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REDUCTION OF NITRIC OXIDE AT A PLATINUM CATHODE IN AN ACIDIC SOLUTION

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Abstract—The reduction of nitric oxide at a platinum electrode in 4 M H_2SO_4 was investigated by the measurement of potential/current relations and by the determination of the current efficiencies for the hydroxylamine, nitrous oxide, ammonia, hydrazine and hydrogen formation at fixed potentials in the potential range from 0 to -400 mV vs sce.

The potential/current curve for the reduction of nitric oxide has two waves, of which the limiting currents depend strongly on the potential and the time of the pretreatment of the electrode and on the direction of the potential change during the measurements. In the potential range of the first wave (viz $\epsilon > -30$ mV) nitric oxide is reduced only to nitrous oxide. In the whole potential range of the second wave (viz from -50 to -250 mV) nitric oxide is reduced to hydroxylamine, ammonia and nitrous oxide. Formation of hydrazine has not been detected.

From the literature and from the relations of the current efficiencies a possible mechanism is proposed for the reduction of nitric oxide.

1. INTRODUCTION

Nitric oxide can be reduced to hydroxylamine at a platinum electrode in an acidic solution[1]. This reduction was also studied by Dutta and Landolt[2] and by Savodnik *et al*[3, 4]. Potential/current density curves show that the reduction of nitric oxide at a platinum electrode proceeds in two steps[2-4]. According to Dutta and Landolt it is likely that HNO or NO^- is formed in the first step and that hydroxylamine is the final product of the second step.

Savodnik *et al* found that at potentials corresponding to the first step nitric oxide is quantitatively reduced to nitrous oxide. Moreover, they concluded that the first step corresponds to a one-electron process, followed by dimerization of HNO :

According to them, hydroxylamine is formed only in the region of the potentials where the second reduction wave occurs. The current efficiency of the hydroxylamine formation depends on the potential and reaches a maximum value of about 78% in the potential region of the limiting current of the second step [3]. At potentials close to the reversible hydrogen potential the current efficiency for hydroxylamine decreases. According to Savodnik *et al* this decrease may be related to the reduction of nitric oxide to ammonia. However, the current efficiency of ammonia and of possibly other products were not determined. This paper presents the determination of the formation of N_2O , NH_2OH , N_2 , N_2H_4 and NH_3 (which are all thermodynamically possible) as a function of the potential, especially in the potential region of the second step. These rates can be of interest to elucidate the mechanism of the NO reduction.

2. EXPERIMENTAL

Apparatus

Figure 1 shows a schematic diagram of the electrolytic cell. The cell was divided by two porous glass

diaphragms into a cathodic compartment of 400 cm^3 , an anodic compartment of 15 cm^3 and an intercompartment of 85 cm^3 .

During the electrolysis the cell was kept at 17°C .

A platinum disc of 44 cm^2 on the bottom of the cell served as the cathode and a platinum foil of 8 cm^2 as the anode. A saturated calomel electrode was used as the reference electrode and all potentials (ϵ) are referred to this reference electrode. The potential of the cathode was adjusted with a Wenking potentiostat (model 68 Fr 0.5). The current/time curves were recorded on a Philips recorder (PM 8010). In the applied current range of 1–100 mA the resistance polarisation, measured oscillographically, was very small and could be neglected.

Fig. 1. Experimental cell.

Fig. 2. Plot of the current vs the time of the electrolysis of NO at various electrode potentials.

Procedure

A 4M H_2SO_4 solution, prepared with chemical grade sulfuric acid and distilled water, was used as the supporting electrolyte. The solution in the cathodic compartment was stirred with a magnetic stirrer. Argon was passed through the cathodic compartment for 1 h prior to the electrolysis to deaerate the catholyte. At the beginning of the electrolysis at a constant potential the argon flow was substituted by a NO flow of $3 \text{ cm}^3/\text{min}$, measured with a flowmeter (Fischer and Porter 08-1/16-16-4/36). To minimize the quantity of NO_2 in the electrolytic cell a low flow-rate of NO gas was chosen, so it took about 2 h before NO gas was present in the electrolytic cell. Prior to this bubbling, the NO-gas, containing 0.3% N_2 and 0.3% N_2O , was passed through two washing

Fig. 4. Plot of the current efficiencies for the formation of hydroxylamine, ammonia, nitrous oxide and hydrogen versus the potential.

bottles, both filled with a 4M NaOH solution, to remove possible NO_2 impurities.

The time of the electrolysis was 20 h for each experiment. After the electrolysis the anolyte (15 cm^3) was removed and argon was bubbled through the catholyte for 15 min. The catholyte and the solution of the intercompartment were then mixed. This mixture was analysed.

Fig. 3. Potential/current relations after an electrolysis for 20 h at -30 mV and -340 mV. These relations were determined for a potential change in both anodic and cathodic directions. The arrow on the curve denotes the direction of the potential change.

Fig. 5. Plot of the ratio between the current efficiencies of the formation of hydroxylamine and of the ammonia formation (two series of experiments) and the ratio between the current efficiencies of the formation of nitrous oxide and hydroxylamine versus the potential. The series of experiments indicated by x and by ● are carried out simultaneously.

Analysis

The concentration of hydroxylamine was determined by the method described by Bray *et al*[5]. The presence of hydrazine was checked by the method of Feigl and Auger[6]. Ammonia was determined in the usual way[7], after the hydroxylamine present in the sample was oxidized quantitatively with an excess of ferric ions.

