those at the first (0.7 V) were also near the value of 2 expected for stepwise reactions involving an equal number of electrons. The  $i - t^{-1/2}$  and  $Q - t^{1/2}$  plots were linear for times between 10 ms and 2 s. At shorter times a positive deviation was observed, probably because of the presence of uncompensated resistance which prevents rapid double layer charging. The positive deviation at times

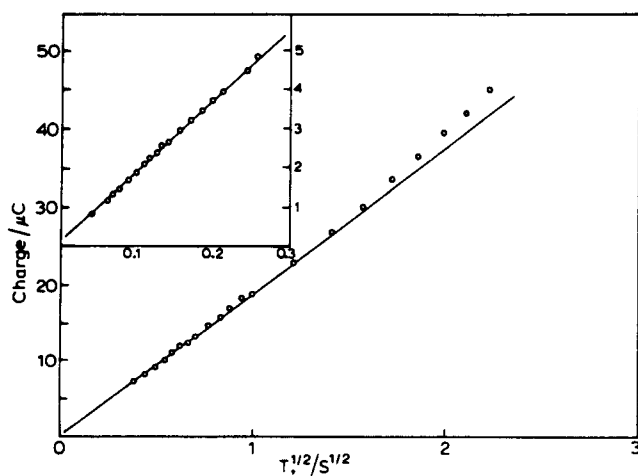


Fig. 5. Chronocoulometric charge vs. time<sup>1/2</sup> plot for the oxidation of *cis*-sTMPE in methylene chloride at a platinum electrode. The insert represents an expansion of the plot for time less than 100 ms.

longer than 2 seconds probably arises from convection due to vibrations of the cell while connected to the vacuum line.

A double potential step chronocoulometric experiment with HMPE was also performed to estimate the extent of adsorption of the dication. A 0.25 mM solution of HMPE dication was prepared by controlled potential oxidation of the parent at +0.6 V. The results of a double potential step (0.5 to 0.0 to 0.5 V) are shown in Fig. 6. The results were analyzed [36,37] assuming that the dication was adsorbed but the product (parent) was not. Under these conditions the charge during the forward (0.5 to 0.0 V) step is given by

$$Q_f = Q(t < \tau) = nK'c_0t^{1/2} + nFA\Gamma_0 + Q_{d1} \quad (8)$$

where  $c_0$  is the bulk concentration of dication and  $\Gamma_0$  the amount of dication adsorbed. At time  $t = \tau$  the potential is stepped back to 0.5 V and the charge on reversal is given by

$$Q_b = Q(\tau) - Q(t > \tau) = nK'c_0 (1 + nFAa_1\Gamma_0/Q_c) \theta + a_0nFA\Gamma_0 + Q_{d1} \quad (9)$$

where  $\theta = (t - \tau)^{1/2} + \tau^{1/2} - t^{1/2}$  and  $a_0$  and  $a_1$  are the slope and intercept of the plot of  $1 - (2/\pi) \sin^{-1}[(\tau/t)^{1/2}]$  vs.  $\theta/\tau^{1/2}$  [36]. The plot of Fig. 6 yields the following results

$$\begin{aligned} \text{Slope } Q_f - t^{1/2} &\equiv S_f &= 2.02 \mu\text{C s}^{-1/2} \\ Q_f \text{ intercept} &\equiv {}^0Q_f &= 0.122 \mu\text{C} \end{aligned}$$

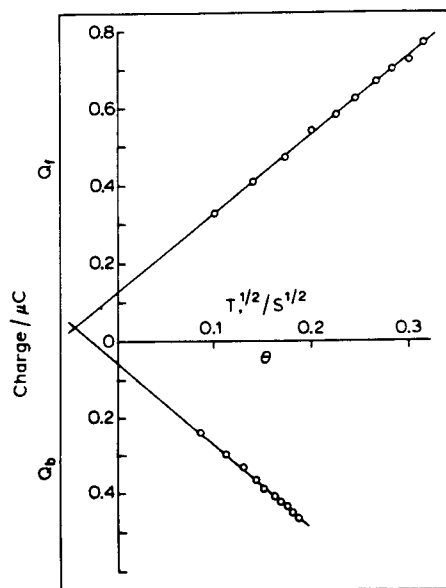


Fig. 6. Charge vs. time<sup>1/2</sup> and charge vs.  $\theta$  plots for double potential step chronocoulometry for a solution of HMPE dication in methylene chloride. The potential was stepped from 0.5 to 0.0 to 0.5 V vs. SCE.

