According to Eq. [11] a large decrease in the magnitude of D_o* for γ-Nb_2O_5 at oxygen pressures less than 10^{-3} atm would be primarily caused by the variation in D. The existence of this variation has been confirmed by the present measurements. Hence, the unusual pressure dependence of the parabolic oxidation kinetics is associated with the formation of a γ-Nb_2O_5 scale consisting of a series of structures changing with the oxygen potential. These structures would be distinct Magneli phases or blocks of a basic structure joined by regular discontinuities (18). If, as it has been suggested (6), the vacancy concentration in such berthollides is largely independent of composition, the observed decrease in oxygen diffusion rate in γ-Nb_2O_5 with stoichiometry would be sufficient to account for the decrease in oxidation rate of niobium with oxygen pressure. To determine the validity of these considerations, the self-diffusion coefficient of oxygen in γ-Nb_2O_5 must be determined as a function of both stoichiometry and structure.

Acknowledgments

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1968 JOURNAL.

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The Electrochemical Behavior of 4,4'-Azopyridine-1,1'-Dioxide

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ABSTRACT

The electroreduction of 4,4'-azobispyridine-1,1'-dioxide (APDO) in dimethylformamide solutions was studied by polarography, cyclic voltammetry, controlled potential coulometry, and electron spin resonance, Voltammetric reduction showed two well-defined, reversible one-electron transfers. Coulometric reduction at a potential corresponding to the plateau of the first wave gave evidence of chemical reactions following the initial electron transfer producing intermediates which were also electroactive at the same potentials. Coulometry at the second wave gave an over-all value of six Faradays per mole for the complete reduction of APDO to the dianion of azopyridine (AP), identified by electrochemical and electron spin resonance techniques. A mechanism for the reduction process consistent with the experimental evidence is presented.

The polarographic behavior of a number of tertiary amine oxides in aqueous systems has been reported (1-9). Kubota and Miyazaki (6a) performed a polarographic study of pyridine N-oxide and its alkyl derivatives followed by a study (6b) of the effect of substituents on the polarographic reduction of pyridine N-oxide derivatives. Recently, Date (7a) reported a thorough polarographic investigation of dimethylaniline N-oxide, followed by an investigation of the relationship between the $E_{1/2}$ values of a series of similar compounds and the pKa's of their parent amines (7b). Chambers (8) studied the polarographic and adsorption behavior of dimethyldodecylamine N-oxide and Elving and Warner (9) have reported a study of the polarographic behavior of adenine 1-N-oxide.

In all of the above work, the amine oxide group gives a well-defined, irreversible polarographic wave between pH values of 1 to 6. Date proposed that the amine oxide group is reduced to the corresponding parent amine in a reaction involving two electrons, the first electron addition being rate controlling. This mechanism agrees quite well with his experimental data and is further supported by Chambers' work on N,N-dimethyldodecylamine N-oxide.

Recently Nasielski and co-workers (10) studied the polarographic reduction of pyridine N-oxide and other heterocyclic N-oxides in DMF solution. They proposed that the reduction involves a single, two-electron wave (composed of reduction to the anion radical, fast protonation, and further reduction, protonation, and dehydration), leading to the free base. We report here a study of the amine oxide 4,4'-azobispyridine-1,1'-dioxide (APDO) in DMF, in which a clear separation of the step leading to formation of the anion radical and to formation of the dianion is obtained.

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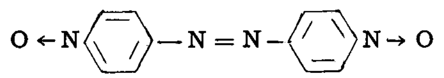
* Electrochemical Society Active Member.

Results

Voltammetric methods. The polarographic reduction of APDO,



in a N,N-dimethylformamide (DMF) solution containing 0.1 *M* tetra-n-butyl-ammonium perchlorate (TBAP) showed two well-defined waves (Fig. 1) with half-wave potentials ($E_{1/2}$) of —0.73 and —1.35v *vs.* an aqueous saturated calomel electrode (SCE). The values of $E_{3/4}$—$E_{1/4}$ for the two waves (Tômes criterion for reversibility) 0.06 and 0.07v, respectively, suggested that the first wave involved a reversible, one-electron reduction and that the second wave may be complicated by a following chemical reaction. The diffusion currents of both waves were directly proportional to the square root of the height of the head of the dropping mercury electrode (dme). The diffusion current constants for the first and second waves were 2.97 and 5.45 μa-sec$^{1/2}$-mM^{-1}-mg$^{-2/3}$, respectively.

