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Mechanistic Study on the Electrocatalytic Reduction of Nitric Oxide on Transition-Metal Electrodes

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The mechanism of the electrochemical reduction of nitric oxide (NO) on a series of metals (Pd, Rh, Ru, Ir, and Au) has been studied, both for the reduction of adsorbed NO and for the continuous NO reduction. All metals show a high selectivity to N_2O at high potentials and a high selectivity to NH_3 at low potentials, whereas N_2 is formed at intermediate potentials (although gold forms mainly N_2O, and very little NH_3). The behavior of the transition metals is very similar to that of platinum, suggesting that the reaction schemes are essentially the same (especially the potential windows in which the products are formed are similar). The mechanism that leads to N_2O is believed to involve the formation of a weakly adsorbed NO dimer intermediate, similar to recent suggestions made for the gas-phase reduction of NO. The reduction of adsorbed NO leads only to formation of NH_3 and not to N_2O or N_2. The electrochemical measurements suggest that NH_3 formation involves a combined electron–proton transfer in equilibrium, followed by a nonelectrochemical rate-determining step. The formation of N_2, produced at potentials between the formation of N_2O and NH_3, most likely takes place by the reduction of previously formed N_2O. © 2001 Academic Press

Key Words: **NO reduction; electrocatalysis; transition metals; differential electrochemical mass spectroscopy.**

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1. INTRODUCTION

The reduction of nitric oxide (NO) is an important reaction in environmental catalysis, since it determines the performance of wastewater treatment catalysts for nitrate, nitrite, and NO removal (1), and the scrubbing of NO from gas streams (2). Nitric oxide reduction has also been investigated as the cathodic reaction in fuel cells (3), because of its high reduction potential.

The electrodes employed in the electrochemical reduction of NO are usually noble transition metals, because they are the most active catalysts (4) and show the least formation of metal oxides. Palladium has the highest activity and selectivity to N_2 (3), and therefore is the catalyst of choice. Other metals form, depending on potential, undesirable products such as N_2O and/or NH_3.

There is as yet little or no mechanistic insight into why palladium is the best catalyst in the selective reduction of NO to N_2. The only metal for which reasonably detailed mechanistic information is presently available is platinum (5).

Summarizing the results of our previous publication (5), we found that there are two major reaction paths for NO reduction on platinum, one at high potentials (0.3–0.7 V vs RHE) which leads to nitrous oxide (N_2O), and one at low potentials (0–0.3 V) which leads mainly to ammonia (NH_3). The formation of N_2O was observed to take place only in the presence of NO in the solution. From the Tafel slope, the pH dependence, and the kinetic order in NO solution concentration, the following reaction scheme was suggested:

$$
\begin{aligned}
&{}^* + \mathrm{NO(aq)} \rightarrow \mathrm{NO_{ads}} && \text{fast}\\
&\mathrm{NO_{ads}} + \mathrm{NO(aq)} + \mathrm{H^+} + \mathrm{e^-} \rightarrow \mathrm{HN_2O_{2,ads}} && \text{r.d.s.}\\
&\mathrm{HN_2O_{2,ads}} + \mathrm{H^+} + \mathrm{e^-} \rightarrow \mathrm{N_2O(aq)} + \mathrm{H_2O} + 2\,{}^* && \text{fast,}
\end{aligned}
\qquad [1]
$$

where * denotes a free site at the surface. The most remarkable feature of this scheme is the rate-determining step, in which we proposed a surface-bonded NO to combine with a solution-phase NO. The latter may also be interpreted as a weakly bonded NO, as long as its concentration is first-order in solution NO to explain the experimentally observed first-order kinetics in NO solution concentration.

The reaction scheme suggested for the formation of NH_3 proceeds through the reduction of adsorbed NO_{ads}:

$$
\begin{aligned}
&\mathrm{NO(aq)} + {}^* \rightarrow \mathrm{NO_{ads}} && \text{fast}\\
&\mathrm{NO_{ads}} + \mathrm{H^+} + \mathrm{e^-} \leftrightarrow \mathrm{HNO_{ads}} && \text{fast}\\
&\mathrm{HNO_{ads}} + \cdots\cdot \rightarrow \text{unknown intermediate} && \text{r.d.s.}\\
&\text{Unknown intermediate} + 5\mathrm{H^+} + 4\mathrm{e^-}\\
&\quad \rightarrow \mathrm{NH_4^+} + \mathrm{H_2O} + {}^* && \text{fast.}
\end{aligned}
\qquad [2]
$$

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Presumably, the rate-determining step in this scheme involves a breaking of the N–O bond.

Some nitrogen (N_2) is formed in the intermediate potential region (0.2–0.4 V vs RHE), but we did not discuss the mechanism of its formation in our previous work. However, given the fact that N_2 is the most desirable product and that its selective formation is apparently quite sensitive to the nature of the electrode surface, more detailed investigations into the N_2 formation pathway are clearly of interest.

