

# Reactions of N and NO on Pt(335)

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As part of a study of species important in automotive exhaust chemistry, the reactivity of atomic N and NO on Pt(335) at low temperature has been studied. The atomic N was produced by dissociating adsorbed NO with a 76 eV electron beam. Cross sections for electron-stimulated desorption and dissociation are estimated for NO on terrace and step sites. Terrace NO is at least five times more likely to desorb than to dissociate. Step NO has a lower desorption cross section than terrace NO, but probably a higher dissociation cross section. Temperature-programmed desorption was used to monitor desorption, dissociation, and the formation of N<sub>2</sub> and N<sub>2</sub>O from adsorbed N and NO. Five distinct desorption states of N<sub>2</sub> formed by NO dissociation are identified. The dominant N<sub>2</sub> peak (435 K) comes from electron-dissociated step NO; its desorption temperature is higher than the N<sub>2</sub> peaks from electron-dissociated terrace NO. Co-adsorbed N and NO react to form N<sub>2</sub>O even below 100 K, with an activation barrier of ~6 kcal/mol. Only terrace NO participates in this reaction; step NO does not react to form N<sub>2</sub>O. This site dependence resembles that for CO oxidation on Pt(112) and Pt(335) and can be rationalized with simple steric considerations. All of the forms of atomic N participate in N<sub>2</sub>O formation, but that formed by the dissociation of step NO exhibits the lowest reaction temperature. Hence, the same N atoms that only recombine to form N<sub>2</sub> at 435 K, react with NO to form N<sub>2</sub>O at 100 K. We found no evidence for an NO reaction with N atoms to form N<sub>2</sub> and adsorbed O, or for NO formation from the recombination of adsorbed N and adsorbed O<sub>2</sub>. © 1997 American Institute of Physics. [S0021-9606(97)01246-4]

## I. INTRODUCTION

Catalytic reduction of NO on Pt, Rh, and Pt-Rh surfaces is used to help control automotive tailpipe emissions.<sup>1</sup> Among the desired surface reactions are:



Models suggest that under reaction conditions the surface can be nearly saturated with adsorbed N. We use an artificial procedure to prepare a high coverage of adsorbed N on a well characterized Pt surface in vacuum: NO is adsorbed at low temperature and then bombarded with electrons. By using a stepped surface as the substrate, we are able to learn about the effects of structural defects on the surface chemistry. Practical catalyst surfaces, of course, are highly heterogeneous, and it has been shown that the NO dissociation

reaction on Pt is very sensitive to surface structure.<sup>2-4</sup> For this study our substrate is Pt(335), or Pt(s)[4(111) × (100)] in step-terrace notation. As shown in Fig. 1, it has four-atom wide terraces separated by monatomic-height (100) steps. We have previously studied CO, H, and oxygen on this surface.<sup>5-9</sup>

After electron bombardment, both NO and N (and possibly O) remain on the surface. We focus on the chemistry involving NO and N. In addition to Eqs. (1)–(3) we consider:



The formation of N<sub>2</sub>O [Eq. (4)] is of concern because the product, although unregulated, is a “greenhouse” gas. The conversion of NO to N<sub>2</sub>O over supported Pt catalysts has long been recognized as an important reaction path.<sup>10</sup> Moreover, for the CO+NO reaction over Rh(111), N<sub>2</sub>O formation is the dominant pathway for adsorbed N to react when NO coverages are significant.<sup>11,12</sup> Even so, until recently, most studies of NO on single crystal Pt neglected the N<sub>2</sub>O channel, and those that did consider it found little evidence for its importance—only trace amounts of N<sub>2</sub>O were seen in temperature-programmed desorption (TPD) of NO from Pt(100)<sup>13</sup> and Pt(111).<sup>13,14</sup> There were exceptions: significant

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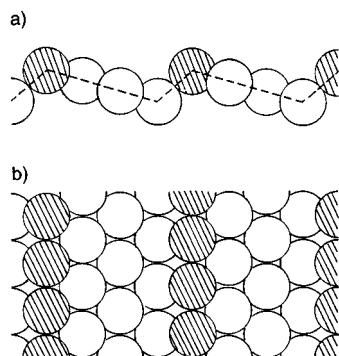


FIG. 1. Side (a) and top (b) views of the ideal Pt(335) surface. The Pt atoms at the step edge are shaded; those on the terrace are clear.

yields of  $N_2O$  were observed from NO on potassium-promoted Pt(111)<sup>14</sup> and from coadsorbed NO and CO on a polycrystalline Pt ribbon that was mostly Pt(111).<sup>15</sup> More recently, significant conversion of NO to  $N_2O$  has been seen on polycrystalline Pt<sup>16</sup> and on a surface that was approximately Pt(112).<sup>17</sup> On Pt(335) we find that  $N_2O$  formation proceeds rapidly at temperatures as low as 100 K, and conclude that reaction (4) can be important if the surface has a high concentration of atomic nitrogen. Reaction (5) has been proposed as a significant pathway on Rh(111),<sup>18–20</sup> but Belton *et al.* found no evidence for it.<sup>11</sup> We also find no sign of this reaction on Pt(335).

We are able to show that only terrace NO participates in the  $N_2O$  formation reaction; NO at step sites is essentially unreactive. This contrasts sharply with the high reactivity of step sites for NO dissociation,<sup>2,13,21–23</sup> but is similar to results for CO oxidation on stepped Pt surfaces.<sup>24–27</sup> In the CO studies the greater reactivity of terrace CO was attributed to steric factors, and it is likely that similar effects influence  $N_2O$  formation.

