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Non-aqueous Polarogrophic Behavior of the Anion Radical Itself of 4-Nitropyridine *N*-Oxide[1]

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Although many reports have been published on the non-aqueous polarography of organic substances, there have been only a few reports on the polarographic behaviour of the anion radical itself, prepared macroscopically,[2] because of the instability of the radicals. However, a comparison of the non-aqueous polarogram for the neutral molecule (mother compound) with that of the anion radical formed from the mother compound also seems to be important in elucidating the reduction mechanism. From this point of view, we tried to make polarographic measurements of the anion radical itself of 4-nitropyridine *N*-oxide (4NPO) and of 4,4′-dinitrobiphenyl, whose polarograms usually show two waves: the first wave is due to the anion-radical formation of the mother compound,[3] while the second one may be caused by dianion formation.[3,4] In this note we would like to report our experimental results, and also our findings on the electrolysis cell, which may be very convenient for carrying out the measurement in a non-aqueous medium in which the contamination of water, *etc.* diffusing from the saturated calomel electrode (SCE) has been completely eliminated.

Experimental

The controlled potential electrolysis cell employed here is illustrated in Fig. 1. The cathode potential of either one of two electrolysis cells of almost the same size is controlled *versus* the SCE. The other cell is then in a parallel connection to the first one, as may be seen in Fig. 1. Now, it can easily be understood that the cathode potential of the second cell is also automatically controlled so as to operate at the cathode potential of the first cell. Since no reference cell is necessary for the second cell, any contamination originating from the reference cell is completely removed. Operation under a vacuum system or at a higher or a lower temperature is also very easy by making a little modification to satisfy this experimental purpose. In the present experiments, dimethylformamide was employed as the solvent, the supporting electrolyte being 0.1 mol/*l* tetra-*n*-propylammonium perchlorate. The capillary used for the dropping mercury electrode had the following open circuit values in distilled water: $m=1.00$ mg/sec and $t=9.55$ sec at $h=70$ cm. When we measured the polarogram of the anion radical produced in the second cell, first the cell circuit was made free from the constant-potential electrolyzer, and then the anode of the cell (right-hand side in Fig. 1) was quickly replaced with SCE in a nitrogen atmosphere. The polarogram was subsequently recorded *versus* SCE. The other experimental procedure was just the same as in previous papers.[3,4]

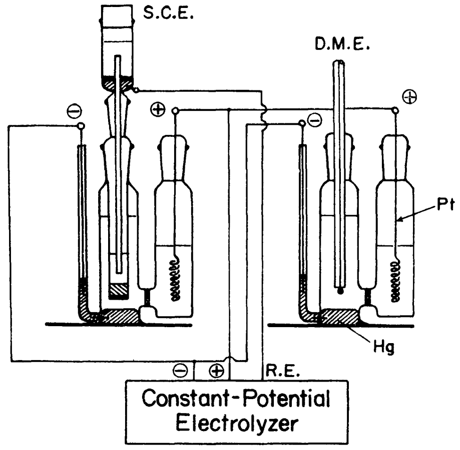

Fig. 1. Cells employed for recording the polarogram of anion radical itself (D.M.E.: dropping mercury electrode). The inlet part of N_2 gas for removing the dissolved oxygen is omitted in this figure for simplicity (see Fig. 1 of the reference 3a in text).

Results and Discussion

The polarograms recorded for 4NPO are shown in Fig. 2 as typical examples. The observed constant values, such as the half reduction (or oxidation) potential, $E_{1/2}$, the DC wave height, i_{DC}, and the AC peak height, i_{AC}, are listed in Table 1. It was previously

Table 1. Polaroglaphic data of 4-nitropyridine *N*-oxide and its anion radical[a]

4-Nitropyridine *N*-oxide	$-E_{1/2}$[b] (V)	i_{DC} (μA)	i_{AC} (μmhos)	$-E_{1/2}$[b] (V)	i_{DC} (μA)	i_{AC} (μmhos)
	1st reduction wave			2nd reduction wave		
Neutral species	0.80	1.66	294	1.69	2.10	172
	Oxidation wave			Reduction wave		
After electrolysis at −1.10 V	0.77	1.38	228	1.66	1.88	128

a) See text for the meaning of each notation, and Fig. 2 for experimental conditions.

b) $-E_{1/2}$ values are *versus* SCE and corrected for so called *IR*-drop term.

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[1] Presented at the 14th Symposium of Polarography, Hiroshima, Oct. 7, 1968.

[2] a) K. S. V. Santhanam and A. J. Bard, *J. Amer. Chem. Soc.*, **88**, 2669 (1966). b) J. L. Sadler and A. J. Bard, *J. Electrochem. Soc.*, **115**, 343 (1968). c) J.-P. Billon, *Bull. Soc. Chim. Fr.*, **1961**, 1923.

