The electrocatalytic reduction of nitrogen compounds, part II : the influence of the electrode material on the electrochemical reduction of nitrite

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nitrocyclohexane³⁴, cyclohexyl nitrite³⁵, cyclohexyl nitrate³⁶) or were available as commercial products. Tank nitrogen dioxide and nitric oxide were purchased from Matheson (>99% purity).

Standard procedure for kinetic experiments

~ 10 ml solutions of **1b** or **1c** in cyclohexane were placed in a 4-necked round-bottomed 25 ml flask equipped with a reflux condenser, a gas inlet, a serum cap and a thermometer.

Via the condenser a gas outlet was connected with a wash-bottle with saturated Ba(OH)₂ solution (optional). At appropriate time intervals samples were withdrawn with a syringe and quenched with 0.25 M NaOC₂H₅ in C₂H₅OH at room temperature for 30 seconds; unconverted **1** was thus transformed into the corresponding ethyl ester, which was subsequently determined by GLC (HP 5700, FID capillary SE-30 column, i.d. 0.4 mm, gas rate 20 cm/sec, oven temperature 140°C, detector 200°C, injector 200°C). Internal standard: *p*-dichlorobenzene. After 6–7 half-lives the reaction was also analyzed by GLC without quenching (HP 5700, same column, temperature programme: 8 min, 80°C, isothermal; 8°C/min from 80°–100°C, 8 min isothermal at 200°C).

Kinetic analysis by UV spectroscopy

Decomposition of **1c** in $\approx 10^{-4}$ M solutions was also followed by UV spectroscopy at 288 nm; conversion into *m*-Cl-C₆H₄CO₂H, peracid and CO₂ led to an overall decrease of the absorbance with 15%. The rate of decrease measured on a Cary-15 apparatus led to rate-constants comparable with those obtained by GLC analysis.

Isolation of peracid

After washing of the reaction mixture (10 ml) with 5 ml water, the organic layer was extracted twice with 5 ml 0.1 N NaOH solution; after acidification with 4 N HCl to pH 1–2 the peracid was isolated by extraction with pentane, drying with molsieves and evaporating of the pentane. The quantity of peracid was determined by weighing and iodometric titration³⁷.

Identification of reaction products

Apart from checking retention times in GLC, most reaction products were also analyzed by GC/MS combination, comparing mass spectra with those of authentic samples.

Acknowledgement

The authors thank Mr. N. P. E. Vermeulen for carrying out mass spectrometric analyses.

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³⁷ D. J. Pasto and C. R. Johnson, "Organic Structure Determination", Prentice-Hall Inc., p. 408 (1969).

The electrocatalytic reduction of nitrogen compounds.

Part II: The influence of the electrode material on the electrochemical reduction of nitrite

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Abstract. The electrochemical reduction of nitrite was studied at several electrode materials in 7.5 M sulfuric acid solutions. The thin oxide films on the noble metals, Pt, Ir and Rh, did not interfere with the reduction process. A thick oxide layer, as on Nb and Ta, however, did shift positively the reducing potential by several hundreds of mV.

In these solutions, the protecting layer on a lead electrode (lead sulfate) behaved in the same manner. From the decrease in the current in repeated cyclic experiments, it could be concluded that poisoning of the active surface sites of the electrodes by oxygen did change the reduction mechanism of nitrite.

Introduction

The electrochemical reduction of nitrous acid has been investigated, using various electrode materials^{1–4}. It appeared, that the mechanism (and so the reducing potential) depends on the nature of the electrode material used. So, Khomutov et al.¹ found, that the reduction of nitrous acid in a 2 M potassium chloride solution takes place in one or more reduction steps, dependent on the electrode material. They also found a periodic relationship between the half-wave potential and the atomic number for the 38 different metals, investigated. Tamayo Garcia, et al.² studied the reduction of nitrous acid in concentrated sulfuric acid with gold and platinum electrodes. At the gold electrode only a reversible, one-electron reduction was observed, in accordance with the reduction of NO⁺ (the electroactive species of nitrous acid) to nitric oxide. The investigations of the process at a platinum electrode were hindered by the formation of an oxide layer on the platinum electrode. In our study³ of the reduction of nitrite at a rotating platinum ring-disc electrode, we discussed the occurrence of a nitroxyl (HNO)

surface complex as an intermediate in the reduction of nitrite to hydroxylamine.

