the average energy transferred in one collision to be small.

The very wide spread in the energy of reacting methylene (which is practically the same as the initial energy dispersion for CDMC* given in Table III) may originate either from energy partitioning between reaction products in the photolytic act or from energy transfer in collisions prior to reaction. Although probably both effects operate in our systems, the dispersion caused in energy partitioning is believed to be dominant. This is supported by the increase in the spread with increasing energy release and by the inefficiency of collisional energy transfer.

Further research is in progress to study energy partitioning in the photolytic production of $CH_2({}^{1}A_1)$ and energy transfer in collisions between methylene and heat bath molecules.

Registry No. cis-Dimethylcyclopropane, 930-18-7; trans-dimethylcyclopropane, 2402-06-4; ketene, 463-51-4; diazomethane, 334-88-3; cis-2-butene, 590-18-1; methylene, 2465-56-7.

Kinetics of NO Decomposition on Silica-Supported Rhodium

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Temperature programmed desorption (TPD) spectroscopy was used to study the desorption and decomposition of NO adsorbed on a Rh/SiO_2 catalyst. At room temperature, less than about 9% of the NO is adsorbed dissociatively, and hence associative adsorption predominates. Upon heating the catalyst, the adsorbed NO undergoes extensive decomposition to form N_2 and O_2 , as well as small amounts of N_2O . The TPD spectra show two peaks for N_2 , but only single peaks for NO, N_2O , and O_2 . It is suggested that the two N_2 peaks are attributable to the following two processes: $N_s + NO_s \rightarrow N_2 + O_s + S$ and $2N_s \rightarrow N_2 + 2S$. N_2O is taken to be formed by the process $N_s + NO_s \rightarrow N_2O + 2S$. Rate parameters for the elementary processes involved in NO desorption and decomposition were determined by forcing agreement between simulated and observed TPD spectra. The preexponential factor and activation energy for NO desorption determined this way are $1\times10^{-15}~{\rm s}^{-1}$ and 23.7 kcal/mol, respectively.

Introduction

Temperature programmed desorption (TPD) spectroscopy can be used to elucidate the elementary processes occurring on the surface of a catalyst during the desorption and decomposition of an adsorbate.¹⁻¹¹ Relatively few efforts, however, have been made to apply this technique to the study of reactions which occur on supported metal catalysts or to use it as a basis for deducing the rate parameters for elementary surface reactions. In this paper we report on a study of the kinetics of NO desorption from, and decomposition on, a silica-supported Rh catalyst. TPD spectra were obtained by observing the composition of a helium stream passed through a shallow bed of catalyst as the catalyst temperature was raised in a linear fashion. The rate parameters for individual surface processes were determined by simulation of the observed TPD spectra.

On single-crystal and polycrystalline Rh surfaces, NO adsorbs with a sticking coefficient near unity.¹²⁻¹⁵ Dissociative adsorption predominates at low coverages but becomes less probable as the coverage increases. Infrared studies¹⁶⁻¹⁸ of NO adsorption on silica- and alumina-supported Rh suggest that at room temperature molecular adsorption of NO occurs preferentially.

To date, all TPD studies of adsorbed NO have been carried out with unsupported Rh. In most cases, the primary products observed are NO, N₂, and O₂.¹²⁻¹⁵ The formation of N_2O has also been observed in two of these investigations.^{13,14} Desorption of NO occurs primarily from a single peak, the position of which is independent of coverage. This peak is observed only at high initial exposures. At low initial coverages of NO, dissociation takes place before the desorption temperature is attained and consequently little, if any, NO desorbs from the surface. The principal nitrogen-containing product observed in all studies is N_2 . This species desorbs from two states. A low-temperature peak appears at high initial coverages, the position of which is independent of coverage. A hightemperature peak is found at all coverages. The position of this peak shifts to lower temperatures with increasing initial NO coverage in a manner characteristic of secondorder kinetics. It is generally accepted that the high-temperature peak is due to the recombination of adsorbed nitrogen atoms, but there is disagreement as to the origin of the low-temperature peak. Where N_2O is observed to form, it appears in a single peak, which is positioned in close proximity to the NO peak and the low-temperature N_2 peak. The desorption of O_2 occurs at significantly

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higher temperatures than those at which nitrogen-containing products are observed.