In this paper, we study the metal dependence of the electrocatalytic reduction of NO. The metals investigated are Ru, Rh, Ir, Pd, Pt, and Au. We will show that the two separate pathways for N_2O and NH_3 exist for all these electrodes, and we will argue that they take place via reaction schemes similar to those on Pt. Most importantly, we will present more detailed results on the formation of N_2 on the different metal electrodes. From these results, we will suggest that the key intermediate in the N_2 formation is N_2O rather than surface-bonded N_{ads}.

2. EXPERIMENTAL

Rotating disk electrodes (RDEs) were used in a home-made setup. Platinum, palladium, and gold were pretreated by repeated cycling in the hydrogen and oxygen evolution region in 0.1 M H_2SO_4, after which the electrolyte was replaced with clean electrolyte. Rhodium, iridium, and ruthenium were electrodeposited from the metal trichloride solution at 0.1 V (vs RHE) onto disk electrodes made from the same metal prior to a measurement in the electrochemical cell, and traces of chloride were removed by thorough rinsing while the electrode was kept at −0.2 V. Iridium was deposited at ca. 80°C. The blank cyclic voltammogram of the disk electrode was compared to that of a flag electrode, to check for the absence of contaminations and surface oxides.

Differential electrochemical mass spectroscopy (DEMS) electrodes consisted of platinum gauzes with the metal of interest electrodeposited onto it, except for gold, in which case a gold gauze was used. The electrodes were pretreated in the same manner as the rotating disk electrodes.

Adsorbate studies were performed on a flag electrode of the pure metal. All flag electrodes were flame annealed prior to each measurement, except for gold, which was cleaned by repeated cycling between the hydrogen and oxygen evolution regions. The electrodes were quenched in clean water under an argon atmosphere, except for ruthenium, which was quenched in an argon/hydrogen atmosphere to reduce residual surface oxides (ruthenium is more susceptible to the formation of irreversible surface oxides than the other metals). The cyclic voltammogram in a clean solution was taken to check for the absence of surface oxides and contaminations.

The counter electrode in all cases consisted of a platinum flag. An AUTOLAB Pgstat 20 potentiostat was used for all RDE and adsorbate experiments. DEMS measurements were performed employing a Balzers Prisma QMS 200 mass spectrometer. Details of the setup are described elsewhere (6). The DEMS signals of N_2, N_2O, and NO were calibrated by oxidizing a monolayer of CO and measuring the amount of CO_2. The signal was corrected for differences in sensitivity and fragmentation probability (7).

A $Hg/HgSO_4$ reference electrode was used for all measurements in acidic solutions. In alkaline solutions a Hg/HgO reference electrode was used. All potentials reported in this paper, however, are converted to the RHE scale. All measurements were performed at room temperature (20°C).

All glassware was cleaned in boiling H_2SO_4/HNO_3 to remove organic contaminations. All solutions were prepared with p.a. grade chemicals (Merck) and Millipore Gradient A20 water. All solutions were deaerated by purging with argon. NO was bubbled through two 2 M KOH washing flasks in order to remove NO_2 (8).

Adsorbate studies were performed by saturating the surface in a solution of saturated NO or 2 mM $NaNO_2$ under potential control (usually 0.37 V) in a 0.1 M H_2SO_4 solution in order to avoid oxidation of the surface by NO (9).

3. RESULTS AND DISCUSSION

3.1. Selectivity of the NO Reduction

We will first discuss the various products of the NO reduction and the potential dependence of their transformation. The selectivity of the NO reduction in the presence of NO in the solution has been measured both in the DEMS setup by measuring the amount of N_2O and N_2 formed, and in the RDE setup by determining the number of electrons transferred per NO molecule from the Levich equation:

$$\frac{1}{I} = \frac{1}{I_{\mathrm{kin}}} + \frac{1}{0.62nFC^*D^{2/3}\nu^{-1/6}\omega^{1/2}}.$$

In this equation, I_{kin} is the kinetic limited current density, n is the number of electrons per NO molecule, C^* is the bulk concentration of NO, D is the diffusion constant of NO in water, and ν is the kinematic viscosity. The following values were used: $C^* = 1.40 \times 10^{-6}$ mol cm^{-3}, $D = 2.5 \times 10^{-5}$ cm^2 s^{-1}, and $\nu = 8.5 \times 10^{-3}$ cm^2 s^{-1} (10). The kinetically limited current cannot be determined exactly at potentials where several reactions occur simultaneously, and was therefore only determined in potential windows where the selectivity to N_2O was 100%.

On all metals the potential window in which NO reduction takes place can be divided into three regions: at high potentials (0.4–0.7 V) N_2O is the main product, N_2 is formed with varying selectivity at intermediate potentials (0.2–0.4 V), whereas NH_3 is the main product at low potentials (0–0.3 V). It is known that hydroxylamine (H_2NOH)

