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Anodic Oxidation of *N*,*N*-Dimethyl-*p*-phenylenediamine with Sodium Sulfite

Tatsuo Erabi, Fumihiro Arifuku, and Masaya Tanaka
Department of Industrial Chemistry, Faculty of Engineering, Tottori University, Koyamacho, Tottori 680

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The sulfonation reaction occurs in the anodic oxidation of *N*-methyl-substituted-*p*-phenylenediamine, in the presence of sodium sulfite,[1–3] and the electrode reaction proceeds through the so-called ECE mechanism: that is the electro-oxidation of *N*-methyl-substituted-*p*-phenylenediamine, followed by a chemical sulfonation reaction with sodium sulfite and furthermore with a successive electro-oxidation of the sulfonated compound. However, the reaction intermediate with sodium sulfite has still not completely been revealed. The present paper aims to clarify the reaction intermediate, and to examine whether any regularity is found in these sulfonation mechanisms or not.

Apparatus for voltammetry have been described previously.[3]

When *N*,*N*-dimethyl-*p*-phenylenediamine (DMPPD) was oxidized anodically, two successive waves were observed in the region between pH 3.75 and 6.50, and only one wave was observed in its upper and lower regions. In addition, when the comparison of the wave height of DMPPD oxidation to the one of *p*-phenylenediamine (PPD) oxidation was attempted using the rotating electrode, the first wave height for DMPPD oxidation in the region between pH 3.75 and 6.50 was equal half to the wave height for PPD oxidation, and therefore the number of electron transfer involved in the reaction for the first wave was estimated to be 1. In its upper and lower regions, the wave height of DMPPD was equal to that of PPD, and therefore the number of electron transfer was estimated to be 2. However, it has been known that DMPPD forms the stable cation radical (so-called Wurster's red) in the measured pH region.[4] Moreover, from the analysis of the products by the controlled-potential electrolysis at the half-wave potential at pH 2.70, it was observed that DMPPD cation radical produced partly. Therefore, it seems probable that two successive one-electron transfers actually occurred in these pH regions. Furthermore, when the Tafel plots were tried for the polarograms obtained with the rotating electrode, α n values were estimated to be about 0.5. Hence, α was equal to 0.5 since the number of electron transfer for the initial reaction was estimated to be 1, and therefore the initial reaction is an oxidation of DMPPD with reversible one-electron transfer.

The anodic oxidation of DMPPD with sodium sulfite was carried out at pH 2.70, 4.00, 6.00, 8.00, and 10.00. As the typical examples, the anodic polarograms at pH 2.70 and 6.00 were shown in Figs. 1 and 2, and the relationships of half-wave potentials and peak currents to concentration of sodium sulfite based on the polarograms in Figs. 1 and 2 were illustrated in Figs. 3 and 4.

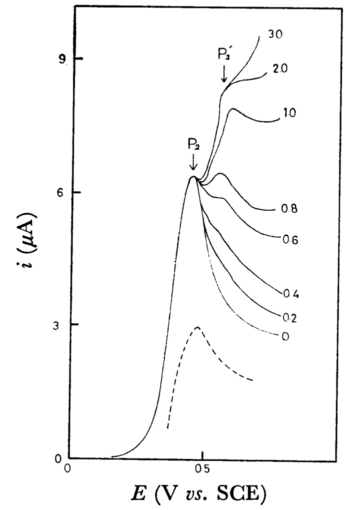

Fig. 1. Typical polarograms of DMPPD oxidation at pH 2.70. Numbers in the figure represent the mole ratio of Na_2SO_3 to DMPPD. The dotted line shows oxidation wave of DMPPD monosulfonate.[5,6]

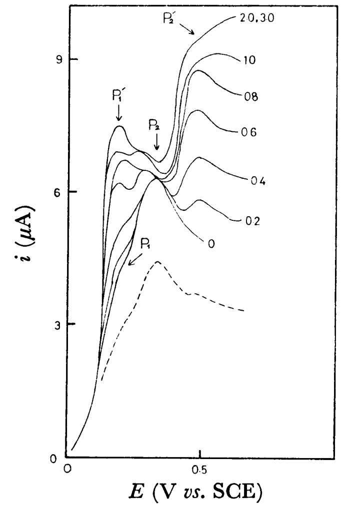

Fig. 2. Typical polarograms of DMPPD oxidation at pH 6.00. Numbers in the figure represent the mole ratio of Na_2SO_3 to DMPPD. The dotted line shows oxidation wave of DMPPD monosulfonate.

