Adsorption of nitrogen dioxide and nitric oxide on Pd(111)

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Received 14 April 1990; accepted for publication 18 September 1990

The adsorption of NO₂ on Pd(111) was studied by using HREELS and TPD. NO₂ adsorbs molecularly at 110 K in a μ-N₂O nitrito bonding geometry. The assignment of this bonding geometry is made by comparison of the vibrational data obtained in this study with IR measurements of the NO₂ symmetric and asymmetric stretching frequencies of a bridge-bonded nitro palladium complex. Chemisorbed NO₂ dissociates upon heating to 180 K (at low coverages) into NO(a) and O(a). Below θ(NO₂) = 0.25 ML, NO₂ desorption is not detected; NO₂ adsorption is irreversible. Above θ(NO₂) = 0.25 ML, reversible NO₂ adsorption occurs with desorption energies of 14 and 16 kcal mol⁻¹ as determined by desorption activation energies. NO adsorption on Pd(111) was also studied by HREELS and TPD, in order to further understand NO₂ dissociation. The NO TPD data agree well with other studies of NO on Pd(111) with desorption activation energies of 38, 21, and 20 kcal mol⁻¹. For saturation coverages of NO at 100 K, two NO species are observed with N–O stretching modes at 1575 and 1735 cm⁻¹. These species are assigned as NO bonded at bridge and atop sites, respectively. We also note the lack of measureable adsorption of N₂O on Pd(111) at 100 K.

1. Introduction

Catalytic reactions of NO₂ are of interest in several commercial processes, including automotive exhaust catalysis [1] and atmospheric NO₂ measurement at very low levels [2]. Consequently, studies of the elementary reaction steps in this catalysis, such as adsorption and desorption of NO₂ on metal surfaces, are important. Also, NO₂ when coordinated as nitrite (NO₂⁻) in inorganic complexes is well known to be a versatile linkage isomer [3]. We have been trying to extend this concept of linkage isomerism to metal surfaces and thus have undertaken studies of NO₂ adsorption on a number of transition metals [4]. The surfaces that we have studied to date, in addition to Pd(111), are Pt(111) [5], polycrystalline Pt [6], Au(111) [7], polycrystalline Au [8], and Ni(111) [9]. In addition, results are available for the adsorption geometry of NO₂ on Ru(001) [10] and Ag(110) [11]. The coadsorption of NO₂ and oxygen adatoms has also been studied on Pt(111) [12], Au(111) [13], and Pd(111) [9].

These studies have clearly shown that NO₂ is a versatile linkage isomer on metal surfaces. It bonds in at least three different, stable geometries upon chemisorption. Each linkage isomer has a characteristic vibrational spectrum as measured by high resolution electron energy loss spectroscopy (HREELS) and electronic structure as measured by ultraviolet photoelectron spectroscopy (UPS). These isomers include a bridge-bonded μ-N₂O nitrito species with C₂ᵥ symmetry on Pt(111) [5], an N-bonded nitro isomer with C₂ᵥ symmetry on oxygen precovered Pt(111) [12] and Ru(001) [10], and an O,O'-chelating isomer also exhibiting C₂ᵥ symmetry on Au(111) [7] and Ag(110) [11]. Studies of the decomposition of NO₂ on Pt(111) have shown that the μ-N₂O nitrito species is irreversibly adsorbed, whereas the N-bonded nitro species is reversibly adsorbed, and thus the μ-N₂O nitrito species may be the required precursor for NO₂ decomposition into NO(a) and O(a). We have also

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shown that the O,O’-chelating isomer on Au(111) undergoes unique radical addition reactions [7]. One hypothesis is that each adsorption isomer has a unique reactivity associated with it [4,14], but this needs to be verified. Progress in establishing these new structure-reactivity relationships in surface chemistry can be made by systematic studies of the NO₂ adsorption geometry and chemical reactivity on a series of transition metals. We are particularly interested in exploring the group of Pt, Pd, and Ni.

NO₂ adsorption has not been studied previously on palladium surfaces. The adsorption of NO has been investigated on Pd single crystal surfaces [15–19], but much less so than on Pt surfaces. NO adsorption studies are important for understanding NO₂ decomposition. This is required in order to isolate the effects of coadsorbates resulting from NO₂ decomposition and formation on Pd(111). TPD studies of NO on Pd(111) show the existence of two NO desorption states separated by approximately 20 kcal mol⁻¹. Conrad et al. [19] and Bertolo et al. [18] suggest that these two states result from NO bonding on bridge and atop sites, while Schmick et al. [16] propose that the formation of NO dimers at higher coverages accounts for the separate desorptions peaks.

In this paper, we report our results of investigations of NO and NO₂ adsorption on a clean Pd(111) surface using HREELS and TPD. Studies of the influence of coadsorbed oxygen on the bonding of NO and NO₂ to the Pd(111) surface will be reported elsewhere [9].