TPD spectra show multiple species of adsorbed N following electron bombardment of NO. All of these species can participate in  $N_2O$  formation. The most active for  $N_2O$  formation is N derived from the dissociation of step NO. Surprisingly, this N species is less active for  $N_2$  formation than other N species (from dissociation of terrace NO) that form  $N_2O$  less readily.

## II. EXPERIMENT

Our experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure of  $3 \times 10^{-11}$  Torr. The sample was spot-welded to two Ta wires, which were used for heating and cooling. The sample temperature could be controlled between 90 and 1300 K. The sample was cleaned by cycles of Ar sputtering and oxygen treatment between 623 and 1023 K. Detailed sample cleaning procedures can be found elsewhere.<sup>7</sup> The sample cleanliness was always checked by Auger spectroscopy.

Isotopically labeled  $^{15}NO$  was used, enabling us to distinguish among CO (mass 28),  $N_2$  (mass 30), NO (mass 31),  $O_2$  (mass 32),  $CO_2$  (mass 44), and  $N_2O$  (mass 46) in the TPD

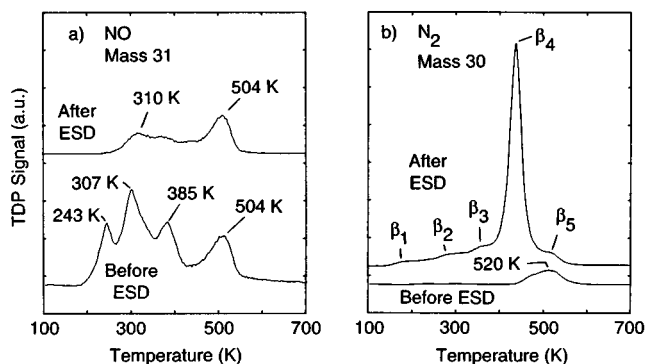


FIG. 2. (a) NO (mass 31) desorption signal from a saturation coverage of NO before (lower trace) and after (upper trace) 5 min of electron bombardment at an energy of 76 eV and sample current of 1.2 mA. (b)  $N_2$  (mass 30) signal from a saturation coverage of NO before (lower trace) and after (upper trace) electron bombardment. Signal has been multiplied by 0.1 relative to (a).

spectra. Gas was dosed with the sample at 90–95 K and in front of an NO doser. The doser's enhancement over background dosing was approximately  $10^2$ . The TPD spectra were measured with the sample facing the aperture of a cone covering the mass spectrometer, at a distance of about 1 cm. The aperture prevented detection of desorption from the back of the sample or from the heating leads. The heating rate was 10 K/s, and masses 28, 30, 31, 44, and 46 were all monitored simultaneously.

The electron-stimulated desorption (ESD) system was the same as that used in Refs. 11 and 28. Four thoriated iridium filaments mounted in parallel on Ta posts provided thermal electrons at ground potential. The sample was placed about 1 cm from the filaments and a positive bias of about 76 V was applied to the sample. The current between the filament and the sample was typically 1.2 mA with a filament current of 19 A. The electron bombardment generally lasted about 5 min, during which time the sample temperature rose from 90 to 140 K.

## III. e-STIMULATED DESORPTION AND DISSOCIATION OF NO

Figure 2 compares TPD spectra for NO (mass 31) and  $N_2$  (mass 30), with and without ESD, all from a saturation coverage of NO on Pt(335). The lower curves show the desorption from an NO layer prepared by simply dosing at 90 K to saturation coverage. There are four NO desorption peaks, at 243, 307, 385, and 504 K. One  $N_2$  peak is found, at about 520 K. In an unpublished study we have used high-resolution electron energy loss spectroscopy (HREELS) to show that the highest temperature NO peak is from NO adsorbed at step sites; the other three peaks are from NO adsorbed on the (111) terraces. The  $N_2$  desorption at 520 K comes from the recombination of atomic N derived from thermally dissociated step NO.

The absolute coverage of NO on Pt(335) at saturation at 90 K is estimated by equating the coverage of NO on the

(111) terraces at saturation with the saturation coverage of NO on Pt(111), from the literature. Several TPD experiments have obtained it by comparison with CO. The values obtained in this way are 0.55 ML (at 90 K),<sup>13</sup> 0.3 ML (at 260 K),<sup>22</sup> 0.25 ML (at 250 K),<sup>23</sup> and 0.54 ML (at 120 K).<sup>29</sup> Independently, a comparison<sup>13</sup> of the oxygen 1s photoemission peak between a saturated layer of atomic oxygen and a saturated layer of NO on Pt(111), gave 0.7 ML. A dynamical low energy electron diffraction (LEED) analysis<sup>30,31</sup> of a NO overlayer on Pt(111) that was prepared at 90 K and then heated to 250 K, gave 0.25 ML. This must be corrected for the desorption caused by heating. From Ref. 13, heating from 90 to 250 K desorbs 35% of the NO. Consequently, at 90 K, the LEED analysis implies a saturation NO coverage of 0.39 ML. Similarly, upon correcting to 90 K, the TPD results from Refs. 22 and 23 give 0.46 ML and 0.39 ML, respectively. Each measurement is given equal weight. The final value for the saturation coverage of NO on Pt(111) at 90 K is  $0.51 \pm 0.11$  ML.

