

# The electrocatalytic reduction of nitrogen compounds. Part I. The electrochemical reduction of nitrite at a rotating platinum ring-disk electrode

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## The electrocatalytic reduction of nitrogen compounds

### Part I: The electrochemical reduction of nitrite at a rotating platinum ring-disc electrode

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**Abstract.** The mechanism of the electrochemical reduction of nitrite has been studied at a rotating ring-disc electrode. It is found that the reduction of nitrite to nitric oxide is a reversible process. The reduction of nitric oxide to hydroxylamine involves the intermediate HNO, from which dinitrogen oxide can be formed in a side reaction to the reduction process.

#### List of symbols:

$E$	potential
$E_D$	potential of disc electrode
$E_R$	potential of ring electrode
$I$	current
$i$	current density
$I_D$	current at disc electrode
$I_D(E)$	current at disc electrode, when disc potential is $E$ volts
$I_R$	current at ring electrode
$I_R(E)$	current at ring electrode, when ring potential is $E$ volts
$I_R^0(E)$	value of $I_R(E)$ when $I_D = 0$
$N_0$	collection efficiency
$r_1$	radius of disc electrode
$r_2$	internal radius of ring electrode
$r_3$	external radius of ring electrode
$S$	shielding factor
$\beta$	$(r_3/r_1)^3 - (r_2/r_1)^3$ , geometrical parameter for the ring
$\omega$	rotation speed

oxide (which is found as a possible reduction step only at mercury and platinum electrodes) especially, has not been investigated thoroughly.

As part of our research, on the influence of electrode materials on the selectivity and reactivity of the nitrite (nitrate) reduction, it was imperative to study the different steps of the reduction process. We chose the voltammetric technique with a rotating ring-disc electrode in order to detect, and to study the mechanism and the kinetics of, the formation of intermediate reaction products. With this technique a steady state mass transport is maintained to and across the surface of the electrode, so that a homogeneous convective diffusion regime is maintained over the whole disc and ring. Moreover, a characteristic feature of this technique is, that if the potentials of disc and ring are chosen so that products formed at the disc electrode are reversibly converted to the original substrate at the ring electrode, the ring current divided by the disc current gives a constant, called the collection efficiency,  $N_0$ <sup>8</sup>, dependent only on the electrode geometry and not on the speed of rotation. Because experimentally measured currents can be compared with theoretically calculated currents, information can be obtained about the reversibility of the electrode reactions and the stability of intermediates and reaction products. Hence a chemical reaction following an electron transfer results in a decreasing value of  $N_0$ .

#### Introduction

The mechanism of the electrochemical reduction of nitrite has been investigated by different electrochemical techniques such as polarography<sup>1</sup> and (cyclic) voltammetry with and without rotation of the electrode<sup>2-5</sup>. These investigations have proved insufficiently decisive to attribute the intermediate products of the reduction of nitrite to hydroxylamine to separate reduction steps. For instance, the reduction at mercury and platinum electrodes is found to occur with three reduction steps, while at a gold electrode only two steps can be distinguished. The stable intermediate products of the different reduction steps of nitrite to hydroxylamine are, as verified by most authors, nitric oxide and dinitrogen oxide.

In the majority of cases further reduction to ammonia has not been observed<sup>3</sup>. Special attention has been paid to the electrochemical reduction of nitrite to nitric oxide and Schmidt et al.<sup>2</sup> especially have investigated the influence of added nitrate during the reduction of nitrite. They found that nitrate gives a catalytic wave in the presence of nitrite as a result of the autocatalytic reduction of nitrate by nitric oxide to nitrite. Therefore, we studied the reduction of nitrite instead of nitrate. The reduction steps of nitrite from nitric oxide to dinitrogen oxide and to hydroxylamine have been studied only partially. Some studies<sup>6,7</sup> started from nitric oxide, but the reduction of nitric oxide to dinitrogen

#### Experimental

To obtain  $I-E$  and  $I-\omega$  relations with the rotating ring-disc electrode, a Tacussel bipotentiostat, type BI-PAD, was used in combination with a Wenking linear voltage scangenerator, type VSG 72; the curves were recorded with a Hewlett Packard X (t) - Y-Y-recorder, type 7046 A, and the ring and disc potentials were measured with Philips DC-microvoltmeters, PM 2435. The rotation speed of the electrode could be varied between 100 and 5000 rpm and was kept constant at a desired value by means of a tachogenerator, type Motomatic, see Figure 1.