Experimental Section

Apparatus. The apparatus used in the present study has been described previously.^{19,20} The central part of this apparatus is a quartz microreactor, which can be heated at up to 1 K/s. The desorbing gas was swept from the microreactor by a continuous flow of helium. Analysis of the effluent flow was done with a quadrupole mass spectrometer. A microprocessor-based data acquisition system was used to direct the mass spectrometer to a series of preselected masses and to record the signal intensity at each mass setting together with the catalyst temperature. For the conditions of these experiments, the transfer time from the microreactor to the mass spectrometer was less than 1.5 s.

Adsorption isotherms were measured at room temperature for H_2 and NO with a static adsorption apparatus. Gas was added to the sample volume from a fixed dosing volume, and the equilibrium pressure was determined by means of an electronic capacitance manometer.

Materials. A 5% Rh/SiO₂ catalyst was prepared by impregnation of Davison 70 silica with an aqueous solution of RhCl₃·3H₂O. The resulting slurry was dried overnight in air at 378 K. A 30–60 mesh fraction was screened and reduced in flowing hydrogen for 4 h at 623 K. The concentration of Rh surface sites was determined by H₂ chemisorption. The amount of H₂ adsorbed on the freshly reduced catalyst was 73.3 μ mol/g, corresponding to a dispersion of 30.2%. After several TPD experiments, the Rh dispersion declined to 16.4% (38.8 μ mol of H₂/g), but remained constant thereafter.

Helium (99.998%) was purified of oxygen down to about 200 ppb by passage through an Oxyclear (Labclear) filter. Water was removed by a trap filled with Linde 13X molecular sieve and immersed in liquid nitrogen. High-purity H_2 (99.999%) was passed through a Deoxo purifier (Engelhard) to convert any oxygen to water and then passed through a liquid nitrogen cooled trap filled with Linde 13X molecular sieve to remove the water. The static adsorption of NO was carried out with NO (99.0% minimum) purified by passage through a trap filled with Linde 13X molecular sieve immersed in a dry ice-acetone slush. For the TPD studies, NO was adsorbed from a mixture containing 0.32% NO in ultrapure helium. The studies of N_2O desorption were conducted with a mixture containing 440 ppm of N_2O in ultrapure helium.

Experimental Procedure. The procedure for all experiments was similar. A 25-mg sample of the catalyst was placed in the microreactor, and the air in the reactor was evacuated with a mechanical pump. The reactor was then backfilled with helium and reevacuated. This procedure was repeated several times to reduce the oxygen impurity level to below 1 ppm. Next, the catalyst was reduced at 723 K for at least 4 h in pure H₂ flowing at 200 STP cm³/min. Following reduction, the microreactor was evacuated, and the catalyst was heated to 1073 K at 0.25 K/s. The catalyst was then cooled to room temperature while still under vacuum. At this point, the reactor was repressurized with helium.

The adsorption of NO was carried out by passage of pulses of a mixture of 0.32% NO in helium through the catalyst bed. After the desire amount of gas had been adsorbed, the reactor was evacuated for 5 min to remove any gaseous NO. The reactor was then repressurized with



Figure 1. TPD spectra of N₂, N₂O, and NO, following NO adsorption at 295 K. β = 1 K/s.

helium, and the helium flow rate set to 50 STP cm³/min. Heating of the catalyst was now commenced at 1 K/s, and the data acquisition system was activated to initiate analysis of the desorbing gas. Following each TPD experiment, the mass spectrometer was calibrated against helium mixtures containing specified concentrations of NO, N₂, or N₂O.

The absolute rate of desorption was determined in the following manner. To correct for mass spectrometer baseline drift, we normalized the observed intensity for each mass to the intensity of helium, mass 4. The absolute rate of formation of species i, r_i , was then determined from the expression

$$r_i = \frac{(I_{i,\text{obsd}} - I_{i,\text{bg}})}{S_i N_{\text{T}}} \frac{Q}{273R}$$

where $I_{i,\text{obsd}}$ and $I_{i,\text{bg}}$ are the normalized intensities observed for the experiment and background, respectively; S_i is the calibration factor for species i; N_{T} is the total number of surface Rh sites on the sample; and Q is the flow rate of helium at STP.

Results

Static Adsorption. The amount of NO adsorbed at saturation on the silica-supported Rh sample was determined from the NO adsorption isotherm obtained at room temperature. Comparison of this amount with the saturation coverage by H_2 gives an NO/H ratio of 0.92. This suggests that, at saturation, more than 91% of the Rh surface is covered by molecularly adsorbed NO and less than 9% by dissociatively adsorbed NO. The predominance of molecular adsorption is confirmed by independent infrared observations, which show that the room temperature adsorption of NO on a Rh/SiO₂ catalyst produces a major feature at 1660 cm⁻¹, attributable to a negatively charged, linearly adsorbed, nitrosyl species.¹⁶⁻¹⁸ The absence of a NO band at 1910 cm⁻¹ indicates that the surface is not oxidized by dissociative chemisorption of NO.