$$\begin{aligned} \text{Slope } Q_b - \theta &\equiv S_b = 2.22 \mu\text{C s}^{-1/2} \\ Q_b \text{ intercept} &\equiv {}^0Q_b = 0.055 \mu\text{C} \\ Q_c \text{ (Cottrell charge)} &\equiv 2K'\tau^{1/2} = 0.64 \mu\text{C} \end{aligned}$$

From these parameters, the amount of adsorbed dication calculated by eqn. (9) was  $2.5 \times 10^{-11}$  moles  $\text{cm}^{-2}$ . This amount adsorbed represents less than monolayer coverage. Using the internal consistency check advocated by Christie et al. [36], the measured slope ratio  $S_b/S_f$  was 1.10 which agrees exactly with the theoretical value.

$Q_{dl}$  was found to be  $0.06 \mu\text{C}$  which was somewhat less than the  $0.08 \mu\text{C}$  double layer charging term measured in a blank solution under identical conditions.

TABLE 4  
Coulometric data on selected tetraarylethylenes in methylene chloride <sup>a</sup>

Compound	Oxidation control potential/V (vs. SCE)	$n_{app}$	Reversal coulometry <sup>b</sup>	
			Reduction control potential/V (vs. SCE)	$n_{app}$
OMPE				
1.16 mM	0.6	2.01	-0.4	2.06
HMPE				
1.51 mM	0.8	2.04	0.0	1.96 <sup>c</sup>
0.97 mM	0.6	2.00	-0.2	1.99
<i>trans</i> -sTMPE				
1.53 mM	0.6	2.01	0.0	1.98
<i>cis</i> -sTMPE				
1.58 mM	0.8	1.98	0.0	2.02
uTMPE				
1.57 mM	0.7	1.1 <sup>d</sup>	0.0	0.1
3.36 mM	0.7	0.98		
TAE				
0.44 mM	0.95	0.86 <sup>e</sup>		
	1.20	2.1		

<sup>a</sup> The solution was 0.2 M TBAP.

<sup>b</sup> These data refer to reversal coulometry on the completely oxidized parent. In general, the time between completion of oxidation and initiation of reduction was about one hour.

<sup>c</sup> The oxidized solution was allowed to remain overnight; the reduction was initiated the next morning.

<sup>d</sup> Electrolysis was terminated at a steady-state current of about one percent of the initial current.

<sup>e</sup> E.s.r. examination indicated the presence of an intense singlet radical spectrum, with some superimposed hyperfine structure.

### *Controlled potential coulometry in methylene chloride*

Coulometry experiments at a platinum gauze electrode controlled at a potential on the limiting current plateau were undertaken to determine definitive  $n_{app}$ -values, to determine if any slow chemical reactions of the primary electrode reaction product occurred, and to prepare solutions of the electrode reaction product for further voltammetry studies. The results are given in Table 4. The type (c) compounds all show  $n_{app}$ -values near 2.0 corresponding to the oxidation of the parent to the intensely colored dication. As expected, no e.s.r. spectrum was observed for a completely oxidized solution of OMPE. To determine the long-time stability of the type (c) dications, reversal coulometry [38] experiments were conducted on the completely oxidized solutions. In all cases,  $n_{app}$ -values near 2.0 were found. In one experiment, a 1.51 mM HMPE solution was completely oxidized, then left overnight exposed to the atmosphere. Twelve hours later, reversal coulometry showed  $n_{app} = 2.0$ . These experiments provide conclusive evidence that the group (c) compounds are reversibly oxidized to extremely stable dications. Voltammetric studies on the oxidized solutions will be given below.