To estimate the saturation coverage of NO on Pt(335), 75% of the total area is assigned to (111) terrace sites, on which the saturation NO coverage is assumed to be the same as it is on Pt(111): 0.51 ML. With dissociation during TPD taken into account, 19% of the NO is at step sites. Consequently, at saturation at 90 K, 29% of the step sites are occupied by NO. Overall, the estimated saturation coverage of NO on Pt(335) at 90 K is  $0.46 \pm 0.10$  ML.

The upper spectra in Fig. 2 come from a surface saturated with NO at 90 K followed by 5 min of electron bombardment. Compared to TPD of the same surface without electron bombardment, the total amount of N<sub>2</sub> that desorbed increased by a factor of 8 while the NO decreased by a factor of 3—the electron bombardment partially dissociated the NO. A similar effect has been reported for NO on Rh(111).<sup>11</sup> Electron-stimulated dissociation of NO on Pt(111) has been reported,<sup>32</sup> but the sample was a recrystallized ribbon that produced considerable thermal dissociation and thus probably had a high defect density. We will show that the majority of the stimulated dissociation of NO on Pt(335) occurs at the step edges, although a significant amount occurs on the terraces as well. This site preference mimics that for thermal dissociation, and may be related to the orbital symmetry arguments of Banholzer *et al.*<sup>2</sup>

There are five distinct desorption features in the N<sub>2</sub> (mass 30) signal in Fig. 2(b), labeled  $\beta_1$  to  $\beta_5$ . We estimated the peak temperature and fraction of the total intensity for each peak by deconvolving the desorption spectrum, assuming Gaussian peaks with independently adjustable heights, widths and peak temperatures. The results are given in Table I. By far the most intense peak, containing 71% of the total intensity, is the  $\beta_4$  peak at 435 K. Only the  $\beta_5$  peak is seen in the absence of electron bombardment [Fig. 2(b), lower trace].

Determining the origin of the five N<sub>2</sub> peaks is complex. The highest temperature peak,  $\beta_5$ , is observed even without electron bombardment, and is only a few degrees higher than the highest temperature NO desorption. In its peak temperature and correlation with NO desorption it strongly re-

TABLE I. Peak temperature and fraction of the total integrated desorption intensity for each of the five N<sub>2</sub> desorption peaks observed upon heating a saturated NO layer after 5 min of electron bombardment [Fig. 2(b), upper trace]. The uncertainty in each fractional intensity is less than 10% of its value.

	$\beta_1$	$\beta_2$	$\beta_3$	$\beta_4$	$\beta_5$
Peak temperature (K)	185	290	360	435	520
Fraction of total intensity (%)	3	8	11	71	7

sembles the N<sub>2</sub> desorption observed from the thermal dissociation of NO on nominally flat or vicinal Pt(111)<sup>2,21,33</sup> and on polycrystalline Pt.<sup>16,32,34</sup> The peak temperature is about 40 K higher than was observed on surfaces close to (111) (with appropriate corrections for differences in heating rate<sup>35</sup>), but very similar to the peaks seen on Pt(114) and Pt(112).<sup>3</sup> We attribute it to N formed by *thermal* dissociation of the NO left intact by the electron bombardment. Since the N atoms formed at low temperature by *stimulated* dissociation leave the surface at lower temperatures, we conclude that the kinetics of the  $\beta_5$  peak is limited by NO dissociation. The kinetics of NO dissociation may in turn be limited by the NO desorption required to produce vacant sites, as suggested by Wickham, Banse, and Koel.<sup>34</sup>

The four lower temperature peaks  $\beta_1 - \beta_4$ , at 185, 290, 360, and 435 K, respectively, appear only after electron bombardment. We assign them to the recombination of N atoms that remain on the surface after electron bombardment at 140 K. It has been reported that molecular nitrogen adsorbed at low temperature desorbs at about 180 K,<sup>36</sup> close to the temperature of our  $\beta_1$  peak, so it is possible that the  $\beta_1$  peak arises from a small amount of nitrogen that recombines even at very low temperature.

The dominant  $\beta_4$  peak occurs at 435 K. There have been a number of observations of N<sub>2</sub> desorption from N-atom recombination on flat and vicinal Pt(111). In general, the results for stepped and flat surfaces are not significantly different, except for the extent of thermal dissociation; in particular, no desorption feature can be associated with step sites.<sup>21,33,37,38</sup> The desorption temperatures for the main peaks range from 450 to 520 K. When the N atoms come from NO dissociation<sup>21,32-34</sup> it is uncertain whether the rate-limiting step in N<sub>2</sub> desorption is NO dissociation or N<sub>2</sub> recombination; our results suggest NO dissociation, as discussed above. Schwaha and Bechtold avoided this difficulty; they deposited N atoms directly by exposing flat and vicinal Pt(111) surfaces at room temperature to activated nitrogen generated in a high-frequency discharge.<sup>37</sup> The primary N<sub>2</sub> peak occurred at 500 K at low coverage, and shifted to 450 K at the highest coverage studied. Consideration of the heating rate (80 K/s in Ref. 37) would lower the high-coverage peak to about 430 K,<sup>35</sup> very close to our  $\beta_4$  peak. Atomic N generated by ammonia dissociation on Pt(111) produces N<sub>2</sub> desorption at 520 K, even though the dissociation is largely