2. Experimental

These experiments were carried out in a stainless steel UHV chamber that has been described in detail elsewhere [20]. The UHV chamber is equipped with the instrumentation necessary to perform Auger electron spectroscopy (AES), low energy electron diffraction (LEED), ultraviolet photoemission (UPS), TPD and HREELS. The chamber pressure was maintained at 2×10⁻¹⁰ Torr by a 220 l s⁻¹ ion pump and a titanium sublimation pump.

The TPD experiments were performed line-of-sight with the mass spectrometer, with the Pd(111) face (1 cm diameter) approximately 4 cm away from the ionizer. The heating rate for all experiments was 7.9 K/s. An IBM-XT was interfaced to the mass spectrometer in order to monitor several masses simultaneously during TPD.

The HREELS experiments were performed using a beam energy of 5 eV and a beam current of 0.1 nA. For these conditions, the elastic peak intensity was 20–40 kcps within a resolution of 75 cm⁻¹ FWHM routinely. All of the HREELS figures shown were obtained for scattering in the specular direction, with θ_{in} = θ_{out} = 65° from the sample normal.

High purity NO₂ was prepared in our laboratory [5,14]. Nitric oxide (99%, Scientific Gas Products) was passed through a dry ice/methanol bath for additional purification. Ultrahigh purity oxygen (99.97%, Scientific Gas Products) was used without further purification.

The Pd(111) crystal was heated resistively and cooled by close contact with a liquid nitrogen reservoir. It was cleaned by argon ion sputtering at 800–1000 K for 22 h. This treatment resulted in a surface that was free of sulfur contamination as determined by AES. However, following O₂ exposure at 110 K, the O₂ TPD peak due to O(a) was not observed even though the low temperature O₂ TPD peaks due to O₂(a) agreed well with those reported by Matsushima [21]. The surface then was cleaned by exposure to NO₂ for two hours at 1000 K. Following this treatment, the ratio of the TPD peak areas due to O₂(a) agreed well with those reported by Matsushima [21]. Initially, an oxygen signal was detected with AES which did not disappear when the crystal was heated to 1000 K. The contaminant responsible for this tenacious oxygen was removed by argon ion sputtering for 15 min at low temperature. After the crystal was annealed at 1000 K for 5 min, the LEED pattern exhibited sharp spots with the expected hexagonal symmetry. Reproducible AES and TPD spectra during the course of the experiments confirmed that the surface was always kept free of contamination.

Activation energies for desorption in TPD experiments were estimated using Redhead analysis
For first-order desorption kinetics of NO, a pre-exponential factor of $1 \times 10^{16}$ s$^{-1}$ was used as has been suggested [23]. A pre-exponential factor of $1 \times 10^{13}$ s$^{-1}$ was used for other first-order kinetics, while a value of $1 \times 10^{-2}$ cm$^2$ s$^{-1}$ was used in calculations for second-order kinetics.

3. Results

3.1. NO adsorption

3.1.1. TPD of NO after NO exposure

The NO TPD spectra following NO exposures on Pd(111) at 100 K are shown in fig. 1. NO coverage was determined by TPD areas, using the saturation NO coverage of 0.75 ML reported in previous work [19] and confirmed recently by Bertolo et al. [18]. Low exposures show clearly the behavior of the high temperature ($\beta_3$) state as this state is initially populated. With an NO coverage of 0.02 ML (curve a), the $\beta_3$ state is observed at 540 K. As the NO coverage increases, this state grows and the peak temperature gradually shifts to lower temperatures. When $\theta_{\text{NO}} = 0.43$ ML (curve e), the amount of NO desorbing from the $\beta_3$ desorption state is saturated and the temperature of the peak maximum is 510 K. As the NO coverage increases to 0.75 ML (curve j), two low temperature states, $\beta_2$ at 290, and $\beta_1$, at 270 K are sequentially filled. The NO TPD spectrum that results from a saturation exposure of 4.0 L NO is in good agreement with that of Conrad et al. [19]. The decomposition of NO, as would be evidenced by the desorption of N$_2$, O$_2$, or N$_2$O, was not observed under any conditions that were employed here. (Separate experiments were performed in which N$_2$O was exposed on the Pd(111) surface at 100 K. However, no desorption of N$_2$O or other species was observed in TPD so that we conclude that no adsorption occurred.)

Although the peak temperature for the $\beta_3$ desorption state shifts to lower temperatures with increasing NO coverage, the desorption of NO is likely to be a first-order process with a coverage dependent activation energy. Using this assumption (along with the pre-exponential value discussed earlier in section 2) the activation energies for NO desorption from the $\beta_1$, $\beta_2$, and $\beta_3$ states were calculated to be 20, 21, and 38 kcal mol$^{-1}$, respectively.

