Anodic Voltammetry of Hydroxylamine at Rotating Disc Electrode of Platinum

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Hydroxylamine has been examined by anodic voltammetry at platinum electrode in sulphuric acid media. Obedience to Levich relationship was shown at platinum electrode in 0.01 M sulphuric acid concentration in the range 2.0×10^{-4} to 1.0×10^{-3} M, (M=mol dm^{-3}). Electrode kinetics parameters have been evaluated and a possibility of the reaction mechanism path is suggested.

The chemistry of hydroxylamine is extremely fascinating because it exhibits different oxidation routes and gives different products. It can serve as either an oxidizing[1—11)] or a reducing[12—14)] agent and primarily used as the latter. The reactions involved in the oxidation of hydroxylamine have been the subject of several previous studies[2—11)] which have demonstrated the variety of products which may be formed.

In this paper oxidation of hydroxylamine in aqueous sulphuric acid was investigated at platinum electrode by means of single scan and cyclic voltammetry for the purpose of determining kinetic parameters and seeking a plausible mechanism for its oxidation.

Experimental

Quartz processed high purity distilled water out-gassed and used throughout.

Apparatus: Rotating Electrode Assembly.[15)] The electrode disc, split disc, ring disc, and split-ring-disc, of platinum are self centering to within a run-out of 5 μm, and can be interchanged within 15 s. The disc area is 0.503 cm^2. The rotator shaft is driven by a powerful, reversible, dc tacho-servo motor on a massive, rigid, vibration-free mount, and shaft speed is photoelectrically monitored via a frequency standard counter, the SM 200. The relaxation time to a speed constancy of ±0.01 Hz is 15 s from rest to maximum speed, or from 5 to 50 Hz, and the drift is<0.03 Hz h^{-1} at 50 Hz and <0.006 Hz h^{-1} at 5 Hz. A full description is given elsewhere.[16)] The electronics[15)] incorporate a ±2 V −100 mA potentiostat and amperostat, a bidirectional ramp generator of 0.001 mV min^{-1} cyclic voltammetry from 0.001 to 1200 Hz, voltage and current follower outputs, and output offset and attenuation/expansion. Measurements of current (through a calibrated standard resistance) and potential were made on a 7-digit SEL transfer standard digital voltmeter (DVM) Model SM 215 and of lapsed time on a 10-MHz frequency standard counter. The readout was displayed on a Bryans A3X-Y/T recorder 20170/s or a calibrated dual-beam measuring oscilloscope HP 1200A. Assembly and instruments were driven from a 1.5 KW saturable reactor, additionally loaded by heating elements to 96—98% of full output. Dummy loads with fast TTL switching were used on thermostats and electrolytic cells. Brush noise was smoothed and filtered. The thermostated, jacketed cell was provided with a ceramic plug separated side-arm filled with the same supporting electrolyte as the cell for connection of the platinum spiral counter electrode, and an entry for the Luggin capillary bridge, similarly filled (and replaced every hour), into which the ceramic-terminated, saturated potassium chloride bridge, from the large capacity saturated calomel electrode, was fitted. A machined and drilled PTFE cap on the cell permitted reproducible presentation by elevator to the rotating electrode, and carried gas entry and exit ports.

Electrode Activation: The following pre-treatment was applied before each scan or other individual operation:

1) Inspect the electrode surface for imperfection or staining, and, if necessary polish metallographically to an optical flat.

2) Remove adsorbate by immersion in warm aqua regia for 1 min and rinse with pure water.

3) For a working anode, anodise, then cathodise for 30 s at 30 mA cm^{-2} for three cycles in 0.5 mol dm^{-3} Aristar sulphuric acid and finally anodise for 60 s at 60 mA cm^{-2}. For a working cathode, cathodise then anodise for 30 s at 30 mA cm^{-2} each operating for three cycles, and finally cathodise for 60 s at 30 mA cm^{-2}. For a clean electrode, treat as for a cathode and then short circuit to a working saturated calomel electrode for 6 min. Rinse with pure water and transfer it to the working electrolyte without allowing it to dry.

Reagents: Sulphuric Acid: Aristar grade was used. Hydroxylamine: Freshly prepared from Analar hydroxylammonium sulphate predried in a vaccuum oven a 40 °C over magnesium perchlorate and dissolved in acidified water. Working solutions were prepared by dilution of the stock solutions that were freshly prepared.

General Procedure: Voltammetry: A set is run on a supporting electrolyte of the same composition and volume as a check on electrode performance before performing any measurements on a sample.

