

Transient Kinetic Studies of the Catalytic Reduction of NO by CO on Platinum

B. A. BANSE, D. T. WICKHAM, AND B. E. KOEL

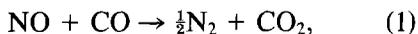
Department of Chemistry and Biochemistry and the Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Campus Box 449, Boulder, Colorado 80309-0449

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Transient kinetic experiments were performed in order to study the catalytic reduction of NO by CO over a polycrystalline platinum surface. The experiments were performed by preadsorbing one reactant on the Pt surface at the reaction temperature and then rapidly introducing the second reactant in a pressure jump while monitoring the transient production of CO₂. The CO₂ production rate, R_{CO_2} , was modeled as a function of NO and CO coverages (θ_{NO} and θ_{CO}). When NO was preadsorbed, the reaction rate can be described by $R_{\text{CO}_2} = k\theta_{\text{NO}}\theta_{\text{CO}}$ (for the onset of the reaction) and $R_{\text{CO}_2} = k'\theta_{\text{NO}}\theta_{\text{free sites}}$ (for the final portion). The onset of CO₂ production showed no detectable induction period in these experiments. When CO was preadsorbed, the reaction rate is described by $R_{\text{CO}_2} = k''\theta_{\text{NO}}\theta_{\text{free sites}}$ (for the onset of the reaction) and $R_{\text{CO}_2} = k'''(\theta_{\text{CO}})^2$ (for the final portion). For CO preadsorption, a time delay in the onset of CO₂ production which varied with temperature and the initial amount of preadsorbed CO was observed. Our transient kinetic results indicate that the reaction proceeds over a wide range of reaction conditions via a dissociative mechanism in which NO_(a) first dissociates into N_(a) and O_(a), and then O_(a) reacts with CO_(a) to form CO₂. © 1989 Academic Press, Inc.

I. INTRODUCTION

The fundamental catalytic aspects of the reaction of nitric oxide (NO) and carbon monoxide (CO) on various metal single-crystal surfaces, especially rhodium and platinum, have been the topic of much research in recent years (1–14). The reaction between NO and CO,



is a fundamentally important oxidation reaction since it is slightly more complicated than the classic oxidation reaction between CO and O₂. The added complexity of reaction (1) is due to the formation of an additional product which could inhibit the reaction and to the more likely reaction of the reactants through either a bimolecular or a dissociative pathway. In addition, the study of this reaction has practical importance because of continued interest in improving the

performance of automotive catalytic converters.

The mechanism of nitric oxide reduction on Pt has been studied and different mechanisms which depend upon the surface structure and reactant conditions used in the experiments have been proposed. Studies using Pt (111) have shown almost no activity for reaction (1) (7), while Pt (100) has been shown to be very active (6, 8, 11). Pt (410) has shown unique behavior, dissociating both NO and CO under UHV conditions (5, 12). Nitric oxide reduction has also been studied under some conditions on polycrystalline Pt, which is of more practical interest, since working catalysts are obviously composed of microcrystallites. Klein *et al.* (13) studied the steady-state kinetics of reaction (1) using pressures between 1 and 10⁻⁸ Torr and proposed that the reaction occurred via the bimolecular mechanism, in which the surface reaction

between molecular NO and CO is the rate-limiting step. However, Aldoch *et al.* (14) used total reaction pressures ranging from 1.75×10^{-4} to 4.2×10^{-3} Torr and found evidence for the dissociative mechanism in which NO dissociation to produce adsorbed O atoms is the rate-limiting step. According to a recent review, the majority of the literature suggests that at low pressures the dissociative mechanism dominates (15). However, this reaction has not been investigated using a transient titration technique.

Kinetic studies utilizing transient methods are very useful for providing mechanistic information. An extensive review which discusses a variety of transient techniques including the pressure jump transient technique like that used in this paper, temperature-induced transients, and molecular beam techniques, has been published recently (16). The objective of this paper is to investigate the kinetics of the NO + CO reaction by a transient titration technique and model these results in order to differentiate between the bimolecular and the dissociative mechanisms for the catalytic reduction of NO by CO over Pt. The titration technique is a powerful probe of reaction kinetics, since it allows the reaction rate to be measured as a function of reactant coverage. Thus, the rate laws can be expressed in terms of reactant surface coverages rather than partial pressures, and the kinetic effects of reactant adsorption are transparent to the analysis.

II. EXPERIMENTAL

The apparatus used in these experiments has been described in detail previously (17). The 1.3-L reaction chamber was continuously pumped, and therefore, the reaction rate is directly proportional to the CO₂ partial pressure (above background) as measured by a quadrupole mass spectrometer. The areas under the pressure vs. time profiles could be accurately converted into units of molecules per square centimeter on the surface by using the system volume,

pumping speed, and mass spectrometer sensitivity for the gas of interest. All coverages were calculated relative to the Pt substrate using the Pt atom density of 1.5×10^{15} cm⁻². The pumping speeds for CO₂, CO, NO, and N₂ were measured using the standard decay method.