To determine the rate of the nitrous oxide formation during the electrolysis, the gas which left the cathodic compartment at the end of the electrolysis was analyzed with a Hewlett-Packard gaschromatograph (model 5710 A), using a 180 cm column filled with molecular sieve 5 Å (size 60–80 mesh) at 80°C to separate the peaks of hydrogen, nitrogen and nitric oxide in the chromatogram. After evolution of NO the temperature of the column was increased to 250°C at a rate of 30°C/min[8]. In the potential range from –300 to –400 mV additional experiments were carried out for the determination of hydrogen. In these experiments argon was used as the carrier gas.

3. RESULTS

Relations between potentials, current and time of electrolysis

Figure 2 shows some current/time curves at fixed electrode potentials. During the first hours of the electrolysis the current is very low, especially at potentials higher than the reversible hydrogen potential; thereafter the current increases to a limiting value. This value is reached after about 13 h due to long time necessary for obtaining the saturation situation. From preliminary experiments it appeared that the pretreatment of the platinum cathode has also a great influence on the ϵ/i curve.

Figure 3 shows stationary ϵ/i curves, measured during potential change both in anodic and cathodic direction, for a platinum electrode which had been polarized during 20 h at two different constant potentials, *viz* –30 mV and –340 mV (no current interruption occurred after the polarization and during the determination of the ϵ/i curve). The ϵ/i curves for $\epsilon = -340$ mV have clearly two reduction waves; for $\epsilon = -30$ mV the second wave is not clearly distinguishable. The current at a given potential during a scan in anodic direction is smaller than that of a scan in cathodic direction. This difference is not caused by a bulk concentration change, since the ϵ/i curve was measured at practically stationary conditions.

Current efficiency, R

The electrolysis at constant cathodic potential was performed in the potential range from –30 to –370 mV. It was necessary to electrolyse for a long period, due to the small currents obtained during the NO electrolysis (*viz* about 1 mA at –30 mV and about 100 mA at –370 mV). The current efficiency for NH_2OH and for NH_3 were calculated from their quantities present in the electrolytic cell after the 20 h electrolysis, whereas, the current efficiency for N_2O and H_2 were determined gaschromatographically from their formation rates at the end of the elec-

trollysis. In Fig. 4 the current efficiencies R for NH_2OH , NH_3 , N_2O and for H_2 are plotted versus the cathodic potential. The results for hydroxylamine are in agreement with those of Savodnik *et al*[3].

The decomposition of NH_2OH at electrolytic conditions without electric current flow was investigated by measuring the rate of the decrease of the NH_2OH concentration during NO bubbling for 16 h. It appeared that the decomposition of NH_2OH could be neglected in 4M H_2SO_4 . In the investigated potential range no detectable quantities of N_2H_4 and of N_2 were formed.

4. DISCUSSION

The ϵ/i curve of the reduction of NO at a platinum electrode in 4M H_2SO_4 has two waves (Fig. 3). Savodnik *et al*[4] have established that the first wave (*ie* the wave between 400 and 100 mV) corresponds with the reduction of NO to N_2O , at which HNO is an intermediate. This conclusion is supported by the results represented in Fig. 4. From this figure it can be concluded that the current efficiencies of the hydroxylamine and of the ammonia formation decrease strongly with increasing potential $\epsilon > -100$ mV and are practically zero at $\epsilon > -30$ mV. On the other hand the current efficiency for N_2O increases very strongly and will be 100% $\epsilon > -30$ mV.

In the potential range of the second wave, *viz* from –50 to –250 mV, three species (NH_2OH , NH_3 and N_2O) are formed by reduction of NO; at potentials lower than about –250 mV also hydrogen is evolved. At potentials where the limiting current of the second wave occurs, N_2O is still formed by reduction of nitric oxide. The ratio of the current efficiencies for the formation of NH_2OH and of NH_3 are shown in Fig. 5. It appears that both the $R_{\text{N}_2\text{O}}/R_{\text{NH}_2\text{OH}}$ and the $R_{\text{NH}_2\text{OH}}/R_{\text{NH}_3}$ ratio decrease with decreasing potential and approach limiting values, *viz* respectively 0.20 and 3.5. A second series of experiments, where only the current efficiencies for the NH_2OH and the NH_3 formation were determined gave the same results.

We conclude from the fact that the ratio $R_{\text{N}_2\text{O}}/R_{\text{NH}_2\text{OH}}$ becomes a constant with increasing overpotential that the intermediate HNO, formed during the first step is not directly reduced electrochemically but this intermediate may react with protons forming HNOH^+ and dimerizes to $\text{H}_2\text{N}_2\text{O}_2$. The limiting ratio of $R_{\text{N}_2\text{O}}/R_{\text{NH}_2\text{OH}}$ is determined by the ratio between the rate of the protonation and of the dimerization. The species NH_2OH can be formed from HNOH^+ by an eHe-mechanism.

Analogously to the preceding reasoning this ratio may be explained by desorption of adsorbed NH_2OH . The ratio $R_{\text{NH}_2\text{OH}}/R_{\text{NH}_3}$ has also a finite limiting value (Fig. 5). Summarizing the foregoing discussion, the mechanism of the reduction of nitric oxide, satisfying the experimental results, can be given by

Further experiments are necessary to establish the mechanism proposed.

The ϵ/i curve of the NO reduction, especially the limiting current of both waves, depends on the potential during the pretreatment of the electrode and on the direction of the potential-change during the measurement of the ϵ/i curve (Fig. 3).

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