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ANODIC VOLTAMMETRY AND ESR STUDIES OF P-PHENYLENEDIAMINE AND SOME OF ITS DERIVATIVES IN ACETONITRILE

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The electrochemical oxidation of p-phenylenediamine and its derivatives was studied on platinum electrode in acetonitrile. The oxidation mechanism was composed of two successive one-electron reversible waves. The hyperfine ESR spectra of the cation radicals were observed by electrolysis on the first wave. The generation of the same cation radicals could be performed by electrolysis on the second wave, indicating the presence of an electron exchange reaction between the dication and the parent molecule in solution.

The anodic voltammetric behavior of p-phenylenediamine(PPD) in aqueous medium has already been reported.[1,2] In aqueous medium, p-phenylenediamine is oxidized in a two-electron process to the diimine, which is hydrolyzed to the diquinoid. To avoid complications arising from the hydrolysis, we have examined the electrochemical behavior of this compound in acetonitrile where hydrolysis should not take place for substances of this kind, and our investigations have been extended to some its derivatives : N,N-dimethyl-p-phenylenediamine(DMPPD), N,N,N',N'-tetramethyl-p-phenylenediamine(TMPPD), tetramethyl ester of p-phenylenediamine-N,N,N',N'-tetraacetic acid(EPDTA). Another and more fundamental reason for investigating the electrochemical behavior of these compounds in acetonitrile is to understand the properties and behavior of the cation radicals and the dications expected in aprotic solvent.

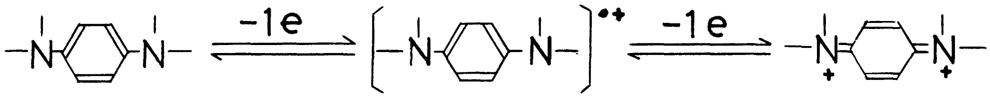
Experimental. PPD and TMPPD (reagent of Wako Pure Chemical Co.) were purified from ethyl alcohol and petroleum ether, respectively. DMPPD(reagent of Wako Pure Chemical Co.) was used without further purification. EPDTA was synthesized by esterification(CH_3OH-HCl) of p-phenylenediamine-N,N,N',N'-tetraacetic acid prepared according to the reported method[3] (Found: C, 54.49 ; H, 5.98 ; N, 7.18%. Calcd for $C_{18}H_{24}N_2O_8$: C, 54.53 ; H, 6.11 ; N, 7.07%). Acetonitrile was purified by the method of Coetzee et al.[4] Moisture in the purified acetonitrile was determined by the Karl-Fischer titration to be 0.01-0.02%. Tetraethyl ammonium perchlorate(TEAP) was used as a supporting electrolyte. TEAP was prepared following Fujinaga et al[5]., and was recrystallized five times from distilled water before drying at 60°C in vacuo.

Polarographic curves were recorded using a Yanagimoto P-8 type Polarograph.

Cyclic voltammetry was performed with a versatile solid-state instrument constructed in this laboratory following the design of Goolsby and Sawyer.[6] A rotating platinum disk electrode (RPDE) was used as a working electrode. The electrode surface was polished with the fine emery paper before each run. Reference electrode was constructed by dipping a coil of silver wire into a solution of 0.1M $AgClO_4$ in acetonitrile-0.1M TEAP contained in a glass tube having a medium-porosity glass frit and salt bridge at one end. A platinum wire was used as a counter electrode. ESR spectra were recorded on a Hitachi MES-4001 ESR spectrometer with *in situ* generation of radical species using a platinum wire working electrode.[7)]

Results and Discussion. Two successive voltammetric waves were observed with all p-phenylenediamines studied. The height of the two successive waves for each p-phenylenediamines was nearly the same, but the second wave was slightly smaller than the first. The values of the half-wave potentials for the compounds studied are reported in Table 1. The potential separation between the two successive oxidation waves was considerably large. The half-wave potentials for each successive wave were independent of the rotating speed. These successive waves showed a linear relation between the limiting current and $\omega^{\frac{1}{2}}$ (where $\omega=2\pi n$, and n = rotating speed). This result shows that these waves are diffusion-controlled in acetonitrile.