Fig. 2 shows the plot of NO coverage as a function of NO exposure at 110 K on Pd(111). The slope of the uptake curve does not change with increasing coverage up to the saturation coverage of NO ($\theta_{\text{NO}} = 0.75$ ML). This behavior is generally attributed to the presence of a weakly bound precursor state which controls the adsorption kinetics.

3.1.2. HREELS after NO exposure

The vibrational spectra for NO(a) for NO coverages between 0.26 and 0.75 ML on Pd(111) at 100 K are presented in the top panel of fig. 3. The simple vibrational spectra obtained indicate that NO does not decompose or form new compounds (e.g., via disproportionation) on this surface. The top panel of fig. 3 shows a single
energy loss peak at 1570 cm\(^{-1}\) when \(\theta_{\text{NO}} = 0.26\) ML. This peak is attributed to the N–O stretch mode, \(v_{\text{NO}}\), of NO adsorbed in a bridge site. As the coverage of NO is increased to 0.51 ML, a shoulder appears on the high energy side of the original peak due to the occupation of a new NO adsorption site. At saturation NO coverage, this second site is characterized by \(v_{\text{NO}} = 1735\) cm\(^{-1}\) and a peak intensity nearly equal to that of the bridge-bonded peak at 1595 cm\(^{-1}\). We assign this second site as an atop site. The correlation of these two NO stretching frequencies to adsorption sites is discussed further in section 4.1.

The spectra showing an annealing sequence after a saturation exposure of NO are shown in the bottom panel of fig. 3. At 100 K, two energy loss peaks are present at 1595 and 1735 cm\(^{-1}\). As the temperature is increased to 475 K, the peak at 1735 cm\(^{-1}\) is no longer observed and only the single peak corresponding to bridge-bonded NO remains. This also occurs following the anneal to 505 K. No adsorbed species are observed after the temperature is increased to 1000 K.

3.2. NO\(_2\) adsorption

3.2.1. TPD of O\(_2\), NO, and NO\(_2\) after NO\(_2\) exposure

The O\(_2\), NO, and NO\(_2\) TPD spectra following NO\(_2\) exposure at 110 K on Pd(111) are shown in figs. 4–6. The O\(_2\) and NO desorption spectra are unambiguous evidence that NO\(_2\) decomposes on the Pd(111) surface. Desorption of N\(_2\) was not observed after NO\(_2\) exposure under any of the conditions employed here.

The O\(_2\) TPD spectra in fig. 4 show a desorption peak that appears to follow second-order kinetics. The peak maximum shifts from 860 K following a 0.6 L NO\(_2\) exposure (curve b) to 790 K after a 2.8 L NO\(_2\) exposure (curve h). The activation energy for O\(_2\) desorption was calculated to be 49 kcal mol\(^{-1}\) for \(\theta_{\text{O}} = 0.0–0.4\) ML. These results are in agreement with O\(_2\) TPD spectra that result from the recombination of adsorbed O atoms produced by O\(_2\) exposure on Pd(111) [21,24]. We did not observe any lower temperature O\(_2\) TPD states. The maximum oxygen coverage attainable from NO\(_2\) exposure on Pd(111) at 110 K is 0.4 ML. This is 1.6 times larger than the maximum value of \(\theta_{\text{O}} = 0.25\) ML from O\(_2\) exposure at 300 K [21,24]. (We
have reported on the efficient oxidizing power of NO$_2$ on Pd(111) in more detail elsewhere [25].

Fig. 5 shows the NO TPD spectra after NO$_2$ exposure. A single desorption state, $\beta_1$, at 540 K occurs following the 0.05 L NO$_2$ exposure (curve b). As the exposure is increased to 0.2 L NO$_2$ (curve d), the $\beta_1$ peak height increases with a small shift in peak temperature. After 0.6 L NO$_2$ (curve f), the $\beta_1$ peak temperature shifts to 500 K. A new desorption peak, $\alpha_2$, appears at 460 K following NO$_2$ exposures larger than 0.8 L (curves h–k). In addition to this $\alpha_2$ state, higher NO$_2$ exposures give rise to a distribution of low energy states, $\alpha_3$, between 300 and 400 K. The NO TPD peak at 225 K, which appears for exposures greater than 2.0 L NO$_2$ (curve j), is due to an NO cracking fragment of NO$_2$ and not to the presence of an additional NO desorption state. The activation energies for NO desorption can be estimated to be 40 to 36 kcal mol$^{-1}$ for the $\beta_1$ state, 34 kcal mol$^{-1}$ for the $\alpha_2$ state, and 26 to 18 kcal mol$^{-1}$ for the multiple $\alpha_3$ states, assuming that the desorption rates are always described by first-order kinetics.