TPD of NO. Four species were detected during the thermal desorption of adsorbed NO: NO, N₂O, N₂, and O₂. Figure 1 shows the spectra for the nitrogen-containing products obtained following the passage of 30 pulses (1.05)

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Figure 2. TPD spectra of O₂, following NO adsorption at 295 K. β = 0.5 K/s.

cm³) of helium containing 0.32% NO. The spectra for NO and N₂O each exhibit a single narrow peak centered at 445 K. The spectrum for N₂ is composed of narrow peak centered at 450 K and a second broader peak centered between 500 and 550 K. The spectrum for O₂ desorption is shown in Figure 2 and appears as a single, broad peak centered at 1060 K. A heating rate of 0.5 K/s was used to obtain the O₂ spectrum, since the power supply could not maintain a linear temperature ramp up to 1200 K at a heating rate of 1 K/s.

The amount of NO present on the catalyst prior to TPD was determined by summing the integrated TPD spectra for the nitrogen-containing species. An NO coverage of 0.60 was determined by this means, for the adsorption conditions noted in the caption for Figure 1. The distribution of desorbed products based on the number of nitrogen atoms adsorbed as NO is 87.8% N₂, 3.3% NO, and 8.9% N₂O. It is interesting to note that the amount of oxygen which leaves the catalyst surface as O₂ is significantly smaller than the amount corresponding to the oxygen released in the formation of N₂ and N₂O. This suggests that most of the atomic oxygen produced during NO decomposition remains on the catalyst surface or diffuses into the bulk of the Rh microcrystallites.

The amount of dissociatively adsorbed NO present at room temperature was estimated by passing pure CO through the reactor following saturation of the catalyst surface with NO. Introduction of the CO resulted in a small, transient CO_2 signal. It is assumed that the CO_2 observed is produced by the reaction of CO with adsorbed atomic oxygen released upon dissociative adsorption of NO. Integration of the CO_2 transient indicates that approximately 4% of the NO dissociates at room temperature. Complementary infrared experiments indicated that at room temperature none of the adsorbed NO was displaced by CO.

The influence of NO dose on the TPD spectrum for N_2 is illustrated in Figure 3. The dose levels are indicated as fractions of the saturation dose rather than as fractional NO coverages, since as will be discussed below uniform coverage of the catalyst surface could not be achieved in these experiments. The intensity of the low-temperature N_2 peak decreases rapidly with decreasing NO dose, but the peak position is unchanged, as might be expected for first-order kinetics. By contrast, the position of the high-temperature N_2 peak shifts to higher temperatures with decreasing NO dose. This suggests that the process giving rise to the high-temperature peak follows secondorder kinetics. It is also apparent that, with decreasing NO dose, the high-temperature peak accounts for an increasingly larger fraction of the total N_2 signal.



Figure 3. Effect of NO dose on the TPD spectrum of N₂. β = 0.5 K/s.

The NO and N₂O spectra associated with the N₂ spectra shown in Figure 3 rapidly decline in intensity as the NO dose decreases. For the doses corresponding to spectra C through G in Figure 3, the NO and N₂O peaks disappear altogether, and N₂ is the only nitrogen-containing product observed.

Theoretical studies by Chin²¹ indicate that, for the condition of the present experiments, adsorption of NO in the catalyst bed occurs chromatographically. Each of the porous particles making up the bed experiences a wave of adsorption that begins at the exterior surface and propagates to the center of the particle. Particles located near the upstream end of the bed reach saturation coverage earlier than those located farther downstream. As a consequence, for NO doses which only partially saturate the entire bed, gradients in NO coverage are expected both along the axis of the bed and across the radius of each particle.

Several experiments were undertaken to determine whether a more uniform coverage of NO could be achieved by increasing the adsorption temperature to 373 K and by maintaining the catalyst at 373 K for a fixed period prior to the initiation of the temperature ramp. The results of these experiments are illustrated in Figure 4. Adsorption of NO at 373 K and further heating at this temperature for 10 min produces an N₂ spectrum which is virtually the same as that obtained when NO adsorption is carried out at 295 K. The N₂ spectrum changes substantially, though, when the period of annealing at 373 K is increased to 15 min. Spectrum C shows that, relative to spectrum B, the

⁽²¹⁾ Chin, A. A. M.S. Thesis, University of California, Berkeley, CA, 1982.



