The dissociation kinetics of NO on Rh(111) as studied by temperature programmed static secondary ion mass spectrometry and desorption

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Temperature programmed static secondary ion mass spectrometry (TPSSIMS) and temperature programmed desorption (TPD) have been used to study the kinetics of adsorption, dissociation, and desorption of NO on Rh(111). At 100 K, NO adsorption is molecular and proceeds via mobile precursor state kinetics with a high initial sticking probability. SSIMS indicates the presence of two distinct NO adsorption states, indicative of threefold adsorption at low coverage, and occupation of bridge sites at higher coverages. Three characteristic coverage regimes appear with respect to NO dissociation. At low coverages \( \theta_{\text{NO}} < 0.25 \text{ ML} \), NO dissociates completely at temperatures between 275 and 340 K. If we neglect lateral interactions and assume pure first order dissociation kinetics, we find effective values for the activation barrier and preexponential factor of \( 40 \pm 6 \text{ kJ/mol and } 10^{8 \pm 1} \text{ s}^{-1} \) for the dissociation of 0.15–0.20 ML NO. However, if we assume that a NO molecule needs an ensemble of three to four vacant sites in order to dissociate, the preexponential factor and activation energy are \( \approx 10^{11} \text{ s}^{-1} \) and 65 kJ/mol, in better agreement with transition state theory expectations. The \( \text{N}_2 \text{ads} \) and \( \text{O}_2 \text{ads} \) dissociation products desorb as \( \text{N}_2 \) and \( \text{O}_2 \), respectively, with desorption parameters \( E_{\text{des}} = 118 \pm 10 \text{ kJ/mol and } \nu_{\text{des}} = 10^{10.4 \pm 0.9} \text{ s}^{-1} \) for \( \text{N}_2 \) in the zero coverage limit. At higher coverages, the desorption kinetics of \( \text{N}_2 \) is strongly influenced by the presence of coadsorbed oxygen. In the medium coverage range 0.25 \( \leq \theta_{\text{NO}} \leq 0.50 \text{ ML} \), the NO desorption limit. At higher coverages, the desorption kinetic parameters of elementary reaction steps calls for spectroscopies which are able to monitor the surface reaction in real time. The combination of temperature programmed desorption (TPD) and temperature programmed static secondary ion mass spectrometry (TPSSIMS) has appeared particularly powerful, as TPD is sensitive to gas phase products and TPSSIMS is sensitive to adsorbed species.26–28 Recently, Schmatloch et al.16 reported the first temperature programmed SSIMS study on the decomposition of low coverages of NO on the Rh(110) surface. For 0.16 ML, NO dissociation starts at 170 K and the rate maximizes around 240 K. Kinetic parameters were determined by fitting appropriate SSIMS intensity ratios to a first order rate equation. This procedure resulted in an activation energy of 15 kJ/mol and a surprisingly low preexponential factor of \( 10^{1.9} \text{ s}^{-1} \).

In this study, we use TPSSIMS and TPD to study in situ the kinetics of the dissociation and desorption of NO on Rh(111) and the reactions leading to the desorption of \( \text{N}_2 \). The results show that NO dissociates already below room

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I. INTRODUCTION

Rhodium is an efficient catalyst for the reduction of NO to \( \text{N}_2 \), applied in the automotive exhaust gas converter.1 Studies on the interaction of NO with polycrystalline Rh,2 Rh(111),3–8 Rh(100),9,11 and Rh(110) (Refs. 12–16) generally indicate that at low temperatures, NO adsors molecularly on Rh surfaces. When present at low coverages, NO dissociates completely upon heating as witnessed by the desorption of the dissociation products \( \text{N}_2 \) between 450 and 700 K and \( \text{O}_2 \) at much higher temperatures. At higher coverages, part of the NO desorbs molecularly and an additional desorption state of \( \text{N}_2 \) arises. The mechanisms underlying these phenomena and their kinetics are only partially understood, especially due to the pronounced dependence on surface coverage.

The best way to study the overall kinetics of such a complicated reaction mechanism is to isolate the various elementary reaction steps and study their kinetics over a wide range of experimental conditions. Lateral interactions in a mixed adlayer can be included in the kinetic scheme by investigating well-defined coadsorption systems. For the Rh(111) surface, efforts in this field have led to studies on the interaction of atomic N with Rh(111),17,18 the coadsorption of N and \( \text{O}_2 \),18 NO and \( \text{O}_2 \),4,19 NO and \( \text{N}_2 \),20 NO and \( \text{CO} \),21–24 and NO and \( \text{H}_2 \).25 Determination of the kinetic parameters of elementary reaction steps calls for spectroscopies which are able to monitor the surface reaction in real time. The combination of temperature programmed desorption (TPD) and temperature programmed static secondary ion mass spectrometry (TPSSIMS) has appeared particularly powerful, as TPD is sensitive to gas phase products and TPSSIMS is sensitive to adsorbed species.26–28 Recently, Schmatloch et al.16 reported the first temperature programmed SSIMS study on the decomposition of low coverages of NO on the Rh(110) surface. For 0.16 ML, NO dissociation starts at 170 K and the rate maximizes around 240 K. Kinetic parameters were determined by fitting appropriate SSIMS intensity ratios to a first order rate equation. This procedure resulted in an activation energy of 15 kJ/mol and a surprisingly low preexponential factor of \( 10^{1.9} \text{ s}^{-1} \).

In this study, we use TPSSIMS and TPD to study in situ the kinetics of the dissociation and desorption of NO on Rh(111) and the reactions leading to the desorption of \( \text{N}_2 \). The results show that NO dissociates already below room
temperature on Rh(111) when the surface coverage is low, whereas dissociation becomes progressively more inhibited when the total surface coverage increases.