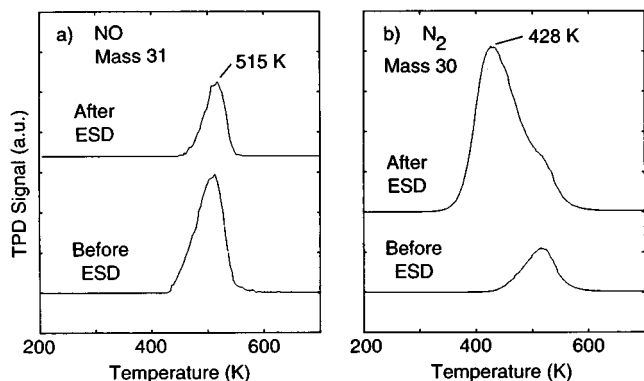


FIG. 3. (a) NO desorption signal from a saturation coverage of *step* NO before (lower trace) and after (upper trace) electron bombardment. The surface was prepared by saturating with NO at  $\sim 95$  K and heating to 433 K. (b)  $N_2$  desorption signal from a saturation coverage of *step* NO before (lower trace) and after (upper trace) electron bombardment. Signal has been multiplied by 0.1 relative to (a).

complete by 400 K.<sup>21,38</sup> The difference between this desorption temperature and that found by Schwaha and Bechtold is not understood. Desorption peaks of  $N_2$  from atomic N layers prepared by activated nitrogen have also been observed at 390 K and 450 K on Pt(100)<sup>37</sup> and at 465 and 525 K on Pt(110).<sup>39</sup>

By comparison with the data of Schwaha and Bechtold we tentatively identify the  $\beta_4$  peak as the recombination-limited peak from atomic N on the (111) terraces. Its low desorption temperature—closer to those seen on Pt(100)—could, however, support its identification with N atoms on the (100)-oriented steps. Quite possibly both explanations are correct and the two signals simply overlap.

We also tentatively assign the  $\beta_2$  and  $\beta_3$  peaks to recombination of terrace nitrogen. The  $\beta_3$  peak (360 K) resembles the 395 K peak seen by Schwaha and Bechtold, although its intensity relative to the  $\beta_4$  peak is smaller in our data than in theirs.<sup>37</sup> A peak near 360 K was also observed at some NO coverages for NO on polycrystalline Pt,<sup>34</sup> but was not identified. The experiments of Schwaha and Bechtold did not extend below room temperature, so the  $\beta_2$  peak at 290 K would not have been detected; it may also be a characteristic feature of N-atom recombination on Pt(111). The association of the  $\beta_1$ – $\beta_3$  features with terrace N is supported by experiments with only *step* NO, discussed below. We could not use isotope labeling to study possible mixing of the  $\beta_1$ – $\beta_3$  peaks, since the necessary electron bombardment after each dose would itself produce site mixing. Consequently we do not know whether they represent distinct adsorption sites.

Further information about the desorption states can be obtained from Fig. 3, which shows NO and  $N_2$  TPD measurements before and after electron bombardment, but with the NO occupying *only step sites*. The lower curves are from a surface prepared by saturation with NO at 90 K followed by heating to 433 K and recooling. In an unpublished HREELS study we have shown that this procedure desorbs NO from the terraces but leaves *step* NO in place. The upper

TABLE II. Fraction of the populations of *step* and *terrace* NO that desorb, dissociate, or remain intact after 5 min of electron bombardment, from Figs. 2 and 3. The values assume a TPD sensitivity to  $N_2$  that is 71 (10 000) times greater than that to NO. Estimated cross sections for desorption and dissociation are calculated using Eq. (6).

	Terrace NO	Step NO
Desorbed fraction	0.60 (0.71)	0.00 (0.53)
Dissociated fraction	0.11 (0.00)	0.59 (0.00)
Intact fraction	0.29 (0.29)	0.41 (0.46)
Desorption cross section $\sigma_{des}$ ( $10^{-19}$ cm <sup>2</sup> )	3.6 (4.3)	0.0 (2.7)
Dissociation cross section $\sigma_{dis}$ ( $10^{-19}$ cm <sup>2</sup> )	0.7 (0.0)	3.1 (0.0)
Fraction of saturated layer before exposure to electron beam	0.80 (0.82)	0.20 (0.18)

curves are from a surface prepared in the same way and then subjected to 5 min of electron bombardment.

Figure 3(b) again shows a large (factor of 5) increase in the total  $N_2$  desorption and a decrease (by a factor of 2) in the NO desorption, after the electron bombardment. The dominant  $N_2$  desorption feature after bombardment is still the  $\beta_4$  peak at 428 K. As expected, the  $\beta_5$  peak (at 520 K) is still seen—the NO that remains after electron bombardment thermally dissociates and the N atoms recombine to form  $N_2$ . The  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  peaks, however, are missing. We conclude that the  $\beta_4$  peak arises in large part from the dissociation of NO at *step* sites, while the three low temperature peaks,  $\beta_1$  to  $\beta_3$ , arise from dissociation of *terrace* NO. This interpretation agrees with the analysis of Gohndrone and Masel for the similar Pt(112) surface.<sup>3</sup> However, it does not tell us where the *N atoms* that produce the  $\beta_4$  peak are adsorbed.