The sample solution is placed in the cell and brought to thermostated temperature while being deoxygenated by outgassing with dry nitrogen (pre-purified by passage through scrubbers containing chromium(II) sulphate and one containing water). The voltammogram is recorded immediately after being activated.

Determination of Number of Electrons *n*: For amperostatic determination of *n* value of hydroxylamine oxidation, the same instrument above is used. A voltammogram is recorded for the sample and electrolyte versus a reference SCE and the limiting current density is defined. A constant current is selected such that the resultant current density expected at the termination of the electrolysis. The sample is then electrolyzed for the required time, then a second voltammogram is recorded and the new limiting current is measured. If the limiting current is 50% of the original then $n=1$; if it is 75% of the original then $n=2$ and so on.

Results and Discussion

Voltammetry of Hydroxylamine: Anodic oxidation of hydroxylamine has been examined in different sulphuric acid concentrations and showed no significant difference in the voltammograms obtained. The optimum condition is 0.01 M sulphuric acid, a typical voltammogram is shown in Fig. 1. As shown a well defined oxidation wave is obtained, which starts at a potential of 0.68 V and extends to a limiting current region of 1.18 V. This wave suggests that the anodic oxidation of hydroxylamine at platinum electrode, is kinetically slow, a charge transfer reaction.

Mass and Charge Transfer Effects: Hydroxylamine solutions ranging between 2.0×10^{-4}—1.0×10^{-3} M were anodically examined for evaluation of mass and charge transfer effects.

The effect of the rotation speed of the disk of the electrode was investigated by applying Levich equation of the following form:

$$I_{L,a} = -0.620\, n\, FA[\text{red}]_b D_{\text{red}}^{2/3} v^{-1/6} W^{1/2} = 0.620, \qquad (1)$$

where:

$I_{L,a}$ is the limiting current in mA
n is number of electrons
F is Faraday constant
A is the area of electrode=0.503 cm^3
D_{red} is the diffusion coefficient of reductant
v is the Kinematic viscocity
W is the rotation speed in rad s$^{-1}=2\,\pi f$

where f=frequency Hz.

So, different concentrations of hydroxylamine were employed each at rotation speed varying between 10 and 50 Hz at room temperature and a scan rate of 5 mV s^{-1}. A representative example is shown in Fig. 2.

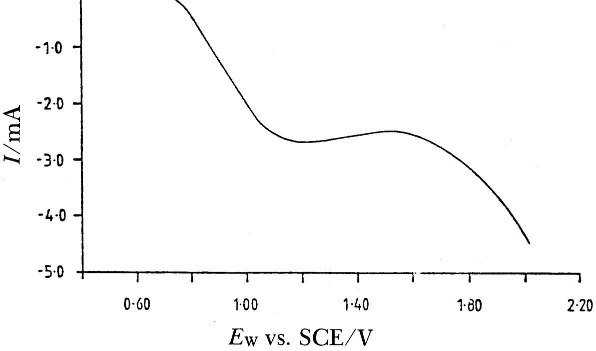

Fig. 1. Anodic voltammogram of 6.0×10^{-4} M hydroxylamine in 0.01 M sulphuric acid at a rotation speed of 20 Hz and a scan speed of 5 mV s^{-1} using platinum electrode.

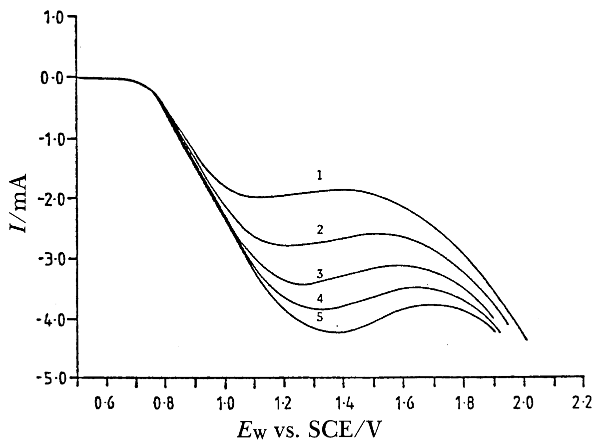

Fig. 2. Voltammetry of 6.0×10^{-4} M hydroxylamine in 0.01 M sulphuric acid at a scan speed of 5 mV s^{-1} using platinum electrode at different rotation speeds: 1, 10 Hz; 2, 20 Hz; 3, 30 Hz; 4, 40 Hz, and 5, 50 Hz.