<sup>1</sup> J. Mašek and H. Przewlocka, Coll. Czech. Chem. Comm. **28**, 670-687; 688-695 (1963).

<sup>2</sup> G. Schmidt, M. A. Lobeck and H. Keiser, Ber. Bunsenges. Phys. Chem. **73**, 189-199 (1969).

<sup>3</sup> N. E. Khomotov, U. S. Stamkulov, V. A. Vinogradov and N. T. Kudryavtsev, Tr. Mosk Khim-Tekhnol. Inst. **65**, 99-103 (1970).

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<sup>5</sup> R. Rao Gadde and S. Bruckenstein, Electroanal. Chem. **50**, 163-174 (1974).

<sup>6</sup> J. Mašek, Z. Anal. Chem. **224**, 99-107 (1967).

<sup>7</sup> D. L. Ehman and D. T. Sawyer, J. Electroanal. Chem. **16**, 541-549 (1968).

<sup>8</sup> W. J. Albery and M. L. Hitchman, Ring-disc electrodes, Clarendon Press, Oxford (1971).

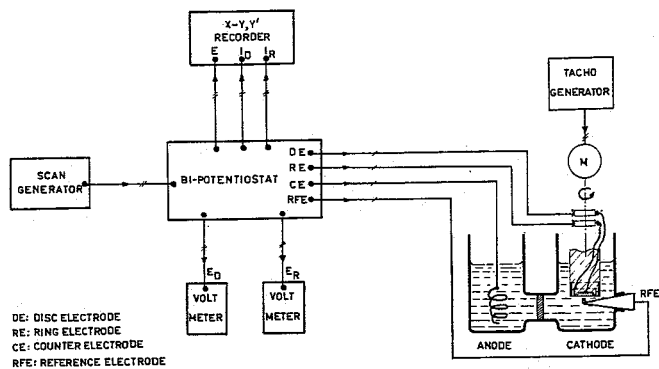


Fig. 1. Scheme of the instrumentation.

The experiments were carried out in a glass cell with an anode compartment, separated from the cathode compartment by means of a frit glass diaphragm. The cell was thermostatted at 25°. The Pt ring and the Pt disc electrode were separated by Kell-F as insulating material and were imbedded in a cylindrical jacket of the same material (see Figure 2).

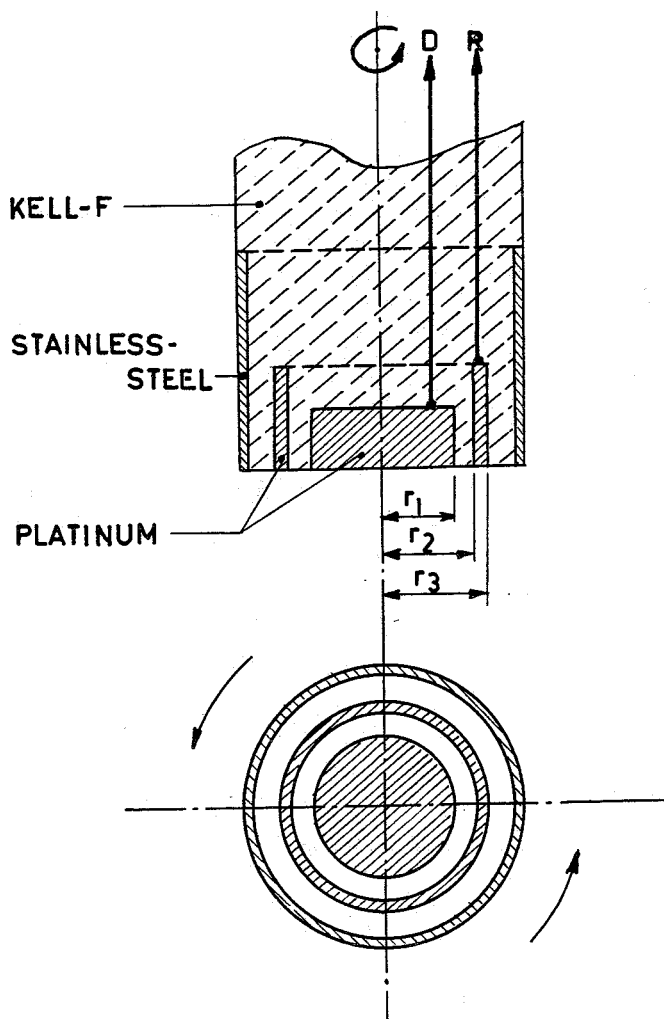


Fig. 2. Side- and bottom-view of the ring-disc electrode. The value for  $r_1$ ,  $r_2$  and  $r_3$  are 4.0525 mm, 4.1875 mm, 4.3350 mm, respectively.