A cyclic voltammogram of APDO in DMF containing 0.1*M* TBAP at a hanging mercury drop electrode (hmde) is shown in Fig. 2. At all scan rates employed, the reverse scan clearly shows two anodic peaks, corresponding to the oxidation of APDO monoanion and dianion. The cyclic voltammogram obtained on a planar platinum electrode is illustrated in Fig. 3. The behavior of the first wave is essentially the same as that observed on a hmde; however, the second wave shows a much larger cathodic-to-anodic peak current ratio. Typical results of cyclic voltammetric (linear potential sweep chronoamperometry with reversal) experiments for both a hmde and platinum disk electrode are given in Table I. At both a platinum disk electrode and a hmde, the ratio of the peak current (i_{pa}) of the first anodic wave to the peak current of the corresponding cathodic wave (i_{pc}) is about 1, as would be expected for the formation of a radical species which is stable during the duration of the measurement. The value of E_{pc}-E_{pa} for this couple is very close to the value (0.057v) for a reversible, one-electron reaction. E_{pc} and E_{pa} for this couple are independent of scan rate *v*, and plots of the current function ($i_p/v^{1/2}$) and i_{pa}/i_{pc} *vs.* scan rate [diagnostic criteria given in the work of Nicholson and Shain (11) show this wave to be reversible].

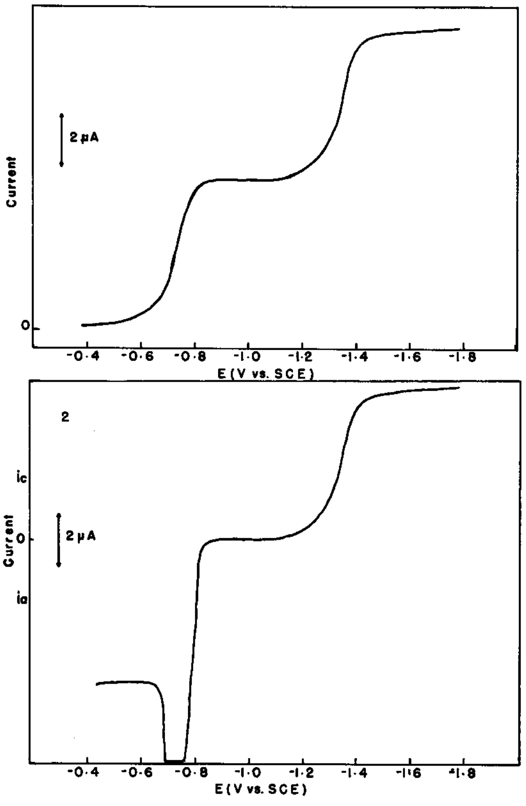


Fig. 1. Polarograms before and after reduction of a 1.32 mM APDO solution in DMF containing 0.1M TBAP at a mercury pool electrode: 1, before reduction; 2, after reduction at —1.0v *vs.* SCE.

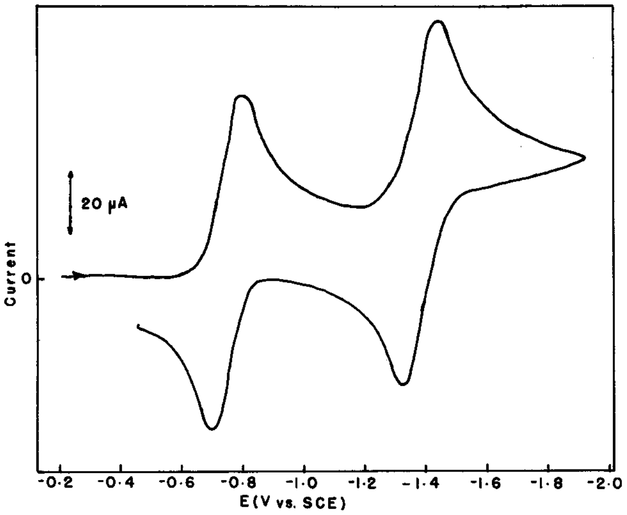


Fig. 2. Cyclic voltammetry of APDO at a HMDE. The solution contained 0.1M TBAP in DMF and was 1.32 mM in APDO.

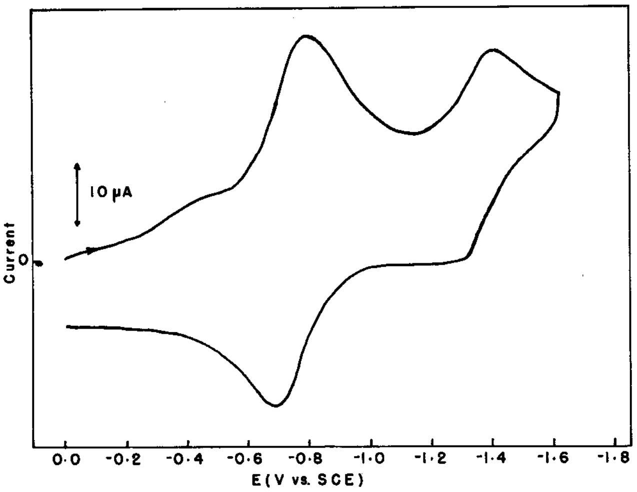


Fig. 3. Cyclic voltammetry of APDO at a planar platinum disk electrode. The solution contained 0.1M TBAP in DMF and was 1.32 mM in APDO.