We use the TPD data in Figs. 2 and 3 to estimate the cross sections for electron-stimulated desorption and dissociation for *step* and *terrace* NO. The calculation requires knowledge of the relative sensitivity of the TPD system to NO and  $N_2$ . We do not have an independent measure of the sensitivity ratio, but Fig. 2 allows us to set a limit. If there is no stimulated desorption of *step* NO, and there are no other channels for removal of nitrogen from the surface, then the TPD system is at least 71 times more sensitive to  $N_2$  than to NO; any lower ratio would imply that the number of nitrogen atoms on the surface is *increased* by the electron bombardment. If stimulated desorption of *step* NO occurs, then the sensitivity ratio must be correspondingly higher. Our data provide no definite upper limit for the sensitivity ratio, but even the lower limit of 71 is unexpectedly large, so we believe that the correct value is probably close to that limit. Table II gives our best estimates of the fractions of *step* and *terrace* NO that desorb, dissociate, and remain intact after 5 min of electron bombardment, calculated with sensitivity ratios of 71 and 10 000. The latter (essentially infinite) value corresponds to the unlikely assumption that essentially no stimulated dissociation occurs; the values listed therefore define the range of values that could be consistent with our experimental results.

The surprisingly high sensitivity to N<sub>2</sub> desorption as compared to NO could be partially caused by the angular distributions of the desorbing species. Our mass spectrometer is sensitive to molecules that desorb within about 20 deg from the surface normal. If the N<sub>2</sub> desorption pattern is highly peaked in that direction, while that of NO is more diffuse, then the sensitivity to N<sub>2</sub> is enhanced. In a study of N<sub>2</sub> (450 K) and NO (420 K) desorption from Rh(335), Ikai *et al.*<sup>40</sup> found that their desorption patterns had angular widths (FWHM) of 65 and 100 deg, respectively. For Pd(110), Ikai *et al.*<sup>41</sup> found an even bigger difference: angular widths of 19 and 120 deg respectively, for N<sub>2</sub> and NO. (The N<sub>2</sub> peak from Pd(110) was directed 37° from the surface normal.) A highly collimated desorption pattern has also been observed for CO<sub>2</sub> desorption from Pt(112).<sup>42</sup> However, even with an infinitely sharp distribution for N<sub>2</sub> and a cos( $\theta$ ) distribution for NO, if the mass spectrometer accepts a cone with angular radius of 20 deg then the sensitivity enhancement for N<sub>2</sub> is only a factor of 10, not enough to explain fully the observed difference.

We assume that the electron flux is uniform over the surface, that the cross sections are independent of coverage, that the NO molecules do not jump between step and terrace sites, and that all NO molecules on a given type of site (step or terrace) are equivalent, so that the population of each species decays exponentially with flux. (Only a single electron dose was used in the experiments.) Then for each species (terrace and step), the cross sections  $\sigma_{\text{des}}$  and  $\sigma_{\text{dis}}$  for desorption and dissociation, respectively, are determined by solving the equations:

$$\sigma_{\text{des}} + \sigma_{\text{dis}} = -\frac{eA}{It} \ln(f_{\text{intact}}), \quad (6)$$

$$\frac{\sigma_{\text{des}}}{\sigma_{\text{dis}}} = \frac{f_{\text{des}}}{f_{\text{dis}}},$$

where  $I$  is the beam current,  $A = 0.79 \text{ cm}^2$  is the sample area, and the  $f$ 's are the fractions of the molecules desorbed, dissociated and intact after time  $t$ . The results are given in Table II.

The dominant effect of the electron beam is to induce desorption. For a saturated layer at least 48% of the NO desorbed while no more than 20% dissociated. For terrace NO, desorption is at least five times more likely than dissociation. This is perhaps not surprising since the Pt(111) surface is completely inactive for thermal NO dissociation.

NO at the step sites is less likely to be activated by the electron beam than is NO at the terrace sites; the overall cross section  $\sigma_{\text{des}} + \sigma_{\text{dis}}$  is  $1.5 \pm 0.1$  times greater at terrace than at step sites. This difference may be attributed to the difference in binding energies: Campbell, Ertl, and Segner found  $E_d = 33.1 \text{ kcal/mol}$  for defect sites on Pt(111), and  $E_d = 27 \text{ kcal/mol}$  on the perfect (111) plane at low NO coverage. With increasing NO coverage,  $E_d$  on terrace sites decreases further.<sup>22</sup> It is likely, however, that the cross section for stimulated dissociation is greater at step than at terrace sites (assuming the TPD sensitivity ratio is close to its mini-

um value). A similar difference in *thermal* dissociation rate has been explained by Banholzer *et al.* with an argument based on orbital symmetry.<sup>2</sup>

Comrie, Weinberg, and Lambert reported cross sections for electron-stimulated desorption and dissociation of NO on a Pt(111) ribbon.<sup>32</sup> Since a large amount of thermal dissociation was also observed it is probable that the ribbon's surface had a high density of defect sites. For an electron beam energy of 2000 eV they found  $\sigma_{\text{des}} = (4.0 \pm 2.0) \times 10^{-19} \text{ cm}^2$  and  $\sigma_{\text{dis}} = (1.0 \pm 0.2) \times 10^{-18} \text{ cm}^2$ . On Pt(110) they found  $\sigma_{\text{des}} + \sigma_{\text{dis}} < 0.2 \times 10^{-19} \text{ cm}^2$ . Their value of the desorption cross section is quite similar to ours, but their dissociation cross section is much larger than we observed. It may be that stimulated dissociation is more sensitive to the electron energy than is stimulated desorption, or the ribbon surface may have contained sites with much higher dissociation cross section than are available on Pt(335). The latter explanation is suggested by the levels of *thermal* NO dissociation— $\sim 2/3$  of the NO dissociated thermally on the ribbon<sup>32</sup> as compared with only about 2% on Pt(335)—and by the wide variation in NO dissociation activity among crystal faces of Pt.<sup>2-4</sup>