It seemed interesting to study the reduction of nitrite at other electrode materials in order to determine the surface conditions which influence the nitrite reduction. To study the electrode reaction, it was necessary to work in strongly acidic media (to avoid kinetic control by a preceding chemical reaction) in which metals, however, form oxide layers, other passivating layers or are stable only at high cathodic potentials. Hence these surface layers also are objects of our research.

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Experimental

We used the voltammetric technique with (rotating) disc electrodes. The instrumentation was the same as previously reported³, with the exception that a different type of electrode holder was used as with the ring-disc electrode experiments. The disc electrodes used consisted of 6 mm diameter metal discs, embedded in a 12 mm diameter Kel-F cylindrical jacket. The whole configuration was held in place by a stainless steel mantle. The reference electrode was a saturated mercury sulfate electrode with a reference potential of +0.70 V vs. SHE. The base electrolyte was a 7.5 M sulfuric acid solution into which a known amount of a concentrated KNO₂ solution was injected, just before starting the experiments. All solutions used were made oxygen-free by leading oxygen-free nitrogen through for at least 30 minutes.

Results

We studied the current-potential relationships for the reduction of nitrite at several electrode materials, viz. Pt, Nb, Ir, Rh, Pb and Ta.

The dependence on acidity of the relationship between the current and the square root of the rotation speed, ω , is shown in Fig. 1 for the reduction of nitrite at a rotating Nb disc electrode. From these curves it is possible to conclude whether the electrode reaction is completely diffusion controlled or whether a kinetic reaction also plays a role in the overall reaction rate (see Discussion). The current-potential relationships at the iridium and rhodium electrodes were almost identical (Fig. 2B, 3). Therefore, only the iridium electrode was investigated in detail. Figures 4 and 5 show the current-potential relationships at a stationary disc electrode (A) and at a rotating disc electrode (B) made of respectively, platinum and niobium. Figure 6 shows this for a rotating lead disc electrode. In the last case a protective layer plays an important role as will be discussed later. In earlier experiments it appeared that the current was time-dependent. Therefore the influence of repeated cycling was investigated, see Figure 7.

Discussion

The mechanism of the reduction of nitrite has been discussed in detail in a previous paper³. The important steps are:

The acid dissociation of nitrite [1] is rapid and complete in 7.5 M sulfuric acid solutions⁴. In less acidic media this reaction becomes rate-determining for the electrochemical reduction of nitrite to nitric oxide. This is clearly shown in the $i - \omega^{1/2}$ relationships (Fig. 1), where a straight line should be obtained, according to the Levich equation⁵, for a completely diffusion controlled process. This condition is complied with only at a minimum molarity of the sulfuric acid solution of 7.5. When reaction [1] becomes rate-determining, mixed control by the diffusion of NO⁺ to the electrode surface and the acid dissociation rate of NO₂⁻ occurs. In this case, according to the Jahn-Vielstich equation⁶, the $i - \omega^{1/2}$ relationship will deviate from a straight line.

This can be seen in Fig. 1 where with lowering the molarity and thus of the acidity of the solution the deviation from the straight line becomes greater. For comparison the curves in Fig. 1 are recalculated from the original curves in order to eliminate the effects of changing viscosity of the solution

and changing diffusion coefficient of the substrate. The method of recalculation was the same as used by Schmid et al.⁴ and performed using their data of diffusion coefficients and viscosities.

Fig. 1. $I - \omega^{1/2}$ relationships of the reduction of nitrite at a rotating niobium disc electrode in sulfuric acid solutions of different molarity and thus of different acidity: scanrate 10 mV/sec, conc. nitrite: 4 mM.

Fig. 2. Current-potential relationships of the reduction of nitrite at a stationary (A) and a rotating (B) iridium disc electrode.

— — without nitrite; — with nitrite. Experimental conditions: Curve A: scanrate 0.1 V/sec; conc. nitrite 5 mM. Curve B: scanrate 10 mV/sec; $\omega = 2000$ rpm; conc. nitrite 5 mM.

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All our further experiments were performed in 7.5 M sulfuric acid solutions, so reaction [1] could not interfere with the electrochemical reaction.

a. Iridium and rhodium

From Figs. 2A and 2B, it can be seen that at an iridium electrode the curves without nitrite show peaks which can be ascribed to the oxygen adsorption and desorption or even to surface oxidation and reduction. When nitrite is added to the solution, reduction taking place to nitric oxide is found anodically to the peaks previously mentioned, so that it may be concluded that the reduction of nitrite at an iridium electrode takes place on an oxidized electrode surface.