The whole configuration was held in place by a stainless steel mantle. The reference electrode was a Hg/Hg<sub>2</sub>SO<sub>4</sub>/sat.K<sub>2</sub>SO<sub>4</sub> - half cell, S.S.E. (Saturated Sulfate Electrode) with a reference potential of +0.70 V vs. RHE; all potentials are referred to it. This electrode was placed at a few mm distance from the working electrodes by means of a Luggin capillary. The counter electrode was a Pt wire, area about 6.3 cm<sup>2</sup>.

The base electrolyte, 7.5 M sulfuric acid solution, was prepared by diluting concentrated sulfuric acid (Merck p.a.) with distilled water, and was made oxygen-free by leading oxygen-free nitrogen through it for 30 minutes. The nitrite was introduced into the solution to a concentration of  $1.2 \times 10^{-3}$  M KNO<sub>2</sub> just before starting the experiments, by injecting a small and known amount of oxygen-free, concentrated KNO<sub>2</sub> solution into the base electrolyte.

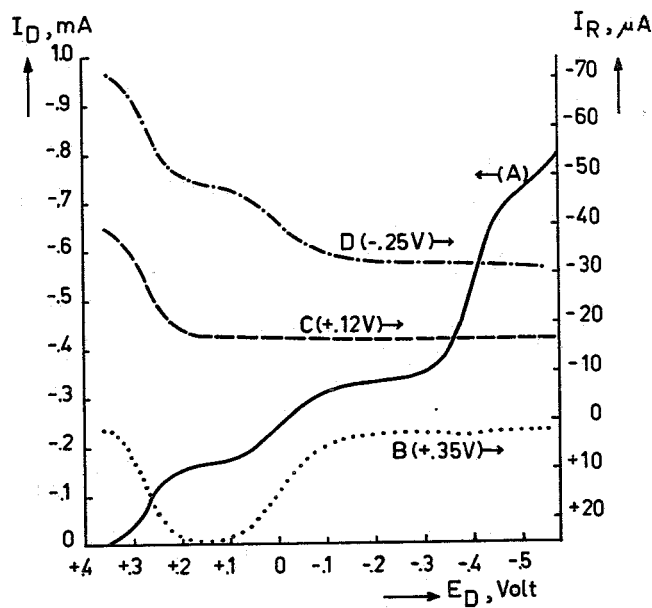


Fig. 3. Current-potential curve for a potential scan with a Pt disc electrode, curve A (—);  $\omega = 105$  rad/sec, scanrate 10 mV/sec, conc. 5 mM KNO<sub>2</sub> in 7.5 M H<sub>2</sub>SO<sub>4</sub>. The current response of the Pt ring electrode is recorded for the following constant potentials of the ring electrode: curve B (···),  $E_R = +0.35$  V; curve C (---),  $E_R = +0.12$  V; curve D (-·-·),  $E_R = -0.25$  V.

## Results

To study the nature and reactivity of the intermediate products of the reduction of nitrite to hydroxylamine, we used linear potential scans over the disc or the ring electrode, keeping respectively the ring or the disc electrode at a fixed potential. By scanning the disc electrode from +0.35 V to a more cathodic potential of -0.60 V, the possible reduction products of nitrite can be detected at the ring electrode, fixed at constant potential values.

Figure 3 gives the results of a potential sweep at the disc electrode (curve A).

The current response of the Pt ring electrode is recorded for the following constant potentials of the ring electrode: +0.35 V (curve B), +0.12 V (curve C) and -0.25 V (curve D). When the ring potential was kept at +0.80 V, another reoxidation process was distinguished, if the disc potential was scanned between -0.30 V and -0.60 V. Sweeping the disc potential between +0.12 V and -0.30 V gave no indication of any reoxidation process at the ring electrode, not even when the ring potential was kept near the potential where oxygen must be formed at the electrode.

Conversely, the reduction process at the disc electrode, kept at a constant potential, was followed by scanning the ring electrode. In this case too, the coupling between the reduction processes at the ring and the disc electrode was studied. Figure 4 gives the result of linear potential scans at the ring electrode, keeping the disc-potential at respectively +0.35 V (curve A), +0.12 V (curve B), -0.25 V (curve C) and -0.55 V (curve D). The curves C and D are exactly the same, although the disc potentials are different.