The oxidations of the type (a) and type (b) compounds were quite different. Oxidation of TAE at 1.2 V vs. SCE gave an  $n_{app}$ -value of 2.1. However oxidation at 0.95 V gave an  $n_{app}$ -value of 0.86; e.s.r. examination of this solution showed an intense singlet with some superimposed fine structure. This cation radical has also been obtained by chemical oxidation with methanesulfonic acid in methylene chloride, and its interpretation has been reported [39].

The controlled potential oxidation of uTMPE at 0.7 V vs. SCE showed an  $n_{app}$  of about one. An e.s.r. examination of the oxidized solution showed the presence of a radical, but the signal was very weak and not well resolved. Apparently, the radical decomposes in a chemical reaction that is slow compared to the voltammetric time scale, i.e., order of seconds, but that is important compared to the coulometric time scale, i.e., order of forty to sixty minutes. Reversal coulometry on this oxidized solution showed only one tenth of an electron per molecule was recovered, indicating extensive decomposition of the radical cation.

### *Voltammetry of oxidized solutions in methylene chloride*

An RDE voltammogram of an 0.97 mM HMPE solution completely oxidized at 0.6 V vs. SCE showed a cathodic wave with an  $E_{1/2}$  of 0.321 V vs. SCE, a Levich constant of 1.63 and a log plot slope<sup>-1</sup> of 38 mV. These data can be compared with data for the original solution which showed an oxidation wave with an  $E_{1/2}$  of 0.318 V vs. SCE, a Levich constant of 1.94 and log plot slope<sup>-1</sup> of 36 mV. With the exception of a lower limiting current, these data are consistent with the reversible two-electron reduction of the dication to the original compound. Similarly the cyclic voltammogram of the totally oxidized HMPE solution was essentially the same as that for the parent solution except

that the peak currents were about 11% smaller for the oxidized solution (Table 2B). Note also that the  $i_{pc}/i_{pa}$  ratio is now slightly less than 1.0, since it is the reactant which is now weakly adsorbed.

The difference in limiting and peak currents between parent and dication suggests that either the concentration of the dication is lower than that of the original parent or that the diffusion coefficient of the dication is considerably smaller than that of the parent. Loss of dication by precipitation of the salt on the large gauze electrode is a possibility; no precipitate was observed in solution or on the electrode surface, however. Note that reversal coulometry showed essentially complete recovery of the dication. The amount of adsorption of the dication determined by the chronocoulometric experiment is much too small, even with electrode areas of 300 cm<sup>2</sup> to account for any appreciable decrease in the solution concentration. A difference of diffusion coefficient of about 25% between parent and dication is required to account for the limiting current differences. While this seems unusually large, it may be caused by the dication existing in the form of an ion pair or ion aggregate with perchlorate ion in this low dielectric constant solvent.

Because of the difficulty of making quantitative correlations of the composite waves with a theoretical model, extensive voltammetry studies on oxidized solutions of TAE were not conducted. Cyclic voltammetry of the completely oxidized solutions demonstrated the presence of a reasonably stable dication which was reduced in the same stepwise manner as the parent was oxidized. Cyclic voltammetric reduction of an oxidized solution of uTMPE showed only a small wave for the reduction of uTMPE cation radical. This observation reflects the extensive decomposition of the cation radical already suggested by the reversal coulometry.

Direct product isolation from the oxidized solutions was unsuccessful as all attempts to separate the dication salt from the supporting electrolyte failed. However, similar products have been isolated from the chemical oxidation of these compounds. Baenziger et al. [40] have reported the isolation of stable dication salts of TAE. Anderson et al. [41] have reported the isolation of the dinitrate and diiodide of OMPE by oxidation of the parent with silver nitrate.

Although direct isolation proved difficult, some information concerning the structure of the dication can be obtained by reducing the dication back to the neutral parent, then isolating the starting material. Product isolation from the reduction of an oxidized solution of OMPE and of HMPE was effected by stripping the MC from the electrolysis solution, extracting the residue with carbon disulfide in a Soxhlet extractor to separate the products from the supporting electrolyte, and finally stripping the carbon disulfide. The product was identical to starting material by n.m.r. and i.r.; recovered yields were 70–90%.