II. EXPERIMENT

The experiments were done in a stainless steel ultrahigh vacuum (UHV) system with a base pressure of $2 \times 10^{-10}$ mbar, equipped with Auger electron spectroscopy (AES) (Leybold EA10), TDS and static SIMS (Leybold SSM200). SIMS spectra were taken by using a defocused 5 keV Ar$^+$ primary ion beam with a current density of 1 nA/cm$^2$ at an incident polar angle of 60$^\circ$ with respect to the surface normal. Secondary ions were collected under a polar angle of 50$^\circ$. An electrostatic field was applied between the sample and the extraction lens of the quadrupole ion optics to average eventual anisotropic ion emission effects due to the crystal structure.

The rhodium crystal of (111) surface orientation has a thickness of about 1 mm and was mounted on a moveable sample rod by two tantalum wires of 0.24 mm diameter, pressed into small grooves on the side of the crystal. This construction allows for resistively heating the sample up to 1500 K. The sample can be cooled by a flow of liquid nitrogen to 100 K. Temperatures were measured with a chromel-alumel thermocouple spotwelded to the back of the crystal.

The crystal surface was cleaned by cycles of argon sputtering and annealing under oxygen and UHV. Argon sputtering (1.5 keV, 2 $\mu$A/cm$^2$) at 925 K was used to remove small amounts of impurities, such as sulphur, phosphorus, and chlorine, until these were no longer detectable with AES. Near-surface carbon was removed by heating the crystal in 10$^{-7}$ mbar O$_2$, cycling the temperature between 900 and 1200 K, until CO and CO$_2$ were absent in TPD spectra taken after saturating the surface with oxygen. Oxygen was removed by annealing the sample to 1400 K.

Nitric oxide (Messer Griesheim, 99.999% pure) was used without further purification. Gas dosing was done with the crystal at 100 K. Temperature programmed experiments employed a heating rate of 10 K/s.

III. RESULTS

A. Adsorption of NO

1. Temperature programmed desorption (TPD)

Temperature programmed desorption spectra obtained after dosing various amounts of NO to Rh(111) at 100 K are given in Fig. 1. During these experiments, the only observed desorption products were NO (at $m/e=30$), N$_2$ (at $m/e=28$), and O$_2$ (at $m/e=32$); N$_2$O was not detected. We only show the desorption spectra of nitrogen containing products, noting that molecular oxygen desorbs at elevated temperatures (~1200–1350 K) with similar desorption kinetics as after dosing to O$_2$. The mechanistic implications of the desorption spectra will be discussed later on in this paper; here we use these data for the calibration of surface coverage vs exposure.

The initial concentration of NO was then determined from the amount of desorbing nitrogen atoms, i.e., by integrating the N$_2$ and NO desorption peaks, multiplying the N$_2$ area by 2, dividing the NO area by the difference in mass spectrometer sensitivity for NO and N$_2$ (= 1.2), and adding these contributions. For the saturation coverage of NO on Rh(111) at 100 K, we tentatively used the value of 0.68 ML, which is in reasonable agreement with the slightly higher values of 0.71 (Ref. 5) and 0.75 ML (Ref. 8) reported for NO on Rh(111) around room temperature.
The uptake of NO as a function of exposure at 100 K is given in Fig. 2. Clearly, the sticking coefficient of NO (proportional to the slope in Fig. 2) decreases only slowly with coverage up to 0.50 ML; for higher coverages, it drops rapidly to zero. This behavior is characteristic for adsorption that proceeds via a mobile precursor state. It implies that a NO molecule impinging on an already occupied site may be trapped in a so-called extrinsic precursor state from which it may diffuse to an empty site on which to adsorb, resulting in the enhanced sticking coefficient with respect to Langmuir adsorption. In the Langmuir adsorption model, the sticking coefficient $S$ depends linearly on the concentration of available sites

$$S(\theta) = S_0(1 - \theta/\theta_{sat})$$  \hspace{1cm} (1)

with $S_0$ the initial sticking coefficient and $\theta_{sat}$ the saturation coverage of NO. If the adsorption proceeds via a mobile precursor, the sticking coefficient $S$ can be written as

$$S(\theta) = S_0 \left( 1 + \frac{k_p \theta/\theta_{sat}}{1 - \theta/\theta_{sat}} \right)^{-1}$$  \hspace{1cm} (2)

$$K = \frac{k_{des}^{extr}}{k_{ads}^{int} + k_{des}^{int}}$$

where $k_{des}^{extr}$ is the rate constant for desorption from an extrinsic precursor state (above an occupied site), whereas $k_{ads}^{int}$ and $k_{des}^{int}$ are the rate constants for adsorption and desorption, respectively, from an intrinsic precursor state (above an empty site). In this formalism, the limiting value $K=1$ corresponds to pure Langmuir adsorption. The solid line in Fig. 2 represents Eq. (2) for equal values of $S_0$ (based on the initial slope of the measured data) and $\theta_{sat}$, but for different values of $K$. The line for $K=0.15$ gives a satisfactory fit, implying that there is a highly mobile precursor state involved in the adsorption of NO on Rh(111) at 100 K. Similar adsorption behavior of NO has been reported for the Rh(110) (Ref. 13) and Pd(111) (Refs. 30 and 31) surfaces.