The second reduction wave in cyclic voltammetric experiments utilizing a hmde shows some evidence of a chemical reaction following the reduction to give another electroactive species. The current function decreases about 20% for a 10-fold increase in scan rate, which indicates an ECE-type process (*i.e.*, an electron transfer reaction followed by a chemical reaction generating a species reducible at these potentials). A simple EC process is eliminated, because it is characterized by a change of only 10% in the current function for a 10-fold change in scan rate (11). The anodic-to-cathodic peak current ratios increase with increasing scan rate, as expected for an ECE process.

The results obtained in cyclic voltammetric experiments using a platinum disk electrode also give evidence for the presence of an irreversible chemical reaction following the second charge transfer step. At scan rates up to 657 mv/sec, however, essentially no corresponding anodic wave is seen for the second reduction wave. This suggests that either the following reaction is catalyzed at platinum or perhaps adsorption of the product at mercury occurs. This difference

Table I. Cyclic voltammetric data for the two-step reduction of 4,4′-azobispyridine-1,1′-dioxide[a]

Scan rate,	First wave						Second wave					
mv/sec	i_{pc}, μa	i_{pa}[b] μa	i_{pa}/i_{pc}	$-E_{pc}$ v vs. SCE	$-E_{pa}$ v vs. SCE	$i_{pc}/v^{1/2}$	i_{pc}[c] μa	i_{pa}[b] μa	i_{pa}/i_{pc}	$-E_{pc}$ v vs. SCE	$-E_{pa}$ v vs. SCE	$i_{pc}/v^{1/2}$
Hanging mercury drop electrode;[d] conc. = 1.03 mM												
73	5.4	5.0	0.93	0.76	0.71	0.63	5.8	3.9	0.67	1.40	1.33	0.68
91	6.0	5.8	0.97	0.76	0.70	0.63	5.9	4.8	0.81	1.40	1.33	0.62
203	8.1	7.9	0.98	0.76	0.70	0.67	8.5	6.1	0.72	1.40	1.33	0.60
298	11.0	10.4	0.96	0.76	0.70	0.64	10.1	7.5	0.74	1.40	1.33	0.59
430	14.0	13.2	0.95	0.76	0.70	0.68	12.2	8.7	0.71	1.40	1.33	0.59
657	17.9	17.0	0.95	0.80	0.69	0.70	15.6	12.0	0.77	1.41	1.30	0.61
Concentration = 1.29 mM												
73	6.5	6.0	0.93	0.76	0.70	0.77	6.1	4.4	0.72	1.42	1.35	0.72
91	7.7	6.5	0.85	0.76	0.70	0.80	6.5	4.4	0.68	1.42	1.35	0.68
203	11.0	10.0	0.91	0.76	0.70	0.77	8.5	6.3	0.74	1.42	1.35	0.60
298	13.3	12.5	0.94	0.76	0.70	0.77	10.4	7.9	0.76	1.42	1.34	0.60
430	15.8	15.0	0.95	0.76	0.70	0.76	11.7	8.9	0.76	1.42	1.34	0.57
657	19.5	18.5	0.95	0.80	0.67	0.76	14.4	9.3	0.65	1.42	1.32	0.56
Concentration = 3.25 mM												
73	20.1	16.1	0.80	0.76	0.70	2.4	23.6	19.7	0.84	1.39	1.31	2.8
91	22.8	18.5	0.81	0.76	0.70	2.4	26.4	22.1	0.84	1.39	1.31	2.8
203	33.0	26.8	0.81	0.76	0.70	2.3	37.0	30.7	0.83	1.39	1.31	2.6
298	40.2	33.1	0.82	0.76	0.70	2.3	44.1	37.0	0.84	1.40	1.31	2.5
430	48.0	41.7	0.87	0.76	0.70	2.3	50.0	43.4	0.87	1.40	1.30	2.4
657	60.0	50.0	0.83	0.77	0.67	2.3	60.0	55.0	0.92	1.41	1.30	2.3
Platinum disk electrode;[e] concentration = 1.74 mM												
73	8.0	6.5	0.81	0.77	0.71	0.94						
91	9.0	7.5	0.83	0.77	0.71	0.94						
203	13.0	13.0	1.00	0.77	0.71	0.91						
298	16.5	16.0	0.97	0.77	0.71	0.95						
430	18.0	17.5	0.97	0.78	0.70	0.97						
657	24.5	23.5	0.96	0.78	0.69	0.96						