The polycrystalline platinum foil (12.0 × 14.0 × 0.1 mm, 99.998% purity) was mounted in a manner previously described (17). Carbon monoxide (99.99%, research grade, Scientific Gas Products) was used without additional purification. Nitric oxide (99%, CP grade, Scientific Gas Products) was purified by passing it through a silica gel trap cooled in a dry ice/methanol bath prior to use.

Initial cleaning of the platinum foil consisted of heating to 1050 K in 2×10^{-6} Torr O₂ for 15 h, followed by treatment in 2×10^{-6} Torr NO₂ for 4 h at 1150 K. In addition, the sample was also cleaned in 2×10^{-6} Torr NO₂ for about 30 min before experiments each day. Temperature programmed desorption (TPD) of CO was used to verify that the surface was free from contamination. After cleaning, the CO TPD spectra agreed well with those obtained by Winterbottom (18) and Collins and Spicer (19).

The titration technique and data analysis used in these experiments is similar to that used by Bonzel and Ku for the reaction between CO and preadsorbed oxygen on Pt (110) (20). In our studies, one reactant (either CO or NO) was adsorbed on the surface at the constant reaction temperature. After the chamber was evacuated, the titrant was introduced into the system by way of a pressure jump. The partial pressures of N₂ (28 amu), CO (28 amu), NO (30 amu), and CO₂ (44 amu) were monitored with the mass spectrometer as a function of time. N₂ was differentiated from CO by monitoring the 14 amu signal. When the CO₂ pressure was below measurable detection (less than 2×10^{-8} Torr, corresponding to a rate of 2×10^{-4} CO₂ molecules (Pt atom · s)⁻¹), the chamber was evacuated

and the Pt temperature was increased at 11 K s^{-1} while monitoring the above masses. We attribute the 44 amu signal to CO_2 and not N_2O molecules because of coadsorption experiments done by Lambert and Comrie (21) and steady-state experiments done by Aldoch and Lintz (14). Both of these studies used isotopic labeling experiments to conclude that CO_2 is the major product formed in reaction (1) on polycrystalline Pt.

A background experiment in which the titrant pressure jump was induced for an inert surface was also performed at each temperature. The CO_2 and titrant signals were monitored as a function of time with the mass spectrometer. This titrant signal was used as a pressure-response curve for determining the amount of titrant adsorbed or reacted during the titration, similar to the way that uptake is measured on a clean surface. The method for calculating coverages

from these profiles can be found in a variety of papers by White and co-workers (16, 22, 23).

A material balance calculation was performed as a check for the accuracy of the coverage determination. The total number of titrant molecules (either CO or NO) was calculated directly using the titrant signal during the titration and the post-titration TPD. This number of molecules was then compared to the number of titrant molecules calculated indirectly using the CO_2 signal from the titration and post-titration TPD, assuming the appropriate stoichiometry of reaction. These values agreed within 20%. The total number of preadsorbed molecules was calculated indirectly by using the CO_2 signal from the titration and post-titration TPD and assuming the appropriate stoichiometry of reaction. These values for the initial coverage of the preadsorbate,