2. Static secondary ion mass spectrometry (SSIMS)

Figure 3 shows a typical static SIMS spectrum of the Rh(111) surface taken after a saturation dose of 10 L NO at 100 K. The spectrum shows intense substrate peaks Rh$^+$ at $m/e=103$ and Rh$_2^+$ at $m/e=206$. The peaks due to the emission of molecular clusters, such as RhNO$^+$ at $m/e=133$, Rh$_2$NO$^+$ at $m/e=236$, Rh(NO)$_2$ at $m/e=163$, Rh$_3$N$^+$ at $m/e=220$, and Rh$_2$O$^+$ at $m/e=222$ are characteristic for the adsorbates and their structure. The high intensity of clusters of the type Rh$_n$NO$^+$ with respect to the intensities of Rh$_n$N$^+$ and Rh$_n$O$^+$ indicates that the adsorption of NO on the close-packed Rh(111) surface at 100 K is molecular, in agreement with high-resolution electron-energy loss spectroscopy (HREELS) studies of NO on Rh(111), which show that dissociation does not occur for temperatures below 250 K. We attribute the small Rh$_n$N$^+$ and Rh$_n$O$^+$ peaks to the fragmentation of molecular NO during the secondary ion emission process, in analogy with the presence of Rh$_n$CO$^+$ and Rh$_2$O$^+$ clusters in SSIMS spectra of molecular CO on Rh(111). The origin of the Rh(NO)$_2$ feature is not quite clear. It may be related to the presence of Rh(NO)$_2$ nitrosyls, in analogy to the observation of Rh(CO)$_2$ nitrosyls in Rh(CO)$_2$ SSIMS cluster ions when Rh(CO)$_2$ carbonyls are present. Otherwise, it may result from the formation of (NO)$_2$ dimers at low temperatures and high coverages, in similarity with findings for Pd(111) (Ref. 33) and Pt(111). Finally, the Rh(H$_2$O)$_2$ cluster is due to the adsorption of tiny amounts of water from the residual gas during cooling to 100 K, for which SSIMS is particularly sensitive.

In general, the quantification of absolute SSIMS intensities in terms of adsorbate surface concentrations is not straightforward due to poorly understood matrix effects on the ionization probability of emitted secondary clusters. Ion intensities are strongly enhanced if the work function of the sample increases due to the decreased ionization probability of emitted ions. To account for these work function...
For NO on Rh(111), we find that the $\text{Rh}_2\text{NO}^+/\text{Rh}^+$ ratio is two times higher than the $\text{Rh}_2\text{O}^+/\text{Rh}^+$ ratio. The SSIMS intensity ratios vary linearly with coverage. In this region, the SSIMS $\text{Rh}_2\text{NO}^+/\text{Rh}^+$ ratio is 1.6 times as high as the $\text{RhNO}^+/\text{Rh}^+$ ratio. On increasing the NO coverage above 0.35 ML, the coverage dependence of the SSIMS intensity ratios becomes more pronounced, which holds especially for the $\text{Rh}_2\text{NO}^+/\text{Rh}^+$ ratio. The SSIMS intensity ratios maximize at the saturation coverage. The increase of slope in Fig. 4 is probably related to increased intermolecular repulsion within the adlayer which leads to ordering and the occupation of a new NO adsorption site, causing a change in the relative intensities for the $\text{Rh}_2\text{NO}^+$ cluster ions. In general, cluster ion intensities are not only sensitive to the molecular structure of the adsorbate, but also to the bonding geometry of the adsorbate and lateral interactions within the adlayer. Systematic studies by Brown and Vickerman$^{37}$ of CO adsorbed on various transition metal surfaces have shown that the intensities of SSIMS $\text{M}_n\text{CO}^+$ clusters bearing more than one metal atom (i.e., $n>1$) increase relative to the $\text{MCO}^+$ intensity when the coordination of the CO adsorption site increases. These authors proposed characteristic fragmentation patterns for CO adsorbed at on-top, twofold bridge, and threefold hollow sites, which were essentially independent of the transition metal.$^{37}$ By comparing the SSIMS fragmentation patterns of CO and NO on Rh(111), we can make a qualitative estimate for the bonding geometry of NO. CO adsorbs linearly on Rh(111) for coverages up to 0.33 ML (Ref. 38) and gives a SSIMS $\text{RhCO}^+/\text{Rh}^+$ intensity ratio which is two times higher than the $\text{Rh}_2\text{CO}^+/\text{Rh}^+$ ratio. For NO on Rh(111), we find that the $\text{Rh}_2\text{NO}^+/\text{Rh}^+$ ratio is larger than the $\text{RhNO}^+/\text{Rh}^+$ ratio irrespective of coverage, implying that the coordination of NO is higher than that of CO for the whole coverage range. Interestingly, a similar increase in slope as that depicted in Fig. 4 has been observed by Brown and Vickerman for CO on Pd(111)$^{39,40}$ which adsorbs at threefold sites at low coverage and increasingly occupies bridge sites at coverages above 0.33 ML.

More detailed information on the adsorption site geometry of NO on Rh(111) comes from HREELS and low energy electron diffraction (LEED) data.$^{6,8}$ These studies suggest that around 100 K, the NO adlayer is disordered and is characterized by a $\nu_{\text{NO}}$ stretching frequency which shifts from 1480 cm$^{-1}$ at low coverage to 1630 cm$^{-1}$ at saturation. By comparison with metal-nitrosyl complexes, this vibrational mode was assigned to bridge bonded NO with its axis perpendicular to the surface (here denoted as $\alpha_\perp$-NO). A new mode at 1840 cm$^{-1}$, appearing at high coverages, was assigned to NO influenced by small amounts of coadsorbed oxygen.$^{6,19}$ The enhanced mobility of NO molecules at higher temperatures induces ordering of the adlayer and an increased adsorption capacity of the Rh(111) surface. Kao et al.$^8$ observed a $(4\times2)$ LEED pattern at a coverage of 0.50 ML NO at 120 K, corresponding with a N–O stretching mode at 1590 cm$^{-1}$. At 0.75 ML coverage, obtained by saturating the surface with NO at 250 K, a $(2\times2)$ LEED pattern was observed, characterized by two N–O modes at 1515 and 1840 cm$^{-1}$, respectively. Again the lower frequency mode was assigned to $\alpha_\perp$-NO adsorbed at twofold bridge sites, however, the high frequency mode was attributed to linear $\alpha_\parallel$-NO. On the basis of these site assignments and dynamical LDIF data, the authors suggested the occupation of two linear and one bridge bonded NO per $(2\times2)$ unit cell.$^8$