[a] The solution was 0.1*M* TBAP in DMF.
[b] For scan reversed at a potential 100mv more negative than E_{pc}. Potentials given may also include some uncompensated iR drop.
[c] Measured using extrapolation of decreasing current of first peak as base-line.
[d] Electrode area = 0.088 cm².
[e] Apparent electrode area = 0.031 cm².

in behavior at platinum and mercury electrodes was not investigated further.

These results suggest that the following reactions occur during voltammetry

$$APDO + e \rightleftarrows APDO^{\overline{\cdot}} \qquad \text{(first wave)} \qquad [1]$$

$$APDO^{\overline{\cdot}} + e \rightleftarrows APDO^{=} \qquad \text{(second wave)} \qquad [2]$$

$$APDO^{=} + HS \rightarrow APDOH^{-} + S^{-} \qquad [3]$$

where HS represents any source of protons and $APDOH^{-}$ is reducible at the potential of the second wave.

Coulometric experiments at a mercury pool electrode controlled at a potential on the diffusion plateau of both the first (—1.0v) and second (—1.8v) reduction waves were undertaken to study the electrochemical behavior of $APDO^{\overline{\cdot}}$ and $APDO^{=}$ and to obtain, via electron spin resonance (esr) techniques, further evidence for the above-postulated mechanism. Reduction of APDO at —1.0v gave values of n_{app} ranging from 1.40 to 1.92 faradays per mole (Table II). In all experiments the electrolysis current decayed to a value significantly higher than the corresponding background currents. For example, in the case of n_{app} = 1.70, the current decreased from an initial value of 38 ma to a steady value of 1.4 ma after 30 min, indicating that continued electrolysis does not bring about complete cessation of all reduction reactions. This behavior is indicative of a slow secondary process which produces a product that is electroactive at the same potential. Reversal coulometry at —0.20v *vs.* SCE gave n_{app} values for oxidation significantly lower than the corresponding initial reduction n_{app} values (Table II).

The solution resulting from reduction of APDO at —1.0v *vs.* SCE was a deep reddish-brown in color and gave an intense esr spectrum of about 75 lines. The spectrum was significantly nonsymmetrical about the center, indicating that the signal obtained was due to a mixture of two or more radical species. The presence of two radical species is also consistent with an ECE mechanism.

Voltammetry after Reduction

Polarograms for a APDO solution before and after reduction at —1.0v *vs.* SCE are shown in Fig. 1. The polarogram for a reduced APDO solution (Fig. 1, curve 2), shows an anodic wave with a large maximum which abruptly drops to near the expected diffusion current value at a potential (—0.68v) near the potential of the electrocapillary maximum for this medium, —0.70v. This behavior is similar to that observed by Santhanam and Bard (12) in their study of 9,10-diphenylanthracene and can probably be attributed to the anodic streaming mechanism proposed by them. The reduction of $APDO^{\overline{\cdot}}$ to $APDO^{=}$ occurs at the same potential as the second polarographic wave in the reduction of APDO (Fig. 1, curve 2). The diffusion current of the second wave is about the same before and after electrolysis at —1.0v. Cyclic voltammetry, utilizing a hmde, on a reduced solution of APDO is shown in Fig. 4, curve 2. The very large anodic current for the oxidation is attributed to the same stirring effect mentioned above. Cyclic voltammetry on a platinum disk electrode does not exhibit this stirring phenomena (Fig. 4, curve 4). The value of i_{pc} for the first wave at a platinum electrode decreases by about 20% after reduction of APDO at —1.0v (24.5 μa before *vs.* 19.4 μa after). Peak potentials (E_{pc} and E_{pa}) for the first reduction step are unchanged.

Further controlled potential reduction of the reduced solution at —1.80v, corresponding to the plateau of the second wave gave an additional 4.1 faradays

Table II. Controlled potential coulometric results[a]

	n_{app}		
Conc., mM	Reduction at −1.0v	Oxidation at −0.20v	Reduction at −1.80v
0.90	1.63	—	5.92
1.05	1.92	—	—
1.32	1.92	—	—
1.73	1.40	0.47	—
3.25	1.70	0.70	—
1.05	—	—	5.84

[a] The solution was DMF containing 0.1*M* TBAP. The cathode was a mercury pool with an approximate area of 12 cm² and the anode was platinum wire, isolated by a fine-porosity, sintered glass disk. Potentials given above are *vs.* SCE. Electrolysis times were 0.5 to 1.5 hr.