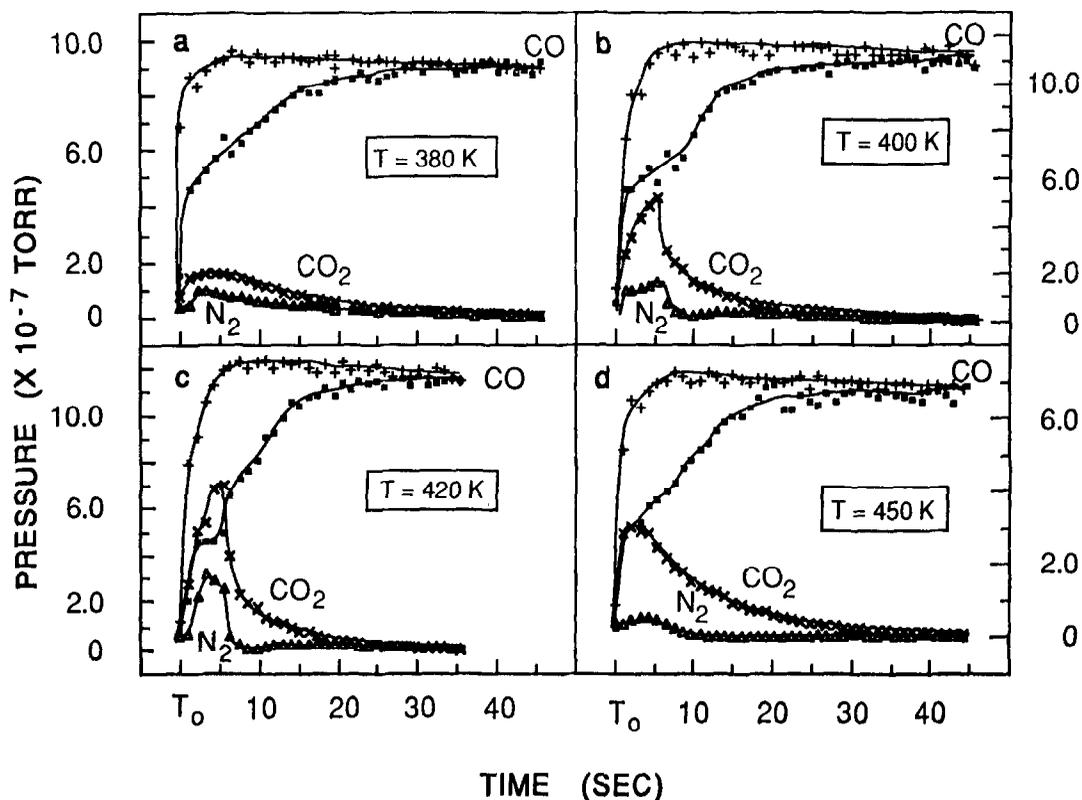


FIG. 1. The CO (+ and ■), CO_2 (×), and N_2 (Δ) signals monitored in the transient experiment where preadsorbed NO was titrated by CO at (a) 380 K, (b) 400 K, (c) 420 K, and (d) 450 K.

calculated using the titration data, were in reasonable agreement with initial coverage values obtained by comparison of the TPD areas from the reaction temperature exposure (30 L) to TPD areas from the saturation exposure (30 L) at 120 K.

III. RESULTS

A. Titration of NO by CO

A series of titration experiments, shown in Fig. 1, in which Pt was preexposed to 30 L of NO at selected reaction temperatures (380, 400, 420, and 450 K) followed by the introduction of CO was carried out. The initial surface coverages of NO in these experiments (referenced to the Pt atom surface density) were 0.10, 0.10, 0.090, and 0.070 at 380, 400, 420, and 450 K, respectively. These initial coverages were 0.34, 0.34, 0.31, and 0.24 when calculated relative to the saturation coverage obtained by a 30-L NO exposure at 120 K. In the titration experiments, signals at 14, 28, and 44 amu were monitored with the mass spectrometer as a function of time. Two major corrections were needed in order to process the raw data collected. First, the contribution of N₂, also a product molecule in reaction (1), to the 28 amu signal was determined by monitoring mass 14. After correction for the relative sensitivities of CO and N₂, the N₂ pressure was subtracted from the 28 amu signal, leaving an accurate CO pressure vs time profile. Second, the background CO₂ signal, resulting from CO introduction, was obtained by measuring the CO₂ pressure during the appropriate pressure jump for an inert sample surface. In Fig. 1, the system response for CO pressure on an inert sample surface (+) is superimposed on the CO (■), N₂ (Δ), and CO₂ (×) signals during a titration experiment. As mentioned in Section II, the pressure-vs-time signals for these molecules can be converted to number of molecules by using the system volume and pumping speeds of the molecules. Since the pumping speeds are not equal for each molecule, the relative

areas under the pressure–time profiles in Fig. 1 should not necessarily reflect the stoichiometry of the reaction until the pumping speeds are considered.

Figure 1c shows titration data at 420 K, where the maximum pressure of CO₂ is observed. This pressure is proportional to the rate of reaction (1). At T_0 , when the CO pressure jump is initiated, the CO₂ pressure increases rapidly. The reaction rate increases to a maximum and then shows a sudden decrease. Thus, there is no detectable induction time for the production of CO₂. After approximately 35 s the reaction rate is below measurable detection. The CO signal initially increases rapidly and then remains relatively constant over the range of maximum CO₂ production (from 3 to 5 s). When CO₂ production decreases, the CO partial pressure gradually increases up to a constant value. TPD at the conclusion of the titration indicates that approximately 14% of the NO does not react at 420 K.

Figure 1b shows titration profiles obtained at a Pt temperature of 400 K. The CO₂ signal is very similar in shape to the CO₂ signal at 420 K discussed above; however, the maximum pressure is only 5.0×10^{-7} Torr, approximately 80% of the maximum pressure observed at 420 K. Again, there is no induction time for CO₂ production. The reaction rate, as monitored by the CO₂ signal, shows a sudden decrease immediately following the peak maximum, followed by a slower decrease. The post-titration TPD reveals that approximately 16% of the NO does not react.

Figures 1a and 1d show the titration data for Pt temperatures of 380 and 450 K, respectively. The overall shape of the CO₂ production transient differs from those described at 400 and 420 K in that a more gradual decrease in CO₂ pressure is observed immediately after the peak maximum. The post-titration TPD shows that 25% of the NO has not reacted after 45 s at 380 K, and about 12% of the NO has not reacted after 52 s at 450 K.