It is interesting to compare these data with results for NO adsorbed on Ni(111),$^{41,42}$ Pd(111),$^{30,31,33}$ Ru(0001),$^{43}$ and Pt(111).$^{34,44,45}$ Initially, a bridge bonded, bent configuration of NO with $\nu_{\text{NO}}=1475–1510$ cm$^{-1}$ has been suggested for low coverages of NO on Ni(111).$^{41,42}$ With increasing coverage, this state is displaced by a new one, characterized by a frequency which shifts from 1540 to 1580 cm$^{-1}$ at 0.50 ML coverage, associated with a $(4\times2)$ LEED pattern. The assignment to bridge bonded perpendicular NO (Refs. 41 and 42) is the same as for Rh(111), where $\nu_{\text{NO}}$ is 1590 cm$^{-1}$ for the $(4\times2)$ structure. However, several studies have recently indicated that the adsorption site assignment of NO on Ni(111) on the basis of vibrational frequencies fails dramatically. Surface-extended x-ray-absorption fine-structure (SEXAFS),$^{46}$ photoelectron diffraction (PD),$^{47}$ and dynamical LEED$^{48,49}$ studies all indicate that NO adsorbs at threefold sites in the $(4\times2)$ Ni(111) structure. On the basis of symmetry arguments and dynamical LEED, a model was proposed in which NO adsorbs at both face-centered-cubic (fcc) and hexagonal close-packed (hcp) threefold sites.$^{46,48,49}$

Inconsistency also exists on the adsorption site of NO on Pt(111). Vibrational studies show two bands ranging from 1475–1500 and 1700–1725 cm$^{-1}$, which have been associated with bridge and linearly bound NO,$^{44,45}$ upright and dimer species,$^{42}$ and both linearly adsorbed NOs. In this case, dynamical LEED analysis$^{49}$ of the $(2\times2)$ structure at 0.25 ML points to a threefold fcc NO adsorption site.
Considering the inconsistency between the site assignments on the basis of vibrational and structure-sensitive spectroscopies, we wonder if twofold bridge and atop bonding assignments for $\sigma_2$-NO and $\alpha_1$-NO on Rh(111), respectively, are correct. Although a dynamical LEED analysis of the (2×2)-3NO structure appears to confirm these bonding configurations, the authors seem to have relied heavily on the interpretation of their HREELS spectra in choosing the input structures for LEED I–V simulations: saturation structures (0.75 ML) containing threefold coordinated NO were not included in the calculations. The SSIMS data in Fig. 4 would be consistent with a model in which $\sigma_2$-NO occupies threefold sites at low coverage, with increasing amounts of bridge bonded $\alpha_1$-NO above a coverage of 0.35 ML.

B. The thermal decomposition of NO

1. Temperature programmed desorption

The desorption phenomena during heating a NO adlayer, as shown in Fig. 1, depend strongly on coverage. For low doses of NO (<0.7 L), the only desorption products are N$_2$ (tentatively denoted as $\beta_2$-N$_2$) and O$_2$, indicating complete NO dissociation during the temperature ramp. The peak temperature of the $\beta_2$-N$_2$ desorption state decreases considerably with increasing coverage from 655 K after a dose of 0.2 L NO to 550 K at saturation. The small peak in the TPD spectra at m/e =28, shifting from 510 K in the 0.2 L spectrum to 460 K in the 0.7 L spectrum, is due to the desorption of a small amount of CO, which adsorbs from the residual gas onto the surface during cooling to 100 K. This assignment was verified by monitoring the C TPD signal (at m/e = 12), which showed the same shift. The decrease of the CO desorption temperature indicates that CO is destabilized by the presence of increasing amounts of nitrogen and oxygen atoms on the surface. For doses higher than 0.7 L, a narrow NO desorption state, denoted as $\alpha_2$-NO, is observed. Its peak maximum shifts slightly towards higher temperature with increasing coverage, from 430 K after a dose of 0.7 L NO to 445 K at saturation. Concomittant with this $\sigma_2$-NO state, a low temperature $\beta_1$-N$_2$ desorption state develops with a constant peak temperature of 460 K. The contribution of CO to this desorption state is negligible, as the intensity of the C TPD spectra decreases with increasing NO dose. For high initial NO coverages, we observe a new $\alpha_1$-NO desorption state with a peak temperature of 380 K. This state was not reported by Root et al. for NO on clean Rh(111), although the other features are in good agreement.

2. Stepwise heating of NO/Rh(111)—SSIMS

Figure 5 shows static SIMS spectra (m/e=200–250) of the Rh(111) surface with initial coverages of 0.20 ML NO (left panel) and 0.65 ML NO (right panel) at 150 K and after heating to the indicated temperatures. The spectra were normalized to the Rh$_2$ intensity to allow a quantitative comparison. After adsorption at 150 K, the spectra exhibit intense Rh$_2$NO$^+$ peaks which are characteristic for the presence of molecular NO; the small intensities of Rh$_3$N$^+$ and Rh$_2$O$^+$ are attributed to the fragmentation of intact NO during the ion emission process. Heating a low coverage of NO [Fig. 5 (left panel)] to 350 K results in the disappearance of the Rh$_2$NO$^+$ peak and a significant intensity rise of the Rh$_3$N$^+$ and Rh$_2$O$^+$ peaks. This, and the absence of desorption phenomena between 150 and 350 K (see the TPD spectra of Fig. 1), indicates that all NO has dissociated. As equal amounts of atomic nitrogen and oxygen are formed during dissociation, and no desorption takes place, it may be concluded that SSIMS is about four times more sensitive towards adsorbed
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FIG. 6. Surface coverages of NO and N on Rh(111) during temperature programmed reaction, reflected by the TPSSIMS $\Sigma_{n=1,2} R_h NO^+/R_h$ and $R_h N^+/R_h^+$ ion intensity ratios for various initial NO coverages (given in monolayers). The adsorption temperature was 100 K; the heating rate was 10 K/s.