The NO$_2$ TPD spectra after NO$_2$ exposure are shown in fig. 6. No desorption of NO$_2$ is seen for exposures smaller than 1.5 L NO$_2$. This indicates that NO$_2$ adsorption is irreversible and the rate of decomposition into NO(a) and O(a) is higher than the rate of molecular NO$_2$ desorption at low coverages. Beginning with an NO$_2$ exposure of 1.5 L (curve b), a reversibly adsorbed NO$_2$ state designated as $\beta_2$ appears with the desorption peak at 280 K. As the exposure is increased to 2.1 L NO$_2$ (curve f), the $\beta_2$ peak maximum shifts downward to 270 K and a new peak, $\beta_1$, is observed at 240 K. The peak for the $\beta_1$ state shifts to 230 K and does not vary with coverage for exposures larger than 2.6 L NO$_2$. The NO$_2$ desorption peak at 140 K in curve (j) is due to desorption from a physisorbed N$_2$O$_4$ multilayer and will be discussed in more detail later (with fig. 7). If we assume that
coverage dependent activation energies cause these minor peak shifts with increasing coverage and that first-order desorption kinetics control NO\textsubscript{2} desorption, then the desorption activation energies are 16 and 14 kcal mol\textsuperscript{-1} for the \(\beta_2\) and \(\beta_1\) states, respectively.

The desorption of NO\textsubscript{2} from physisorbed N\textsubscript{2}O\textsubscript{4} multilayers is shown in more detail in fig. 7. The peak at 140 K exhibits zero-order kinetics and is attributed to the decomposition of a physisorbed N\textsubscript{2}O\textsubscript{4} multilayer [5–8, 10]. An additional NO\textsubscript{2} desorption peak occurs at 170 K for NO\textsubscript{2} exposures of 8.0 L and greater (curves d–f). This desorption state has been observed in other studies [5, 10], however, the origin of this state is still uncertain. (We have been unsuccessful in isolating this state for spectroscopic study.)

Fig. 8 shows the total NO\textsubscript{2} uptake as a function of NO\textsubscript{2} exposure on Pd(111) at 110 K. Adsorbate coverages were determined by integration of the TPD spectra. The coverage of NO(a) was de-
terminated by calibrating the NO TPD area after NO₂ exposure to the NO TPD area following NO exposure (a saturation NO exposure at 110 K results in $\theta_{\text{NO}} = 0.75 \text{ ML}$ [18,19]). The coverage of O(a) at saturation NO₂ exposures was assumed to be equal to $\theta_{\text{NO}}$, since no other decomposition or reaction products were observed. Calculation of the NO₂ coverage is based on two assumptions: (i) the sticking coefficient of NO₂ as it condenses into the multilayer on the surface is unity at 110 K [5,7]; and (ii) the sticking coefficient of NO₂ on Pd(111) at 110 K is also unity at all coverages prior to formation of the N₂O₄ multilayer [5,7,10]. It follows that the slope of the NO₂ uptake curve must be independent of exposure at 110 K. The initial slope of the uptake curve where no NO₂ desorption occurs can be unambiguously determined from $\theta_{\text{NO}}$ and $\theta_{\text{O}}$ calibrations. At high exposures, where NO₂ desorption is observed, $\theta_{\text{NO₂}}$ can be derived by forcing the slope of the NO₂ uptake curve to be equal to the initial slope.

Fig. 8 shows that NO₂ decomposes completely into NO(a) and O(a) upon heating, with irreversible adsorption of NO₂ for $\theta_{\text{NO₂}} < 0.25 \text{ ML}$. Some reversible adsorption occurs at higher coverages and molecular NO₂ desorption is observed for $\theta_{\text{NO₂}} = 0.25 \text{ ML}$. For $0.25 \leq \theta_{\text{NO₂}} \leq 0.50 \text{ ML}$, the coverage of reversibly adsorbed NO₂ increases along with the irreversibly adsorbed coverage. Therefore, NO₂ desorption and decomposition are competitive processes at these coverages. Above $\theta_{\text{NO₂}} = 0.5 \text{ ML}$, $\theta_{\text{N}_2\text{O}_4}$ increases. In summary, the maximum coverage of chemisorbed NO₂ at 110 K is 0.5 ML, and at this coverage 80% (0.4 ML) of the chemisorbed NO₂ is decomposed into NO(a) and O(a) during heating while 20% (0.15 ML) is desorbed intact.