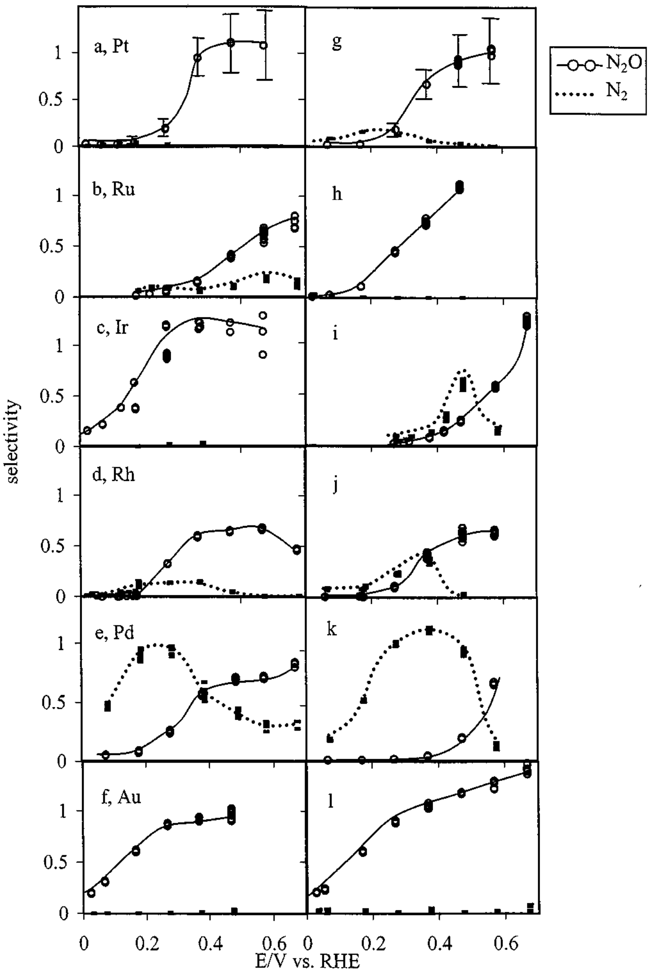

FIG. 1. Selectivity of the reduction of NO in the solution. Solution saturated with NO, (a–f) 0.1 M H_2SO_4, (g–l) 0.1 M KOH, (a, g) Pt, (b, h) Ru, (c, i) Ir, (d, j) Rh, (e, k) Pd, (f, l) Au. Solid lines and filled circles, selectivity to N_2O; dotted lines and rectangles, selectivity to N_2. The error bars given in (a) and (g) also apply to the other figures.

can be formed as a minor product at low potentials (0 V) on platinum (11); however, as the number of electrons per NO molecule at low potentials is close to 5, indicating that NH_3 is the major product, and a quantitative determination is quite complicated, we will exclude H_2NOH formation from our discussion. Figure 1 shows the selectivity to N_2O and N_2 of the six metals studied in this paper, as obtained from the DEMS measurements. At high potentials both the electrical current and the DEMS signal become very small, resulting in a large experimental uncertainty, reflected in some of the selectivities reported being higher than unity. The amount of N_2 produced varies with the metals used, as do the boundaries of the three potential regions. The selectivity to N_2 on palladium, for instance, is very high and covers a larger potential window than on the other metals. As will be further discussed below, we believe that the similarities in selectivity are an indication that the reaction mechanism is similar on all transition metals. The results will be discussed in three separate sections, according to the three potential regions.

TABLE 1

Tafel Slope of the Adsorbed NO Reduction, in mV/dec

	Pt	Rh	Ir	Ru
0.1 M H_2SO_4	54 ± 3(5)	70 ± 3	76 ± 5	66 ± 10
0.1 M KOH	58 ± 3(5)	106 ± 3	88 ± 5	63 ± 1

3.2. Reduction of NO to NH_3

The reduction of NO to NH_3 can be studied by continuous NO reduction in the potential region 0–0.3 V, or by the reduction of an NO adsorbate layer in a clean NO-free electrolyte. In the latter case, information about the rate-determining step in the overall reaction scheme can be obtained relatively easily by measuring a so-called Tafel plot, which gives the potential dependence of the overall reaction rate. Under the assumption that the reduction rate is first- (12) or second-order (13) in the adsorbate coverage, it can be shown that a plot of the peak potential (i.e., the potential at which a maximum current is measured during the reductive stripping voltammetry) vs the logarithm of the scan rate is equivalent to a Tafel plot. Lateral interactions between NO molecules are neglected, as the coverage at the peak potentials is relatively low (ca. 0.2, i.e., in approximately half of the maximum coverage).

Table 1 summarizes the slopes of the Tafel plots obtained for the NO adsorbate reduction on Pt, Rh, Ir, and Ru in acidic and alkaline solution. The maximum coverage of NO is in all cases similar (0.4–0.5 monolayer), and similar to values reported for single-crystal surfaces (14–16). Pd and Au are not included, as in the case of palladium the peak potential overlaps with the hydrogen evolution reaction, and in the case of gold because no NO adsorbate layer is formed. As an example a typical Tafel plot for the NO reduction of Ru in acidic solution is shown in Fig. 2. A value of ca. 60 mV/dec indicates the existence of an electron-transfer

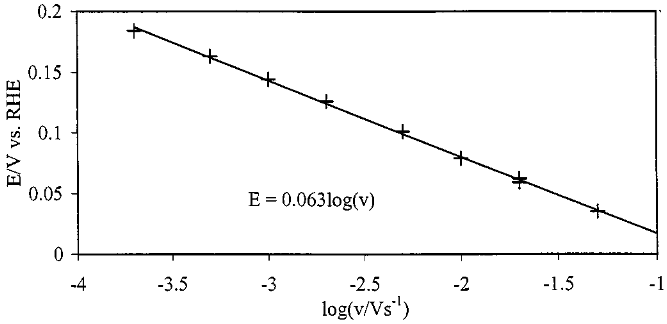

FIG. 2. Dependency of the peak position of the NO reduction with the scan rate on ruthenium in 0.1 M H_2SO_4; surface at maximum NO coverage.