N sub than to $\Omega_{sub}$, in agreement with the SSIMS results of DeLouise and Winograd. We note that diatomic RhN$^+$ and RhO$^+$ cluster ions were virtually absent in the SSIMS spectra of dissociated NO, which is related to the fact that nitrogen and oxygen atoms reside in threefold hollow sites on the Rh(111) surface. As mentioned before, high coordination adsorption sites favor the emission of secondary ion clusters containing multiple metal atoms. Heating the crystal further to 500 K results in an intensity loss of the Rh$_2$N$^+$ cluster; this ion is absent in the SSIMS spectrum after annealing to 800 K. The observed decrease of the nitrogen surface concentration is attributed to the recombination to and desorption of N$_2$.

SSIMS spectra of NO on Rh(111) at a high coverage [0.65 ML; [Fig. 5 (right panel)] reveal interesting differences with respect to dissociation kinetics. Only a minor part of the NO molecules has reacted at 350 K, as indicated by a small decrease of the Rh$_2$NO$^+$ intensity. This is probably due to desorption, but a small increase of Rh$_2$N$^+$ and Rh$_2$O$^+$ indicates also that some NO may have dissociated. Clearly, the dissociation of NO is significantly hindered on the heavily occupied surface. Heating to 500 K removes all molecular NO from the surface due to desorption and dissociation of NO. Again, heating to 800 K removes all nitrogen and leaves only oxygen on the surface.

3. Temperature programmed static SIMS (TPSSIMS)

Characteristic cluster ions in SSIMS can be monitored as a function of time by multiplexing the mass spectrometer, enabling in situ studies of surface reactions. Figure 6 shows the temperature evolution of the SSIMS intensity ratios $\Sigma_{n=1,2} R_h NO^+/R_h$ and $R_h N^+/R_h^+$, characteristic of adsorbed NO and N, respectively, after exposing the Rh(111) surface to various amounts of NO at 100 K. The heating rate of 10 K/s was the same as that during TPD. The first ratio corresponds to the surface concentration of NO according to the calibration given in Fig. 4. The $R_h N^+/R_h^+$ ratio is linearly proportional to the amount of adsorbed nitrogen atoms, as deduced from the low coverage region where all NO dissociates.

For NO coverages below 0.25 ML, a decrease of the NO coverage and a concomitant increase of the nitrogen concentration are observed around 275 K, indicative for the onset of NO decomposition. Molecular NO is detected above 350 K. Between 500 and 750 K, a continuous decrease of the nitrogen coverage takes place which is due to the recombinative desorption of N atoms as N$_2$.

For coverages exceeding 0.25 ML, variations in the $\Sigma_{n=1,2} R_h NO^+/R_h$ ratio may reflect both dissociation and desorption of NO; here the dissociation rate of NO is reflected more directly by the increase of the Rh$_2$N$^+/R_h^+$ ratio. Clearly, the onset of dissociation shifts to significantly higher temperatures with increasing NO doses. For a coverage of 0.30 ML, atomic nitrogen is detected above 300 K and its coverage maximizes at 425 K. Close to saturation, NO dissociation does not start until 400 K. Above this temperature, the nitrogen coverage increases rapidly and reaches its maximum at 450 K.

IV. DISCUSSION

A. Elementary reactions of NO on Rh(111)

The adsorption studies indicate two states of NO on Rh(111), a state labeled $\alpha_1$ fills at low coverages, while an additional state $\alpha_2$ becomes occupied at coverages above 0.35 ML. As discussed before, we think that the $\alpha_2$ state is associated with NO in threefold sites and the $\alpha_1$ state with bridge bonded NO. Irrespective of this assignment, the TPD
This mechanism is slightly different from that suggested previously by Root and co-workers, who alternatively proposed \( \text{NO}_{\text{ads}} + \text{N}_{\text{ads}} \rightarrow \text{N}_2 + \text{O}_{\text{ads}} \) instead of reaction (3a). In the following sections, we focus on each of the elementary steps except the desorption of \( \text{O}_2 \). However, we note that the desorption of \( \text{O}_2 \) from dissociated \( \text{NO} \) is essentially the same as that after dosing the crystal to \( \text{O}_2 \).

### B. NO dissociation vs desorption

TPD and TPSSIMS experiments indicate that at low coverages, i.e., \( \theta_{\text{NO}} < 0.25 \text{ ML} \), NO dissociates readily on Rh(111). At higher coverages, dissociation and desorption become competitive reactions. As summarized in Fig. 7, of all NO in excess of 0.25 ML, about half of the molecules desorb molecularly. At saturation, approximately 65% of the NO dissociates, whereas the remaining 35% of NO desorbs. These numbers are somewhat different than those reported by Root et al., who found 55% for the extent of NO dissociation on Rh(111) on the basis of x-ray photoelectron spectroscopy (XPS). Comparable values, between 54 and 65%, were reported for the degree of NO dissociation on Rh(100).

Temperature programmed SSIMS provides data on the kinetics of NO dissociation, which is not directly accessible by TPD due to the absence of desorption products during this elementary reaction step. The complementary nature of TPD and TPSSIMS is illustrated by Fig. 8, showing that three characteristic coverage regimes exist in the competition between NO dissociation and NO desorption, which we designate here as the low, medium, and high coverage ranges.

The low coverage range \( \theta_{\text{NO}} < 0.25 \text{ ML} \) is characterized by complete NO dissociation when the surface is heated to 350 K. At these coverages, all NO is adsorbed in the \( \alpha_2\text{-NO} \) state, attributed to NO in threefold positions. Decomposition

![Figure 7](image1.png)

**FIG. 7.** The distribution of nitrogen atoms over \( \text{N}_2 \) and NO desorbing during temperature programmed reaction of NO on Rh(111) as a function of the initial NO coverage. The data were obtained by integrating and weighting the TPD spectra in Fig. 1.