Figure 4. Effects of NO dose and annealing time on the TPD spectrum of N₂. β = 0.5 K/s.

low-temperature N_2 peak is substantially reduced in intensity and shifted to lower temperature, at the same time that the high-temperature peak is increased in intensity and shifted to higher temperatures. These effects result in a clear resolution of the two peaks. When the period of annealing is increased to 20 min, the low-temperature peak disappears completely, and concurrently the hightemperature peak increases in intensity and shifts to 640 K. Increasing the dose of NO fivefold and the period of annealing to 60 min results in spectrum E. Here again, only a single, high-temperature peak is observed. The intensity of the peak in spectrum E is greater than that in spectrum D, but the peak temperature is lower (i.e., 600 K in spectrum E vs. 640 K in spectrum D).

TPD of N_2O . Figure 5 illustrates the TPD spectra obtained for N_2O and N_2 following a 20-min exposure of the catalyst to a stream containing 440 ppm of N_2O in helium. N_2O desorbs as a sharp peak at 373 K and a broad peak at about 730 K. The N_2 spectrum consists of a single broad peak near 600 K. While the intensity at mass 30 was followed in this experiment, no evidence was found for NO desorption. Based on the integrals of the N_2O and N_2 spectra, it is estimated that roughly 0.04 μ mol of N_2O adsorbed at room temperature. This is equivalent to 0.04 of a Rh monolayer. The very small extent of N_2O adsorption is consistent with the results of infrared studies,¹⁷ which show little evidence for adsorbed N_2O following extended exposure of the catalysts to pure N_2O at room temperature.

Discussion

Model of NO Adsorption and Surface Stoichiometry. The static adsorption results presented here indicate that



Figure 5. TPD spectra of N₂O and N₂, following N₂O adsorption at 295 K. β = 0.5 K/s.

at saturation silica-supported Rh can chemisorb one NO molecule per surface Rh site. A maximum coverage of θ_{NO}^0 = 0.6 was achieved, though, following the passage through the catalyst bed of 30 pulses of helium containing 0.32% NO. Failure to achieve full saturation can be explained in the following manner. NO from the intial pulse is rapidly adsorbed by that portion of the Rh sites present near the surface of the particles, which make up the catalyst bed. Once these sites are saturated, further adsorption can occur only on those sites located deeper within the catalyst particles. Thus, the adsorption of NO can be envisioned to proceed as a wave into the interior of the particles, as more and more pulses of the adsorbate are passed through the bed. If the pulses of gas are too small, a point can be reached where the time during which the pulse is present in the bed becomes shorter than the time needed for diffusion of adsorbate into the internal recesses of the particles. When this happens, the diffusion front does not reach the center of the particle before the pulse exits the bed. Since each pulse is followed by a period of a few seconds, during which the flow of helium through the bed is free of adsorbate, the NO accumulated in the catalyst pores diffuses back out of the particles. As a consequence of these effects it becomes difficult to saturate those sites present near the center of the largest particles in the bed. Rough estimates of the pulse residence time and the diffusion time for the circumstances of the present experiments indicate that particles with diameters larger than the average value of 0.04 cm may not have achieved saturation coverage by NO near the center of the particles for the conditions used in the present experiments.

The extent of NO dissociation upon adsorption was estimated to be roughly 4% for the experiment shown in Figures 1 and 2. This level must be regarded as a lower limit since it is not certain that CO would remove all of the atomically adsorbed oxygen formed upon dissociative adsorption of NO. The observation of a low level of dissociative adsorption is consistent, though, with recent infrared studies,¹⁷ which indicate that the proportion of molecularly adsorbed NO present on a Rh/SiO₂ catalyst, following exposure to a few torr of NO at 298 K, is close to 100%. It is also of interest to note that Campbell and White¹² have estimated that for saturation NO coverage on a Rh wire, at 330 K, approximately 85% of the NO adsorbed is present as molecular NO, and the remaining 15% is dissociatively adsorbed.