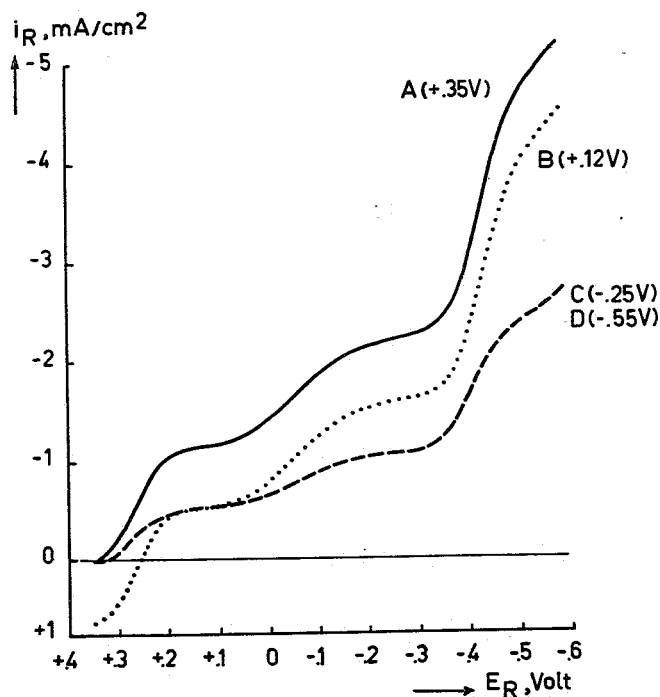
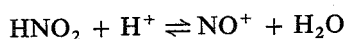


Fig. 4. Current density-potential curves for a potential scan at the Pt ring electrode with the following fixed Pt disc electrode potentials: curve A (—),  $E_D = +0.35$  V,  $i_D = 0$ ; curve B (⋯),  $E_D = +0.12$  V,  $i_D = 0.36$  mA/cm<sup>2</sup>; curve C (---),  $E_D = -0.25$  V,  $i_D = 0.72$  mA/cm<sup>2</sup>; curve D (-·-·-),  $E_D = -0.55$  V,  $i_D = 1.74$  mA/cm<sup>2</sup>. Experimental conditions:  $\omega = 105$  rad/sec, scanrate 10 mV/sec, conc. 5 mM KNO<sub>2</sub> in 7.5 M H<sub>2</sub>SO<sub>4</sub>.

## Discussion

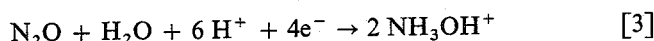
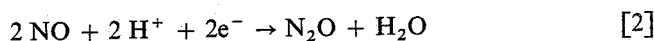
In the acid solutions used, nitrite is completely dissociated in water and the electroactive nitrosonium ion, NO<sup>+</sup>, according to:



So, when in the text the reduction of nitrite is spoken of, the species actually reducible is NO<sup>+</sup>, reduced according to:



This reaction is followed by the overall reduction steps<sup>2</sup>:



As already mentioned, these three steps are found to appear separately only at platinum and mercury electrodes. On other metals the half-wave potentials of steps [2] and [3] merge so that only one 3-electron reduction step appears. Figure 3, curve B, gives the ring current due to the disc current when the potential of the ring electrode is kept at +0.35 V. From this curve it is possible to calculate the experimental collection efficiency,  $N_0$ , of the ring disc electrode for the three plateaus in curve A of Figure 3 – respectively 0.140, 0.0 and 0.0 – and to compare these values with the collection efficiency calculated from the electrode geometry<sup>8</sup>, viz. 0.136.

A reaction is reversible, when the experimentally found  $N_0$  is equal to the theoretical value, provided the ring potential is set at a value, where  $i_D = 0$  and  $\delta(i_D)/\delta(E) > 0$ . The measured values confirm, that the first reduction step, because of the chosen potentials, is a reversible one, corresponding to the reduction of nitrite to nitric oxide. Almost no ring current can be measured when the disc potential becomes less than -0.25 V, indicating that the products formed at the disc electrode, at these potentials, are not,

or almost not, oxidizable at the ring electrode. The small residual current may be attributed to NO, escaped from the disc. Moreover, from Figure 3, curve C and D; it can be seen that at disc potentials less than +0.12 V and -0.25 V, respectively the ring current no longer changes. In other words, when the ring potential is fixed at such a value that no oxidation of nitric oxide can occur, no other products are oxidized at the ring electrode. The decrease of the cathodic ring current in Figure 3, curve C and D, when the disc potential is scanned in the cathodic direction up to the corresponding fixed ring potential, respectively, is a result of the increase of the so-called shielding effect on the ring electrode.

