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REDUCTION OF NITRIC OXIDE AT A FLOW-THROUGH MERCURY PLATED NICKEL ELECTRODE

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Abstract—The electrochemical reduction of nitric oxide at a flow-through mercury-plated nickel gauze electrode in sulphuric acid was investigated. The current efficiencies of hydroxylamine, nitrous oxide and of hydrogen formation were determined. The main experimental results are:

1. The ratio between the NH_2OH and N_2O formation depends on the cd and on the flowrate of the electrolyte through the electrode, but does not depend on the H_2SO_4 concentration in the investigated range from 0.25 to 2.0 M and likewise not on the temperature.

2. The rate of the reduction of nitric oxide to NH_2OH and N_2O increases with increasing cd up to a maximum value, thereafter this rate decreases with increasing cd .

3. The ratio between the current efficiency of the NH_2OH formation and the current efficiency of the N_2O formation increases slowly with increasing cathodic potential.

It seems that at low cd (much lower than the cd where the rate of the reduction of NO reaches its maximum) the reduction of NO is affected by both the electrochemical parameters and by the transport of NO to the electrode surface. However, at high current densities the reduction is dominated by mass-transport of NO only. NOH is an intermediate for both the NH_2OH and the N_2O formation.

1. INTRODUCTION

The electrochemical reduction of nitric oxide to hydroxylamine can be of interest for oximation processes. The effect of a number of factors on the electrochemical reduction of NO to NH_2OH is already published by Janssen and Hoogland[1,2]. They found that nitric oxide can be cathodically reduced mainly to NH_2OH at various electrode materials. In addition, NH_3 can be formed in solutions with a high acid concentration, eg in 8 M H_2SO_4 [2]. On the other hand N_2O is formed in solutions with a higher pH, eg pH = 5[3]. In this paper additional details are presented.

The effect of several conditions of electrolysis (eg time of electrolysis, potential, current density, flowrate of electrolyte and temperature) on the reduction of NO at a flow-through mercury-plated nickel electrode are studied more extensively in their interrelations.

2. EXPERIMENTAL

2.1 Apparatus and electrolytical conditions

A schematic diagram of the apparatus used for the electrolysis is shown in Fig. 1. The electrolytic cell was separated by a porous glass diaphragm into a cathodic and anodic compartment. The cell was thermostatted. The temperature was usually maintained at 17°C, unless the influence of the temperature between (5–40°C) was studied.

A platinum foil electrode in the anode compartment was used as an anode. A nickel gauze electrode covered with mercury, serving as a cathode, was horizontally clamped between two rubber rings at the bottom of the cathodic compartment of the cell. A saturated calomel electrode served as a reference electrode. The current was supplied by a *dc* power generator (Delta Elektronika D 050-10). The applied cur-

rent was varied between 0.25 and 2.5 A. Potentials of the cathode vs the calomel electrode were measured by means of a high-impedance voltmeter (Philips, PM 2435). These potentials were corrected for the *ir* drop measured oscillographically. Before the electrolytic cell and the other parts of the electrolytic circuit were filled with a solution, a potential difference between anode and cathode was adjusted. Careful attention was paid to this procedure to prevent any corrosion of the cathode. A 1 M H_2SO_4 solution was used as

Fig. 1. Experimental set-up.

the supporting electrolyte, unless otherwise mentioned. The catholyte was pumped by a flow-inducer (W. A. Bachofen type LPA-standard) through the cathodic compartment of the cell in rising direction.

To measure the flowrate of the electrolyte a flowmeter (Fischer and Porter No. 3F-3/8-25-5/36, tantalum or sapphire float) was used. The volume of the catholyte was 550 cm³ and that of the anolyte 150 cm³.

The flowrate of the catholyte was adjusted between 500–2000 cm³/min, usually 1600 cm³/min. To determine the current for the production of hydroxylamine a 5–10 cm³ sample of the catholyte was tapped by means of a tap in the catholyte circuit. Immediately after the sampling an equal volume of the supporting electrolyte was added to the catholyte. The first sample was taken 1 h after the passage of NO was started through the catholyte and the sampling was repeated with intervals of 1 h. The average time of an electrolysis was about 6 h.