TABLE 2

Peak Potential of the NO Adsorbate Reduction at 5 mV/s, Compared to the Potential at Which the Selectivity of the Reduction of Solution NO Changes According to the RDE

		Pt	Pd	Rh	Ir	Ru
0.1 M H_2SO_4	E_{peak}	0.21	0.01[a]	0.11	0.17	0.102
	RDE	0.25	[b]	0.2	0.25	[b]
0.1 M KOH	E_{peak}	0.18	0.03[a]	0.14	0.10	0.101
	RDE	0.2	[b]	0.15	0.15	0.2

[a] Measured on a gold electrode with a thin (2–3 ML) palladium overlayer, and at 1 mV/s.

[b] There is no change in the selectivity.

step in equilibrium, followed by a rate-determining chemical (potential-independent) step. The value reported for platinum (5), together with the observed pH dependence, has led us to suggest that the NO reduction on platinum follows scheme [2] discussed in the Introduction. The very similar Tafel slopes observed for the other metals, and the similar pH dependence (Table 2), may be interpreted according to a similar scheme, where a higher Tafel slope could point toward a slower first electron-transfer step.

We believe that the continuous reduction of NO to NH_3 in the potential range of 0–0.3 V takes place through the same mechanism as the adsorbate reduction, as the onset in NH_3 production in the continuous reduction occurs at roughly the same potentials as the adsorbate reduction (Table 2). It is difficult to obtain kinetic information however, as the selectivity to NH_3 at 0.2–0.3 V is not 100%.

Two metals behave differently from the other metals and have to be discussed separately, namely palladium and gold. On palladium the reduction of adsorbed NO takes place at significantly lower potentials than on the other noble metals (ca. 0 V). Also, the potential at which NH_3 is formed in the continuous reduction is low compared to the other metals (ca. 0.1 V). On gold the selectivity to N_2O does not drop to zero, as on the other noble metals, since the adsorption of NO on gold is weak and little formation of NH_3 is observed.

The mechanism of the formation of NH_3 from NO must include the breaking of the N–O bond. The nature of this step, and its relationship to the rate-determining step, is an important mechanistic issue. In scheme [2], the dissociation of the N–O bond is assumed to take place after the protonation. However, NO is known to dissociate at room temperature on metals like rhodium, iridium, and ruthenium, and hence we must consider this possibility in the overall reaction scheme. Since the possibility of NO dissociation is also an important mechanistic issue in the formation of N_2O and N_2, we postpone its discussion to Section 3.5, where we will discuss a number of general mechanistic features in relation to the gas-phase reduction.

3.3. Reduction of NO to N_2O

The Tafel slopes of the NO reduction to N_2O on the various metals, as derived from the kinetic limiting current of the RDE measurements, are given in Table 3. The Tafel slope was found to be close to 120 mV/dec in three cases: platinum and ruthenium in acidic solutions, and iridium in alkaline solutions. This implies that the first electron transfer is rate-determining in these three cases. In all other cases the Tafel slope was found to be significantly higher than 120 mV/dec, indicating that the rate-determining step is a chemical step prior to the electrochemical steps. The values given in Table 3 are significantly different from those given by Colucci *et al.* (8) (78, 116 and 408 mV/dec on respectively Pd, Rh, and Ru in acidic solutions), as determined from voltammetry at stationary electrodes. Since reactions with mass-transport limitations should preferably be studied at rotating electrodes, and because we took extreme care to avoid surface oxidation of the less noble transition metals (17, 18), we believe our values reflect more accurately the "real" Tafel slopes.

Colucci *et al.* (8) suggested that the mechanism of the NO reduction to N_2O on platinum, palladium, rhodium, and ruthenium includes only species which are adsorbed at the surface. Gootzen *et al.* (19) suggested for platinum electrodes that the key step in the N_2O formation is the dissociation of NO, which also implies that only adsorbed species are involved in the formation of N_2O. However, we find that NO from the solution must be involved in the reaction scheme for two reasons. The first reason is that the potential window in which the reduction of adsorbed NO takes place (0–0.3 V) is much lower than the potential window considered here (0.4–0.7 V). Second, N_2O is not produced during the reduction of adsorbed NO. Since the only difference between the reduction of adsorbed NO and the reduction of NO at high potentials is the presence of dissolved NO, solution NO *must* be directly involved in the reaction sequence to produce N_2O. Since these observations hold for all metals studied here, we suggest that the formation of an $(NO)_2$ dimer as the rate-determining step, as has been proposed for platinum (5), is also valid for the other metals. The higher Tafel slopes observed for some of the systems could be explained by assuming that the first electron transfer shifts to a stage after the rate-determining step, and the surface dimerization reaction becomes the rate-determining chemical step.

