Cyclic Voltammetry of Aromatic Amine *N*-Oxides in Nonaqueous Solvents and the Stability of the Free Radicals Produced[1)]

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Cyclic voltammograms of aromatic amine *N*-oxides were recorded in nonaqueous solvents at various sweep rates less than 10 V/s. The measurement was carried out for both cathodic and anodic sweeps, and the sweep rate for obtaining a good cyclic voltammogram was correlated with the wave height of the a.c. polarogram in the reduction and oxidation processes, respectively. A good correlation was found between the sweep rate and the wave height in both the reduction and oxidation processes. This confirmed that the two values serve as good measures of the stability of the anion or cation free radical produced by the electrode reaction of the aromatic amine *N*-oxides. The data were also examined by comparison with results from an electron spin resonance study. Finally, the temperature effect on the cyclic voltammogram of pyridine *N*-oxide was investigated in detail.

The study of cyclic voltammetry (CV) of aromatic amine *N*-oxides was carried out in nonaqueous solvents to compare the results with those of our previous polarographic and electron spin resonance (ESR) investigations on the same compounds.[2–7)] The results of these CV studies are considered to be good measures of the reversibility of the electrode reaction[8)] and were expected to display good correlation with the previous results mentioned above.

Experimental

The CV measurement was made using a combination of a Yanagimoto Applied Potential Sweep Unit Model PE-21-TB2SS, a Yanagimoto polarograph P8-AP, a Hitachi Synchroscope Model V-104, and a Riken Denshi XY-Recorder Model D-51P to obtain a cyclic voltammogram at a sweep rate of 0.0017—10 V/s. As working electrodes, a PAR Model 9323 hanging mercury drop electrode (HMDE), a hanging mercury electrode (HME), and a platinum disk electrode (PDE: 2 mm in diameter) were used. All the measurements of samples, except for pyridine *N*-oxide (PNO: *vide infra*) were done at 25±0.1 °C by using the so called three-electrode-technique, a saturated calomel electrode (SCE) being employed as a reference electrode except for the low temperature measurement. The solvents used were *N*,*N*-dimethylformamide (DMF) and CH_3CN containing 0.1 mol dm^{-3} tetrapropylammonium perchlorate (TPAP) as the supporting electrolyte.

The cathodic sweep cyclic voltammogram of PNO was measured in the temperature range between 23.5 °C and −40

TABLE 1. POLAROGRAPHIC, CYCLIC VOLTAMMETRIC, AND ELECTRON SPIN RESONANCE (ESR) DATA OF AROMATIC AMINE *N*-OXIDES IN REDUCTION AND OXIDATION PROCESSES