[3] a) T. Kubota, K. Nishikida, H. Miyazaki, K. Iwatani, and Y. Ōishi, *J. Amer. Chem. Soc.*, **90**, 5080 (1968); b) K. Nishikida, H. Miyazaki, T. Kubota, S. Katsumata, and S. Nagakura, Presented at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1969.

[4] T. Kubota, Y. Ōishi, K. Nishikida, and H. Miyazaki, This Bulletin, **43**, 1622 (1970).

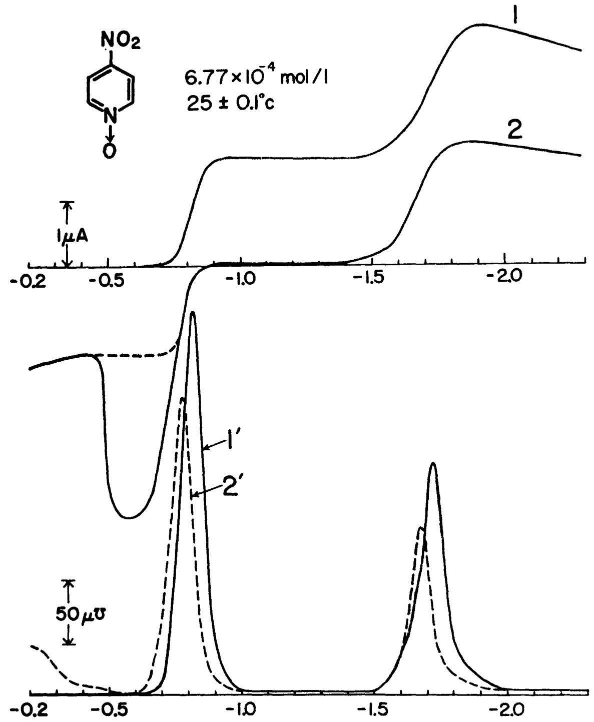

Fig. 2. DC (upper part) and AC (lower part) polarograms of 4-nitorpyridine *N*-oxide (1 and 1′) and its anion radical (2 and 2′).

shown that the first wave of the 4NPO neutral species is caused by the formation of the anion radical, which is quite stable,[5] and that the second wave may be due to the dianion formation, since: (i) DC wave-heights of the first and the second waves are almost the same and (ii) controlled potential electrolysis at the second wave gives the ESR signal of the 4NPO anion radical, perhaps because of a rapid electron exchange between neutral and dianion species. The results in Fig. 2 now give additional evidence for the interpretation of the reduction wave. That is, in the polarogram (curve 2) taken after reduction at -1.10 V for 60 min,[6] we see that the first wave disappears almost completely and that the oxidation wave appears at a potential close to that of the first wave of the polarogram 1.[7] In addition, (i) the second wave of the polarogram 1 decreases in wave height an amount corresponding to a one-electron reduction, so that the wave height of the polarogram 2 at ~ -2.0 V is almost the same as that of the first wave of the polarogram 1, and (ii) the AC peak-height (curve 2′) after reduction is also quite high in both the oxidation and reduction waves. These experimental results may indicate that the anion radical (A^-) formed at the first wave of the neutral species (N) is in an oxidation and reduction equilibrium like $N \rightleftarrows A^- \rightleftarrows A^=$, where $A^=$ stands for the dianion of the N species. Of course, the reversibility of the equilibrium between A^- and $A^=$ is less than that between N and A^-, since the reactivity of the $A^=$ species is quite high.[6] A polarographic behaviour of the anion radical similar to that described above was also observed in 4,4′-dinitrobiphenyl.[7]

In the case of 4-methylpyridine *N*-oxide, whose first reduction wave is not responsible for the anion radical formation, *i. e.*, in which the succeeding reaction also occurs at the first wave,[3a] no oxidation wave such as is seen in Fig. 2 could be observed in the polarogram of the substance produced after electrolysis at the first wave. This result seems to be reasonable because there is no good equilibrium between the A^- and N species.

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5) K. Ezumi, H. Miyazaki, and T. Kubota, *J. Phys. Chem.*, **74**, 2397 (1970).

6) The color of the solution varied from pale yellow to pale blue→deep blue→and finally deep blue-greem, which again changed to pale yellow upon the introduction of dry air. In addition, polarographic measurements after reduction at -2.0 V (second wave: see Fig. 2) showed that the polarogram is somewhat complicated and time-dependent, indicating that the dianion generated macroscopically is not so stable as, and more reactive than, the monoanion radical.

7) Here, one remarkable point is that a quite strong maximum wave is superposed on the oxidation wave of the anion raidcal (see Fig. 2). This phenomenon seems to be generally observed in the experiments by us and by Bard *et al.*[2] The later authors explained it in terms of a pronounced streaming mechanism occurring on the dropping mercury electrode during the oxidation of the A^- species.