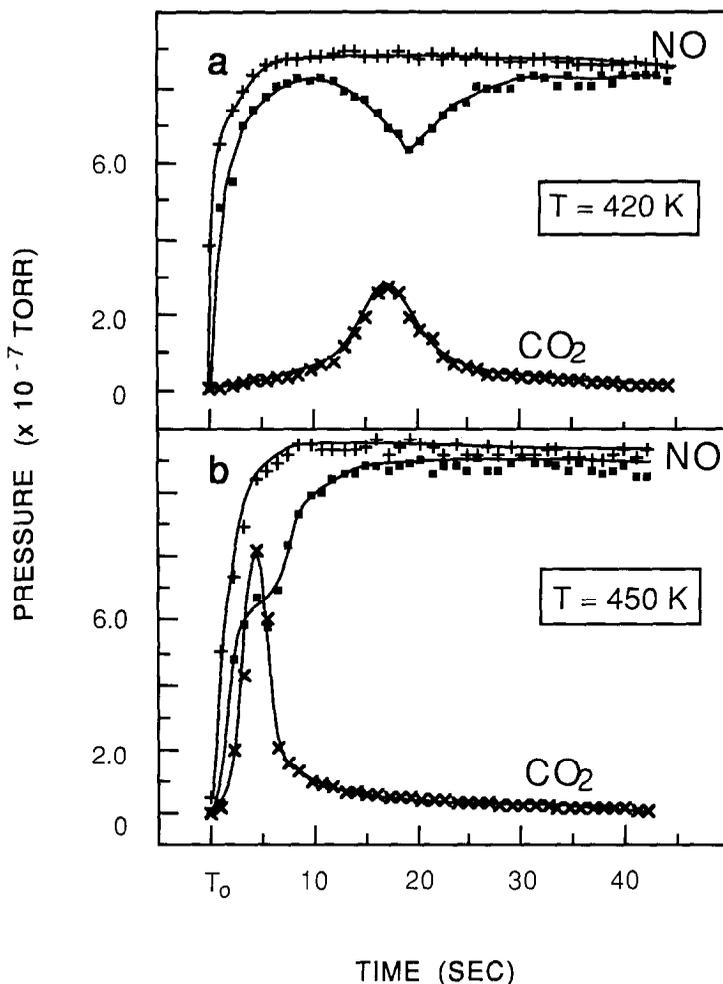


FIG. 2. The NO (+ and ■) and CO₂ (x) signals monitored during the titration of preadsorbed CO by NO at (a) 420 K and (b) 450 K.

B. Titration of CO by NO

Another series of experiments was performed where CO was preexposed to the surface followed by a jump in NO pressure. Figures 2a and 2b show titration data from a 30-L preexposure of CO at 420 and 450 K, which resulted in initial CO coverages of 0.10 and 0.090, respectively (referenced to the Pt atom surface density). These initial coverages were 0.41 and 0.33 when calculated relative to the saturation coverage obtained by a 30-L exposure at 120 K. The reaction profile at 420 K, in Fig. 2a, is markedly different from those observed

when NO was preadsorbed. The CO₂ signal shows only a slight increase initially and then reaches a maximum of 2.8×10^{-7} Torr after 18 s. This induction time is not seen when NO is preadsorbed. The titrant (NO) signal (■) also shows little variation initially from the system response curve (+), increasing almost immediately, and then decreasing when the rate of CO₂ production begins to increase. The post-transient TPD shows that 50% of the preadsorbed CO does not react during the NO titration measurement.

Figure 2b shows the data for a Pt temperature of 450 K, where the maximum CO₂

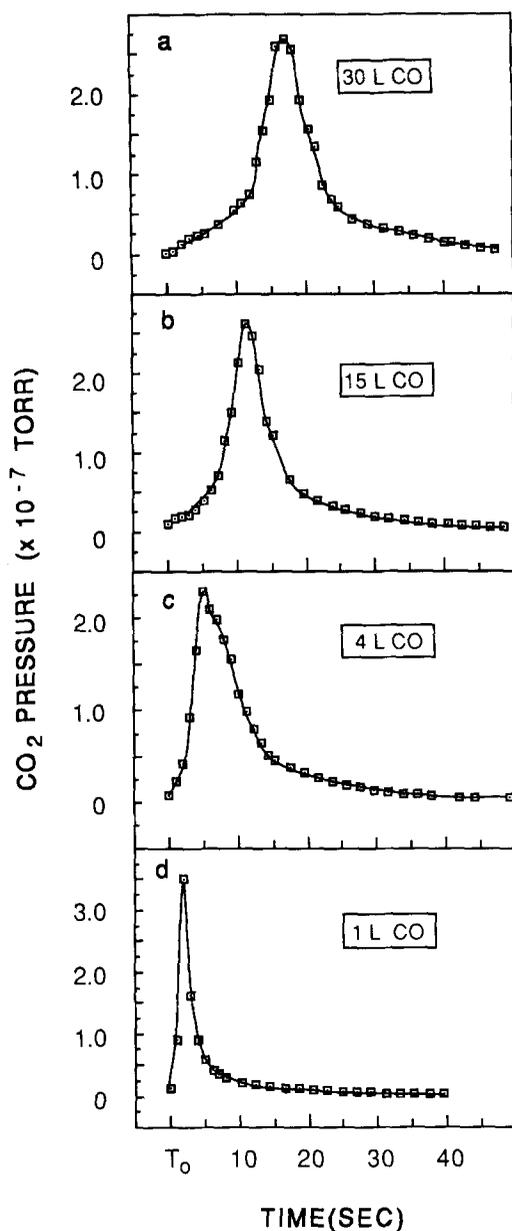


FIG. 3. The CO₂ production rate at 420 K following CO preexposures varying between 1 and 30 L.

rate was observed. The CO₂ induction time has diminished to about 1 s and the reaction is complete after 10 s. After this transient experiment, 25% of the preadsorbed CO was unreacted.