Compound	Reduction[a)]							Oxidation[b)]						
	Polarography[c)]		Cyclic voltammetry[d),h)]				ESR[e)]	Polarography[f)]		Cyclic voltammetry[g),h)]				ESR[e)]
	$(-E_{1/2}^{\mathrm{red}}$ *vs.* SCE)/V	$I_{\mathrm{a.c.}}/\mu\mho$ mol m^{-3}	$(-E_{\mathrm{p.f}}$ *vs.* SCE)/V	$(-E_{\mathrm{p.b}}$ *vs.* SCE)/V	$(-E_{1/2}^{\mathrm{red}}$ *vs.* SCE)/V	Sweep rate[i)] / V s^{-1}		$(E_{1/2}^{\mathrm{oxd}}$ *vs.* SCE)/V	$I_{\mathrm{a.c.}}/\mu\mho$ mol m^{-3}	$(-E_{\mathrm{p.f}}$ *vs.* SCE)/V	$(-E_{\mathrm{p.b}}$ *vs.* SCE)/V	$(E_{1/2}^{\mathrm{oxd}}$ *vs.* SCE)/V	Sweep rate[i)] / V s^{-1}	
Phenazine 5,10-dioxide	0.833	306	0.849	0.785	0.817	$\approx 1\times10^{-3}$	Yes	1.344	400	1.374	1.30	1.337	1.12×10^{-2}	Yes
Phenazine 5-oxide	0.972	348	0.983	0.922	0.953	$\approx 1\times10^{-3}$	Yes	1.745	78	—	—	—	>10	No
Acridine 10-oxide	1.300	180	1.361	1.262	1.312	—	Yes	1.280	137	1.30	1.238	1.269	≈ 0.1	Yes
Quinoxaline 1,4-dioxide	1.241	293	1.236	1.171	1.204	$<1\times10^{-3}$	Yes	1.598	335	1.619	1.492	1.556	0.18	Yes*
Quinoxaline 1-oxide	1.419	315	1.427	1.344	1.386	$<1\times10^{-3}$	Yes	1.971	—	—	—	—	>10	No
Quinoline 1-oxide	1.809	317	1.859	1.736	1.798	$\approx 1\times10^{-3}$	Yes	1.537	59	—	—	—	>10	No
Isoquinoline 2-oxide	1.946	231	1.918	1.839	1.879	0.4	Yes*	1.600	51	—	—	—	>10	No
Pyrazine 1,4-dioxide	1.616	306	1.659	1.566	1.613	0.025	Yes	1.741	331	1.788	1.685	1.737	≈ 0.3	Yes*
Pyrazine 1-oxide	1.837	325	1.859	1.773	1.816	$<1\times10^{-3}$	Yes	2.312	55	—	—	—	>10	No
Pyridine 1-oxide	2.297	106	—	—	—	>10	Yes*	1.802	90	—	—	—	>10	No
4-(dimethylamino)-pyridine 1-oxide	—	—	—	—	—	—	—	0.759	145	0.820	0.744	0.782	4	Yes

a) Data in DMF. b) Data in CH_3CN. c) Obtained with DME, and taken from Refs. 2, 3, 4, and 5. d) Obtained with HMDE. e) Taken from Refs. 2, 3, and 6. Here "Yes" means that the ESR spectra due to the anion or cation free radicals were recorded at room temperature. However, the free radicals of several *N*-oxides were obtained only at below 0 °C; in such a case the asterisk is put on "Yes" as superscript. f) Obtained with PDE at 600 r.p.m., and taken from Ref. 5. g) Obtained with PDE. h) The equation, $E_{1/2}=(E_{\mathrm{p.f}}+E_{\mathrm{p.b}})/2$, was used to determine the half-wave potential. Each value of $E_{\mathrm{p.f}}$ and $E_{\mathrm{p.b}}$ is for the CV curves at the sweep rate where the backward sweep wave becomes evident. See text for details. i) This is the value corresponding to the $(i_{\mathrm{p.b}}/i_{\mathrm{p.f}})=0.5$. See text for details.

°C.[10] A platinum wire was employed instead of the SCE, since the SCE can not be used at the lower temperatures.[9] HME was employed as a working electrode, the solvent being DMF containing TPAP. Note here that, since the PNO anion radical is unstable at room temperature (*vide infra*), checking the reversibility of the electrode process at the lower temperature was the most important problem for PNO.

The aromatic amine *N*-oxides used here, listed in Table 1, are the same ones previously studied with polarographic and ESR techniques.[2–7]