Comparison with Previous Studies. The TPD spectra presented in Figures 1–4 bear many similarities to those reported previously for unsupported Rh.^{12–15} For example, the desorption of molecular NO is observed only when the initial NO coverage approaches the saturation level. This pattern can be ascribed to the fact that, at low coverages, dissociation of NO occurs upon both adsorption and desorption. As was noted above, it appears that the extent of NO dissociation upon adsorption onto silica-supported Rh is small and, hence, that the majority of NO dissociation from such a catalyst must occur during TPD.

The N₂ TPD spectra reported here and those obtained previously for unsupported Rh¹²⁻¹⁵ show clear evidence for two peaks and the increasing dominance of the high-temperature peak as the NO coverage is reduced. Campbell and White¹² attributed the high-temperature peak to the recombination of nitrogen atoms via the process $2N_s \rightarrow$ $N_2 + 2S$. This interpretation was based on the close agreement of the peak temperature with that for the N_2 peak observed in the TPD spectrum of adsorbed atomic nitrogen. Two explanations were offered for the appearance of a low-temperature N_2 peak at high NO coverages. The first is that during TPD a significant proportion of the energy released upon the dissociation of molecularly adsorbed NO remains in the nascent nitrogen atom. The higher translational energy associated with such an atom would increase its probability of finding another adsorbed nitrogen atom with which to react and produce N₂. The second explanation is that the low-temperature peak is due to the reaction of an adsorbed nitrogen atom with an adsorbed NO molecule. This process can be represented by the reaction $N_a + NO_a \rightarrow N_2 + O_a + S$. Castner and Somorjai^{13,14} and Baird et al.¹⁵ have also ascribed the high-temperature N2 peak to the recombination of atomic nitrogen, but these authors offer no mechanistic interpretation for the low temperature peak.

The data presented in Figure 4 show that only a hightemperature N_2 peak is observed when a small amount of NO is adsorbed at 373 K and then heated at this temperature for 20 min or more. Heating the adsorbed NO for shorter time results in the observation of both N_2 peaks. These experiments can be interpreted in the following manner. The initial adsorption of NO is into a molecular state and, because of the high sticking coefficient of NO, the Rh crystallites present near the exterior of the Rh/SiO_2 particles are essentially saturated. With heating, more and more of the initially adsorbed NO desorbs and migrates into the interior of the porous catalyst pellets. Since the surface of the Rh crystallites in the pellet interior are largely vacant, NO dissociation can occur quite readily. If the period of heating at 373 K is sufficient, than all of the molecularly adsorbed NO will dissociate. Subsequent elevation of the catalyst temperature will then produce a single N_2 peak attributable to the recombination of the adsorbed N atoms. The shift of the high-temperature peak to lower temperatures with increasing NO dosage is consistent with the assignment of this peak to a process which is second order in the coverage by atomic nitrogen.

The low-temperature N_2 peak observed with both supported and unsupported Rh is probably best attributed to the reaction of atomic nitrogen with adsorbed NO. This interpretation is supported by the spectra shown in Figure 4, which demonstrate that a low-temperature peak is observed only in those cases where a portion of the originally adsorbed NO remains in the molecular state. Recent

steady-state rate measurements of NO reduction by CO and H₂ over a Rh/SiO₂ catalyst also suggest that N₂ is formed by the process N_a + NO_a \rightarrow N₂ + O_a + S.²² Neither Campbell and White¹² nor Baird et al.¹⁵ ob-

served the formation of N₂O during the thermal decomposition of adsorbed NO. Two N₂O peaks were observed, though, by Castner and Somorjai in studies carried out with Rh(331) and Rh(S)–[6(111)×(100)] surfaces.^{13,14} The high-temperature peak was attributed to reactions involving dissociated NO and the low-temperature peak to reactions involving molecularly adsorbed NO. In the present study, the N₂O peak appears at the same temperature as the NO peak, which is slightly lower than the temperature of the low-temperature N_2 peak. The fact that N₂O is observed only under conditions where NO desorption occurs concurrently suggest that the formation of N_2O is related to the presence of molecularly adsorbed NO. A possible mechanism for the formation of N_2O is the reaction $N_a + NO_a \rightarrow N_2O + 2S$. The occurrence of such a reaction has also been inferred from studies of the kinetics of NO reduction over Rh/SiO₂.²²

The position of the O_2 peak, shown in Figure 2, agrees closely with that observed by Campbell and White¹² and Baird et al.¹⁵ in the TPD spectrum of NO for polycrystalline Rh wire and a Rh(110) surface, respectively. Similar peaks have been reported for O_2 desorption from Rh(111), Rh(331), and Rh(S)–[6(111)×(100)] surfaces.^{13,14,23} These latter studies clearly indicate that this peak is consistent with second-order kinetics and can be ascribed to the recombination of atomically adsorbed oxygen.