Gas (N₂ or NO) was passed through a flowmeter (Fischer and Porter No. 08-1/16-16-4/36, sapphire float) and then through two wash bottles containing 6 M KOH. Thereafter the gas was brought into the catholyte by a glass frit in the form of a ring placed in the absorption column. In all experiments the flowrate of NO was 75 cm³/min to ensure saturation. The gas and the catholyte were pumped together through the cathodic system. The cathodic compartment of the cell has a gas outlet. The gas passed this outlet, flowed through the gas sample loop of the gas chromatograph and then through a wash bottle containing water.

After the adjustment of the current and the flowrate of the electrolyte, N₂ gas with a flowrate of about 80 cm³/min was bubbled through the catholyte during the first hour of the electrolysis. Thereafter the N₂ gas was replaced by NO gas containing 0.50% N₂O and 0.60% N₂, both values determined gas chromatographically. The first gas chromatographic analysis during the electrolysis was carried out 55 min after the start of the bubbling through of NO; and then repeated every hour.

2.2 Cathode

The cathode consisted of a nickel gauze of 42 mm dia, spotwelded to a nickel ring with an o.d. of 50 mm and an i.d. of 35.6 mm. A nickel strip (5 × 35 mm) was also spotwelded to the nickel ring and served as current connection. The nickel gauze had a mesh-width of 0.050 mm, and wire diameter was 0.035 mm. A geometric surface area of 10 cm² of the gauze was exposed to the electrolyte. Taking into consideration a roughness factor of 2.58 for this gauze, the surface area of the wires serving as cathode surface was 25.8 cm².

To cover the nickel electrolyte with a mercury layer the following room temperature procedure was adopted. The electrode was cleaned by a cathodic treatment in 1 M KOH with 1 A for 15 min and thereafter by washing with distilled water. The cleaned electrode was immersed in 4 M HNO₃ for 2 min and a further cathodic treatment in 1 M HClO₄ at 0.5 A for 30 min. Mercury was deposited on the oxide-free electrode by polarizing the electrode cathodically with 30 mA in a solution of 1 M HClO₄ and 0.01 M

HgNO₃ for 1 hr a calculation gives that a mercury layer with a thickness of about 0.006 mm was formed. Thereafter the mercury plated nickel electrode was maintained cathodically with 0.6 A in 1 M HClO₄ till the electrode was used for the experiments. To obtain reproducible results it was necessary to deposit a new mercury layer before each experiment on to the nickel electrode. This was brought about by a cathodic polarization of the electrode in the HClO₄/HgNO₃ solution at 30 mA for 10 min.

2.3 Analyses

2.3.1 Hydroxylamine and ammonia. To determine the amount of NH₂OH, 5 or 10 cm³ catholyte was added to a 20 cm³ solution consisting of 10 cm³ 2 M H₂SO₄ and of 10 cm³ 0.85 M Fe NH₄(SO₄)₂ + 0.1 M H₂SO₄. The solution was boiled for 5 min, cooled to room temperature and then potentiometrically titrated[4] with 0.05 M Ce(SO₄)₂ or 0.02 M KMnO₄. Before the concentration of NH₃ in a catholyte sample of 10 cm³ could be determined in the usual way[5] the hydroxylamine present in the sample oxidized quantitatively by adding 15 cm³ 0.1 M Ce(SO₄)₂ + 0.1 M H₂SO₄ to the sample and boiling the solution for 20 min.

2.3.2 Nitrogen oxides, nitrogen and hydrogen. The analyses of the gas in the gas sample loop were performed with a gas chromatograph (F and M, model 720). The volume of the sample loop was 2.85 cm³. The carrier gas was argon. A 180 cm column of molecular sieve 5 A (size 45–60 mesh) at 80°C was used to obtain separately the peaks of hydrogen, oxygen, nitrogen and nitric oxide in the chromatogram. After the appearance of the nitric oxide peak the temperature of the oven was brought from 80° to 220°C with a rate of 30°C/min and then the temperature was held at 220°C. After about 15 min the N₂O peak if present, appeared. The detector block was always maintained at 230°C.