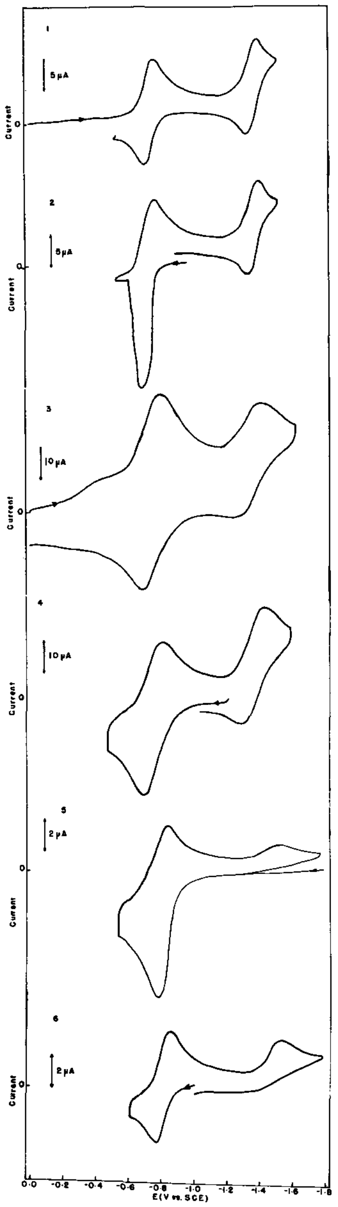


Fig. 4. Cyclic voltammetry of APDO on a hmde and platinum disk electrodes at various stages of reduction at a mercury pool working electrode. The solution was 1.73 mM in APDO in DMF containing 0.1M TBAP: 1, C.V. at hmde of original solution; 2, C.V. at hmde after reduction at —1.0 v; 3, C.V. at platinum disk electrode of original solution; 4, C.V. at platinum disk electrode after reduction at —1.0 v; 5, C.V. at a platinum disk electrode after reduction at —1.80 v; 6, C.V. at a platinum disk electrode of an authentic sample of azopyridine in the same medium as described above.

per mole for an over-all value of $n_{app} = 5.84$. Cyclic voltammetry, employing a platinum disk electrode, of an APDO solution after complete reduction at —1.80v, is shown in Fig. 4, curve 5. With the scan initiated in a positive direction from —1.80v, an oxidation wave occurs at —0.76v followed, on reversal, by two reduction steps at —0.84 and —1.53v. These peak potentials are significantly different from those observed for APDO itself.

Reversal coulometry (oxidation) at —1.0v resulted in no anodic current flow, indicating that the reduced species was not oxidizable at this potential. On changing the potential to —0.20v, however, this species was oxidized, giving a value of $n_{app} = 1.44$. Cyclic voltammetric reduction and oxidation of the species resulting from this oxidation showed waves at the same potentials as those observed for the completely reduced species as noted above; the first charge transfer was apparently reversible with a reduction wave at —0.84v and was followed by an irreversible reduction with a peak potential of —1.53v.

Controlled potential electrolysis of this product at a potential corresponding to the first reduction step (—1.0v) gave a value of $n_{app} = 1.30$. The solution was sampled at this stage for esr analysis. The resulting esr spectrum, containing approximately 40 lines, was significantly different from the spectrum of APDO$^{\cdot -}$ mentioned above.

The most logical product of the complete reduction of APDO, based on the behavior of other amine oxide systems, would involve the 4,4′-azobispyridine (AP) system; hence, the electrochemical behavior of AP was examined. Cyclic voltammetry, employing a platinum disk electrode, of AP is shown in Fig. 4, curve 6. The voltammetric behavior of AP is the same as that of the reduction product of APDO obtained by complete reduction at —1.8v. Controlled potential electrolysis of AP, using conditions identical to those employed for APDO, was performed at a potential of —1.0v, which corresponds to the plateau of the first reduction wave. An n_{app} value of 1.09 electrons per molecule was observed for this reduction. A sample was taken at this stage for esr analysis. The resulting esr spectrum was identical to that obtained from reversal coulometry reported in the previous paragraph.