The previous results show that the induction time for the onset of reaction (1) is a function of reaction temperature. Figure 3

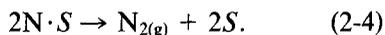
shows that this induction time is also a function of the initial CO coverage. Titration profiles following 30-L, 15-L, 4-L, and 1-L CO exposures at 420 K are shown in Figs. 3a, 3b, 3c, and 3d, respectively. These figures show that the induction time is shifted from 20 s to about 5 s as CO exposure is decreased from 30 L to 1 L.

IV. DISCUSSION

A. General Discussion of Mechanisms for the Reaction between NO and CO

We first discuss two general mechanisms through which the NO + CO reaction is likely to take place. The results of modeling the experimental titration curves using the rate laws derived from these mechanisms are discussed in the next section. All of the data for the titration experiments were analyzed assuming a Langmuir-Hinshelwood (LH) type of mechanism, where the reaction occurs between CO and NO adsorbed on the surface, since current literature suggests that the NO reduction reaction takes place between surface reactants (15). Also, an Eley-Rideal (ER) mechanism, by which one reactant on the surface reacts with a gas phase reactant molecule to form the product, did not fit our CO₂ production curves for either the CO or the NO titration experiments. Two possible mechanisms and their corresponding rate laws are discussed here: the bimolecular mechanism involving the direct reaction between coadsorbed CO and NO molecules, and the dissociative mechanism where CO₂ formation occurs via the reaction between coadsorbed CO and O atoms that are liberated by NO dissociation.

Bimolecular reaction mechanism. The bimolecular reaction mechanism has been found to fit data for steady-state kinetic studies at high pressures, as mentioned in the introduction (13). The following elementary steps would result if the mechanism of CO₂ formation proceeded through a direct bimolecular reaction between CO and NO (where $\cdot S$ denotes a surface site):

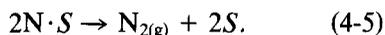


If step (2-3) is rate determining, the resulting rate law would be

$$R_{\text{CO}_2} = k\theta_{\text{NO}}\theta_{\text{CO}}. \quad (3)$$

Since our titration experiments allow us to measure changes in θ_{NO} and θ_{CO} , we can evaluate the contribution of this mechanism directly.

Dissociative mechanism. The dissociative mechanism was proposed by Bell and co-workers on supported catalysts (24, 25). It has also been shown to fit steady-state data (14) under conditions different from those used by Klein *et al.* (13). If the dissociation of NO were necessary for the reaction between CO and NO to proceed, the following elementary steps would result:



If NO dissociation (step (4-3)) is the rate-determining step, the rate law would have the form

$$R_{\text{CO}_2} = k'\theta_{\text{NO}} \cdot S. \quad (5)$$

The number of free sites is calculated from the data using the expression $\cdot S = \theta_{\text{free sites}} = (S_{\text{T}} - \theta_{\text{NO}} - \theta_{\text{CO}})$, assuming that the residence time for both N_2 and CO_2 at the reaction temperature is small. S_{T} is equal to the total number of reactive sites.

However, if step (4-4) above is rate determining, the resulting rate law would have the form

$$R_{\text{CO}_2} = k''\theta_{\text{CO}}\theta_{\text{O}}. \quad (6)$$

This expression is also proportional to Eq. (3) derived in the previous section because

one O atom is liberated from every NO molecule that dissociates. The importance of this proportionality will be discussed in a later section.

These two mechanisms, in addition to other rate laws, were used to model our experimental titration curves. The results are discussed for the two cases studied, (i) titration of preadsorbed NO by CO, and (ii) titration of preadsorbed CO by NO.