![Figure 8](image2.png)

**FIG. 8.** The NO (---) and \( \text{N}_2 \) (---) TPD rates (top) and \( \Sigma_{\text{RhNO}}/\text{Rh}_{\text{ads}} \) (---) and \( \text{RhNNO}^+ / \text{Rh}^+ \) (---) TPSSIMS ion intensity ratios (bottom) during the temperature programmed reaction of NO on Rh(111) for low (left panel), medium (central panel), and high (right panel) initial NO coverages. The NO TPD spectra have been divided by a factor of 4 with respect to the \( \text{N}_2 \) TPD spectra. The adsorption temperature was 100 K; the heating rate was 10 K/s.
of the $\alpha_2$ state starts $\sim$275 K and is complete at 340 K, well below the temperature where $\alpha_2$-NO is seen to desorb at higher initial coverages. These temperatures agree well with HREELS data,\textsuperscript{6} exhibiting NO dissociation between 270 and 325 K for low coverages.

The medium coverage range $0.25<\theta_{\text{NO}}<0.50$ ML is characterized by partial desorption of $\alpha_2$-NO. The desorption of $\alpha_2$-NO, starting at 400 K for initial NO coverages higher than 0.75 ML, indicates that further dissociation is hindered by the increased occupation of the surface. As soon as $\alpha_2$-NO desorption (followed by $N_2$ desorption) starts, additional NO dissociates due to the creation of vacancies. $\alpha_2$-NO is the dominant NO species in this range, although the SSIMS data in Fig. 4 suggest increasing occupation of the $\alpha_1$-NO state above 0.35 ML.

At high coverages close to saturation $\theta_{\text{NO}}>0.50$ ML, dissociation is completely self-inhibited up to 400 K. In this coverage range $\alpha_1$-NO, presumably bridged NO, coexists with $\alpha_2$-NO. Interestingly, the desorption of $\alpha_1$-NO, with a peak maximum near 380 K, does not create the required vacancies that affect the energetics of the dissociation reaction. Therefore, we restrict the determination of the NO dissociation rate parameters to low-coverage cases $\theta_{\text{NO}}<0.25$ ML. Figure 9 shows the coverages of NO$_{\text{ads}}$ and N$_{\text{ads}}$, as derived from TPSSIMS, as a function of temperature during a 10 K/s heating ramp. The complementarity of the NO and N concentrations confirms that all NO decomposes. The dissociation rate was modeled by a differential equation of Arrhenius form

$$-\frac{d(\theta_{\text{NO}}/\theta_{\text{sat}})}{dT} = \nu_{\text{dis}}\theta_{\text{NO}} \theta_{\text{sat}}^n \exp\left(-\frac{E_{\text{dis}}}{RT}\right),$$

where $\theta_{\text{NO}}$ is the absolute NO coverage, $\theta_{\text{sat}}$ is the absolute coverage of available sites, $\nu_{\text{dis}}$ is the preexponential factor for dissociation, $E_{\text{dis}}$ is the activation barrier for dissociation, and $\beta$ is the heating rate. Coverages are normalized to a saturation value $\theta_{\text{sat}}$ of 0.50 ML, i.e., the concentration of threefold hollow sites available for the adsorption of $\alpha_2$-NO, N$_2$, and O. The parameter $n$ can be considered as an effective ensemble size required for the dissociation of NO. The pronounced coverage dependence of the NO dissociation rate, and the fact that two atoms are produced by dissociating one NO molecule, imply that at least one vacant site ($n=-1$), or more generally an ensemble of vacancies ($n>1$), is required.

This differential equation was integrated numerically for independent values of the preexponential factor and activation energy to obtain the best fit for both the measured NO$_{\text{ads}}$ and N$_{\text{ads}}$ concentrations.

The case $n=0$ assumes pure first order dissociation kinetics and neglects lateral interactions such as site blocking. The fits for 0.15 and 0.20 ML result in rather low values for the activation energy for dissociation $E_{\text{dis}}=40\pm6$ kJ/mol and the preexponential factor $\nu_{\text{dis}}=10^{4.0\pm1}$ s$^{-1}$. As discussed below, we consider these numbers as effective values rather than as "fundamental" values for the dissociation of a NO molecule on an empty surface. With increasing ensemble size (i.e., increasing $n$), the values for the activation energy and preexponential factor increase. We find $E_{\text{dis}}=45\pm6$ kJ/mol and $\nu_{\text{dis}}=10^{5.2\pm1}$ s$^{-1}$ for $n=1$, $E_{\text{dis}}=53\pm6$ kJ/mol and $\nu_{\text{dis}}=10^{8.5\pm1}$ s$^{-1}$ for $n=2$, $E_{\text{dis}}=60\pm6$ kJ/mol and $\nu_{\text{dis}}=10^{10.2\pm1}$ s$^{-1}$ for $n=3$, and $E_{\text{dis}}=70\pm6$ kJ/mol and $\nu_{\text{dis}}=10^{12.1\pm1}$ s$^{-1}$ for $n=4$.