However, from the anodic scan at the rotating electrode (Fig. 2B), it can be seen that the limiting current of the nitrite reduction shows no change over several hundreds of mV (drawn line), while the electrode surface is changing from an oxidized form to a reduced form.

So, it is clear, that the overall kinetics of the reduction of nitrite to nitric oxide at an iridium electrode is not influenced by the surface state of the electrode. A further reduction of nitric oxide occurs near the hydrogen evolution potential, in a three-electron reduction step of nitric oxide to hydroxylamine, as could be calculated from the limiting current using the equation derived by Levich⁵ for the limiting current at a rotating disc electrode. The same results were obtained with a rhodium electrode as can be seen by comparing Figs. 2B and 3.

Fig. 3. Current-potential relationship of the reduction of 5 mM nitrite at a rotating rhodium disc electrode. — — — without nitrite; — with nitrite. Scanrate: 10 mV/sec; $\omega = 2000$ rpm.

b. Platinum

The reduction of nitrite at a platinum electrode (Fig. 4) is different from that at an iridium electrode. The mechanism of the reduction has been discussed in a previous paper³. Here, only the surface effect of the electrode will be discussed. The peak currents of the oxygen adsorption and desorption on platinum, as measured in cyclic voltammetric experiments, were less than 1% of the reducing currents of nitrite and are therefore not detectable in Fig. 4.

The peak potential of the desorption process, however, is in the potential range at which the reduction of nitrite to nitric oxide occurs.

The next reducing step of nitric oxide to nitroxyl, NOH (reaction 3) occurs therefore on an oxygen free (reduced) platinum surface.

Fig. 4. Current-potential relationships of the reduction of 10 mM nitrite at a stationary (A) and a rotating (B) platinum disc electrode. Experimental conditions: Curve A, scanrate: 0.1 V/sec. Curve B, scanrate: 10 mV/sec; $\omega = 2000$ rpm.

This may explain why in the reduction of nitrite at iridium and rhodium electrodes, the reduction of the nitric oxide formed takes place only near the hydrogen evolution potential, where the electrode surface is in a reduced state.

c. Niobium

It was interesting to study the reduction of nitrite at an electrode with a thick oxide layer to determine whether the electrode reaction will be hindered on such a surface. We therefore used a niobium electrode (Fig. 5A and 5B).

The cyclic voltammogram showed one irreversible reduction reaction. From the rotating disc curves it could be determined, as shown previously, that the reduction process was still completely diffusion controlled and that only reduction of nitrite to nitric oxide took place.

The half wave potential (-0.05 V vs. SHE) of the reduction of nitrite to nitric oxide at the rotating niobium electrode was about 1 volt more cathodic than that at the iridium or platinum electrode ($+0.92$ V vs. SHE). This can be ascribed to the oxide layer on niobium. It is known that Nb_2O_5 is formed on the surface of niobium in acidic solutions⁸. This

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⁸ H. V. K. Udupa and V. K. Venkatesan, Encyclopedia of Electrochemistry of the Elements, ed. A. J. Bard. Marcel Dekker Inc., New York, p. 104 (1974).

Fig. 5. Current-potential relationships of the reduction of 7 mM nitrite at a stationary (A) and a rotating (B) niobium electrode.

--- without nitrite; — with nitrite. Experimental conditions: Curve A, scanrate 0.1 V/sec. Curve B, scanrate 10 mV/sec, $\omega = 2000$ rpm.

Fig. 6. Current-potential relationships of the reduction of 5 mM nitrite at a rotating lead electrode.

--- without nitrite; — with nitrite. Scanrate: 10 mV/sec, $\omega = 2000$ rpm.

oxide is a poor electron conductor. When this layer is partly reduced to NbO_2 , a much better electron-conducting oxide layer is formed which facilitates the nitrite reduction. In this case the overpotential of the nitrite reduction is dependent on the potential of the reduction of the Nb_2O_5 surface layer. At a tantalum electrode the oxidized surface remains non-conducting, so that in this case no reduction wave of nitrite could be observed.

d. Lead

The same type of surface effects as for the niobium electrode is found when a lead electrode is used. In this case, the surface layer that influences the reducing potential of the nitrite consists of lead sulfate.

From Fig. 6, it can be seen that, without nitrite in the solution, a strong cathodic peak is obtained at -0.45 V (vs. SHE), corresponding to the reduction of the lead sulfate layer. In the presence of nitrite, a second reduction wave after the reduction of the surface layer occurs. This wave corresponds to a 4-electron reaction, as could be calculated using the Levich equation as mentioned already, and this means that as soon as the lead surface is free of lead sulfate, nitrite is reduced in one step to hydroxylamine. The half-wave potential of the wave corresponding to the nitrite reduction is therefore -0.5 V vs. SHE.