Kinetics of NO Desorption and Decomposition. The discussion presented in the preceding section suggests that the desorption and decomposition of NO can be represented by the following set of elementary processes.

$$NO + S \rightarrow NO_{a}$$
 (1)

$$NO_a \rightarrow NO + S$$
 (2)

$$NO_a + S \rightarrow N_a + O_a \tag{3}$$

$$NO_a + N_a \rightarrow N_2O + 2S$$
 (4)

$$NO_a + N_a \rightarrow N_2 + O_a + S \tag{5}$$

$$N_a + N_a \rightarrow N_2 + 2S \tag{6}$$

The desorption of NO is assumed to be reversible. Under the conditions of the present experiments, the partial pressures of NO will be sufficiently large for rapid readsorption of NO to occur. The remaining processes, reactions 3–6, are taken to be irreversible. The desorption of oxygen is neglected, since no O_2 is formed in the temperature range in which nitrogen-containing products are observed. The readsorption of N_2O is also neglected on the basis of the TPD experiments shown in Figure 5, which indicate that N_2O adsorbs very weakly on silica-supported Rh.

Reactions 1–6 were used to develop a theoretical representation of the kinetics for the formation of the nitrogen-containing products during the TPD of NO. The catalyst is treated as a uniform bed through which the carrier gas moves in plug flow. Because the concentrations of the gaseous species are small, it is assumed that the average gas concentration within the voids of the bed and the catalyst particles is given by $\bar{C}_i = (C_i^{(i)} + C_i^{(o)})/2$, where $C_i^{(i)}$ and $C_i^{(o)}$ are the concentrations of species *i* at the inlet

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 TABLE I: Parameters Used for Simulation of TPD Spectra

$\beta = 1.0 \text{ K/s}$	$Q = 0.833 \text{ cm}^3/\text{s}$
$\epsilon = 0.40$	$v = 0.066 \text{ cm}^3$
$\rho_{\rm b} = 0.38 {\rm g/cm^3}$	$\sigma = 7.52 \times 10^{-16} \text{ cm}^2/\text{Rh}$ site
$N_{\rm T}$ = 3.88 μ mol	$s_1 = 1.0$

and outlet of the reactor. The diffusion of gas through the pores present in the individual catalyst particles can be neglected, based on an analysis of the intraparticles diffusion problem presented by Chin^{21} and Rieck and Bell.²⁴

The conservation of species in the gas phase and adsorbed on the catalyst surface are expressed by

$$\frac{\mathrm{d}\bar{C}_i}{\mathrm{d}t} = \frac{Q}{\epsilon V} (C_i^{(i)} - C_i^{(o)}) + \frac{\rho_{\mathrm{b}} N_{\mathrm{T}}}{\epsilon} \sum_j \nu_{ij} r_j \qquad (\mathrm{I})$$

$$\mathrm{d}\bar{\theta}_i/\mathrm{d}t = \sum_j \nu_{ij} r_j \tag{II}$$

where $\bar{\theta}_i$ represents the average fractional coverage by species *i*. Definitions for the remaining quantities appearing in eq I and II are given in the Nomenclature section.

The form of r_j depends on the nature of the *j*th step. The rate of NO adsorption is described by

$$r_1 = k_1 \bar{C}_i (1 - \sum \bar{\theta}_i) \tag{III}$$

where

$$k_1 = s_1 \sigma (RT / 2\pi M_i)^{1/2}$$
 (IV)

For desorption processes, such as reactions 2 and 6, r_j is expressed as

$$r_j = k_j \bar{\theta}_i^n$$
 $n = 1 \text{ or } 2$ (V)

where

$$k_j = k_j^0 \exp(-E_j/kT) \tag{VI}$$

And for a Langmuir-Hinshelwood reaction between dissimilar adspecies, r_j is given by

$$r_j = k_j \bar{\theta}_i \bar{\theta}_k \tag{VII}$$

Equation VII is used to describe k_j for this type of process as well.

The initial conditions for eq I-III are

$$\bar{C}_i = 0$$
 for all i (VIII)

$$\bar{\theta}_1 = \theta_{\rm NO}^{(0)} \qquad (\rm IX)$$

$$\bar{\theta}_{i\neq 1} = 0 \tag{X}$$

where $\theta_{NO}^{(0)}$ is the initial coverage of the Rh surface by molecularly adsorbed NO.