TABLE 3

Tafel Slopes of the NO Reduction between 0.4–0.7 V in a Solution Saturated with NO, in mV/dec

	Pt	Pd	Rh	Ir	Ru	Au
0.1 M H_2SO_4	117 ± 4	160 ± 18	436 ± 32	201 ± 39	133 ± 13	356 ± 16
0.1 M KOH	322 ± 23	246 ± 26	201 ± 39	113 ± 34	242 ± 21	207 ± 18

It is unclear whether dissolved NO reacts directly from the solution, or from a weakly adsorbed state at the surface. Either possibility will lead to the same N_2O formation kinetics and the same adsorbate reduction kinetics, since this weakly adsorbed NO will desorb when the solution is replaced with clean electrolyte.

Finally, we note that reaction scheme [1] predicts the rate of the reaction to be first-order in the concentration of solution NO, because the surface is always covered with NO_{ads} and hence only the amount of NO(aq) changes with the NO concentration. A kinetic order of unity has indeed been observed on platinum in acidic solutions. Due to the large error bars in the determination of the kinetic limited current (Table 3), we have not pursued these measurements for the other systems, but both DEMS measurements and an analysis of the RDE data for palladium, using the procedure suggested by Markovic *et al.* (20), suggest a kinetic order close to one.

3.4. *Reduction of NO to N_2*

As mentioned in the Introduction, there is only scant mechanistic information available on the formation of N_2 from the electrocatalytic NO reduction. However, it seems that one may assume two alternative working hypotheses. The first hypothesis is that N_2 is formed by the reduction of N_2O, i.e., in series with the N_2O formation. This is a known reaction in electrocatalysis that has been studied by a number of authors (21–25). The second hypothesis is that N_2 is formed by a reaction of surface species (such as NO_{ads}, N_{ads}, NOH_{ads}, or other yet unidentified species), i.e., in parallel with the N_2O formation.

If the first hypothesis would be true, i.e., N_2 would be formed from the reduction of N_2O, one would expect a correlation between N_2O reduction activity and the selectivity toward N_2 in the reduction of NO. Figure 3 gives the activity of the various metals in the N_2O reduction in alkaline solutions. The activity found in alkaline solutions increases in the order Au $<$ Ru $\ll$ Ir $<$ Rh $\approx$ Pt $\ll$ Pd, with the onset of the reaction being 0, 0.1, 0.4, 0.45, 0.45, and 0.6 V, respectively (Fig. 3). This ordering is comparable to the production of N_2 in alkaline solutions shown in Fig. 1, the potentials of the onset showing a reasonable agreement with the onset of the N_2O reduction (Au $\approx$ Ru $\ll$ Pt $<$ Rh $<$ Ir $\ll$ Pd, the onset of the reaction being 0, 0, 0.45, 0.45, 0.55, and 0.6 V, respectively). Iridium is more active in the N_2 production than suggested by its N_2O reduction activity, which makes it an exception.

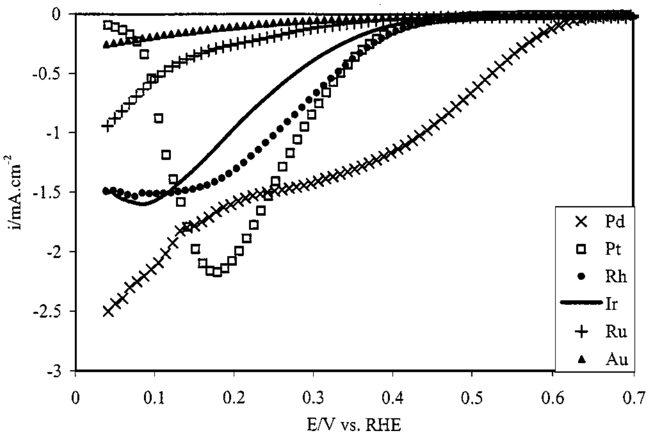

FIG. 3. Activity of the transition metals and gold in the N_2O reduction: 0.1 M KOH saturated with N_2O. Crosses, Pd; squares, Pt; circles, Rh; thick solid line, Ir; plusses, Ru; triangles, Au.

To compare the activity and selectivity in acidic solutions is more problematic, since the N_2O reduction is known to be very sensitive to the competitive adsorption of SO_4^{2-} anions (21, 22). The measurements should therefore be carried out in an $HClO_4$ solution instead of H_2SO_4. Unfortunately, the activity of rhodium and iridium cannot be obtained in $HClO_4$, since these metals can reduce ClO_4^- to Cl^- (26), which is known to adsorb strongly. In general, however, the series for the N_2 production from NO in acidic solutions is similar to the series of the N_2O reduction activity. Gold, for instance, is inactive in both cases, followed by iridium, rhodium, and ruthenium, whereas palladium is very active. Platinum does not fit in the series, as the rate in N_2O reduction in both $HClO_4$ and H_2SO_4 is higher than on palladium, whereas palladium is more active in the selective formation of N_2 from NO.