For the calculation of the rate of the production of H₂, resp. N₂O during the electrolysis, the rate of the gas flow passing the sample loop had to be known. This flowrate was calculated by correcting the flowrate of NO before entering the electrolytic cell by the rate of the H₂ and N₂O production and of the consumption of NO in the electrolytic cell.

3. RESULTS AND DISCUSSION

3.1 Product analysis

Experimentally[2, 3] it was found that NO can be reduced to NH₂OH, N₂O and NH₃. The formation of hydrazine which is also thermodynamically possible, was not mentioned in the literature. The analysis of the catholyte after an electrolysis at a current of 1 A of a 1 M H₂SO₄ solution at 17°C through which NO gas was bubbled for 2 h, showed that beside hydroxylamine a small quantity of ammonium (and no detectable quantity of hydrazine) were present in the catholyte. The hydrazine concentration was determined as described by Watt and Crisp[6]. The quantity of ammonia corresponds to a current efficiency of only 2.7%. The formation of ammonia is only important for solutions with a high H₂SO₄ concentration[2], therefore the formation of ammonia will not be considered further. The analysis of the gas

showed that besides large quantities of NO and H_2 , very small quantities of N_2 and N_2O were present. Moreover, it was found that the NO gas of the cylinder gas contained already small quantities of N_2 and N_2O , 0.60% resp. 0.50%.

Experimentally it appeared that N_2O is formed whereas N_2 is not formed at the reduction of NO. The N_2O content in the NO gas depended on the electrolytic conditions.

This content was about a factor 2-4 higher than that in the NO gas of the cylinder. Consequently, during the electrolysis a small quantity of N_2O is formed. The formation of N_2O may be produced electrochemically by the reduction of NO and/or chemically by the decomposition of NH_2OH which had been formed during the electrolysis. To investigate the decomposition of NH_2OH , we determined the rate of the formation of N_2O and the rate of the decomposition of NH_2OH in the cathodic compartment during NO bubbling through a 1 M H_2SO_4 solution containing NH_2OH . In this case the diaphragm was completely closed by a rubber disk. The rate of the catholyte flow was $1600\text{ cm}^3/\text{min}$ and the temperature 17°C . The cathode had been removed. Comparing the rate of the N_2O formation and that of the decomposition of NH_2OH it appeared that 1 molecule N_2O is formed from 1 molecule NH_2OH . The compound N_2O may be formed by the reaction of hydroxylamine with nitrite[7] according to the reaction, $NH_2OH + HNO_2 \rightarrow N_2O + 2H_2O$.

The occurrence of HNO_2 is likely since it is very difficult to remove all traces of NO_2 from NO gas[8]. Moreover, oxygen gas can enter the cathodic compartment, since the experimental set-up might not completely be air-tight. Oxygen reacts with NO to form NO_2 , so nitrite is formed in the cathodic compartment. The N_2O formation by decomposition of NH_2OH appeared to be independent of the NH_2OH concentration for our experimental conditions. The rate of the decomposition of NH_2OH , J_{NH_2OH} in mA/cm^2 , assuming 3 electrons per 1 molecule, was equal to $3.4\text{ mA}/\text{cm}^2$. The rate of the N_2O formation during the electrolysis was a factor 2-4 greater than corresponds with $3.4\text{ mA}/\text{cm}^2$. Thus during the electrolysis N_2O is formed both by reduction of nitric oxide (J_{N_2O}), and by decomposition of hydroxylamine.

3.2 The effect of the electrolytic conditions

In Fig. 2 characteristic results of the electrolysis of a NO-containing sulphuric acid solution are given. In this figure J_{NH_2OH} , J_{N_2O} and J_{H_2} are plotted vs the time t of electrolysis for which NO gas was passed through the catholyte.