Results and Discussion

For the analyses of CV curves, the following methods were applied. The peak current of the backward sweep was measured by the switching potential current (SPC) method reported by Nicholson.[11–12] The value of the half-wave potential $E_{1/2}$ was cyclovoltammetrically determined by the equation $E_{1/2}=(E_{p.f}+E_{p.b})/2$, which is in principle applicable to the reversible redox system.[13] Here, $E_{p.f}$ and $E_{p.b}$ are the forward and the backward peak potentials, respectively. This equation gave $E_{1/2}$ values almost independent of the sweep rate and compatible with those determined polarographically. In the case of the cathodic sweep, generally speaking, the CV curves recorded in DMF with HMDE were almost the same as those obtained with PDE, and the difference is not remarkable. The CV data recorded with HMDE are given in Table 1, which also lists the other experimental results and, as references, our previously reported data. In the cathodic sweep cyclic voltammograms of the *N*-oxides in DMF the backward sweep waves were always observed for all the samples, except for PNO, at room temperature and at a sweep rate less than 10 V/s. Comparison with previous ESR and polarographic studies of the *N*-oxides[2–7], clearly shows that this backward sweep wave is due to the oxidation process of the anion radical produced by the cathodic sweep. The sweep rate to obtain the backward sweep wave would be related to the stability of the anion radical. In the case of PNO, we could not observe the backward sweep wave at room temperature even when the sweep rate is increased to 10 V/s, as shown in Fig. 1a. However, when the voltammogram was recorded at −30 °C and at a moderate sweep rate, the backward sweep wave was clearly observed, as is seen in Fig. 1b.[14] Since our previous study indicated that the ESR spectrum of the PNO anion radical was clearly obtained at about −50 °C by employing the electrochemical technique,[2] the above backward sweep wave must be due to the oxidation process of the PNO anion radical, in agreement with the ESR study.

Next we would consider the anodic sweep cyclic voltammogram in CH_3CN. Only four of the aromatic amine *N*-oxides studied here showed the backward sweep wave under the present experimental conditions (see Table 1). A typical compound, phenazine 5,10-dioxide, shows a clear backward sweep wave even at 0.1 V/s. This agrees with observations by other workers.[15] The cyclic voltammogram of quinoxaline 1,4-dioxide (Fig. 2) showed no clear backward sweep wave at the rate 0.1 V/s, but the curve is obviously observed at 2 V/s. The cation radical of this *N*-oxide is unstable compared with that of phenazine 5,10-dioxide. In the case of pyrazine 1,4-dioxide, the cation radical was more unstable and therefore the backward sweep wave required a higher sweep rate. These observations agreed well with the results derived from our ESR study of cation radicals.[6]

Based on the discussion mentioned hitherto the sweep rate of the cyclic voltammogram should be closely correlated with the life time of the anion or cation free radical produced by the electrode reaction. Alternative-

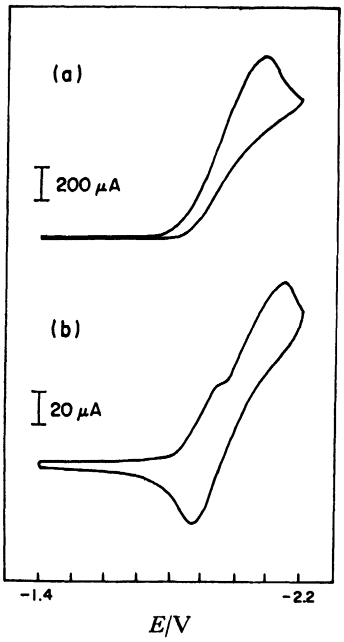

Fig. 1. Cyclic voltammograms of pyridine *N*-oxide (2.51 × 10^{-3} mol dm^{-3}) in DMF containing 0.1 mol dm^{-3} TPAP. Sweep rate and temperature were, respectively, 10 V/s and 23.5 °C for (a), and 8 V/s and −30 °C for (b). The electrode system was HME and platinum wire, the latter being used instead of SCE (see text).