Effect of Proton Donor

To gain some insight into the intermediate steps involved in the reduction of APDO, its electrochemical behavior in the presence of varying amounts of a proton-donating agent was studied. Hydroquinone (HQ), previously employed in a study of 9,10-diphenylanthracene (12) was used as the proton donor. The effect of varying amounts of HQ on the polarographic behavior of APDO is shown in Fig. 5. The first wave is unaffected by increasing concentrations of HQ; however, the second wave is shifted in an anodic direction and the *diffusion* current is increased as the HQ concentration is increased. The second reduction step changes from near reversible behavior, at zero concentration of HQ ($E_{3/4} - E_{1/4} = 65$ mv), to completely irreversible character ($E_{3/4} - E_{1/4} = 150$ mv) in the presence of excess HQ (HQ/APDO ratio = 8.0). The cyclic voltammetric behavior of APDO at a hmde in the presence of HQ is illustrated in Fig. 6. The first reduction step is unaffected by addition of excess HQ with the second reduction showing behavior analogous to that seen in polarography (i_{pc} increasing and E_{pc} shifting anodically with increasing HQ concentration). These results suggest that if the chemical reaction following the first reduction step involves protonation, its rate is still negligible during the duration of the voltammetric experiment. However, the rate of the reaction following the second reduction step is increased considerably. Controlled potential electrolysis at —0.80v was performed on the above-mentioned solution with a resulting n_{app} of 5.92 electrons, which is the same as the n_{app} found for the over-all reduction in the absence of proton donor.

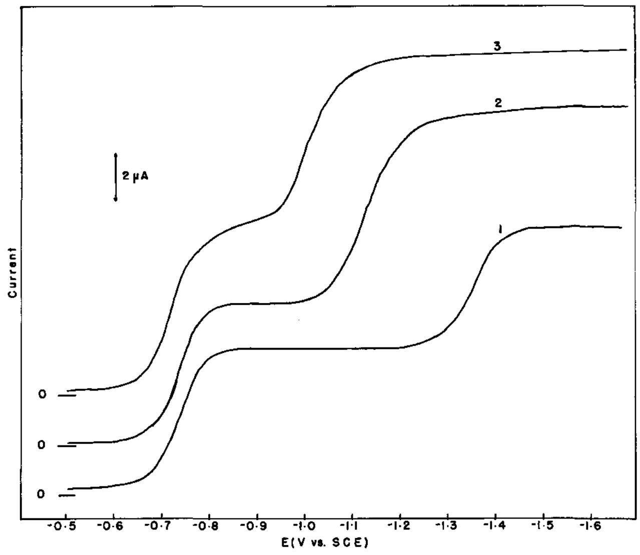


Fig. 5. Polarograms for reduction of 1.05 mM APDO in 0.1M TBAP in DMF in the presence of varying amounts of hydroquinone (HQ): 1, no HQ added; 2, HQ concentration is 1.77 mM; 3, HQ concentration is 8.10 mM.

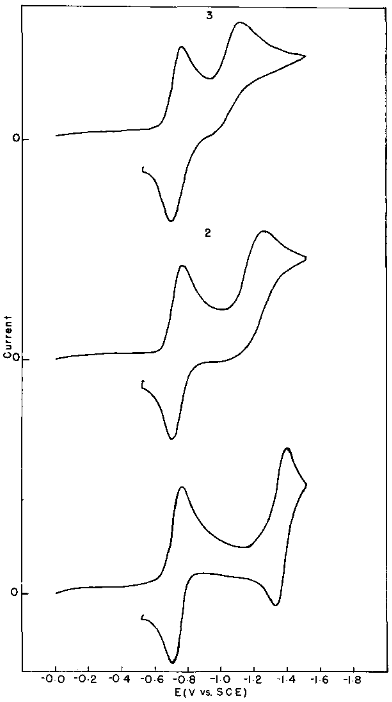


Fig. 6. Cyclic voltammograms for the reduction of 1.05 mM APDO at a hmde in 0.1M TBAP in DMF in the presence of varying amounts of hydroquinone (HQ): 1, no HQ present; 2, 1.77 mM HQ; 3, 8.10 mM HQ.

Discussion

The mechanism of the electrochemical reduction of APDO is shown in the schematic diagram in Fig. 7. In this diagram electron transfer processes at the electrode are indicated by straight lines and chemical reactions are shown as wavy lines. Compounds which are reduction products of APDO are shown as lines below the APDO line; these lines are spaced in increasing numbers of electrons added to the parent molecule. Where the appropriate electrode potentials are known, they are indicated next to the couple. Downward arrows show reduction and upward ones oxidations.