Fig. 2. Plot of J_{NH_2OH} , J_{N_2O} and J_{H_2} at $J = 100\text{ mA}/\text{cm}^2$ vs the time t of electrolysis at which NO gas was passed through the catholyte.

Fig. 3. Plot of $R_{NH_2OH}^0$ and $R_{N_2O}^0$ vs J .

through the catholyte. J_{NH_2OH} was determined from the increase of the concentration of NH_2OH in the catholyte during 1 h of electrolysis taking into account the rate of decomposition of hydroxylamine during NO bubbling, viz. $3.4\text{ mA}/\text{cm}^2$ and the effect of dilution of the electrolyte are averaged over 1 h. J_{N_2O} is calculated from the rate of N_2O formation during the electrolysis, corrected for the N_2O formation due to NH_2OH -decomposition. The sum of the corrected experimental values for J_{NH_2OH} , J_{NO} and J_{H_2} is equal to the total measured current density. Here, only J_{NH_2OH} and J_{N_2O} at the stationary state, (mentioned $J_{NH_2OH}^0$ and $J_{N_2O}^0$) with the corresponding current efficiencies $R_{NH_2OH}^0$ and $R_{N_2O}^0$ will be considered. It appeared that both $R_{NH_2OH}^0$ and $R_{N_2O}^0$ increased with the number of times a mercury layer was deposited on the nickel electrode. After the mercury/nickel electrode has been used for 3 times as cathode for the NO reduction, $R_{NH_2OH}^0$ and $R_{N_2O}^0$ reached constant values. These limiting values are somewhat different for various mercury/nickel electrodes. However, this ratio $R_{NH_2OH}^0/R_{N_2O}^0$ remained practically equal. After about 3 times mercury had been deposited on the electrode, the thickness of the mercury layer on the nickel wire may reach a maximum value.

In Fig. 3, $R_{NH_2OH}^0$ and $R_{N_2O}^0$ are plotted vs the total cd J . This figure shows that the current efficiency for both the NH_2OH formation and the N_2O formation decreases with increasing current density and that at low current density only a small quantity of hydrogen is formed.

The influence of the diffusion of NO to the electrode surface can be more clearly represented by plotting $m_{NO} = (\frac{1}{3} R_{NH_2OH}^0 + R_{N_2O}^0) J/F$ mmole/s cm^2 vs J where J is expressed in mA/cm^2 and $F = 96500\text{ C}/\text{mol}$. For the formation of 1 molecule NH_2OH are used 3 electrons and for 1 molecule N_2O 2 electrons. The m_{NO}/J relation is plotted in Fig. 4;

Fig. 4. Plot of m_{NO} vs J .

Fig. 5. $\epsilon/\log J$ relations during H_2 and during NO bubbling.

its data are deduced from those of Fig. 3. The curve of Fig. 4 reaches a maximum at about $J = 120 \text{ mA/cm}^2$; at higher cd the rate of the reduction of NO decreases with increasing total cd . This decrease may be caused by the decrease of the NO concentration at the cathode due to stripping caused by an increasing rate of the H_2 evolution. Obviously, the current efficiency for the reduction of NO at $J > 120 \text{ mA/cm}^2$ is determined by the net decreased mass transport. The maximum value of $m_{NO} = 24 \times 10^{-5} \text{ mmole/cm}^2$ (Fig. 4) appear to be smaller than the maximum value, which might be obtained when hydrogen gas is not formed at the cathode. This conclusion is based on the much higher maximum rate of NO reduction when a 1 M $(NH_4)_2SO_4$ solution of pH of about 9 is used as a supporting electrolyte. In this solution practically only N_2O was formed. The experimental maximum rate of NO reduction was about 100 mA/cm^2 which corresponds with $m_{NO} = 52 \times 10^{-5} \text{ mmole/s cm}^2$. Consequently, it follows that for a 1 M H_2SO_4 solution the rate mass transfer of NO at the maximum of the m_{NO}/J curve was at least a factor 2 smaller than the limiting rate of mass transfer if no hydrogen gas is formed.