Levich plots of $I_{L,a}$ versus $W^{1/2}$ for various concentrations of hydroxylamine were drawn as in Fig, 3. Levich dependances are statistically reasonable with a non-zero intercepts, even though calibration graphs can be used in quantitative analysis. Diffusion coefficients (D_{red}) were recorded in Table 1. It is obvious that the reaction is a mixed mass and charge transfer controlled predominantly by the latter.

On the other hand, the anodic limiting current was found to be completely independent of the hydroxylamine concentration.

The mass transfer rate constants (Table 1) have been

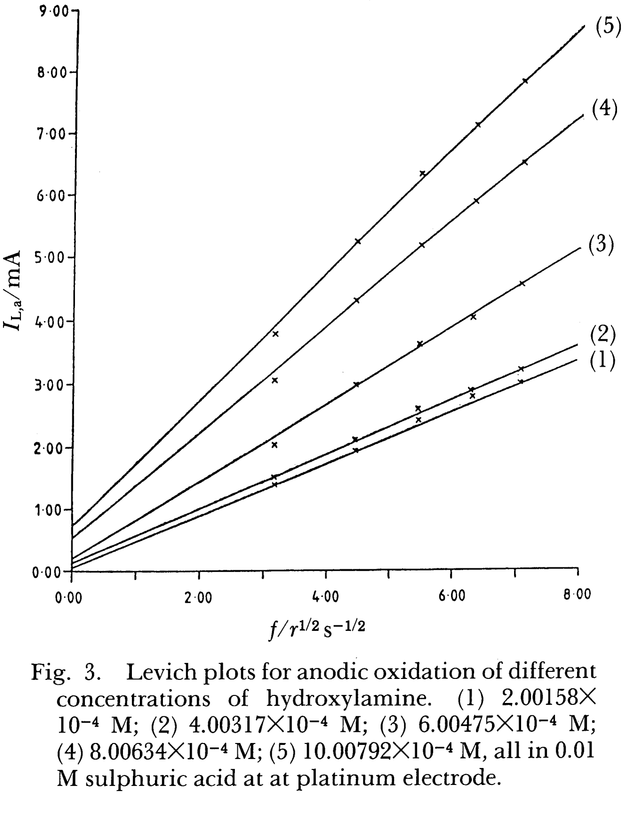

Fig. 3. Levich plots for anodic oxidation of different concentrations of hydroxylamine. (1) 2.00158×10^{-4} M; (2) 4.00317×10^{-4} M; (3) 6.00475×10^{-4} M; (4) 8.00634×10^{-4} M; (5) 10.00792×10^{-4} M, all in 0.01 M sulphuric acid at at platinum electrode.

Table 1. Kinetic Parameters Obtained from Voltammograms Obtained at Platinum Electrode with a Scan Speed of 5 mV s^{-1} for Different Concentrations of Hydroxlamine in 0.01 M Sulphuric Acid

No.	[NH$_2$OH] 10^{-4}M	k_m $\times 10^5$	k'' cm s$^{-1}\times 10^{-6}$	β	D cm^2 s$^{-1}\times 10^{-5}$
1	4.00	6.697	5.686	0.514	3.770
2	6.00	6.284	8.542	0.483	3.602
3	8.00	6.735	10.226	0.529	4.066
4	10.00	6.542	8.689	0.46	3.608

determined at different hydroxylamine concentrations using the following form of equation:

$$K_m = \frac{-I_{L,a}}{nFA[\text{red}]}. \tag{2}$$

The charge transfer coefficient (β) were determined at different hydroxylamine concentrations using platinum electrode and scan rate 5 mV s^{-1}. Pattern theory[20] was used for calculations that are introduced in Table 1, and the following form of equations have been used:

$$\log K = \frac{E_1 - E_0'}{\Delta E} \log_{10} \frac{f_1(1-f_2)}{f_2(1-f_1)} + \frac{f_1}{(1-f_1)} + \log_{10} k_m, \tag{3}$$

$$\beta = \frac{2.303\,RT}{(E_1 - E_2)nF} \log_{10} \frac{f_1(1-f_2)}{f_2(1-f_1)}, \tag{4}$$

where f_1 and f_2 are fractions of the limiting currents at two points on the voltammogram.

$I_1 = f_1 L_2$ and $I_2 = f_2 I_{L,a}$ at the corresponding potentials E_1 and E_2 respectively.

Number of Electrons (*n*): An example of the experiments done, 8.0×10^{-4} M hydroxylamine in 0.01 M H_2SO_4 that was electrolyzed at a constant current of 3.0 mA for 1287 seconds and for another 1280 seconds that reduces the limiting current 18.5% and 37% of its original value respectively. Applying Faraday's laws n was calculated to equal 2.7.