Experimentally determined dissociation parameters for NO on different rhodium surfaces are summarized in Table I. Although the scatter in the available data is large, some general trends can still be recognized. In order to dissociate, an initially vertically adsorbed NO molecule has to bend the oxygen atom in the vicinity of the surface. According to De Koster et al.\textsuperscript{33} and Van Daelen et al.,\textsuperscript{54} dissociation
is highly favored if the molecule bends and stretches over one of the three rhodium surface atoms to which it is coor-
inated, such that the overlap between metal d orbitals and
the antibonding 2p* orbital of NO increases, resulting in a
weakened N–O bond.55 Experimental evidence for such a
mechanism was provided in a HREELS study of NO on
Rh(100). For low coverages, Villarrubia and Ho15 observed a
very low N–O stretching frequency at 920 cm⁻¹ which was
assigned to a flat-lying or highly inclined NO species. This
low frequency was taken as an indication for a significantly
weakened N–O bond, and consistently this inclined NO spe-
cies dissociates already near 170 K with an activation energy
of 44 kJ/mol and a preexponential factor of 10¹² s⁻¹. At
higher coverages, the authors observed an N–O stretch fre-
quency at 1580–1675 cm⁻¹, attributed to twofold bridge
NO. The dissociation rate of this perpendicular species ap-
peared strongly coverage dependent, but was essentially the
same as that of the inclined species in the zero coverage
limit. These results for NO on Rh(100) point to a mechanism in
which the decomposition of the inclined species is rate
limiting at low coverage, whereas the reorientation of the
vertically adsorbed NO molecule into the inclined configu-
ratio limits the rate at higher coverages. A similar reorien-
tation mechanism is likely for the dissociation of α₂-NO on
Rh(111). Although on Rh(111) an inclined NO species does
not appear stable enough to be detected spectroscopically,6 it
may serve as a transition state during the decomposition pro-
cess. Transition state theory predicts that the entropy loss when going from a perpendicular NO molecule to a con-
strained, inclined transition state results in a preexponential
factor for dissociation that is smaller than kT/h (≈6×10¹²
s⁻¹ at 300 K).29 For the dissociation of threefold NO on
Cu(111), Van Daelen et al.54 have calculated that the parti-
tion function of the inclined transition state is lower than that
of perpendicular NO by a factor of 5. This would imply a
preexponential factor of ~10¹² s⁻¹ for the dissociation of
NO on Rh(111). Our parameters are in agreement with this
theoretically predicted value if we include the requirement of
an ensemble of three to four vacant sites to enable NO dis-
sociation. It should be noted that inhomogeneities in local
adsorbate concentrations due to lateral interactions have not
been included in this approach: such inhomogeneities will
also lead to lower effective preexponential factors. To sort
out these effects, Monte Carlo simulations of NO decompo-
sition and desorption are currently in progress in our labora-
tory. Within the concept of transition state theory, the values
reported by Root and co-workers in a HREELS study of NO
on Rh(111),6 E_diss=80 kJ/mol and ν_diss=10¹⁴ s⁻¹, seem rather
high, whereas the kinetic parameters for NO dissociation on
Rh(110) given by Schmatloch et al.16 E_diss=15±2 kJ/mol and ν_diss=10⁸±2×10⁵
s⁻¹ are extraordinarily low and hard to ex-
plain.

The rapid decrease of the NO dissociation rate with in-
creasing surface coverage is in qualitative agreement with the
reorientation mechanism and the requirement of an en-
ssemble of vacancies. The probability that a NO molecule
crosses the transition state barrier for dissociation through
reorientation depends on the number of vacancies next to the
adsorbed molecule, and therefore the rate of dissociation
goes down with increasing coverage. The accumulation of
dissociation products contributes to site blocking. In support
of the site-blocking argument, we mention that the highest
coverage at which all NO dissociates is 0.25 ML, producing a
total atomic coverage of 0.50 ML. This is generally as-
sumed to be the saturation surface coverage of atomic oxy-
gen on Rh(111), which orders in domains of (2×1) structure
with the oxygen atoms at threefold hollow sites.52,57 The highest reported coverage of atomic nitrogen on Rh(111) is
~0.60 ML (Ref. 17); generally, these atoms are also assumed
to occupy threefold hollow sites.20 A second point in agree-
ment with site blocking being the main reason for inhibition of
the dissociation is that the partial dissociation of NO stops
as soon as the total coverage reaches 0.50 ML.

The activation energy of dissociation depends on the
heats of adsorption of NO, N, and O.58,59 As lateral interac-
tions between adsorbates modify (generally weaken) the ad-
sorption bonds, the energetics of the dissociation becomes
coverage dependent as well. Bond order conservation morse
potential (ROCMR) calculations59 for NO on fcc (111) sur-
faces predict that the energetics remain unchanged for total
adsorbate coverages up to 0.33 ML (i.e., for initial NO cov-
erages up to 0.17 ML), whereas above this value, the activa-
tion energy for NO dissociation will increase considerably.
An activation energy of 30–38 kJ/mol has been calculated
for the dissociation of NO on the empty Rh(100) and
Rh(111) surfaces, while the barrier goes up to 100–113 kJ/
mol for Rh(100) containing N_ads and O_ads at a total coverage
of 0.50 ML. Clearly, the dissociation of NO is favored at low
coverages, whereas NO desorption has the lower activation
barrier at high coverages.

Another contribution to the coverage-dependent disso-
ciation rate may be due to the interaction between NO_ads and
coadsorbed oxygen. HREELS and TPD6,10 of coadsorbed
NO and O on Rh(111) exhibit identical spectral features for
NO adsorbed next to oxygen and the α₁-NO species in a
compressed NO overlayer, indicating that oxygen forces
α₂-NO into the lower coordinated α₁-NO adsorption state.
As discussed before, this latter state does not dissociate, but
instead desorbs molecularly. It is conceivable that some
α₁-NO is produced during α₂-NO decomposition due to the
accumulation of atomic oxygen on the surface, although we
have no direct spectroscopic evidence for this. For low NO
coverages, it is possible that eventually formed α₁-NO dif-
fuses to another site and decomposes there. At higher cover-
ages, α₂-NO decomposition proceeds mainly at temperatures
above the α₁-NO desorption temperature, so that α₁-NO de-
sors immediately after it is formed. The α₁-NO and α₂-NO
desorption states cannot be distinguished in this case.