We proposed to explain the experimental results with the following mechanism:

At potentials corresponding to the first wave:

$$\mathrm{APDO} + e \rightleftarrows \mathrm{APDO}\overset{-}{\cdot} \qquad [4]$$

$$\mathrm{APDO}\overset{-}{\cdot} + \mathrm{HS} \rightarrow \mathrm{APDOH}\cdot + \mathrm{S}\ \text{(very slow)} \qquad [5]$$

$$\mathrm{APDOH}\cdot + 3\mathrm{H}^+ + 3e \rightarrow \mathrm{AP} + 2\mathrm{H_2O} \qquad [6]$$

$$\mathrm{AP} + e \rightleftarrows \mathrm{AP}\overset{-}{\cdot} \qquad [7]$$

At potentials corresponding to the second wave:

$$\mathrm{APDO}\overset{-}{\cdot} + e \rightleftarrows \mathrm{APDO}^{--} \qquad [8]$$

$$\mathrm{APDO}^{--} + \mathrm{H}^+ \rightarrow \mathrm{APDOH}^- \qquad [9]$$

$$\mathrm{APDOH}^- + 3\mathrm{H}^+ + 2e \rightarrow \mathrm{AP} + 2\mathrm{H_2O} \qquad [10]$$

$$\mathrm{AP} + 2e \rightarrow \mathrm{AP}^{--} \qquad [11]$$

$$\mathrm{AP}^{--} + \mathrm{HS} \rightarrow \mathrm{APH}^- + \mathrm{S}^- \qquad [12]$$

The polarographic and cyclic voltammetric results show that during the small duration of these experiments (3-20 sec), the results can be explained by reactions [1] to [3]. Only a small contribution of the following reactions [9] through [11] is found, resulting in the ECE-type behavior of the second voltammetric wave.

Controlled potential coulometric reduction at a potential corresponding to the plateau of the first wave gives n_{app} values significantly greater than one and evidence of production of an electroactive species (current not decaying to the background value). Reversal coulometry (oxidation at the foot of the first wave) gives a smaller value of n_{app}, for example (n_{app} reduction $= 0.70$, Table II). This behavior is ascribed to a very slow reaction of the anion radical $\mathrm{APDO}\overset{-}{\cdot}$ to form an electroactive species; a protonation reaction to APDOH· seems reasonable. Since the first reduction wave of APDO is unaffected by addition of a proton donor, this reaction must be slow, even in the presence of excess hydroquinone. Further reduction and protonation eventually leads to azopyridine (AP), which is reduced at these potentials to the stable anion radical $\mathrm{AP}\overset{-}{\cdot}$. Since APDOH· is reduced at these potentials in a series of steps involving 4 electrons, only a small amount of reaction of $\mathrm{APDO}\overset{-}{\cdot}$ will give an appreciable contribution to n_{app}. For example, the decomposition of about 20% of the $\mathrm{APDO}\overset{-}{\cdot}$ would account for these results. The fact that voltammetry of the reduced solution shows a cathodic peak current, on reversal, of about 80% of the original cathodic peak current, is also in agreement with this mechanism and suggests that some of the intermediates involved in [6] are not oxidizable. Since the second reduction wave is about the same after reduction as in the original solution, reduction of both products and intermediates is suggested. The esr spectra obtained following reduction at potentials of the first wave are probably those of $\mathrm{APDO}\overset{-}{\cdot}$, $\mathrm{AP}\overset{-}{\cdot}$ and perhaps some intermediates.

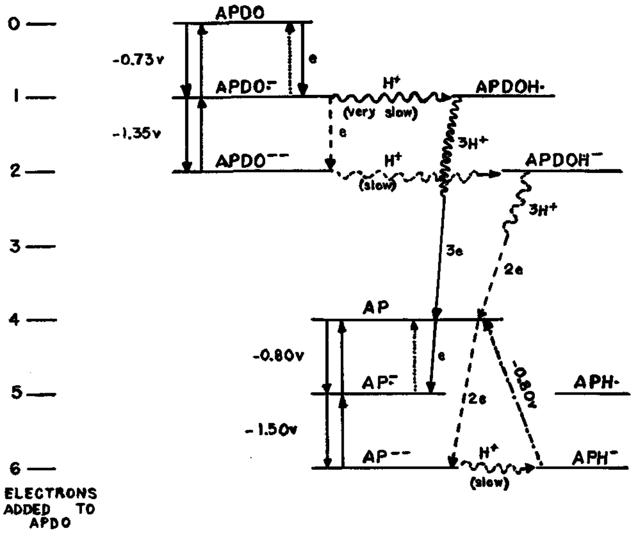


Fig. 7. Schematic diagram of mechanism of the electroreduction of APDO. Electron transfer processes at the electrode are indicated by straight lines (reductions downward and oxidations upward) and chemical reactions by wavy lines. The extent of reduction, in terms of electrons added to APDO, is indicated by the distance down from the APDO line. The potentials at which reactions occur ($E_{1/2}$, vs. SCE) are indicated near the appropriate couple, when known. Some qualitative measure of the rates of chemical reactions has been given ("slow" denotes a reaction which does not proceed to an appreciable extent during a time characteristic of voltammetric experiments but is appreciable on the coulometric time scale; "very slow" denotes a reaction which proceeds only partially even in coulometric experiments). ——— Reduction at —1.0v; .... oxidation at —0.20v following this reduction; — — — — — — reduction at —1.8v; — ● — ● — ● oxidation at —0.2v following this reduction.