3.2.2. HREELS after NO₂ exposure

NO₂ is irreversibly adsorbed at low coverages and HREELS was used to determine if this state was dissociatively or molecularly adsorbed at 110 K. HREELS spectra as a function of NO₂ exposure on Pd(111) at 110 K are shown in fig. 9. Spectrum (a) shows a clean Pd(111) surface. After 0.8 L NO₂ (spectrum (b)), energy loss peaks are observed at 790, 1170, and 1545 cm⁻¹. Infra-red spectroscopy studies of gas phase NO₂ by Arakawa et al. [26] identified the peaks for ONO bending ($\delta$(ONO)), ONO symmetric stretching ($\nu_s$(NO₂)) and ONO asymmetric stretching ($\nu_a$(NO₂)) modes of NO₂(g) to occur at 750, 1318, and 1618 cm⁻¹, respectively. Therefore, we attribute the modes of NO₂(a) at 800, 1170, and 1545 cm⁻¹ to $\delta$(ONO), $\nu_s$(NO₂), and $\nu_a$(NO₂), respectively. The assignment of the bonding geometry of NO₂ on the Pd(111) surface will be discussed later (in section 4.3). Since the NO stretching frequency of bridge-bonded NO is 1570 cm⁻¹, we cannot rule out the possibility that some NO₂ decomposition occurs at 110 K. However, this cannot be a reaction of major importance, since the intensity ratio of the peaks at 1545 and 800 cm⁻¹ does not change dramatically with coverage. The weak loss peak near 600 cm⁻¹ may be due to a Pd–NO₂ stretching mode.
When the exposures are increased to 2.5 L NO₂ (spectrum (e)), where saturation coverage of the chemisorbed NO₂ layer occurs, only two changes are observed in the HREELS spectra. First, the frequency of the ν₃₅ mode shifts 15 cm⁻¹ higher to 1560 cm⁻¹. Secondly, the relative intensity of the ν₁ peak at 1170 cm⁻¹ increases with respect to the other two peaks. We believe that these subtle changes in intensity are an effect of crowding of NO₂ on the Pd surface and not an indication of a change in bonding geometry.

Following the 5.6 L exposure (spectrum (f)), peaks occur at 775, 1290, and 1760 cm⁻¹ with intensities of 3:2:1. These peaks correspond to the formation of N₂O₄(s) multilayers [5,7,10].

3.2.3. HREELS warm-up study after low exposure of NO₂

Two annealing experiments were performed so that the thermal stability of both high and low coverages of NO₂ could be explored. In fig. 10, the HREELS spectra after 0.9 L NO₂ (where no NO₂ desorption was observed in TPD) are shown as the annealing temperature is increased from 110 to 1000 K. Three peaks due to molecular NO₂ at 110 K are present at 800, 1175, and 1535 cm⁻¹, which is similar to the low NO₂ exposure case shown in fig. 9b. When the temperature is raised to 180 K, the peaks at 800 and 1175 cm⁻¹ are attenuated and the peak at 1535 cm⁻¹ increases in intensity and shifts to 1560 cm⁻¹, indicating that some decomposition of NO₂(a) has occurred. After warming to 230 K, the two peaks indicative of molecular NO₂(a) (δ(ONO) and ν₃₅(NO₂)) disappear entirely, indicating that NO₂(a) has completely decomposed. Now, only loss peaks at 1575 and 465 cm⁻¹ remain. These peaks are due to the ν(NO) mode of bridge-bonded NO(a) and to the ν(Pd–O) mode of O(a), respectively. Warming to 505 K causes a 60 cm⁻¹ decrease in ν(NO) to 1515 cm⁻¹ and the O–Pd stretch mode also shifts to a lower frequency of 425 cm⁻¹. No peaks are present at 600 K indicating that NO(a) and O(a) have desorbed completely to leave a clean surface. The TPD data in figs. 4 and 5 show that NO desorption should be complete by 600 K, but O(a) should be stable at this temperature. We speculate that the relatively small amount of O(a) in this experiment was removed by reaction with background CO or H₂ during successive anneals.

3.2.4. HREELS warm-up study after saturation exposure of NO₂

An annealing study utilizing HREELS at saturation coverage of the chemisorbed NO₂ layer is shown in fig. 11. At 110 K, three peaks corresponding to NO₂(a) are apparent and consistent with the results in fig. 9e. Little change occurs in the relative intensities of the three peaks upon heating to 180 K at this coverage. Thus, no significant amount of NO₂(a) decomposes. There is an additional peak at 315 cm⁻¹, which we attribute to the Pd–NO₂ stretch mode. Increasing the temperature to 230 K decreases the intensity of the δ(ONO) and ν₃₅ peaks at 790 and 1175 cm⁻¹ relative to the peak at 1610 cm⁻¹. This indicates that a significant amount of the chemisorbed NO₂
4. Discussion

The discussion section is organized into four parts. In the first two sections, we summarize the adsorption behavior and bonding geometry of NO on Pd(111) and then compare this to previous results for NO on Pt(111). In the last two sections, we discuss the bonding geometry of NO₂ on Pd(111) and then compare the adsorption behavior of NO₂ on Pd(111) and Pt(111) in order to identify trends in the reactivity of NO₂.