It is also interesting to compare our results with the measurements of electron-stimulated desorption and dissociation of step NO on Pt(112) by Heiz *et al.*<sup>43,44</sup> They monitored the step NO population through the infrared absorption intensities of two vibrational bands, at about 1600 and 1800  $\text{cm}^{-1}$ . They assigned these two bands to bridge and terminal NO, respectively, on the step edges. Since only the NO population was measured, they could not directly distinguish between desorption and dissociation, but they argued that dissociation was negligible because no O<sub>a</sub> or N<sub>a</sub> was detectable with Auger spectroscopy after electron bombardment and thermal desorption of the NO. Our results, however, show that the N-containing species desorb at temperatures lower than or the same as the NO desorption temperature. If O<sub>a</sub> were present, it would desorb at a higher temperature,<sup>9,21,33</sup> but we have found *no* O<sub>2</sub> desorption from Pt(335) after either thermal or electron-stimulated dissociation of NO; we believe the ‘‘hot’’ O produced by NO dissociation leaves the surface immediately. Consequently, dissociation could have occurred in the experiments of Heiz *et al.*<sup>43</sup>

For electron-stimulated desorption (possibly including dissociation) they measured cross sections of  $2.3 \times 10^{-18} \text{ cm}^2$  for the 1800  $\text{cm}^{-1}$  species and  $8.7 \times 10^{-19} \text{ cm}^2$  for the 1600  $\text{cm}^{-1}$  species. Our cross sections for step NO, which do not distinguish between the two species, are much smaller. The difference may be due to the difference in beam energies (76 eV versus 275 eV) or to structural differences—the (112) surface is similar to the (335) surface, but the average terrace width is three, rather than four atoms.

## IV. N<sub>2</sub>O FORMATION BY COADSORBED N AND NO

### A. Reaction kinetics

When the overlayer formed by 5 min of electron bombardment of a saturation coverage of NO was heated, a small

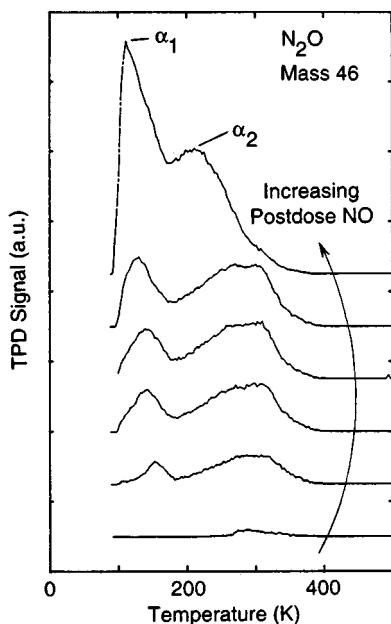


FIG. 4.  $N_2O$  (mass 46) signal from a surface prepared by 5 min electron bombardment of a saturation coverage of NO at  $\sim 95$  K and then post-dosed with varying amounts of NO. During the post-dose the NO pressure at the sample was roughly  $5 \times 10^{-10}$  Torr. The post-dose exposure times were, from bottom to top, 0, 8, 15, 22, 30, and 100 s.

amount of  $N_2O$  (mass 46) was found to desorb near 300 K, indicating a reaction between NO and the N atoms created by electron-stimulated dissociation of NO. As discussed in Sec. I, on clean Pt(111)  $N_2O$  production has been attributed to defect sites. We explored the dependence of the  $N_2O$  formation reaction on NO coverage by post-dosing various amounts of NO on the surface *after* the electron bombardment. Figure 4 shows the  $N_2O$  desorption as a function of NO post-dose. Two  $N_2O$  desorption peaks are evident,  $\alpha_1$  at about 110 K, and  $\alpha_2$  at 210–320 K. With increasing NO exposure the intensities of both peaks increase while the peak temperatures decrease,  $\alpha_2$  from 310 to 210 K, and  $\alpha_1$  from 155 K to 115 K. The increase in the intensity of the  $\alpha_1$  peak occurs mainly at the highest NO exposures.

In Fig. 5 we plot the integrated  $N_2$  desorption signal against the integrated  $N_2O$  desorption signal, for various NO post-doses. With the exception of the last point (discussed below) the data fall on a straight line, indicating that the postdosed NO is simply titrating the adsorbed N atoms. The slope of the line is then the ratio of the mass spectrometer sensitivities for the two species; the mass spectrometer is 2.8 times more sensitive to  $N_2O$  than to  $N_2$ . At the highest NO post-dose the  $\alpha_1$   $N_2O$  peak has shifted to such a low temperature that significant reaction and desorption occurs even at 95 K, before the TPD spectrum is measured. By extrapolating the linear fit, we estimate that 2/3 of the total amount of  $N_2O$  produced desorbed prior to the TPD measurement.