The qualitative agreement between the N_2O reduction activity and the selectivity in the NO reduction to N_2 is a strong argument in favor of the "N_2O serial pathway." Also the fact that no N_2 is produced during the NO adsorbate reduction in the absence of NO in the solution disfavors the "adsorbate parallel pathway." In fact, the NO adsorbate is generally not reactive at all at potentials for which N_2 is produced during the continuous NO reduction.

3.5. *Mechanistic Issues and Comparison to Gas-Phase Reduction of NO*

3.5.1. NO dissociation. As noted in Section 3.2, it is known that NO may dissociate at room temperature on metals such as Rh, Ir, and Ru, whereas it is generally adsorbed molecularly on Pt and Pd. An overview of the NO dissociation behavior on metal surfaces was recently given by Brown and King (27). At higher coverages, the NO dissociation process may be inhibited because of the lack of adjacent empty sites or because strong lateral interactions between the dissociation products render the molecular state more stable. The necessity of having empty surface sites for triggering NO dissociation has been shown recently in detailed UHV surface science studies of NO reactivity on Rh (28, 29). In most UHV studies, the N_{ads} species is considered as an intermediate in the N_2O, N_2, and NH_3 formation. Hence, we will have to consider the possibility of NO dissociation on Rh, Ru, and Ir in the electrochemical context.

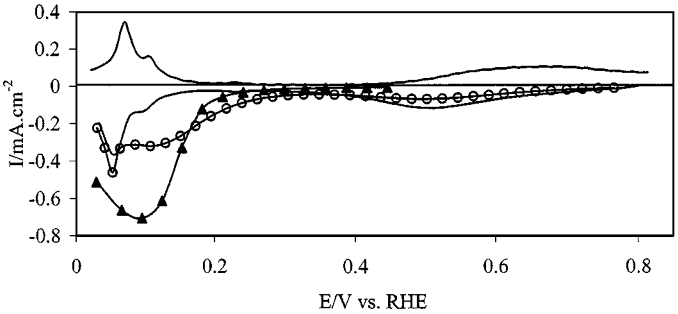

FIG. 4. Reaction of NO adsorbed under OCP (open circles) and at 0.45 V (filled triangles) on polycrystalline rhodium compared to the blank (solid line); scan rate, 20 mV/s.

It is difficult to obtain any direct evidence for NO dissociation from electrochemical experiments. Gootzen *et al.* (19) suggested that the observation of an oxide reduction peak after NO adsorption on Pt at open-circuit potential (OCP) was due to the reduction of the adsorbed oxygen formed from NO dissociation. However, we showed recently that the peak is observed only on roughened electrodes (5), suggesting quite a different mechanism, and in keeping with the gas-phase situation where NO adsorbs molecularly on Pt at room temperature. Interestingly, an oxide reduction peak *is* observed, at ca. 0.5 V, on a smooth flame-annealed Rh electrode after adsorption of NO at OCP (ca. 0.8 V), as illustrated in Fig. 4. When NO is adsorbed at 0.45 V, no oxide reduction peak is observed, and a much higher NO reduction charge is measured (see Fig. 4), indicating a higher coverage of NO under these conditions. However, these observations still do not prove the occurrence of NO dissociation. On Rh, surface oxides are known to be more stable than on Pt, and therefore on Rh, certainly at a potential of 0.8 V, a more competitive co-adsorption of oxides and NO is expected than on Pt. The peak at 0.5 V can hence be explained by the reduction of co-adsorbed oxides, which are not formed by NO dissociation, but similar to the formation of surface oxides on roughened platinum.

An interesting observation to be made from Fig. 4 that could point toward the role of NO dissociation is the fact that the apparently lower coverage of NO formed at 0.8 V starts to be reduced at a significantly less negative potential than a saturated layer formed at 0.45 V. This could mean that the surface sites that become available after reduction of the surface oxides trigger the NO dissociation. The saturated NO adlayer is not reactive or is much less reactive at these potentials, as is also evidenced by the observation of a stable NO stretching peak in FTIR experiments of NO on single-crystal Rh (14). A similar—though less pronounced—shift in the reduction peak is observed when a nonsaturated NO adlayer is formed at 0.45 V by dosing from a less concentrated NO solution. These observations are in stark contrast with the coverage effects observed for the NO adsorbate reduction on Pt, where no such positive shifts in reduction potential with lower NO coverage are observed.

If NO dissociation plays a role on Rh, Ir, and Ru, then the observed Tafel slopes for the adsorbate reduction may suggest that it is not the rate-determining step in the ammonia formation. However, it should be realized that it is not *a priori* clear to what extent the NO dissociation has to be considered as potential or even pH dependent, as the *overall* NO dissociation process at electrochemical interfaces involves protonation of the oxygen:

$$\mathrm{NO} + 2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{N}_{\mathrm{ads}} + \mathrm{H_2O}. \qquad [3]$$

It is obvious that the above experiments are not decisive in pinning down the possible role of NO dissociation on the less-noble transition metals Ru, Ir, and Rh. More direct spectroscopic information is clearly needed.

The results in Fig. 4 do suggest, however, that at high NO coverages, which seems the relevant surface condition for the continuous NO reduction experiments, NO dissociation is not likely to take place at potentials above 0.3 V. Hence, it is suggested that NO dissociation does not play a significant role during N_2O and N_2 formation. Evidence for alternative mechanisms, in relation to gas-phase and UHV experiments, is discussed in the next two sections.