4.1. Adsorption of NO on Pd(111)

NO desorption following NO exposure may occur from up to three different states, and the activation energies of desorption for these states range from 20 to 38 kcal mol⁻¹. Since NO adsorption is not an activated process, the activation energy for NO desorption is equal to the NO adsorption energy. Therefore, the NO adsorption energy on Pd(111) is a strong function of NO coverage, presumably due to different bonding modes or sites on the surface. Two N–O stretching modes exist following a large NO exposure and we interpret this as due to the existence of two types of NO(a) at saturation coverages. The HREELS annealing studies help to correlate the desorption states observed in TPD spectra to the adsorption states detected by HREELS. Peaks at 1735 and 1575 cm⁻¹ after a saturation NO exposure at 100 K are assigned to ν(N–O) modes of bridging and atop-bonded NO, respectively. The assignment of the atop-bonded species from the high frequency mode is based on the reported ranges of ν(N–O) for atop-bonded NO (1650–2000 cm⁻¹) [28,29,31], as well as assignments in previous work on Pd(100) [17] and Pt(111) [32]. The frequency of the ν(N–O) mode assigned to bridge-bonded NO is above the reported range for bridge-bonded species (1480–1545 cm⁻¹) [27–30,32] and is in the reported range of bent NO species (1525–1700 cm⁻¹ [28]). However, we believe that the assignment of the 1575 cm⁻¹ mode to bridge-bonded NO is more consistent with the evidence presented, particularly because of the absence of any bending modes that usually occur...
in the range of 500–800 cm⁻¹ (ref. [15] and references therein). The atop species has a weaker interaction with the metal surface and warming to 475 and 505 K eliminates the peak that is due to the atop-bonded NO with ν(NO) at 1735 cm⁻¹. TPD studies show that warming to 475 K causes the desorption of both the β₁ and β₂ states. Therefore, these desorption states originate from NO that is bonded to atop sites. The β₃ NO desorption state must be derived from bridge-bonded NO. This assignment of β₃ desorption originating from NO adsorbed at Pd bridge sites has been proposed in some previous work on Pd(100) [15,17] and Pd(111) [16,19]. The assignments for both the bridge and atop NO stretching frequencies are also consistent with a very recent study by Bertolo et al. [18].

In addition to the picture presented above, other models of NO adsorption have been presented in the literature. In these models, neighboring adsorbed NO molecules interact strongly with each other at high coverages, either forming dimers [17] due to attractive interactions or weakening the NO-metal bond and strengthening the NO bond (with an increase in the ν(NO) frequency) due to repulsive interactions [16]. In the dimerization model, the NO molecules remain bridge-bonded at all coverages, however, dimerization causes an abnormally large shift in the NO stretching frequency to 1677 cm⁻¹. This model has been proposed in previous work on Pd(100) (ref. [17], and references therein) and on stepped Pd(111) surfaces [16], however, only the Pd(100) study uses HREELS evidence for support of the dimer model. The HREELS results on Pd(100) show a shift in ν(NO) from about 1500 to 1700 cm⁻¹ as the NO coverage increases. At high NO coverages, only the mode attributed to dimerized NO is present. Our HREELS spectra on Pd(111) are significantly different from the spectra of NO on Pd(100) [17]. In our work, the ν(NO) peak at 1570 cm⁻¹ that is present at low NO coverages does not attenuate with increasing NO coverage. At high coverages there is an approximately equal intensity of the two loss peaks for the weakly bound and strongly bound NO molecules. We believe that there is a distribution between bridged and atop NO at high coverages and that there is no support the dimer model invoked for previous studies [16,17].

Using information about the adsorption sites of NO obtained from studies after NO exposure on Pd(111), the adsorption sites of NO corresponding to NO desorption states after NO₂ exposure can be identified. The HREELS spectrum following a 2.5 L exposure of NO₂ and anneal to 325 K, where all NO₂ is desorbed or dissociated, shows a large peak at 1575 cm⁻¹ which indicates that NO is bridge-bonded to the Pd surface. Since this mode is separated from that observed for atop NO by 160 cm⁻¹, we can conclude that there is not a distribution of atop and bridged NO under these conditions. These results demonstrate that β₃ and α₂ NO desorption states following NO₂ exposure are exclusively due to desorption from bridged sites. The observed decrease in activation energy for NO desorption from the α₂ state relative to that from the β₁ state is due to the destabilization of NO on bridged sites rather than a change from bridged to atop NO bonding. This destabilization is a result of coadsorbed oxygen atoms which are also produced by NO₂ dissociation. (This topic will be addressed much further in another paper focusing on the coadsorption of NO and O on Pd(111) [9].) The identification of the adsorption state of NO that gives rise to the α₁ NO desorption feature following NO₂ exposure is not so clear. In this case, HREELS evidence is ambiguous and some atop NO could be formed by warming to 230 K at large initial NO₂ coverages.