Cyclic voltammograms of p-phenylenediamines were recorded under the polarization sweep rate of 0.025-0.5 V/sec. An example of these cyclic voltammograms is represented in Fig. 1 in the case of PPD. The oxidation of each p-phenylenediamines exhibited two anodic peaks corresponding to the two oxidation waves obtained by the RPDE. Similarly, two cathodic peaks were also recorded. The difference between the anodic and cathodic peaks was about 60 mV compared to the theoretical value of 58 mV for a one-electron reversible process. The heights of the voltammetric and cyclic voltammetric waves corresponded to one electron for each successive wave. In the time range of these voltammetry the oxidation process can be represented as follows :



Stability of the cation radicals was sufficient to allow its observation by ESR spectroscopy. The ESR spectra of p-phenylenediamines were obtained by controlled potential electrolysis at the potential of the first oxidation wave in acetonitrile. The examples of the resultant ESR spectra for the present study are given in Fig. 2 in the case of PPD and EPDTA. Although these spectra were very complex and couldn't be readily resolved, we have completed an unambiguous interpretation and have accurately measured all hyperfine coupling constants. These coupling constants are given in Table 2. The ESR spectrum of the PPD cation radical in this study was identical with that obtained previously by Melchior and Maki[8)] in acetonitrile. The ESR spectrum of the DMPPD cation radical showed some line broadening due to the nearly overlapping lines of the amine protons and nitrogens. The values listed in Table 2 gave the best fit to the observed spectrum. A complete analysis of the ESR spectrum of the TMPPD cation radical gave nearly identical couplings with those reported by Carrington *et al.*[9)] The ESR spectrum of the EPDTA cation radical has

Table 1. Half-wave potentials of the two successive voltammetric waves of p-phenylenediamines

	$E_{\frac{1}{2}}$, V vs.Ag/Ag$^+$	
	1st wave	2nd wave
PPD	-0.082	+0.422
DMPPD	-0.173	+0.400
TMPPD	-0.300	+0.280
EPDTA	+0.135	+0.730

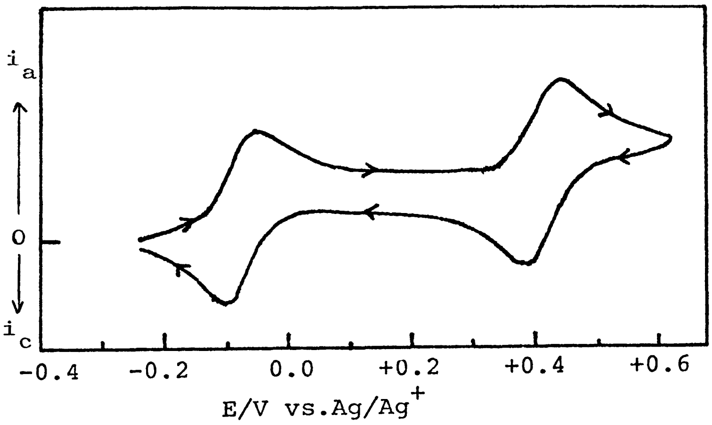
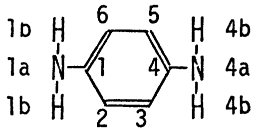
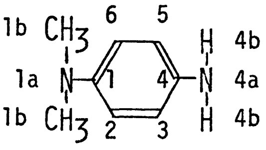
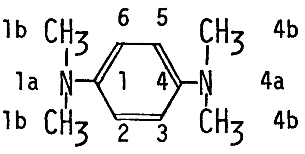
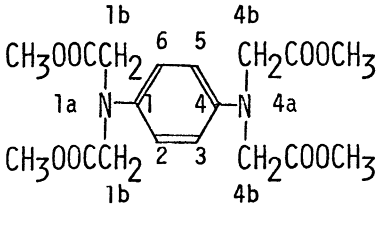


Fig. 1. Cyclic voltammetric curves of 1mM PPD oxidation in acetonitrile containing 0.1M TEAP recorded at stationary platinum electrode.

scan rate : 0.2 V/sec

Table 2. Hyperfine coupling constants for p-phenylenediamine cation radicals

	Nuclei	Positions	Coupling constants (gauss)
PPD			
	N	1a, 4a	5.13
	H	1b, 4b	5.75
	H	2,3,5,6	2.11
DMPPD			
	N	1a	7.19
	N	4a	4.53
	H	1b	7.39
	H	4b	4.69
	H	2,6	1.67
	H	3,5	1.11
TMPPD			
	N	1a, 4a	6.88
	H	1b, 4b	6.94
	H	2,3,5,6	1.99
EPDTA			
	N	1a, 4a	9.88
	H	1b, 4b	3.66
	H	2,3,5,6	2.01