The adsorption of  $N_2O$  on Pt(111) has been previously studied with TPD<sup>45–47</sup> and HREELS,<sup>45</sup> to the best of our knowledge there have been no studies of  $N_2O$  on a stepped Pt surface. On Pt(111),  $N_2O$  adsorption is molecular. For

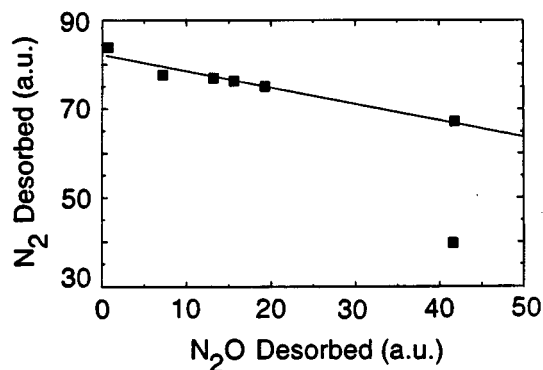


FIG. 5. Integrated intensity of the  $N_2$  desorption as a function of the integrated intensity of the  $N_2O$  desorption, from the data in Fig. 4. A straight line indicates a constant rate of  $N_2O$  production per dissociated NO molecule.

coverages below one monolayer a single first-order desorption peak is observed, with a peak desorption temperature between 90 and 105 K, depending on the coverage. Assuming that the (111) terraces of Pt(335) are similar to the (111) surface, we would expect any  $N_2O$  that forms before the sample is heated to desorb immediately and not be detected in our TPD spectrum. Indeed we believe this occurs for the highest NO post-dose and accounts for the discrepant point in Fig. 5. For lower NO doses it appears from Fig. 4 that little or no desorption occurs before the start of the TPD scan. We argue below that for both peaks the reaction occurs predominantly at terrace sites, and the rate-limiting step is the reaction  $N_a + NO_a \Rightarrow N_2O_a$ , rather than  $N_2O$  desorption. If we assume a preexponential factor of  $10^{13} \text{ s}^{-1}$  then the activation energy for the reaction is  $< 6$  kcal/mol.

## B. Identification of the active sites

In a series of studies of CO oxidation on the stepped Pt(112) and Pt(335) surfaces, Yates and co-workers have found that the reaction probability depends on the binding sites of the reactants.<sup>24–27</sup> Adsorbed CO is more reactive at terrace sites than at step sites, while O is marginally more reactive at step sites than at terrace sites. They have offered a qualitative explanation based on steric factors, the most important being that the CO's carbon atom can get closer to the  $O_a$  when the CO is on the terrace than when it is at the step edge. (Their analysis assumed that step O occupies “trough” sites at the bottom of the step; there are now strong indications that it actually sits on the exposed step edge;<sup>9,48</sup> but this does not affect the argument regarding the reactivity of the different CO species.) In many respects the NO+N reaction is similar to CO oxidation so we might expect terrace NO to be more reactive than step NO.

Indeed, only terrace NO participates in  $N_2O$  formation. TPD from a surface prepared by electron bombardment of a layer that contained only step NO (as in Fig. 3) revealed *no* detectable  $N_2O$  signal. A surface prepared in this way contains no terrace NO or  $\beta_1$ – $\beta_3$  N species, but does contain step NO and  $\beta_4$  terrace N. We show below that the  $\beta_4$  N

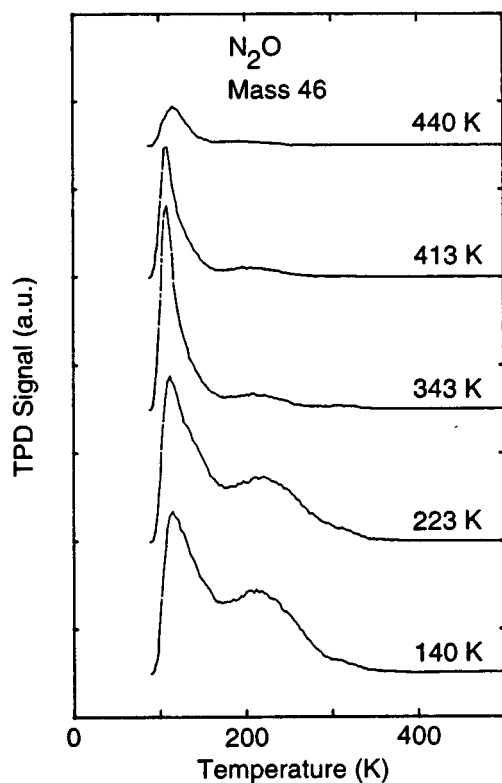


FIG. 6.  $\text{N}_2\text{O}$  desorption spectra that show the effect of varying the initial N coverage (with saturation NO coverage). Before desorption, the surface was prepared by saturating with NO at  $\sim 95$  K, electron bombardment for 5 min, heating to the indicated temperature (to desorb selected N species), and saturating again with NO at 95 K.

species is reactive, so the absence of  $\text{N}_2\text{O}$  production must be due to the lack of terrace NO. The steric reactivity model that Yates and co-workers proposed to explain their CO data also explains our NO data.

All of the observed forms of atomic nitrogen can react with terrace NO to form  $\text{N}_2\text{O}$ , but it appears that the  $\beta_4$  form, derived from dissociation of step NO, reacts more readily than do the forms derived only from terrace NO. Figure 6 shows  $\text{N}_2\text{O}$  TPD spectra from a saturated layer of NO subjected to electron bombardment, annealed to various temperatures to remove selected species of adsorbed N, and finally recooled to 90 K and saturated again with NO. The integrated intensities of the  $\alpha_1$  and  $\alpha_2$   $\text{N}_2\text{O}$  desorption peaks are plotted in Fig. 7 as a function of the annealing temperature. (The intensity of the  $\alpha_1$  peak is understated, however, since at saturation NO coverage roughly 2/3 of it desorbs before the start of the TPD scan.)