4.2. Comparison of the adsorption of NO on Pd(111) and Pt(111)

The results of this study indicate that the difference in stabilities of bridge-bonded NO relative to atop-bonded NO is greater on the Pd(111) surface than it is on the Pt(111) surface even though the maximum NO coverages following NO and NO₂ exposures are similar on both surfaces. TPD results indicate that the difference in adsorption energies for the two forms of NO is 18 kcal mol⁻¹ on Pd(111) compared to only 3 kcal mol⁻¹ on Pt(111) [32,33]. Approximately 60% of the NO at saturation coverage on Pd(111) is bridge-bonded, while 40% is atop-bonded. However, a
majority of the NO is adsorbed in atop sites at high NO coverages on Pt(111) [30]. Finally, following the heating of large NO₂ coverages on Pd(111), NO adsorption occurs exclusively in bridged sites. In contrast, after saturation NO₂ coverages on Pt(111) have been annealed, NO is primarily atop-bonded [5,33].

4.3. Adsorption of NO₂ on Pd(111)

NO₂ adsorbs molecularly on Pd(111) at 110 K, even for the 0.9 L exposure, where no NO₂ desorption is observed in TPD. In this section we give a detailed explanation of our assignment of the bonding geometry of chemisorbed NO₂.

NO₂⁻ has a variety of linkage isomers in inorganic transition metal complexes [3]. These isomers suggest surface species exhibiting C₃ symmetry that include the μ-N,O nitrito (bridge-bonded or side-bonded NO₂, bonded through the N and O atoms), nitrito (with just one O bonded to the surface), and a three-coordinated nitrite (with all atoms of NO₂ bonded to the surface and the molecular plane of NO₂ parallel to the surface) species and those with C₃ᵥ symmetry that include an N-bonded nitro isomer and an O,O'-chelating isomer (bonded through both of the oxygen atoms). According to the dipole scattering selection rule in HREELS [28], only those modes that are completely symmetric within the point group of the adsorbed complex are detected as fundamentals in specular HREELS spectra. Therefore, the two isomers, i.e. N-bonded nitro or the O,O'-chelating, that would be likely to have adsorption geometries with C₃ᵥ symmetry can be ruled out since the asymmetric NO₂ stretch is clearly present at 1170 cm⁻¹, but would not be allowed for C₃ᵥ symmetry.

Of the isomers exhibiting C₃ᵥ symmetry, we believe that NO₂ adsorbs on the Pd(111) surface with a geometry similar to the bridge-bonded, μ-N,O nitrito species. As pointed out previously [5,14], the three-coordinate nitrite (all three atoms of NO₂ bonded to the surface) should not have strong perpendicular components of the dynamic dipole moments associated with the asymmetric and symmetric ONO stretching modes and thus should not have strong peaks in HREELS. Also, the three-coordinate nitrite species would not be expected to have a large splitting between the symmetric and asymmetric stretches since the two N–O bonds would be equivalent. A nitrito complex (bonded through one oxygen) is more difficult to rule out since ligands with this geometry in transition metal complexes have asymmetric NO₂ stretches in the range of 1380–1460 cm⁻¹ and symmetric NO₂ stretching frequencies in the range of 1000–1170 cm⁻¹ [3]. Although these frequencies are near those reported for NO₂ on Pd(111), the asymmetric stretching modes for μ-N,O nitrito species are higher in energy and are in better agreement with our results for the chemisorbed NO₂ species. Also, some inorganic nitrito complexes are known to be thermodynamically unstable [3] and are therefore not likely to be formed on a surface. Our determination of the total chemisorbed NO₂ coverage of 0.5 ML is also consistent with our assignment of the bridge-bonded NO₂ adsorption geometry.

Additional support for this bonding geometry assignment is found in IR studies of inorganic transition metal complexes containing nitro ligands. Chatt et al. [34] identified absorption bands at 1230 and 1472 cm⁻¹ for the palladium complex, dinitrobis(tri-n-butylphosphine)-μ₂-dinitropalladium(II) or (PBu₃)₂Pd₂(NO₂)₂, and assigned these bands to the ν₁(ONO) and ν₈(ONO) modes of the bridge-bonded NO₂ ligands, respectively. Underhill et al. [35] report peaks at 1148 and 1537 cm⁻¹ and attribute these to ν₁(ONO) and ν₈(ONO) modes, respectively, for NO₂ bridge-bonded to two platinum atoms. Nakamoto [36] studied NO₂ in cobalt complexes and reported peaks at 1200 and 1516 cm⁻¹ which were similarly assigned, and also observed the ONO bend mode at 830 cm⁻¹. We feel that this agreement in the vibrational frequencies of NO ligands bridge-bonded in coordination compounds and NO₂ chemisorbed on the Pd(111) surface confirms our assignment of the bridge-bonded adsorption geometry for NO₂ on Pd(111) at 110 K. This assignment is consistent with the analogous surface species identified on Pt(111) [5] and is in keeping with the prediction that the individual adsorption isomers of NO₂ will have vibrational spectra that
are similar, regardless of the metallic substrate [37].