The product of the oxidation–reduction of sTMPE was more revealing. A 2.14 mM solution of *cis*-sTMPE was subjected to complete oxidation and subsequent complete reduction, and the products were isolated. An n.m.r. spectrum of the product dissolved in carbon disulfide demonstrated that a mixture of isomers was recovered, which was quite similar to that obtained from the



initial preparation of these substituted ethylenes. Apparently the dication isomerizes in solution. This observation suggests that the bond order of the central ethylene bond in the dication decreases considerably and thus allows free rotation about this bond.

### Oxidations in acetonitrile

In general, the voltammetric data for the oxidation of the type (c) compounds in MC deviated slightly from theoretical expectations for a direct two-electron oxidation. For example, the peak potential separations were about 10 mV greater than theoretical predictions and slopes<sup>-1</sup> of  $\log i/(i_L - i)$  vs.  $E$  plots were greater than expected, i.e., 34–36 mV compared to 29.5 mV. These differences could be caused by uncompensated  $iR$  drops in the measured potential values and by the reactions occurring by two very closely spaced one-electron transfers, where  $E_2^0$  is equal to or slightly less than  $E_1^0$ . To investigate these possibilities e.s.r. experiments were conducted on partially oxidized OMPE solutions to search for radical cation; these are described below. In addition voltammetric studies were conducted on OMPE and TAE in acetonitrile (ACN), where uncompensated  $iR$ -effects are negligible with our apparatus, and where the effects of solvation on the nature of the electrode reactions could be probed. The cyclic voltammetry of OMPE in ACN showed only a single, reversible wave. The pertinent voltammetry results (Table 5) are as follows: the

TABLE 5

Typical cyclic voltammetric data for the oxidation of TAE and OMPE in acetonitrile<sup>a</sup>

Scan rate/Vs <sup>-1</sup>	$E_{pa}/V$ (vs. SCE)	$E_{pc}/V$ (vs. SCE)	$i_{pa}/\mu A$	$i_{pc}/\mu A$	$i_{pc}/i_{pa}$	$i_{pa}v^{-1/2}c^{-1}/\mu A$ $s^{1/2}V^{-1/2}mM^{-1}$
Tetra- <i>p</i> -anisylethylene (TAE): 2.19 mM						
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
0.152	0.895	0.845	24.6	24.8	1.01	28.8
0.203	0.895	0.845	28.3	28.5	1.01	28.6
0.254	0.895	0.845	31.6	31.9	1.01	28.6
0.304	0.895	0.845	34.7	34.7	1.00	28.7
0.356	0.895	0.84	37.0	37.4	1.01	28.2
Tetrakis( <i>p</i> -N,N-dimethylaminophenyl)ethylene (OMPE): 1.23 mM						
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
0.152	0.161	0.131	16.7	17.0	1.02	34.9
0.203	0.161	0.131	18.9	19.1	1.01	34.2
0.254	0.161	0.131	21.2	21.4	1.01	34.2
0.304	0.16	0.13	23.7	24.1	1.02	34.9
0.356	0.16	0.13	26.2	26.9	1.01	35.4

<sup>a</sup> The solution was 0.1 M in TBAP. The working electrode was a platinum disk with geometric area 0.013 cm<sup>2</sup>.

separation between  $E_{pc}$  and  $E_{pa}$  is 30 mV; the separation between  $E_{pa} - E_{pa/2}$  is 28.5 mV; the ratio of  $i_{pc} / i_{pa}$  is invariant with scan rate and equal to 1; the current function is invariant with scan rate and equal to about 3.4. The potential separations correspond very well with theoretical values of 29.5 mV and 28.2 mV expected for a simple, reversible two-electron oxidation [42]. Moreover, the current function is only slightly less than  $2^{3/2}$  times the value [13] found for a known one-electron oxidation of a similar compound,  $\mu$ TMPE. All of these data are consistent with a reversible two-electron oxidation of OMPE in ACN to a stable dication.