Reduction at a potential on the plateau of the second wave leads in a series of protonation and reduction reactions to APH^-, with $n_{\mathrm{app}} = 6$ (within experimental error). The electrochemical behavior of the solution resulting from this reduction is identical with that obtained from reduction of AP itself.[1] After complete

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[1] A complete study of the electrochemistry of azopyridine and other aromatic azocompounds in DMF has been completed (J. Sadler, Ph.D. Dissertation, The University of Texas at Austin, 1967) and has been submitted for publication elsewhere. The behavior of azopyridine shown in the lower part of Fig. 7 has been established in this study.

reduction, oxidation at −0.2v, and re-reduction, an esr signal which can unequivocally be ascribed to $AP^{\overline{\cdot}}$ is obtained, giving further support to this mechanism.

Experimental

The cell and vacuum line used were essentially the same as reported by Santhanam and Bard (12). DMF purification and storage also followed the procedure outlined there. The filling of the electrochemical cell was accomplished by first evacuating the cell containing the supporting electrolyte and mercury pool, cooling with liquid nitrogen, then distilling DMF under vacuum into the cell. After the distillation had been completed, the cell and contents were allowed to warm to room temperature with continuous evacuation. The cell was then brought to atmospheric pressure by introducing helium through the vacuum line. The helium was obtained from the Matheson Company, LaPorte, Texas. It was passed successively through anhydrous magnesium perchlorate, copper turnings (heated to 350°C), activated charcoal cooled to liquid nitrogen temperature, and finally to the cell. A helium blanket over the solution was maintained throughout the experiment. The auxiliary electrode was a platinum wire. The reference electrode was an aqueous SCE connected via an agar plug and sintered glass disk to the test solution. Stirring was by a magnetic stirrer.

The voltammetric experiments were carried out using a multipurpose instrument employing operational amplifier circuitry with three-electrode configuration, similar to those discussed in the literature (13). Controlled potential coulometry was carried out using a previously described apparatus (14).

The APDO was from Aldrich Chemical Company. It was recrystallized twice from absolute ethanol and twice from benzene. The melting point of the resulting product was very sharp at 236.5°C (decomp.). AP was synthesized by reduction of APDO in ethanol with zinc dust and ammonia. The melting point of the product after recrystallization from petroleum ether, was 106.5°C as compared to a literature value of 107°C (15). The TBAP was obtained from Southwestern Analytical Chemicals, Austin, Texas. It was dried in a vacuum oven for 8 hr at 70°-80°C and stored in a desiccator until use.

A Varian Associates V-4502 spectrometer employing 100-kc field modulation was used for esr spectroscopy.

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The Cu/CuF$_2$ Couple in Anhydrous Hydrogen Fluoride

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ABSTRACT

The electrochemical behavior of a Cu electrode was investigated in basic, anhydrous HF. Anodization of Cu established the Cu/CuF$_2$(s) couple. Micropolarization and bias tests indicated that this couple was reversible, and its potential *vs.* an H$_2$ electrode in the same solution agreed well with that predicted from thermodynamic data. Thus the couple is suitable for use as a reference electrode in basic HF. The formation of a relatively thick, insoluble anodic film at a copper electrode was demonstrated by cyclic voltammetry and chronopotentiometry. Anodic-cathodic cycling of an electrode gave rise to significant roughening of the electrode surface as shown by i-E curves, E-t curves, and differential capacitance measurements on cycled electrodes. X-ray analysis of the anodic film confirmed the presence of crystalline copper fluoride. The formation of CuF$_2$ appears to proceed via dissolution of Cu to form Cu^{2+} ions, followed by precipitation of the CuF$_2$ on the electrode surface. The polarization behavior of Cu electrodes in anhydrous HF solution containing added KF showed that anodic film formation can be approximated by Tafel lines with an apparent exchange current density of about 3×10^{-6} amp/cm^2. Properties of the anodic film of CuF$_2$ are quite similar to those observed for noncontinuous anodic films formed in aqueous solutions.

Very little work on the characterization of electrode reactions in anhydrous or aqueous HF has been reported. A small number of potentiometric investigations have been made (1-3); a brief report on the construction of a rotating nickel electrode for use in anhydrous HF is available (6), and a dropping mercury electrode using a Teflon capillary in aqueous HF

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