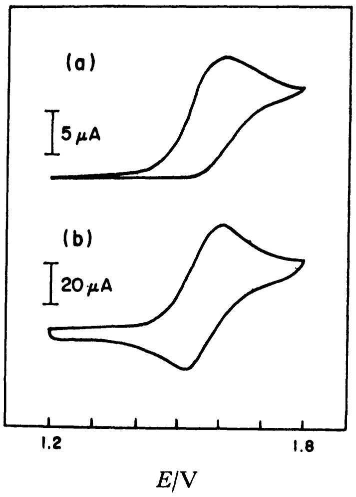

Fig. 2. Cyclic voltammograms of quinoxaline 1,4-dioxide (8.02 × 10^{-4} mol dm^{-3}) in CH_3CN containing 0.1 mol dm^{-3} TPAP at 25 °C. Sweep rate was 0.1 V/s and 2 V/s for (a) and (b), respectively. Reference electrode was SCE.

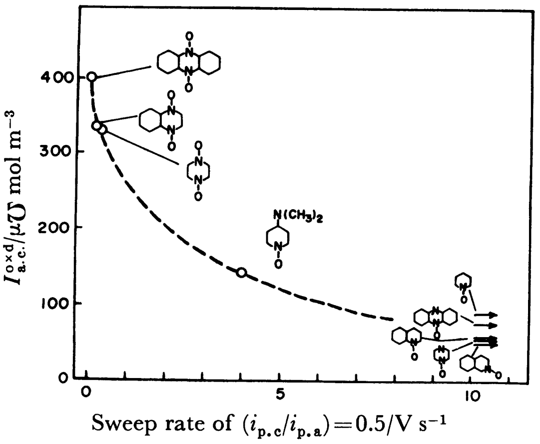

Fig. 3. Relationship between the wave height of the a.c. polarograms and the sweep rate at $(i_{p.c}/i_{p.a})=0.5$ of the cyclic voltammograms in the oxidation process of aromatic amine N-oxides in CH_3CN. The backward sweep wave was not observed for the compounds designated by arrows.

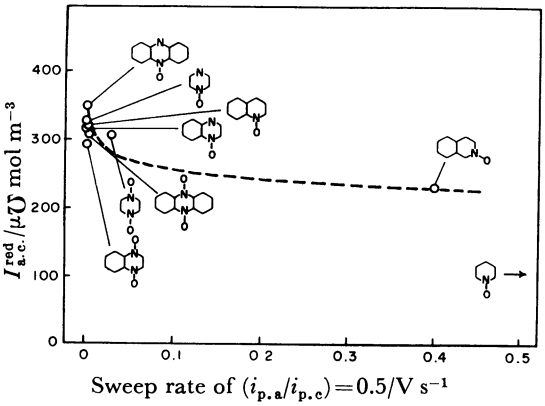

Fig. 4. Relationship between the wave height of the a.c. polarograms and the sweep rate at $(i_{p.a}/i_{p.c})=0.5$ of the cyclic voltammograms on the reduction process of aromatic amine N-oxides in DMF. See text on the pyridine N-oxide, the backward sweep wave of which was not observed at room temperature.

ly many reports support the fact that the wave height of an a.c. polarogram is a good measure of the reversibility of the electrode reaction.[16] Accordingly, the correlation between the sweep rate of the cyclic voltammograms and the wave height of a.c. polarograms was examined for the N-oxides studied. As a sweep rate of the former, the value of $(i_{p.b}/i_{p.f})=0.5$ was conveniently chosen (see Table 1), since the half wave height of a backward sweep against the forward sweep wave height would be considered to be related to the life time of the free radical.[8c] This value was obtained by plotting the $i_{p.b}/i_{p.f}$ value to the sweep rate, where $i_{p.b}$ and $i_{p.f}$ are the peak height of the backward and the forward sweep waves, respectively. The wave heights of a.c. polarograms, reported in our previous papers,[2-5] were obtained under the same experimental conditions and with the same compounds as those employed here. The data are cited in Table 1. In Figs. 3 and 4 the above correlation was illustrated. Figure 3 indicates that the wave height $I^{oxd}_{a.c}$ of the a.c. polarograms for oxidation and the sweep rate value at $(i_{p.c}/i_{p.a})=0.5$ have a good correlation with each other and that the larger the $I^{oxd}_{a.c}$ value and the smaller the sweep rate value, the more stable is the cation radical. The ESR spectra of the cation radicals of the three N,N'-dioxides and the 4-(dimethylamino)pyridine 1-oxide shown in Fig. 3 were successfully measured (*vide supra*).[6] As seen in Fig. 4, a correlation of the $I^{red}_{a.c}$ (wave height of a.c. polarogram for reduction) to the sweep rate value at the $(i_{p.a}/i_{p.c})=0.5$ was also obtained, although the relation was somewhat ambiguous compared with the case of Fig. 3. This is due to the high stability of the anion radicals of the N-oxides[2-5] as discussed hitherto, so that the $I^{red}_{a.c.}$ values are rather large and the sweep rate values defined above are also small. From the results shown in Figs. 3 and 4, we may say that the potential sweep rate for yielding a cyclic voltammogram with a good backward sweep wave is a good measure for checking the reversibility of the electrode reaction of the aromatic amine N-oxides in nonaqueous solvents, and that a good correlation exists between the potential sweep rate and the wave height of a.c. polarograms or the stability of the free radicals of the N-oxides as studied by the ESR technique.