The cyclic voltammetry of TAE in ACN is qualitatively the same as the oxidation of OMPE in ACN: one undistorted reversible wave was observed. However, quantitative results for TAE in ACN are quite different. The cyclic voltammetric results (Table 5) show  $E_{pa} - E_{pc}$  of 50 mV and  $E_{pa} - E_{pa/2}$  of 43 mV. These larger than theoretical potential separations cannot be ascribed to quasi-reversible charge transfer, since  $E_{pc}$ ,  $E_{pa}$ , and the current function are essentially independent of scan rate. Nor are these larger potential separations attributable to uncompensated resistance, since the data for OMPE showed less than 1 mV deviation from theoretical values. These results are best explained by two successive, reversible one-electron transfers where the two  $E^0$ 's are very closely spaced. Using the working curve of Myers and Shain [43], one can calculate from  $E_{pa} - E_{pa/2}$  of  $43 \pm 1$  mV the separation between the  $E^0$  values ( $E_2^0 - E_1^0$ ) of the two steps as  $7 \pm 4$  mV.

The oxidation of OMPE in ACN at an RDE showed a single, well-defined wave with a half wave potential of 0.145 V vs. SCE and a Levich constant of 2.01. A log plot for this wave resulted in a straight line with slope<sup>-1</sup> of 29.5 mV, in excellent agreement with the log plot slope<sup>-1</sup> expected for a two-electron oxidation. Thus both cyclic voltammetric and RDE results suggest that OMPE is oxidized in a direct two-electron transfer to a stable dication.

The oxidation of TAE at an RDE also showed a single, well-defined wave with an  $E_{1/2}$  of 0.875 V vs. SCE and a Levich constant of 1.97, about the same as that of OMPE.

The log plot for TAE in ACN, unlike that for MC, is quite linear. However, the slope<sup>-1</sup> is 49 mV, which is intermediate between a slope<sup>-1</sup> of 59 mV expected for a one-electron oxidation and a slope<sup>-1</sup> of 29.5 mV expected for a direct two-electron oxidation. Again, this apparent discrepancy can be reconciled by assuming that TAE in ACN is oxidized in the same stepwise mechanism proposed for MC. The experimental log plot was fitted to the family of calculated curves for a stepwise mechanism; the best fit was obtained when  $K = 1.6$ , which corresponds to an  $E_2^0$   $12 \pm 5$  mV more positive than  $E_1^0$ , in reasonable agreement with the cyclic voltammetric results.

Controlled potential coulometric oxidation of OMPE in ACN at 0.4 V vs. SCE required 2.0 electrons per molecule, corresponding to complete oxidation of OMPE to a dication. An e.s.r. experiment after complete electrolysis confirmed the absence of a paramagnetic species. Reversal coulometry [38] also required 2.0 electrons per molecule; voltammetric results of the reduced dica-

tion were identical to the parent solution. Coulometric oxidation of TAE in ACN at 1.2 V vs. SCE required 2.1 electrons per molecule, again corresponding to the formation of a dication; an e.s.r. experiment also confirmed the absence of a cation radical. Reversal coulometry required slightly less than 2.0 electrons per molecule, and a RDE voltammogram of the reduced dication exhibited a smaller limiting current (some 5% less) than the original solution. Both observations indicate slow decomposition of the dication.

If the electrolysis was performed at the foot of the wave, an  $n_{app}$ -value of less than 1.0 is obtained, and an e.s.r. spectrum shows the presence of a very intense singlet. Resolution of the hyperfine splittings which is attainable in methylene chloride [39] was never observed.