This is due to the increasing reduction rate of nitrite at the disc electrode. Hence, the concentration of reducible species in the fluid passing the ring electrode is lowered.

At ring potentials more anodic than +0.35 V, another reduction product of nitrite is oxidized. It is found when the disc potential is scanned between -0.30 V and -0.60 V, indicating, that this is hydroxylamine being partly reoxidized. The collection efficiency of this process is, however, less than 0.01, which indicates that the oxidation process is a very slow one. No oxidation of dinitrogen oxide formed in the second wave (Figure 3, curve A) is found, so that the reduction from nitric oxide to dinitrogen oxide is completely irreversible.

Figure 4 shows the current at the ring electrode as a function of its potential when the disc potential is kept constant. These curves can be calculated theoretically from the electrode geometry and the disc current, keeping the model, as pictured above, in mind. The current measured in curve A (Figure 4), coincides with the calculated current according to a formula derived by Albery et al.<sup>9</sup> (see list of symbols):

$$I_R^0(E) = \beta^{2/3} I_D(E) \quad [4]$$

For a reversible electrode reaction at fixed disc potential,  $E_D$ , Albery et al.<sup>8</sup> derived the expression:

$$I_R(E) = I_R^0(E) - N_0 I_D(E_D) \quad [5]$$

Substituting [4] into [5]:

$$I_R(E) = I_R^0(E) - N_0 \beta^{-2/3} \cdot I_R^0(E_D) \quad [6]$$

The curve B, found experimentally, agrees with [6]. This implies that the first reduction step is a reversible electrode reaction, as has been concluded already. Curves C and D do not obey formula [6], because dinitrogen oxide and hydroxylamine, generated at the disc electrode, cannot be oxidized reversibly at the ring electrode. When no oxidation takes place at the ring electrode, the ring current is determined by the amount of reducible species at the ring electrode and by its potential. As long as the fixed disc potential is more cathodic than the ring potential, the disc electrode intercepts reducible species and so reduces the ring current. The decrease of the ring current due to this already mentioned shielding effect can be described, for an irreversible reaction, by<sup>8</sup>:

$$I_R(E) = I_R^0(E) [1 - N_0 \beta^{-2/3}], \text{ if } E_R > E_D \quad [7]$$

where:  $(1 - N_0 \beta^{-2/3}) = S =$  shielding factor (always positive). Curve C fits [7] for  $E_R > -0.25$  V, indicating that dinitrogen oxide formed at the disc electrode at -0.25 V is not oxidizable at the ring electrode.

When  $E_R = +0.12$  V,  $I_R^0(E)$  is  $I_R^0(+0.12$  V), which implies that, according to [4], [6] and [7]:

$$\begin{aligned} I_R(+0.12) \text{ (curve C)} &= I_R^0(+0.12) - I_R^0(+0.12) N_0 \beta^{-2/3} = \\ &= I_R^0(+0.12) - N_0 I_D(+0.12) = I_R(+0.12) \text{ (curve B)} \end{aligned}$$

<sup>9</sup> W. J. Albery, S. Bruckenstein and D. T. Napp, Trans. Faraday Soc. 62, 1932–1937 (1966).

The experimental results confirm this, as shown in Figure 4. When the ring potential is more cathodic than the disc potential shielding no longer takes place. The ring electrode is now able to reduce the species coming from the more anodic disc electrode. Indeed  $I_R(E)$  will increase in the same manner as  $I_R^0(E)$ :

$$I_R(E) = I_R^0(E_D)[1 - N_0\beta^{-2/3}] + I_R^0(E) - I_R^0(E_D),$$

for  $E_R < E_D$ ;

$$= I_R^0(E) - I_R^0(E_D)N_0\beta^{-2/3} \quad [6]$$

an equation already derived.

It is possible that the products formed at the disc electrode are too stable to be reduced at the ring electrode. The concentration of reducible species arriving at the ring electrode then is still influenced by the reduction process at the disc electrode. In this case [7] remains still valid, even for  $E_R < E_D$ ; see curves C and D (Figure 4). Curve C is identical to curve D, described by [7], for  $E_R > -0.55$  V. It can be concluded by comparing these curves, that the intermediate product formed at the disc electrode at a potential of  $-0.25$  V is neither oxidizable nor reducible. Because curve D is described too by [7], this confirms our earlier conclusion that the oxidation of hydroxylamine is not a reversible process.