B. Modeling of CO_2 Production Rate for the Titration of Preadsorbed NO by CO

Figure 4 shows the modeling results (solid lines) for the titration of adsorbed NO by CO experimental data (\square). Line (a) models the bimolecular mechanism using Eq. (3), while line (b) models the dissociative mechanism, with step (4-3) as the rate-limiting step, using Eq. (5). As shown in Fig. 4, line (a), the rate law derived from the bimolecular reaction mechanism (Eq. (3)) fits the initial, rapidly increasing portion of the curve. However, this model does not fit the latter portion of the data: the maximum in the simulated data occurs at 10 s while the actual rate maximum oc-

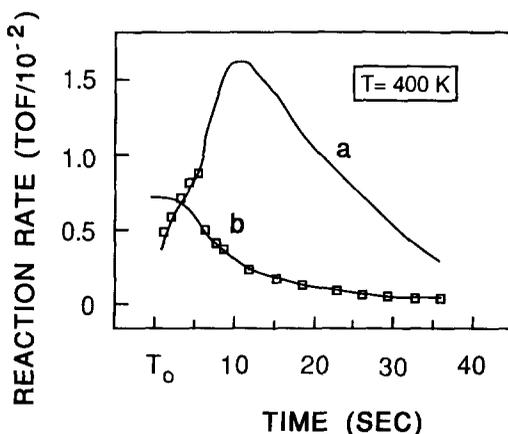


FIG. 4. Models for the CO_2 production rate for the titration of preadsorbed NO by CO experiments at 400 K. Shown are the experimental data points (\square), the bimolecular rate law, $R_{\text{CO}_2} = k\theta_{\text{NO}}\theta_{\text{CO}}$ (curve a), and the dissociative rate law, $R_{\text{CO}_2} = k'\theta_{\text{NO}} \cdot S$, resulting from NO dissociation as the rate-limiting step (curve b).

curs at 6 s. Figure 4, line (b), shows that the rate law derived from the dissociative mechanism with dissociation as the rate-determining step (Eq. (5)) does fit the latter portion of the CO_2 rate. However, this model fails to describe the experimental rate for the initial, sharply increasing portion of the rate. This model, using Eq. (5), does not start at zero because there are some free sites available due to the fact that the reaction is monitored at temperatures near the desorption temperatures for CO and NO. The above results of rate law modeling were found for all the temperatures studied.

It is obvious that neither of these rate laws can be used solely by itself to model the entire CO_2 titration curves. However, it is feasible that a combination of these two rate-limiting cases can describe the rate accurately, particularly when the behavior of NO on the Pt foil is considered. It has been shown in previous work that about 20% of NO dissociates during TPD on the Pt foil surface and that the dissociation is limited by the number of free sites available (26, 27). We propose that initially some preadsorbed NO dissociates into N and O atoms before the titration begins. Then, when CO begins to adsorb on the surface, the rate-determining step is the surface reaction between oxygen and carbon monoxide, step (4-4) above. As mentioned earlier, if this reaction is the rate-determining step, the rate law would have the form shown in Eq. (6). Since we cannot measure θ_{O} directly, the direct calculation of Eq. (6) using experimental data is not possible. However, Eq. (6) is proportional to Eq. (3) (which we can evaluate directly) because the coverage of oxygen is proportional to the coverage of NO, as discussed previously. As shown in Fig. 4, line (a), Eq. (3) describes the initial portion of the rate up to 5 s. We believe that the fit of Eq. (3) for the initial portion of the rate is not a result of the contribution of the bimolecular mechanism. If the bimolecular mechanism were dominant, Eq. (3) should fit the entire reaction rate profile. Instead,

we attribute the fit of Eq. (3) to the fact that Eq. (3) is proportional to Eq. (6). Thus, we propose that step (4-4), the reaction between coadsorbed CO and O, is the rate-determining step for the initial portion of the titration of adsorbed NO by CO.

When step (4-4) is treated as the rate-determining step for the initial portion of the reaction, the fit of Eq. (5) to the latter portion of the data makes consistent, intuitive sense. If the rate of step (4-4) is greater than the rate of step (4-3), O atoms will be consumed more rapidly than they are generated. Eventually, the rate of CO_2 production will be limited by the further production of surface oxygen through NO dissociation, step (4-3). After this point Eq. (5) should then describe the reaction rate. As shown in Fig. 4, this is the case. Therefore, it is not necessary to invoke a change in mechanism from bimolecular to NO dissociation to explain the use of two rate expressions to model the observed rate (although we cannot rule this out completely).

Figure 5 shows that the CO_2 production rate data obtained in preadsorbed NO titration experiments can be modeled accurately using the two-part rate law discussed above for all of the reaction temperatures studied. The initial portion of the CO_2 rate fits a rate law representing a bimolecular expression (Eq. (3)), while the latter half fits a rate law describing NO dissociation as the rate-limiting step (Eq. (5)). We explain the fit of Eq. (3) by the fact that Eq. (3) is proportional to Eq. (6), as discussed earlier. Therefore, two different rate laws can apply even when a single mechanism, NO dissociation, predominates throughout the reaction if the rate-determining step changes from step (4-4) to step (4-3). The kinetic parameters used in the modeling of these data are listed in Table 1.