#### *Electron spin resonance experiments on partially oxidized solutions*

Although electrochemical data for the type (c) compounds, which show essentially a single two-electron oxidation to the dication, cannot provide information about the separation between  $E_1^0$  and  $E_2^0$ , direct observation of the radical cation in solutions containing both parent and dication can be used to estimate this separation. Thus for a type (c) compound the radical cation concentration will vary during the electrolysis, reaching its maximum equilibrium concentration when the electrolysis has consumed one electron per molecule. To detect the radicals of type (c) compounds in MC, a solution of HMPE was partially oxidized, and an e.s.r. spectrum was obtained. The resulting spectrum was a moderately intense singlet similar to that obtained for TAE, thereby clearly demonstrating the existence of the radical cation in solution. Similar experiments with OMPE produced similar results. These results clearly demonstrate that the cation radical exists in significant concentrations in MC and further indicate that type (c) compounds probably undergo a stepwise oxidation with the second step occurring more easily than the first.

These results motivated some e.s.r. experiments in ACN. A solution of OMPE in ACN was partially oxidized and an e.s.r. experiment was conducted. The original experiment was completely negative; no signal was observed. However, after accumulating the spectra with a Varian Model C-1024 Time Averaging Computer for 200 sweeps, the characteristic singlet was resolved. Thus OMPE is probably also oxidized in a stepwise manner in ACN. These results do not contradict the electrochemical results which indicate that OMPE is oxidized in a direct two-electron oxidation; rather, the results suggest that the second oxidation occurs at considerably more positive potentials than the first. In fact, from the e.s.r. and electrochemical results we can estimate that  $E_2^0$  in ACN lies in the range:  $(E_1^0 - 0.08 \text{ V}) > E_2^0 > (E_1^0 - 0.36 \text{ V})$ .

#### DISCUSSION

The question of one- vs. two-electron oxidations has been dealt with previously [1-3]. In general the second oxidation step involves removing an elec-

tron from a positively charged molecule where the electron repulsion of the second electron in the same molecular orbital is not present. From the gas phase ionization potentials the energy of removal of the second electron is of the order of 5.0 eV. In solution however, greater solvation of the dication and its greater tendency to form ion pairs decrease this separation: in the absence of other factors this value is about 0.4 to 0.5 V for the usual aprotic solvents and supporting electrolytes. This behavior, characteristic of type (a) compounds, is observed, with somewhat closer spacing of the two oxidation steps, with uTMPE, and with TMPD.

In a more detailed consideration of the factors influencing the path and potential for the oxidation of substituted ethylenes the following factors must be considered:

#### *Substituent effects*

A comparison of the potentials for TMPE, HMPE and OMPE (Table 1) shows that the oxidation becomes easier with an increasing number of N,N-dimethyl (amino phenyl) groups, an expected result considering the strong electron donating characteristics of this group. Fritsch et al. [19] found similar trends with N,N-dimethylamino ethylenes. Furthermore, since the *p*-methoxy group is a less effective electron donating group than the *p*-N,N-methyl group, TAE is more difficult to oxidize than OMPE.

#### *Solvent effects*

The uncertainty in the junction potential values in the two solvents precludes a direct comparison of the oxidation potentials of a given compound in the two solvents. However some information concerning possible solvent effects can be extracted from the difference in oxidation potential  $E_2^0 - E_1^0$  for a given compound in each of the solvents. For TAE  $E_2^0 - E_1^0$  was about 100 mV in MC and 12 mV in ACN, corresponding to equilibrium constants for the reproportionation reaction (5) of 55 and 1.6, respectively. Similarly OMPE shows a larger concentration of radical cation by e.s.r. upon partial oxidation in MC than in ACN. Thus the results indicate that the dication is more highly solvated in ACN, and that methylene chloride will show better resolution of stepwise electron transfers. Ammar and Savéant [2] have discussed the thermodynamics of successive electron transfers and solvation enthalpy and entropy effects for the stepwise reduction of polynitro-compounds in DMF and ACN.