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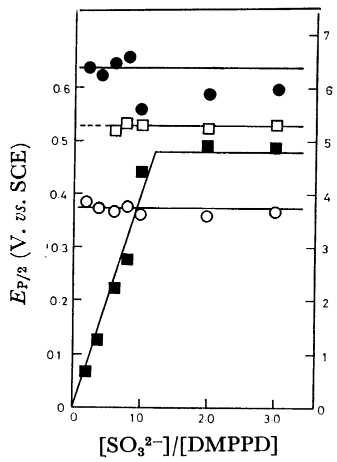

Fig. 3. Relationships of half-wave potential and peak current to Na_2SO_3 concentration at pH 2.70.
○, ●; half-wave potential and peak current for P_2, and □, ■; for P_2'.

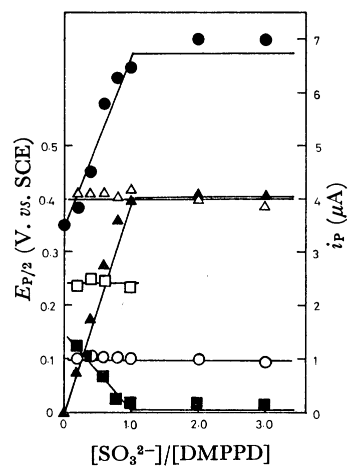

Fig. 4. Relationships of half-wave potential and peak current to Na_2SO_3 concentration at pH 6.00.
○, ●; half-wave potential and peak current for P_1'. □, ■; for P_2, and △, ▲; for P_2'.

Table 1. Controlled-potential electrolysis of DMPPD

Sample	Potential of electrolysis (V *vs.* SCE)	R_f-value	λ_{max} (nm)
DMPPD	—	0.92	248
DMPPD+Na_2SO_3	—	0.92	248
DMPPD+ [4]	—	—	550
DMPPD monosulfonate	—	0.42	250
DMPPD (pH 2.70)	0.36	0.88	548
		0.80	280
	0.44	0.81	285
DMPPD (pH 6.00)	0.18	0.87	551
	0.32	0.89	550
		0.82	281
DMPPD+Na_2SO_3 (pH 2.70)	0.44	0.43	250
		0.36	265
DMPPD+Na_2SO_3 (pH 6.00)	0.18	0.87	550
		0.41	251
		0.31	263
	0.32	0.35	265

The results with DMPPD oxidation can be summarized as follows;

1) The species formed at the first wave (P_1) is DMPPD cation radical, since the initial reaction is oxidation of DMPPD with reversible one-electron transfer. (P_1 is not observed in Fig. 1.)

2) The product at the first wave, DMPPD cation radical, undergoes rapid chemical reaction with SO_3^{--} (or HSO_3^-), and forms DMPPD monosulfonate.

3) This resulting DMPPD monosulfonate is anodically oxidized through second successive one-electron transfers at the same potential range of DMPPD oxidation (P_1'), and forms DMPPD monosulfonate cation radical.

4) The product at P_1', DMPPD monosulfonate cation radical, again undergoes chemical reaction with SO_3^{--} (or HSO_3^-), and forms DMPPD disulfonate.

5) This resulting DMPPD disulfonate is anodically oxidized at the potential of P_2', and forms DMPPD disulfonate cation radical.

That is to say, the sulfonation reaction with DMPPD electro-oxidation seems to proceed through the ECE mechanism. These results are also supported by paper chromatography and spectrophotometric analysis of the products obtained by the controlled-potential electrolysis of DMPPD with sodium sulfite (Table 1).