Cathodic Reduction of Hydroxylamine: Single cathodic scan voltammetry revealed that hydroxylamine is not reducible at platinum electrode. Cathodic reduction to ammonia has been reported using mercury electrode.[21]

Cyclic Voltammetry: Cyclic voltammetry was performed at a stationary platinum electrode using various scan rates, and cycling was repeated until a steady state was obtained. Figure 4 shows cyclic voltammograms (three cycles) of 1.0×10^{-3} M hydroxylamine in 0.01 M sulphuric acid at scan speed 1200 mV s^{-1}. The sweep was initiated in an anodic direction as represented by small arrows. It is obvious that only one oxidation wave is shown at potential 1.0 V and on return cathodic cycle there is a very little evidence of any reversible character to hydroxylamine oxidation since there is no corresponding reduction wave. The drastic deformation of the cyclic voltammogram could be due to the change of the resistance of the test solution during measurement as long as the reference electrode is a sensitive SCE.

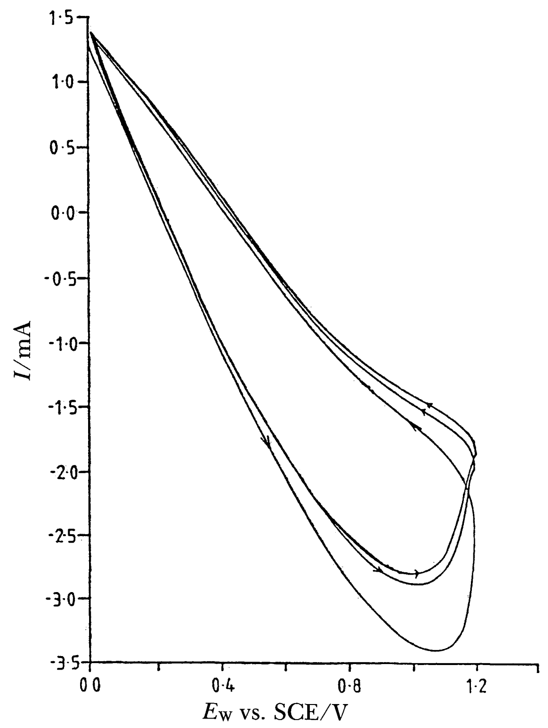

Fig. 4. Cyclic voltammogram of 1.0×10^{-3} M hydroxylamine in 0.01 M sulphuric acid at a stationary 0.503 cm^2 platinum electrode at a scan speed 1200 mV s^{-1}.

Identification of Products: 2×10^{-3} M solution of hydroxylamine was prepared in 0.01 M sulphuric acid and anodically electrolyzed by passing a current of 4.0 mA for 5 h. A 100 ml of this solution was tested for nitrite[22] by adding 0.5 ml of 1% sulphanilic acid in 4 M acetic acid and 2 ml of 1-naphthol in 2 M sodium hydroxide. A pink color developed indicating presence of the nitrite. Thus nitrite could be regarded as a minor product of hydroxylamine anodic oxidation. Nitrite has also been detected previously[23] when hydroxylamine was used as a dc-polarizer in the determination of copper, bismuth, lead, and tin using platinum electrode.

Other expected products were tested for, but all attempts have failed due to the micro amounts of gases evolved if any.

Mechanism: The oxidation of hydroxylamine at a platinum electrode is not a simple one, and reveals that all reaction processes take place in one step. The high over-potential of 500 mV confirms that more than one reaction takes place in one step. Kinetic parameters were calculated by taking the number of electrons as two. No pattern of values or strict proportionality can be claimed at different hydroxylamine concentrations, but the reaction is definitely a mixed mass and charge transfer controlled predominantly by charge transfer. The high overpotential exhibited is a sign of complex reaction steps taking place in one step. As far as the number of electrons involved in the oxidation process is concerned, being a fraction of 2.7, more than one route simultaneously being followed is the most likely mechanism for the reaction. This interpretation could be confirmed by the presence of the micro-amounts of nitrite in the solution after electrolysis. Although the involvement of more than two electrons in one-step electrode process is unlikely, nitrite production in small amounts is a sign of four-electron oxidation of hydroxylamine, which is obscure. The redox irreversible wave exhibited by the cylic voltammogram is not in favor of nitrite being the only product of hydroxylamine oxidation but would certainly suggest that dinitrogen oxide (N_2O) and/or dinitrogen (N_2) species could not be denied as the anodic irreversible wave and final products together with the nitrite. Not only that but these findings reveal that the dinitrogen oxide and/or dinitrogen species predominate and this would explain the reasoning for calculating parameters by taking the number of electrons as two.

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