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1) Most of this work was done at the Shionogi Research Laboratories where T. K. studied until March 31, 1980.

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8) a) R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York and Basel (1969), Chap. 5; b) T. Takamura, *Denki Kagaku*, **39**, 445 (1971); c) K. B. Wiberg and T. P. Lewis, *J. Am. Chem. Soc.*, **92**, 7154 (1970).

9) This was a recommendation (private communication) of Professor Masanori Sato of Kyoto University of Industrial Arts and Textile Fibers. Also, our experiments indicated that the CV curves could be recorded with no difficulty with platinum reference electrode, although the peak potentials could not be accurately determined.

10) The melting point of mercury is −38.89 °C, thus CV measurement at temperatures below −40 °C was not tried.

11) R. S. Nicholson, *Anal. Chem.*, **38**, 1406 (1966).

12) Using ferrocene as the standard (0.1 mol dm^{-3} TPAP/CH_3CN, Pt electrode) we compared the SPC technique with the conventional holding method.[8a,b] The result indicated that the former method is better than the latter, and it always leads to the 1.00 for the value of (backward sweep peak current$=i_{p.b}$)/(forward sweep peak current$=i_{p.f}$) despite of the selection of switching potentials. The value of $(i_{p.b}/i_{p.f})$ is calculated by the equation: $(i_{p.b}/i_{p.f})=(i^{\circ}_{p.b}/i^{\circ}_{p.f})+0.485\times(i^{\circ}_{sp}/i^{\circ}_{p.f})+0.086$. The i°_{sp} is the current at the switching potential. Here superscript zero means the current measured

from the galvanometer zero line, so that $i_{p,f}=i^{\circ}_{p,f}$.

13) S. F. Nelsen, V. Peacock, and G. R. Weisman, *J. Am. Chem. Soc.*, **98**, 5269 (1976).

14) In this case, a pre-wave was always accompanied by the main forward wave, as Fig. 1b shows. The origin of this pre-wave is not clear at the present, but perhaps it may be due to the adsorption phenomena of PNO to the HME surface at lower temperature, as was seen in the cyclic voltammogram of pyridine.[8c)]

15) a) A. Stüwe, M. W. Schäfer, and H. Baumgärtel, *Ber. Bunsenges. Phys. Chem.*, **78**, 309 (1974); b) M. W. Schäfer and H. Baumgärtel, *ibid.*, **78**, 317 (1974); c) A. Stüwe and H. Baumgärtel, *ibid.*, **78**, 320 (1974).

16) See, for example, T. Fujinaga and K. Izutsu, "Bunseki Kagaku II," in "Shin Jikken Kagaku Koza," ed by the Chemical Society of Japan, Maruzen, Tokyo (1977), Vol. 9, p. 389.