Determination of the NO desorption parameters is com-
plicated, as desorption of α₂-NO occurs only on partially
covered surfaces and is always accompanied by α₂ NO de-
composition. Therefore, one achieves at best the desorption
parameters for the first NO molecules desorbing from a
Rh(111) surface covered by 0.25 ML of nitrogen and 0.25
ML of oxygen atoms. The line shape of the NO desorption
spectra is rather peculiar, showing serious deviations from
pure first order desorption curves at both the low and high
temperature sides. Due to these line shape modifications, ap-
FIG. 10. TPD of $\alpha_2$-NO from Rh(111) for doses of 0.82 (bottom) and 1.03 L (top) NO. The solid lines are fits, assuming first order desorption kinetics and neglecting coincident $\alpha_2$-NO dissociation. The fits correspond to a desorption barrier of $113\pm10$ kJ/mol and a preexponential factor of $10^{13.5\pm1.0}$ s$^{-1}$.

The origin of the $\beta_1$-N$_2$ state is under debate. As its area is proportional to that of the NO desorption peak, it has previously been attributed to the NO disproportionation reaction $\text{NO}_{\text{ads}} + \text{N}_{\text{ads}} \rightarrow \text{N}_2 + \text{O}_{\text{ads}}$. However, studies of nitrogen desorption from coadsorbed isotopically labeled NO and N by Belton et al. recently demonstrated that the disproportionation reaction can be ruled out on Rh(111) under the present conditions. These authors alternatively proposed that nitrogen desorption is rate limited by the dissociation of NO, as was also proposed by Pirug and Bonzel for NO on Pt(100).

Additional details on the nitrogen desorption mechanism come from studies of atomic nitrogen on Rh(111) by Bugyi and Solyomosi and Belton and co-workers. These studies show a decrease of 150 K of the $\beta_2$-N$_2$ desorption temperature when going from 0 to 0.5 ML coverage due to mutual repulsions between adsorbed nitrogen atoms. As coadsorbed nitrogen and oxygen are mutually repulsive as well, the desorption kinetics of nitrogen from dissociated NO will deviate considerably from purely second order behavior. The competition between nitrogen and oxygen atoms for the same threefold hollow adsorption sites, where they have comparable adsorption energies, may cause a phase transition at higher coverages, which destabilizes the adsorbed nitrogen atoms and leads to an enhanced nitrogen desorption rate. Theoretical studies demonstrate that desorption phe-
nomens such as the $\beta_1$-N$_2$ and $\beta_2$-N$_2$ states observed here can indeed be explained by repulsive interactions.\textsuperscript{66,67} Experimental support for this explanation is provided by Bugyi and Solymosi,\textsuperscript{17} who observed a $\beta_1$-N$_2$ desorption state resulting from high atomic nitrogen coverages on Rh(111) which is very similar to that observed here. This implies that a high surface coverage of repulsive adsorbates rather than the presence of NO is required to obtain the $\beta_1$-N$_2$ desorption state, and thus invalidates the theory that $\beta_1$-N$_2$ desorption is rate limited by the dissociation of NO.

V. CONCLUSIONS

We have studied the low temperature adsorption and the temperature programmed decomposition and desorption of NO on Rh(111) by using (TP)SSIMS and TPD. With this combination of techniques, which is sensitive to desorption as well as true surface reactions, we determined the kinetic parameters of nearly all elementary reaction steps operative in the thermal decomposition of NO on Rh(111), which are summarized in Table II.

The adsorption of NO at 100 K proceeds via a mobile precursor, resulting in a high, nearly constant sticking coefficient for coverages up to 0.50 ML. SSIMS fragmentation patterns suggest the presence of two distinct NO adsorption states, which we assign to threefold coordinated NO at low coverages up to 0.50 ML, and lower coordinated—presumably twofold bridged—NO at higher coverages. This assignment contradicts earlier reports, but is in agreement with recent revised adsorption site assignments of NO on Ni(111) and Pt(111).

At low coverages, threefold coordinated NO dissociates near 300 K. Assuming pure first order dissociation kinetics, we find an effective activation barrier of 40$\pm$6 kJ/mol and a preexponential factor of $10^{6.2} \pm$ 1 s$^{-1}$. This value for the preexponential is lower than expected on the basis of transition state theory, due probably to lateral interactions which, e.g., result in site blocking and/or inhomogeneous adsorbate concentrations. If we assume that a NO molecule requires an ensemble of three to four vacant sites in order to dissociate, the preexponential factor and activation energy are $\sim 10^{11}$ s$^{-1}$ and 65 kJ/mol, in better agreement with transition state theory expectations. The small value of the prefactor indicates that the transition state for dissociation is tightly bound, consistent with a reorientation mechanism in which the NO molecule has to bend over a rhodium atom in order to bring the oxygen atom in the vicinity of the surface and dissociate. For coverages up to 0.25 ML, NO dissociation is complete. The produced nitrogen and oxygen atoms recombine and desorb as N$_2$ and O$_2$ around 650 and 1350 K, respectively. The nitrogen desorption temperature decreases with increasing coverage due to the repulsive character of the interactions between nitrogen and oxygen atoms, and between nitrogen atoms mutually.

For NO coverages exceeding 0.25 ML, the dissociation temperature gradually increases and part of NO desorbs molecularly, with an estimated desorption barrier of 113$\pm$10 kJ/mol and a preexponential factor of $10^{13.5} \pm 1.0$ s$^{-1}$. This is due to the increased crowding of the surface, which inhibits the reorientation of perpendicular NO and blocks sites for the dissociation products. Concomitant with NO desorption, an additional low temperature nitrogen desorption state is observed. This state was previously attributed to the NO+N disproportionation reaction, or to nitrogen desorption rate limited by the dissociation of NO. We assign this state to the recombination of nitrogen atoms that are strongly affected by repulsive interactions within the highly covered overlayers, possibly resulting in a phase transformation of adsorbed nitrogen atoms.

At coverages close to saturation, NO dissociation is completely inhibited until the desorption temperature of threefold NO. Interestingly, the desorption of the more weakly bound, lower coordinated NO species does not generate the vacancies required for dissociation. Finally, at saturation, 65% of the NO molecules dissociate and 35% desorb molecularly.

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