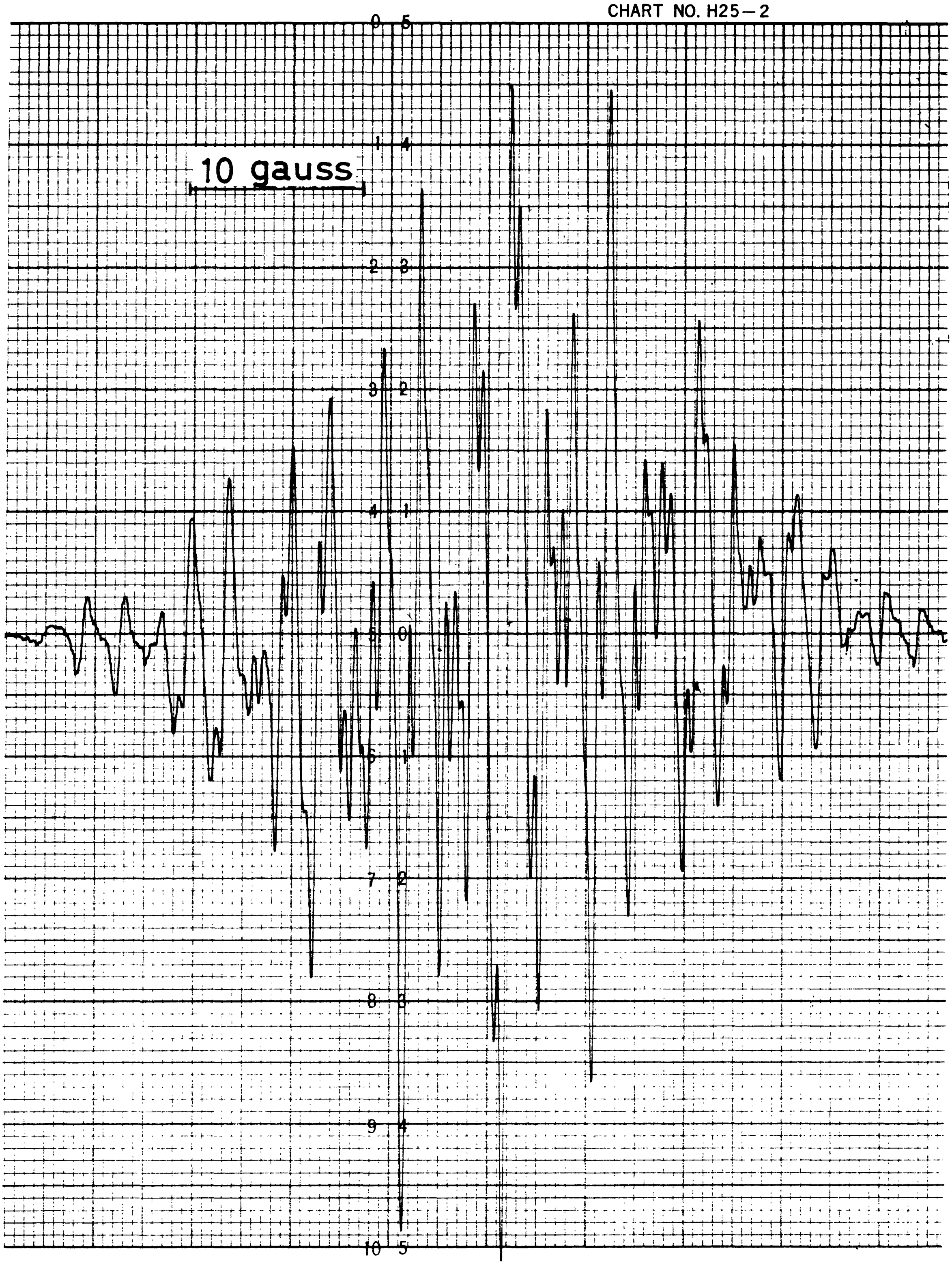


Fig. 2(A). ESR spectrum of PPD cation radical produced by electrolysis on the first wave.