Conclusions

All electrodes mentioned showed strongly decreasing reduction currents at prolonged measurements. Figure 7 shows this in the case of the nitrite reduction at a stationary niobium electrode.

The peak current is lowered by 70% and becomes constant after more than 20 cycles. Measuring the decrease in concentration of the nitrite, due to its instability, by means of

Fig. 7. Current-potential relationships of the reduction of 7 mM nitrite at a stationary niobium electrode in a repeated cyclic experiment. Scanrate: 0.1 V/sec.

spectroscopic methods⁹, made clear that the decrease in current was only partly due to its instability. It is known that oxygen poisons the adsorption sites for nitric oxide¹⁰. So, the lowering of the current can be attributed partly to the poisoning of adsorption sites by traces of oxygen, present in the solution, despite deoxygenation by oxygen-free nitrogen. Also, oxygen may diffuse from the anode compartment (where it is formed) through the glass frit. Further reduction of nitric oxide is than inhibited, because nitric oxide reacts with the oxygen to form nitrogen dioxide. When the electrode surface is oxide-free, the oxygen is no longer adsorbed on the electrode surface and further reduction of nitric oxide is possible.

Because the platinum electrode (compared with the other investigated metals) is still oxide-free at a more anodic

potential, only at this electrode was a separate reduction step of nitric oxide to nitroxyl observed.

In conclusion, from our experiments it can be stated that the oxide layer (or, the lead sulphate layer) does not influence the electrode reaction in such a manner that this reaction becomes slower than the diffusion rate of electroactive species to the electrode surface. It does, however, influence the reducing potential, so that reduction steps merge to form multiple-electron transfer steps. In this respect, it can be stated that the mechanism of the reduction of nitrite to hydroxylamine is influenced by the electrode materials used. This catalytic effect of the electrode materials is due to the surface of the electrode and not due to the bulk metal properties.

Acknowledgement

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Metallation of 1,3-dienyl ethers and 1,3-dienyl sulfides in the 1-position

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Abstract. 1,3-Dienyl ethers and the corresponding sulfides ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{XR}$; X= O, S; R= alkyl, phenyl) are readily metallated at C-1, using *n*-butyllithium and KO-*t*-Bu in tetrahydrofuran. 2*H*-Thiopyran can be lithiated at the 6-position with *n*-butyllithium and tetramethylethylenediamine in tetrahydrofuran. The various metallated compounds react smoothly with methyl iodide, methyl thiocyanate and acetaldehyde to give the expected derivatives. At about -20° a more than 95% trans-formation of the metallated compound from *cis*- $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{S}-t\text{-Bu}$ into the *trans*-isomer occurs; with smaller R groups (isopropyl or ethyl) a less complete inversion is observed.

Introduction

Previous work¹ in our laboratory has shown that the α -hydrogen atoms of cumulenyl ethers and sulfides $\text{H}_2\text{C}=\text{C}=\text{CH}-\text{XR}$ and $\text{CH}_2=\text{C}=\text{CH}-\text{XR}$ (X= O, S) can readily be abstracted by *n*-butyllithium.

Oshima² described a similar lithiation of vinylic sulfides $\text{R}'-\text{CH}=\text{CH}-\text{SR}$ with *sec*-butyllithium in a mixture of tetrahydrofuran (THF) and hexamethylphosphoric triamide (HMPA) while Schöllkopf³ succeeded in removing the α -proton of vinyl ethers $\text{CH}_2=\text{CH}-\text{OR}$ using *tert*-butyllithium.

As 1,3-dienyl ethers and the analogous sulfides have become readily available to us⁴, it seemed worthwhile to search for a good method for converting them into the acyl-anion equivalents, the 1-metallated dienyl ethers and sulfides.

Results and discussion

*a. Reaction of 1,3-dienyl ethers and sulfides with a mixture of KO-*t*-Bu and BuLi in THF*

Addition of a solution of *n*-butyllithium in hexane to a strongly cooled (-65°) solution of the 1,3-dienes $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{XR}$ (X= O, S; R= alkyl, phenyl) and KO-*t*-Bu in THF resulted in a rapid metalation. Subsequent reaction with methyl iodide, methyl thiocyanate or acetaldehyde afforded the compounds **3**, **4** and **5** in good yields (see Scheme 1).

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