#### *Steric effects*

A surprising aspect of the oxidation of the type (c) compounds is the ease of the second oxidation, so that the second oxidation occurs at potentials equal to or more negative than the first. A plausible explanation is that con-

formation changes in the ethylenes occur as the oxidation state changes. Models show that tetraphenylethylene-related compounds exhibit considerable steric strain when constrained to planarity because of the *cis o*-hydrogen interactions. To relieve the strain, either rotation about the C-phenyl bond or torsion about the ethylene double bond occurs. Garst et al. [44] have invoked a similar qualitative explanation to account for the disproportionation of the tetraphenylethylene anion radical. To examine these effects, discussed in more detail in ref. 1, Goldberg [45] performed HMO calculations incorporating varying degrees of rotation and torsion. Although the interpretation is necessarily only semi-quantitative, these calculations suggest that the bond order of the C-phenyl bond increases and that the bond order of the ethylene double bond decreases as the molecule goes from the parent to the cation radical and then to the dication. Thus as the ethylene undergoes oxidation to the cation radical, torsion about the double bond can occur, thus elevating the relative position of the highest occupied molecular orbital and facilitating the removal of the second electron. These conformational changes were experimentally supported by the reversal coulometric experiments on *cis*-sTMPE which clearly demonstrated that isomerization of the cation radical, of the dication, or of both occurred in solution. Similar isomerizations of radical anions are observed in the reductions of substituted ethylenes such as stilbene and diethyl maleate, where addition of an electron to the antibonding orbital weakens the ethylenic double bond.

Finally the results found here are relevant to past studies of similar systems. Kuwata and Geske [16] showed that tetra(dimethylamino)ethylene undergoes two stepwise one-electron oxidations in ACN. Fritsch et al. [18,19] extended this work to include a number of other dimethylamino-substituted ethylenes. In this study too steric repulsion between C- and N-methyl groups can lead to cyclic voltammetric waves characteristic of direct two-electron oxidations. While the original study of Parker et al. [15] suggested a two-electron oxidation of TAE in ACN + LiClO<sub>4</sub>, the results presented here, as well as a recent study of the Parker group [47], show that the reaction occurs by stepwise one-electron transfers in both MC and ACN (where in ACN  $E_2^0$  is about 7 mV more positive than  $E_1^0$ ) and points to the importance of solvation in the separation between the  $E^0$  values.

Two other studies pertinent to the oxidation of TAE have appeared. A series of investigations of the complexes of TAE with various oxidants has culminated in the reported crystal structure of a salt of the dication of TAE [40]. Valenzuela and Bard [39] have reported an e.s.r. study of the cation radical of TAE. All these are thus consistent with stepwise oxidation of TAE.

We have shown that even with the type (c) compounds such as OMPE, which show two-electron electrochemical behavior, appreciable quantities of radical cation can be produced. These results can explain some previous chemical studies [41,46]. Anderson et al. [41] noted that the diiodide salt of OMPE dication exhibited no e.s.r. activity when dissolved in water, whereas this same salt exhibited considerable e.s.r. activity when dissolved in ethylene chloride.

In fact, their results indicated some 20% of the compound existed as the cation radical in ethylene chloride. To account for this curious behavior, they postulated, in somewhat modified form, the following equilibria:



They further postulated that the difference noted could be attributed to solvent effects: more polar solvents favor more highly charged species and less polar solvents favor the less highly charged species. Elofson et al. [46] have also invoked, on the basis of e.s.r. and n.m.r. studies, the intermediacy of OMPE cation radical in the autoxidation of OMPE in benzene.

The equilibrium constants for (9) and (10) can be calculated from the standard potentials of the relevant half reactions in MC.  $E_N(\text{OMPE}^{2+}/\text{OMPE}) = (E_1^0 + E_2^0)/2 = 0.16$  V and  $E^0(\text{I}_2/\text{I}^-) = 0.20$  V (estimated from cyclic voltammetric measurements of a 0.2 M TBAI + MC solution using a platinum electrode). Assuming different values of  $\Delta E^0 = E_1^0 - E_2^0$ , for a 1 mM solution of OMPE, standard equilibrium calculations show that 3 to 6% of the OMPE will be in the form of the cation radical for  $\Delta E^0$  values of 60 to 0 mV. Thus a solution of  $(\text{OMPE}^{2+})(\text{I}^-)_2$  should exhibit e.s.r. activity in MC and probably also in ethylene chloride.

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