Annealing to 345 K largely removes the  $\beta_1$  and  $\beta_2$  species of N and part of the  $\beta_3$  species, and also largely eliminates the  $\alpha_2$   $\text{N}_2\text{O}$  peak. This observation confirms that these N species are reactive, as we asserted above.

The  $\alpha_1$   $\text{N}_2\text{O}$  peak is barely affected by annealing to 345 K. At higher temperatures, however, its intensity drops rapidly, coincident with the removal of N atoms through the  $\beta_4$  desorption channel. It is clear that the  $\alpha_1$   $\text{N}_2\text{O}$  peak is associated with the  $\beta_4$   $\text{N}_2$  desorption. This reinforces our conclu-

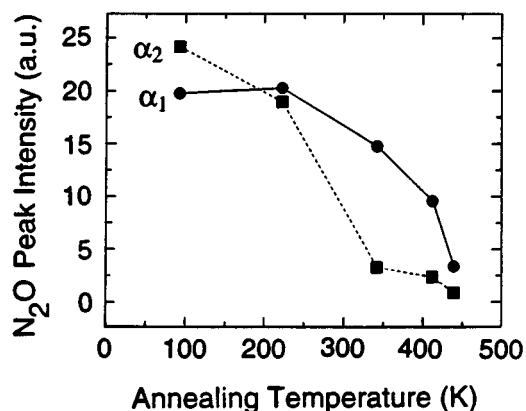


FIG. 7. The integrated intensities of the  $\alpha_1$  and  $\alpha_2$   $\text{N}_2\text{O}$  desorption peaks as a function of annealing temperature, from Fig. 6.

sion that the N-NO reaction rate is a function of the N and NO binding sites.

It is surprising that the  $\beta_4$  species of N is more active for  $\text{N}_2\text{O}$  formation than the  $\beta_1 - \beta_3$  species, but less active for recombination to  $\text{N}_2$ . Assuming that the pre-exponential factors are similar, this difference implies that the activation energy to form  $\text{N}_2\text{O}$  from  $\beta_4$  N is smaller than from  $\beta_1 - \beta_3$  N, but that the order of activation energies is reversed for the recombination reaction. While nothing in principle prevents such a reversal, it contradicts common intuition.

## V. REACTIONS NOT SEEN

We did not find any evidence for reaction (5). It was proposed to occur over  $\text{Rh}(111)^{18-20}$  but was later ruled out over that surface by Belton *et al.*<sup>11</sup> The presence of such a channel might have been revealed by a nonlinear dependence of  $\text{N}_2$  yield on  $\text{N}_2\text{O}$  yield in the NO post-dosing experiments (Fig. 5) or by oxygen desorption. Neither was observed.

We also exposed the electron bombarded overlayer to  $^{18}\text{O}_2$  at 90 K in order to look for a reaction between the N atoms and the oxygen. No mass 33 ( $^{15}\text{N}^{18}\text{O}$ ) signal was found in the TPD spectrum, indicating no reaction between NO and adsorbed oxygen. Moreover, the oxygen desorption spectra showed only the low temperature peaks due to adsorbed  $\text{O}_2$ ; the higher temperature peaks<sup>9</sup> that would have indicated the recombination of atomic O were not seen. In a previous TPD experiment,<sup>9</sup> we showed that  $\text{O}_2$  alone on Pt(335) does partially dissociate to atomic oxygen. With  $\text{O}_2$  alone on the surface, the fraction that dissociates to O depends strongly on whether the  $\text{O}_2$  is at a terrace or edge site; only about 5% of the terrace  $\text{O}_2$  dissociates. It is likely that oxygen dissociation was prevented in the present experiment by saturation of the step edges with N and NO.

## VI. CONCLUSIONS

We have observed low temperature reactions that involve atomic N and NO on the stepped Pt(335) surface. To obtain atomic N on the surface, electron bombardment was used to induce dissociation of adsorbed NO. Electron-

stimulated dissociation occurs at both step and terrace sites. However, for terrace NO, electron-stimulated desorption is much more probable than dissociation.

We have shown that in the  $\text{NO}_a + \text{N}_a \Rightarrow \text{N}_2\text{O}_g$  reaction, only  $\text{NO}_a$  at terrace (and not step) sites participates. Moreover, the  $\text{N}_a$  from dissociated step NO is more reactive than is the  $\text{N}_a$  from dissociated terrace NO. With  $\text{N}_a$  and  $\text{NO}_a$  at their most favorable binding sites, the activation barrier for this reaction is only  $\sim 6$  kcal/mol. In addition, the  $\text{N}_a$  from dissociated step NO is more resistant to recombination to form  $\text{N}_{2g}$  ( $E_a \sim 26$  kcal/mol) than is that from terrace NO, even though it has the lowest barrier to react with  $\text{NO}_a$ .

Adsorbed N and NO did not react to produce  $\text{N}_2$ . Moreover, TPD of a surface with atomic N and molecular oxygen that had been post-adsorbed at 90 K did not produce NO.

Great care is of course required in extrapolating from controlled low temperature UHV studies like these to the radically different operating environment of a catalytic converter. Nevertheless this study explains why  $\text{N}_2\text{O}$  formation is an important reaction path when substantial amounts of adsorbed N and NO are present on supported Pt surfaces.

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