3.5.2. NO dimerization. The reaction scheme [1] suggested for the N_2O formation on Pt involves the formation of a (protonated) surface-bonded $(NO)_2$ dimer. The very similar conditions under which N_2O is formed on the other metals is suggestive of a more general applicability of this reaction scheme.

In fact, there is a growing surface science literature on the formation of NO dimers on silver, copper, molybdenum, tungsten, and palladium, and it has also been suggested to exist on platinum and rhodium (27). It has been shown that on silver the NO dimer is the key intermediate in the N_2O formation. NO is adsorbed weakly on Ag (27). Apparently, strongly adsorbed NO is not required for the formation of the NO dimer or the production of N_2O. Theoretical DFT studies have also supported the existence of the NO dimer on Ag (30).

Even though we are not aware of similar UHV-based evidence for the NO dimer on Au, the generic similarity between Ag and Au suggests that it is reasonable to assume a similar N_2O formation mechanism on Au. This would certainly explain the unique selectivity of Au in reducing NO to N_2O as observed in our electrochemical study. Silver in fact has a similarly high selectivity toward N_2O in the electrochemical NO reduction (31). Also, this weakly adsorbed state of NO involved in the dimer formation may explain the first-order kinetics in the NO solution concentration, as mentioned in the Introduction. Interestingly, there is no clear catalytic effect of any metal in reducing NO to N_2O,

TABLE 4

Current Density of the NO Reduction in Saturated NO at 0.42 V, in mA/cm^2

	Pt	Pd	Rh	Ir	Ru	Au
0.1 M H_2SO_4	0.49	0.55	0.08	0.48	0.11	0.20
0.1 M KOH	0.28	0.52	0.33	0.54	0.43	0.62

as is illustrated by the very similar activities observed for all metals as collected in Table 4. This also strongly suggests the involvement of weakly adsorbed intermediates in the key step of the reaction scheme. As mentioned in the previous section, under these conditions of high surface coverage, NO dissociation does not seem very likely.

The idea that N_2O formation takes place through the formation of a weakly adsorbed NO dimer offers a consistent explanation of our observations. It would certainly explain why the reaction is so similar on all the different metals. However, spectroscopic proof of the existence of NO dimers under electrochemical conditions is certainly necessary to validate our interpretation.

3.5.3. N_2O as intermediate in N_2 formation. The data presented in Section 3.4 offered evidence for the formation of N_2 from N_2O, i.e., in a serial pathway, rather than from other NO-derived adsorbates in a parallel pathway. This interpretation is based on the observation that there is a correlation between the selectivity of a given metal in producing N_2 from NO and its activity in reducing N_2O, and that no N_2, nor N_2O, is formed during the NO adsorbate reduction.

Interestingly, there is a very similar suggestion in the recent gas-phase literature. The formation of N_2O has not been observed under UHV conditions. However, Zaera and Gopinath (32) have suggested on the basis of isotope exchange measurements that the formation of N_2 under a constant flux of NO is not due to the recombination of two N adatoms, but rather via an N_2O-type intermediate formed by the combination of an NO adsorbate and N adatom. According to Zaera and Gopinath, this reaction would only take place under conditions of a high gas-phase pressure of NO.

4. CONCLUSIONS

In this paper, we have studied the mechanism of the electrocatalytic reduction of NO on Ru, Rh, Pd, Ir, Pt, and Au electrodes by a combination of electrochemical measurements and on-line mass spectrometry. Our objectives were to assess to what extent the mechanistic schemes for N_2O and NH_3 formation recently suggested for the NO reduction on platinum can also be applied to the other metals. In addition, we have studied the mechanism of N_2 production from NO.

All transition metals show a high selectivity toward N_2O at high potentials and, with the exception of Au, a high selectivity toward NH_3 at low potentials. At intermediate potentials, all metals, again with the exception of Au, produce N_2, though with varying selectivity.

The NO reduction to N_2O is suggested to take place via the formation of an NO dimer, similar to the mechanism proposed for platinum (5). The varying Tafel slopes found for the different metals may reflect a shift in the rate-determining step with the metal or, more precisely, a shift in the occurrence of the first electron-transfer step in this mechanism. Despite the varying Tafel slopes, the similarities in the onset of the N_2O formation (i.e., at potentials much more positive than the onset of the adsorbate reduction) suggest a common mechanism for the N_2O formation on all metals. The existence of an NO dimer has been proved on various metal surfaces in UHV. Moreover, its weak adsorption strength would explain why all metals show a similar activity in the NO reduction to N_2O.

We have also presented evidence that the mechanism of formation of N_2 is similar on all metals (except for Au, which does not produce N_2), and involves N_2O as the key intermediate. This deduction was based on the correlation between the selectivity of a certain metal toward producing N_2 from NO and its activity in reducing N_2O. Metals that actively reduce N_2O also produce more N_2 in their NO reduction. Moreover, no N_2 and N_2O are formed in the NO adsorbate reduction in the absence of NO in solution, suggesting that there is no parallel pathway for N_2 formation.