C. Modeling of the CO_2 Production Rate in the Titration of Preadsorbed CO by NO

When CO is titrated by NO there is no opportunity for excess oxygen resulting

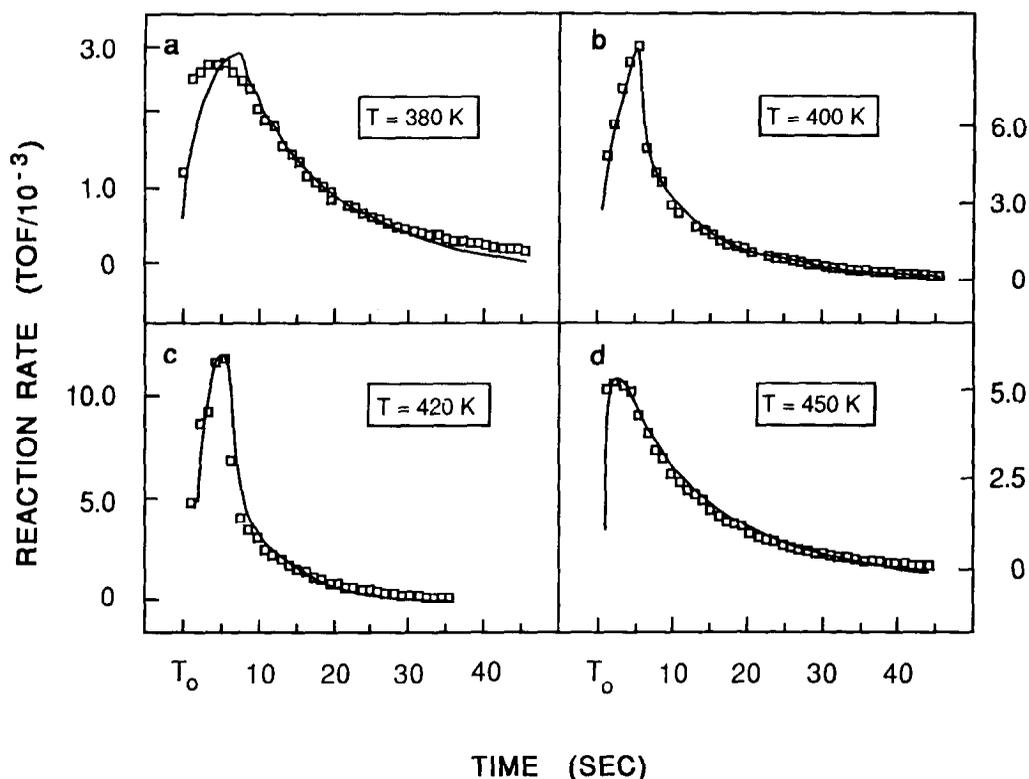


FIG. 5. Summary of the CO_2 production rates (\square indicates experimental data points) modeled using the bimolecular and dissociative rate expressions for the titration of NO by CO experiments at (a) 380 K, (b) 400 K, (c) 420 K, and (d) 450 K.

TABLE 1

Kinetic Parameters Used in Modeling Data for the Titration of NO by CO

Temperature (K)	k (ML s^{-1}) ^a	k' (ML s^{-1}) ^b	S_T ^c
380	1.5	.86	0.22
400	14	1.4	0.15
420	11	2.1	0.15
450	9.3	1.2	0.15

^a k is the rate constant used in the bimolecular rate law given by Eq. (3) in units of ML s^{-1} . Monolayer (ML) is defined here referenced to the Pt atom surface density = $1.5 \times 10^{15} \text{ cm}^{-2}$.

^b k' is the rate constant used in the dissociative rate law given by Eq. (5) in units of ML s^{-1} . Monolayer (ML) is defined here referenced to the Pt atom surface density = $1.5 \times 10^{15} \text{ cm}^{-2}$.

^c S_T is the constant used for the total number of reactive sites in the dissociative rate law of Eq. (5).

from NO dissociation to accumulate on the surface because of site blocking by adsorbed CO molecules. If reaction (4) is the dominant mechanism, the rate law derived using step (4-3) above as rate limiting (Eq. (5)) should describe the data at the beginning of the reaction. Figure 6 shows that this is the case, where the experimental data points (\square) and the modeling results (lines) are both shown. Line (c) is a plot of Eq. (5) and, as can be seen, this model fits the onset of the reaction well. In addition, Fig. 6, line (a), shows that the bimolecular reaction model (Eq. (3)) fits the experimental data poorly. It should also be noted that an additional rate-limiting step in this reaction could be NO adsorption. The resulting rate law,

$$R_{\text{CO}_2} = k' P_{\text{NO}} \cdot S, \quad (7)$$

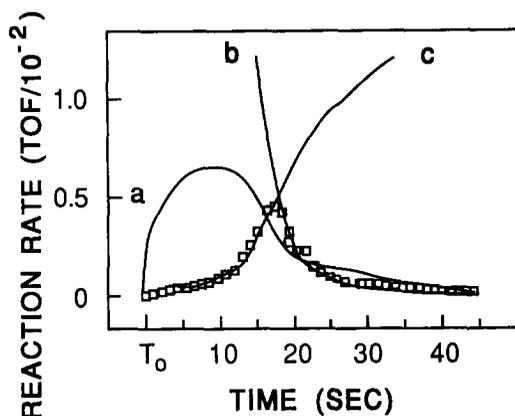


FIG. 6. Models for the CO_2 production rate for the titration of preadsorbed CO by NO at 420 K. Shown are the experimental data points (\square), the bimolecular rate law, $R_{\text{CO}_2} = k\theta_{\text{NO}}\theta_{\text{CO}}$ (curve a), the $(\theta_{\text{CO}})^2$ expression (curve b), and the dissociative rate law, $R_{\text{CO}_2} = k'\theta_{\text{NO}}\cdot S$, resulting from a NO dissociation rate-limiting step (curve c).

also did not fit the data. The above results show that the best fit for the initial portion of the reaction is given by Eq. (5).