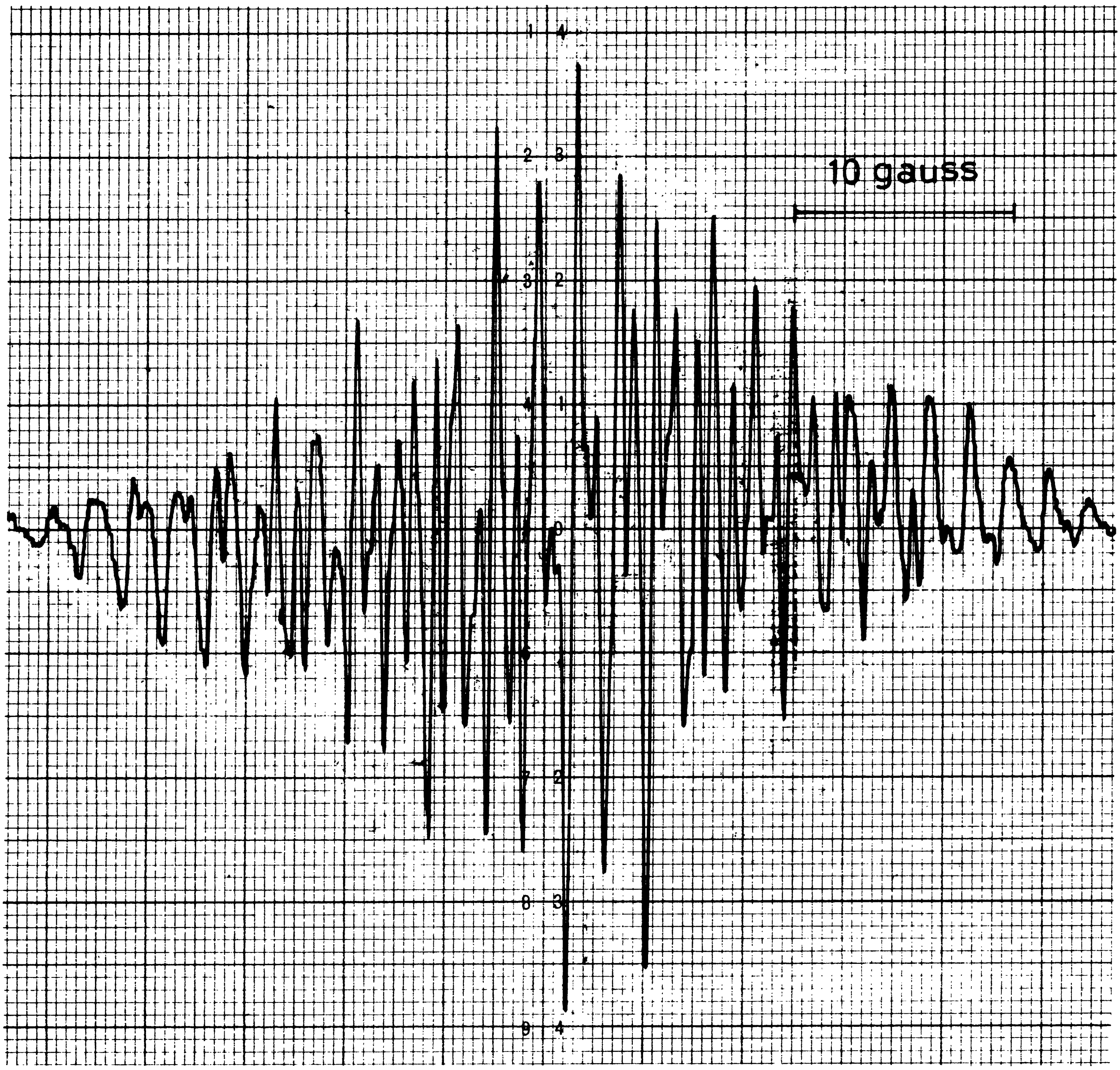
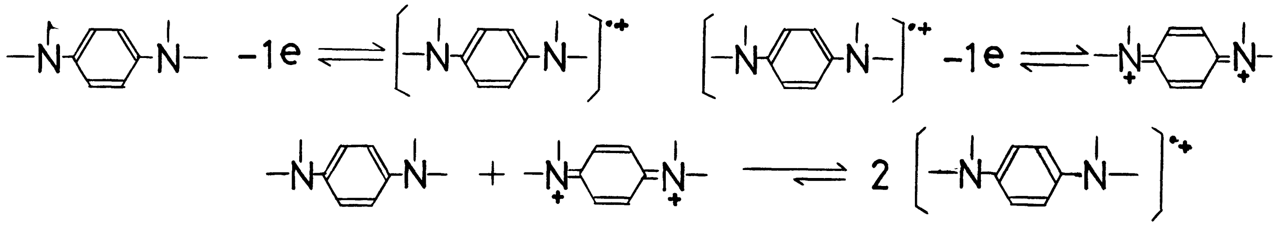


Fig. 2(B). ESR spectrum of EPDTA cation radical produced by electrolysis on the first wave.

not been studied. In this study, EPDTA cation radical had an ESR spectrum which showed the coupling of eight equivalent protons, two equivalent nitrogen nuclei, and four equivalent ring protons.

It is to be noticed that generation of the same cation radicals could be performed in the potential range of the second wave as well as in the potential range of the first one. After the exhaustive electrolysis at the potential of the second wave, the electrolysed solution was transferred into the ESR cavity, but no ESR spectrum was observed. By adding the parent compound to this electrolysed solution, the colour of the solution turned from orange to purple, and the ESR spectrum of the same cation radical was observed. These results mean that the dication when formed at the electrode reacts on the parent molecule to re-generate the cation radical through a fast and quasi-irreversible electron exchange reaction in solution. The oxidation scheme is thus :



Since the potential separation between the two successive oxidation waves is large, the electron exchange reaction is very much displaced toward the right-hand side. This is a new example of electron transfer reactions between the electrogenerated species and the parent molecule in solution.

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