4.4. Comparison of the behavior of NO$_2$ on Pd(111) and Pd(111)

In general, NO$_2$ chemisorption on Pd(111) is similar to that on Pt(111). On both surfaces, NO$_2$ is adsorbed molecularly at 110 K and the $\mu$-N$_2$O nitrito isomer is the stable species. Decomposition initially has a lower activation energy than desorption, but desorption becomes competitive with decomposition at higher coverages. Using the observation that NO$_2$ dissociates upon warming to 180 K on Pd(111) (see fig. 10) and assuming a unimolecular decomposition reaction that follows first-order kinetics, we can estimate that the activation energy for decomposition is 11 kcal mol$^{-1}$. For $\theta_{NO_2} = 0.25$ to 0.5 ML, the activation energy for NO$_2$ dissociation must be comparable to that for NO$_2$ desorption (16 kcal mol$^{-1}$). The NO$_2$ desorption activation energy reported here reflects the heat of adsorption of NO$_2$ in the presence of NO(a) and O(a). This value is a lower limit for the heat of adsorption for NO$_2$ on clean Pd(111), where NO$_2$ should be bound more tightly. On Pt(111), the NO$_2$ dissociation activation energy and desorption activation energy at saturation NO$_2$ coverages were estimated to be 19 kcal mol$^{-1}$ [5,14].

Upon analysis of the adsorption geometry of NO$_2$ on the metals studied thus far, an interesting trend is apparent. It has been proposed in previous work that the bridge-bonded NO$_2$ adsorption isomer is the precursor to dissociation [5,12]. Both the N-bonded nitro isomer [12] and the O,O'-chelating isomer [7] have been detected by HREELS on O-covered Pt(111) and clean Au(111), respectively, but NO$_2$ decomposition was not observed for either of these bonding geometries. However, the bridge-bonded geometry is accompanied by NO$_2$ decomposition on Pt(111) [5,12] and Pd(111). Although there are other parameters such as the specific metal properties and coadsorbate coverages that will also obviously effect the decomposition probability, the results from this study provide additional support for the proposal that bridge-bonded NO$_2$ is the precursor required for dissociation.

5. Summary

We have carried out TPD and HREELS studies of NO chemisorbed on Pd(111) and conclude that NO is bonded to Pd(111) in bridged and atop sites which are characterized by $\nu$(NO) at 1575 and 1735 cm$^{-1}$, respectively. These conclusions are different from previous studies on Pd(100) [17], where a dimerization model was proposed to explain the HREELS results. Bridge-bonded NO desorbs as the $\beta_1$ state with an activation energy of 38 kcal mol$^{-1}$. Atop-bonded NO desorbs as $\beta_1$ and $\beta_2$ states with an activation energy near 20 kcal mol$^{-1}$.

HREELS and TPD results were also presented for NO$_2$ adsorbed on the Pd(111) surface. NO$_2$ chemisorbs molecularly at 110 K, with a saturation coverage of 0.5 ML. Decomposition into NO(a) and O(a) is observed upon heating to 180 K for low NO$_2$ coverages. For $\theta_{NO_2} < 0.25$ ML, NO$_2$ adsorption is completely irreversible. However, for 0.25 < $\theta_{NO_2} < 0.5$ ML, NO$_2$ decomposition and desorption are competitive processes, with NO$_2$ desorption occurring with activation energies of 16 and 14 kcal mol$^{-1}$. The activation energy for decomposition of NO$_2$(a) into NO(a) and O(a) is estimated to range from 11 kcal mol$^{-1}$ at low coverages to greater than 16 kcal mol$^{-1}$ at saturation coverage. A lower limit for the heat of adsorption of NO$_2$ on clean Pd(111) is 16 kcal mol$^{-1}$.

Using vibrational spectroscopy, we have assigned the adsorption geometry for NO$_2$ chemisorbed on Pd(111) as the $\mu$-N$_2$O nitrito or bridge-bonded complex. IR measurements of palladium complexes with bridge-bonded NO$_2$ ligands are in agreement with the $\nu_c$(ONO) and $\nu_m$(ONO) frequencies obtained for NO$_2$(a) on Pd(111). These results on Pd(111) are compared to previous work on Pt(111) and other metals, supporting the hypothesis that the bridge-bonded adsorption geometry is the required precursor to NO$_2$ dissociation on metal surfaces.

In separate experiments, no adsorption of N$_2$O occurred on the Pd(111) surface at 100 K.
Acknowledgments

This work was performed at the University of Colorado at Boulder. Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. Support is also acknowledged from the National Science Foundation. The authors thank Dr. Michael Bartram for a careful reading of this manuscript and helpful suggestions concerning this work. B.A.B. gratefully acknowledges the American Association of University Women for providing an American Fellowship.

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