The temperature of the catalyst bed is assumed to be uniform spatially and to increase with time according to

$$T = T_0 + \beta t \tag{XI}$$

Equations I and II, together with the initial conditions given by eq VIII-X, were solved numerically using a Gear-Hindmarsh algorithm.²⁵ The computed values of concentrations of NO, N₂O, and N₂ at the reactor inlet were then used to determine the rate of appearance of each species as a function of the catalyst temperature. Values for the fixed parameters and variables used in these calculations are given in Table I.

TPD spectra for NO, N_2O , and N_2 generated from the solutions to eq I and II for a fixed set of rate parameters were compared with the spectra obtained experimentally,



Figure 6. Comparison of simulated and observed TPD spectra for N₂, N₂O, and NO. $\theta_{NO}^{0} = 0.6$; $\beta = 0.5$ K/s.

FABLE II :	Rate	Parameters	for	Elementary	Steps
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$k_1^0 = 5 \times 10^{-13} T^{1/2} \text{ cm}^3 \text{ s}^{-1}$	$E_1 = 0$
$k_{2}^{0} = 1 \times 10^{15} \text{ s}^{-1}$	$E_2 = 23.7 \text{ kcal/mol}$
$k_3^{0} = 1 \times 10^3 \text{ s}^{-1}$	$E_3 = 8.0 \text{ kcal/mol}$
$k_{a}^{0} = 1 \times 10^{7} \mathrm{s}^{-1}$	$E_4 = 18.5 \text{ kcal/mol}$
$k_{s}^{70} = 8 \times 10^{7} \mathrm{s}^{-1}$	$E_s = 18.5 \text{ kcal/mol}$
$k_6^{0} = 1 \times 10^9 \mathrm{s}^{-1}$	$E_{6} = 22.5 \text{ kcal/mol}$

shown in Figure 1. The values of the preexponential factor and the activation energy associated with each rate coefficient, k_i (j = 1-6), were varied until the peak temperature and area of the predicted spectrum for each component agreed with the corresponding characteristics of the observed spectrum. The closest agreement between simulation and experiment achieved in this fashion is shown in Figure 6. The rate parameters used for the simulation are given in Table II. It is apparent that the spectra for NO and N₂O obtained from theory are in reasonably close agreement with those observed experimentally. The area of the simulated N_2 spectrum and the positions of the two peaks at which it is made up are also in good agreement with experimental observations, but the shape of the N_2 spectrum is not. As can be seen in Figure 6, the low-temperature component of the simulated N₂ spectrum is too large, but appears to have the correct ratio of height to width. On the other hand, the height of the high-temperature N_2 peak generated from theory is in good agreement with that seen experimentally, but is narrower. Attempts to improve the appearance of the simulated N_2 spectrum were not successful, and it was found that variations in the rate parameters away from the values given in Table II resulted in worsening of the overall agreement between theory and experiment.

The preexponential factor and activation energy for NO desorption, given in Table II, are 1×10^{15} s⁻¹ and 23.7 kcal/mol, respectively. Both parameters are in very close agreement with those reported by Savatsky.¹⁷ From the interpretation of isothermal desorption measurements, Savatsky determined $k_2^0 = 1.2 \times 10^{15}$ s⁻¹ and $E_2 = 25$ kcal/mol. The value of E_2 reported in Table II is also in good agreement with the observation of Castner and Somorjai.^{13,14} Based upon the peak maximum temperature observed in their NO spectra, and an assumed preexponential factor of 10^{13} s⁻¹, they determined the activation energy for NO desorption to be 30 kcal/mol for a Rh(331) surface and 26 kcal/mol for the majority of NO desorbing

⁽²⁴⁾ Rieck, J. S.; Bell, A. T. J. Catal., in press.

⁽²⁵⁾ Hindmarsh, A. "Gear: Ordinary Differential Equation Solver", UDID-3001, REV. 1, Aug 20, 1972.

from a Rh(S)-[6(111)×(100)] surface. If one assumes that the preexponential factor is 10^{15} s⁻¹, rather than 10^{13} s⁻¹, each of these values is decreased by 4 kcal/mol, making the agreement with the present results even better. It is also of interest to note that the preexponential factor for NO desorption reported here is in rough agreement with the value of $1 \times 10^{16\pm0.5}$ s⁻¹ reported by Gorte and Schmidt²⁶ for the desorption of NO from (111), (110), and (100) planes of Pt.