After reaching the maximum rate at about 18 s, the reaction rate decreases rapidly at 420 K as shown in Fig. 6. This implies that the rate is strongly dependent upon the coverage of CO. The best fit for the latter portion of the reaction, shown in Fig. 6, line (b), was obtained by the expression

$$R_{\text{CO}_2} = k''(\theta_{\text{CO}})^2. \quad (8)$$

Other models which included the number of free sites were evaluated; however, none fit as well as Eq. (8). A rate expression that is proportional to $(\theta_{\text{CO}})^2$ was proposed previously by Heyne and Tomkins (28) and Golchet (29) when they suggested the formation of carbonate as an intermediate for CO_2 production on a supported Pt catalyst.

Figure 7 summarizes the modeling results for experiments involving the titration of preadsorbed CO by NO for all the reaction temperatures studied. In these experiments, O atoms cannot accumulate on the surface before reacting with CO to form CO_2 . If NO dissociation is the mechanism

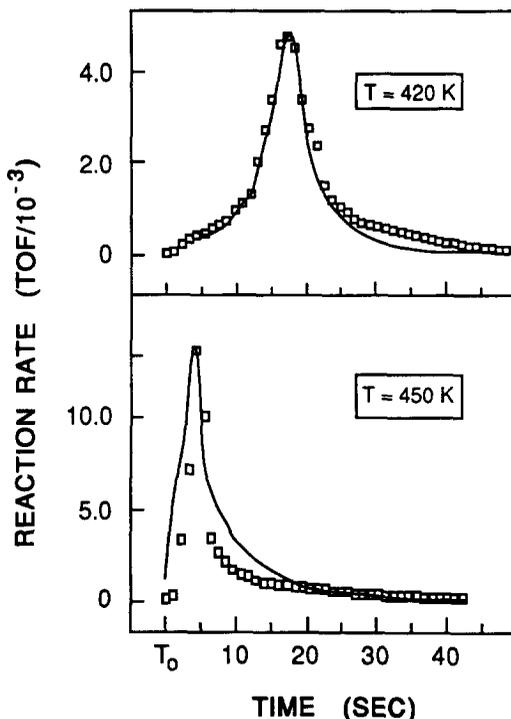


FIG. 7. Summary of the modeling of the CO_2 production rate for the titration of CO by NO at (a) 420 K and (b) 450 K using the dissociative ($R_{\text{CO}_2} = k'\theta_{\text{NO}}\cdot S$) and $(\theta_{\text{CO}})^2$ expressions (\square denotes experimental data points).

of reaction, as predicted by the titration results of preadsorbed NO, the dissociative rate law (Eq. (5)) should describe the CO_2

TABLE 2

Kinetic Parameters Used in Modeling the Data for the Titration of CO by NO			
Temperature (K)	k' (ML s ⁻¹) ^a	S_T ^b	k'' (ML s ⁻¹) ^c
420	15	0.065	8.0
450	53	0.090	8.0

^a k' is the rate constant used in the dissociative rate law given by Eq. (5) in units of ML s⁻¹. Monolayer (ML) is defined here referenced to the Pt atom surface density = 1.5×10^{15} cm⁻².

^b S_T is the constant used for the total number of reactive sites in the dissociative rate law of Eq. (5).

^c k'' is the rate constant used in the $(\theta_{\text{CO}})^2$ rate law given by Eq. (8) in units of ML s⁻¹. Monolayer (ML) is defined here referenced to the Pt atom surface density = 1.5×10^{15} cm⁻².

production rate from the start. The NO dissociative rate law does, in fact, describe the initial portion of the CO₂ production rate (including the induction time) during the titration of CO. The latter portion of the reaction was fit to Eq. (8) which shows a strong dependence on CO coverage. The kinetic parameters used in these modeling results are listed in Table 2.

V. SUMMARY

This paper describes kinetic modeling results of titration experiments involving the reaction between CO and NO on polycrystalline platinum foil. On the basis of the success of our descriptions of the reaction rate laws, we propose that at the coverages of NO and CO studied in these experiments the reaction takes place via a dissociative mechanism in which NO dissociates leaving O atoms on the surface and the adsorbed oxygen atoms then react with adsorbed CO to form CO₂. Our conclusions are further supported by the fact that several other rate laws do not describe the CO₂ production curves accurately.

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