The $\epsilon/\log J$ -relation during H_2 and during NO bubbling give also some information about the reduction of NO. Fig. 5 shows both relations for a 1 M H_2SO_4 solution as supporting electrolyte. These curves determined by changing the potential in anodic direction from the potential at about $J = 300 \text{ mA/cm}^2$. Firstly, the curve during H_2 bubbling was measured after passing hydrogen for 2 h through the solution. Thereafter NO was bubbled for 2 h and the $\epsilon/\log J$ relation determined. The obtained curves agree with the results of Fig. 3. This means that if there is no interaction between H_2 evolution and NO reduction, the obtained curves show that the current efficiency of

Fig. 6. Plot of R_{NH_2OH} and R_{N_2O} at $J = 100 \text{ mA/cm}^2$ vs the rate of the electrolyte flow through the cathode.

Fig. 7. Plot of R_{NH_2OH} and R_{N_2O} at $J = 100 \text{ mA/cm}^2$ vs the temperature T .

the NO reduction decreases and that of the H_2 evolution increases with increasing cd .

The influence of the concentration of sulphuric acid on the reduction of NO was also investigated. In the investigated range from 0.25 M to 2 M H_2SO_4 no influence was found upon the current efficiency of the NH_2OH formation. Figure 6 shows the influence on the rate of the electrolyte flow through the cathode, v_e , upon the current efficiency of the NH_2OH and of the N_2O formation. From this figure it follows that both R_{NH_2OH} and R_{N_2O} increase with increasing v_e . This is in agreement with the theory of hydrodynamics.

The effect of the temperature T appears from Fig. 7. The current efficiency R_{NH_2OH} is constant in the temperature range from 5 to 40°C . In Fig. 8 the ratio R_{NH_2OH}/R_{N_2O} is represented vs ϵ . The value of the potential ϵ is equal to that during the experiments at which the ratio R_{NH_2OH}/R_{N_2O} was determined. Fig. 8 shows that R_{NH_2OH}/R_{N_2O} increases with increasing cathodic potential. According to Mašek[9] nitric oxide yields two polarographic reduction waves in acidic media. He has concluded that the first wave is due to the two electron reduction of the dimer, N_2O_2 $N_2O_2^{2-}$ and that the second wave is due to the direct uptake of three electrons by NO to produce hydroxylamine. The structure of the dimer N_2O_2 [10] is given to

We assume that the structure of $N_2O_2^{2-}$ is the same. No acid association constants of this dimer are given in the literature. The acid-dissociation constants of nitrous acid and hyponitrous acid[10] are well-known, viz. $K_{HNO_2} = 10^{-11} \text{ mole/l}$. From the acid-dissociation constants of the acids mentioned it fol-

Fig. 8. Plot of ratio R_{NH_2OH}/R_{N_2O} vs the potential ϵ .

lows that in sulphuric acid media the compound $\text{N}_2\text{O}_2^{2-}$ formed by the reduction of N_2O_2 reacts with H^+ ions forming $\text{H}_2\text{O}_2\text{H}_2$ with the structure

The formation of N_2O is than only possible after a rearrangement of the dimer $\text{N}_2\text{O}_2\text{H}_2$. For solutions of $\text{pH} = 5$, Ehman and Sawyer[3] found that NO is reduced practically completely to N_2O at a mercury electrode. They proposed the following mechanism:

The species NOH is an intermediate in this mechanism. If NH_2OH is formed with the direct uptake of three electrons by NO it is likely that NOH is also an intermediate which is formed after the uptake of one electron by NO. The intermediate NOH can give N_2O and can be reduced to hydroxylamine according to $\text{NOH} + 2\text{H}^+ + 2e \rightarrow \text{NH}_2\text{OH}$. Both species viz N_2O and NH_2OH are formed also in the potential range where the rate of the NO reduction is determined by the transport of NO to the electrode surface. Moreover, it is found that the

ratio $R_{\text{NH}_2\text{OH}}/R_{\text{N}_2\text{O}}$ increases with increasing cathodic potential. This result supports the conclusion that NOH is an intermediate for both the NH_2OH and the N_2O formation.

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