Since there have been no previous measurements of the rate parameters for reactions 3-6, it is difficult to determine whether the values given in Table II are physically correct or not. The preexponential factor for reaction 3 is quite small, 10^3 s^{-1} . It is hard to see how this magnitude could be explained by purely entropic effects. The only alternative explanation is that a very small fraction of the total Rh sites participate in NO dissociation. By contrast the preexponential factors for reactions 4-6 are roughly in the order of magnitude expected for second-order surface reactions, as predicted by Baetzold and Somorjai.²⁷ It should be noted, though, that in arriving at their estimates, Baetzold and Somorjai assumed that only 10⁻³ of the total sites are catalytically active.

Conclusions

The present investigation shows that at room temperature the adsorption of NO onto silica-supported Rh occurs primarily into a molecular state. From static adsorption measurements, it is estimated that no more than 9% of the adsorbed NO is dissociated. A lower limit of 4% dissociative adsorption is determined from measurements of the amount of atomic oxygen present on the catalyst surface following NO adsorption. By contrast to NO, N_2O adsorbs to only a very limited degree of Rh/SiO_2 .

Adsorbed NO undergoes extensive decomposition when the catalyst is heated to obtain a TPD spectrum. The primary nitrogen-containing species observed is N₂. Small amounts of NO and N_2O are also observed, provided that the initial coverage by NO is large. O_2 also desorbs from the catalyst, but at temperatures well above these where nitrogen-containing species are formed. The TPD spectra for NO desorption from, and decomposition on, Rh/SiO_2 are qualitatively similar to those reported for unsupported Rh. Two overlapping peaks are found for N_2 . The response of these peaks to the manner and extent of NO adsorption suggests that the low-temperature peak is due to the process $N_s + NO_s \rightarrow N_2 + O_s + S$, and that the high-temperature peak is due to the process $2N_s \rightarrow N_2 +$ 2S. The small N_2O peak which occurs at the same tem-

perature as the low-temperature N_2 peak is ascribed to the process $N_s + NO_s \rightarrow N_2O + 2S$.

A theoretical model has been developed to describe the kinetics for the formation of nitrogen-containing species, during TPD. By adjusting the rate parameters associated with the model, a reasonable representation of the observed TPD spectra is achieved. The preexponential factor and activation energy for NO desorption obtained by this means are in good agreement with previous estimates for Rh/SiO_2 and Pt single crystal surfaces. The balance of the rate parameters determined from the fitting procedure cannot be compared with previous measurements, since none have been reported. Comparison of the preexponential factors reported here with those estimated from absolute rate theory by Baetzold and Somorjai²⁷ suggest that with the exception of the preexponential factor for NO dissociation, the present values are physically reasonable. The preexponential factor determined for NO dissociation is a good deal smaller than that estimated from absolute rate theory. It is suggested that this might be explained by the fact that only a fraction of the total sites present on the catalyst surface have the capacity to dissociate NO.

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- gas-phase concentration of species i, mol/cm³
- $C_i \\ E_j$ activation energy for elementary step j, kcal/mol I_i intensity of mass spectrometer signal for species i. A
- k_i rate coefficient for elementary step j, s⁻¹ or cm³ $mol^{-1} s^{-1}$
- k_i^0 preexponential factor for elementary step i, s⁻¹ or cm³ mol⁻¹ s⁻¹
- M_i mass of species i, g
- N_{T} total number of Rh surface sites
- Q volumetric flow rate of helium carrier gas, STP cm³/s
- gas constant, atm cm 3 mol $^{-1}$ K $^{-1}$ R
- experimentally observed rate of formation of r_i species i, s^{-1}
- S_i calibration factor for species i, A/atm
- initial sticking coefficient for NO
- T^{s_1} temperature, K
- t time, s V
 - catalyst bed volume, cm³
- β heating rate, K/s ŧ
 - catalyst bed void fraction
- stoichiometric coefficient for species i in elementary v_{ij} step j
- catalyst bed density, g/cm³ $\rho_{\rm b}$
- area per Rh site, cm² σ
- θ_i fractional coverage of sites by species i
- Registry No. NO, 10102-43-9; Rh, 7440-16-6.

⁽²⁶⁾ Gorte, R. J.; Schmidt, L. D. Surf. Sci. 1981, 109, 367.

⁽²⁷⁾ Baetzold, R. C.; Somorjai, G. A. J. Catal. 1977, 45, 94.