In Figure 5, equation [6], written as:

$$I_R(E)/I_R^0(E) = [1 - N_0\beta^{-2/3}]I_R^0(E_D)/I_R^0(E) \quad [6a]$$

is plotted as a function of  $E_R$  for  $E_D = +0.12$  V (curve A) and  $= -0.25$  V (curve B). Also equation [7], written as:

$$I_R(E)/I_R^0(E) = 1 - N_0\beta^{-2/3} \quad [7a]$$

is plotted as a function of  $E_R$  (curve C).

From Figure 4, the experimental values of  $I_R(E)/I_R^0(E)$  are calculated at different potentials,  $E_R$ , both for curves B and C (D is identical with C). These values are also plotted in Figure 5, and confirm the above-mentioned conclusions. From the stability of the product formed from the reduction of nitric oxide (dinitrogen oxide; second step of Figure 3, curve A), it can be concluded that the further reduction to hydroxylamine does not involve the  $N_2O$  species as a reaction intermediate, but that an unstable reaction intermediate exists, from which dinitrogen oxide is formed. HNO has been proposed as the intermediate product<sup>7,10</sup> and is also found in the catalytic hydrogenation of nitric oxide<sup>11,12</sup>. This intermediate is probably only stable as a surface complex on the electrode and can be reduced further to hydroxylamine (see [8], [9]); or dinitrogen oxide can be formed by dimerisation, dehydration and desorption [10]:

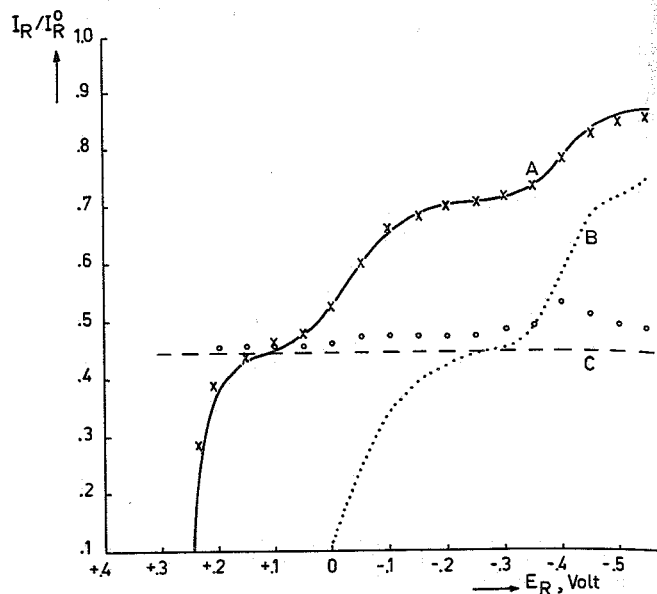
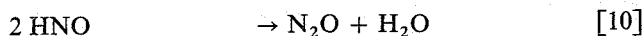
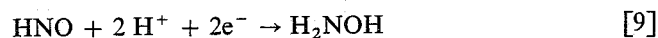
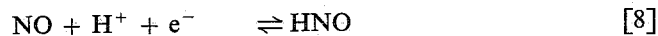
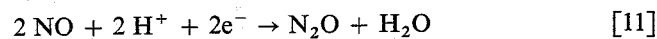


Fig. 5. Theoretical  $I_R/I_R^0 - E$  curves for the ring electrode according to equation [6a]: curve A (—),  $E_D = +0.12$  V; curve B (···),  $E_D = -0.25$  V; and according to equation [7a]: curve C (---).

× × × experimental points derived from Figure 4, curve B.  
○ ○ ○ experimental points derived from Figure 4, curve C.

It might be possible to interpret the above results by assuming that dinitrogen oxide is formed directly from nitric oxide:



by a parallel reaction to [8], but, because the formation of  $N_2O$  involves a dimerisation step of two nitrogen species, this, with reason, can take place only by dimerisation of HNO to the (especially in basic media) moderately stable intermediate  $H_2N_2O_2$ . The formation of a dimer of nitric oxide is highly improbable, because there is loss of energy when dimerisation occurs<sup>13</sup>. We therefore believe that the reduction of nitric oxide occurs solely through the HNO surface complex and, moreover, that dinitrogen oxide is formed as a side reaction product of the HNO surface complex.

Knowledge about the occurrence and manner of adsorption of such an electrode surface complex (as is deduced from the work presented in this paper) is important for understanding the influence of electrode materials on the reduction of nitrite.

#### Acknowledgement

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