The situation for NH_3 formation is less clear. Certainly for the reduction of the NO adsorbate on Rh (and presumably also Ru and Ir) we cannot exclude the role of NO dissociation, which was not considered for Pt. Tafel slope measurements nevertheless suggest an electron-transfer step to be involved in, or prior to, the rate-determining step, even though this cannot be taken as proof for similar mechanisms. At high NO coverages, NO reactivity on Rh is lower, suggesting a suppression of the NO dissociation by the blocking of free sites.

Finally, the best electrocatalyst for the selective reduction of NO to N_2 is palladium. At high potentials this is related to its high activity in reducing N_2O to N_2. At low potentials this is related to its low activity in the reduction of adsorbed NO to NH_3.

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REFERENCES

1. de Vooys, A. C. A., van Santen, R. A., and van Veen, J. A. R., *J. Mol. Catal. A* **154**, 203 (2000).

2. Macneil, J. H., Berseth, P. A., Westwood, G., and Trogler, W. C., *Environ. Sci. Technol.* **32**, 876 (1998).
3. Shibata, M., Murase, K., and Furuya, N., *J. Appl. Electrochem.* **28**, 1121 (1998).
4. Hara, K., Kamata, M., Sonoyama, N., and Sakata, T., *J. Electroanal. Chem.* **451**, 181 (1998).
5. de Vooys, A. C. A., Koper, M. T. M., van Santen, R. A., and van Veen, J. A. R., *Electrochim. Acta* **46**, 923 (2001).
6. Willsau, J., and Heitbaum, J., *J. Electroanal. Chem.* **194**, 27 (1985).
7. Manual Mass Spectrometer, A. G. Balzers, Balzers Liechtenstein, 1991.
8. Colucci, J. A., Foral, M. J., and Langer, S. H., *Electrochim. Acta* **30**, 1675 (1985).
9. Gomez, R., and Weaver, M. J., *Langmuir* **14**, 2525 (1998).
10. Colucci, J. A., Foral, M. J., and Langer, S. H., *Electrochim. Acta* **30**, 521 (1985).
11. Gadde, R. R., and Bruckenstein, S., *J. Electroanal. Chem.* **50**, 163 (1974).
12. Christensen, P. A., and Hamnett, A., "Techniques and Mechanisms in Electrochemistry."Blackie Academic and Professional, Glasgow, 1994.
13. Koper, M. T. M., Jansen, A. P. J., van Santen, R. A., Lukkien, J. J., and Hilbers, P. A. J., *J. Chem. Phys.* **109**, 6051 (1998).
14. Rodes, A., Gomez, R., Perez, J. M., Feliu, J. M., and Aldaz, A., *Electrochim. Acta* **41**, 729 (1996).
15. Alvarez, B., Rodes, A., Perez, J. M., Feliu, J. M., Rodriguez, J. L., and Pastor, E., *Langmuir* **16**, 4695 (2000).
16. Gomez, R., and Weaver, M. J., *J. Phys. Chem. B* **102**, 3754 (1998).
17. Vukovic, M., and Cukman, D., *J. Electroanal. Chem.* **474**, 167 (1999).
18. Iwayama, K., and Wang, X., *Appl. Catal. B* **19**, 137 (1998).
19. Gootzen, J. F. E., van Hardeveld, R. M., Visscher, W., van Santen, R. A., and van Veen, J. A. R., *Recl. Trav. Chim. Pays-Bas* **115**, 480 (1996).
20. Markovic, N. M., Adzic, R. R., Cahan, B. D., and Yeager, E. B., *J. Electroanal. Chem.* **377**, 249 (1994).
21. Ebert, H., Parsons, R., Ritzoulis, G., and VanderNoot, T., *J. Electroanal. Chem.* **264**, 181 (1989).
22. Ahmani, A., Bracey, E., Evans, R. W., and Attard, G., *J. Electroanal. Chem.* **350**, 297 (1993).
23. Furuya, N., and Yoshiba, H., *J. Electroanal. Chem.* **303**, 271 (1991).
24. Attard, G. A., and Ahmadi, A., *J. Electroanal. Chem.* **389**, 175 (1995).
25. Kudo, A., and Mine, A., *Appl. Surf. Sci.* **121/122**, 538 (1997).
26. Ahmani, A., Evans, R. W., and Attard, G., *J. Electroanal. Chem.* **350**, 279 (1993).
27. Brown, W. A., and King, D. A., *J. Phys. Chem.* **104**, 2578 (2000).
28. Borg, H. J., Reijerse, J. P. C-.J. M., van Santen, R. A., and Niemantsverdriet, J. W., *J. Chem. Phys.* **101**, 10052 (1994).
29. Hopstaken, M. J. P., and Niemantsverdriet, J. W., *J. Phys. Chem. B* **104**, 3058 (2000).
30. Perez-Jigato, M., King, D. A., and Yoshimori, A., *Chem. Phys. Lett.* **300**, 639 (1999).
31. Hara, K., Kamata, M., Sonoyama, N., and Sakata, T., *J. Electroanal. Chem.* **451**, 181 (1998).
32. Zaera, F., and Gopinath, C. S., *Chem. Phys. Lett.* **332**, 209 (2000).