

A molecular beam scattering investigation of the oxidation of CO on Rh(111). I. Kinetics and mechanism

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The catalytic oxidation of carbon monoxide on a Rh(111) surface has been investigated using modulated molecular beam techniques. Reaction proceeds via a Langmuir-Hinshelwood mechanism. Under experimental conditions which provide a high coverage of oxygen adatoms and near zero coverage of adsorbed CO, an activation energy of 24.5 ± 0.4 kcal/mol and a preexponential factor of $2 \pm 1 \times 10^{-3}$ cm² s⁻¹ were obtained. The angular distribution of the product CO₂ is sharply peaked toward the surface normal, and cannot be described by a simple $\cos^n \theta$ expression. Present results are discussed in relation to previous work on platinum and palladium surfaces.

INTRODUCTION

Throughout the entire development of surface science, the catalytic oxidation of carbon monoxide over noble metals has been studied extensively. Irving Langmuir chose this reaction for one of the first detailed investigations of surface chemistry,¹ and over the years countless investigators have examined various aspects of what has come to be regarded as a model heterogeneous reaction system. In the past decade, environmental concerns have given the reaction new importance as the catalytic converter for control of automotive exhaust emissions has become the largest single use of both platinum and rhodium.^{2,3} The high cost and limited availability of these metals make them quite unattractive as catalysts for economic reasons, and it has generally been hoped that a more detailed understanding of the reaction could lead to a rational basis for the selection of alternative catalysts.

While the literature relating to CO oxidation on platinum surfaces is vast,^{4,5} rhodium⁶⁻⁹ and palladium^{10,11} have received considerably less attention. In many respects the reaction over the various metals appears to be quite similar, but some rather unexpected differences have also been found, pointing to a need for further comparative studies.

It has by now been well established that the oxidation of CO over noble metals proceeds by a Langmuir-Hinshelwood mechanism, with reaction between molecularly adsorbed CO and atomically adsorbed oxygen leading to the formation of the CO₂ product.⁴ Minor differences in reaction kinetics for the different metals can be reasonably explained in terms of differences in binding energies for the reactants. More puzzling, however, are the apparent differences in the dynamics of reaction which have been observed.

Here again, platinum has been by far the most widely studied catalyst. Several investigations have shown that the oxidation of carbon monoxide on platinum surfaces produces carbon dioxide molecules with excess energy in both translational¹² and internal¹³⁻¹⁵ modes. Molecular beam

time of flight measurements by Becker *et al.*¹² showed that product CO₂ molecules desorbing from both polycrystalline platinum foils and Pt(111) single crystal surfaces carried translational energy well in excess of what would correspond to thermal equilibrium with the surface. Segner *et al.*¹⁶ made detailed measurements of the angular distributions of the product CO₂ from a Pt(111) crystal in another molecular beam scattering experiment, and found that the distributions were sharply peaked along the surface normal. They interpreted their observations in terms of a two-channel model in which a fraction of the molecules desorbs directly from a region of elevated potential energy and the remaining fraction reaches thermal equilibrium prior to desorption. Substantial levels of internal excitation in the product CO₂ have also been reported,¹³⁻¹⁵ and both the angular distributions¹⁶ and internal energies^{13,14} have been shown to depend on surface temperature and reactant coverages.

In the case of palladium, a cosine angular distribution was reported,¹⁰ implying that the CO₂ product interacts more strongly with the surface before desorbing. This is rather surprising, since the binding of CO₂ to platinum and palladium is purely a physisorption interaction,^{17,18} and should be quite similar for the two metals. For rhodium, a sharply peaked angular distribution was reported for angularly resolved thermal desorption experiments by Matsuhashi *et al.*⁷ While this is a rather different experiment than the beam scattering methods used for Pd and Pt, the result indicates that rhodium may behave much more like platinum than palladium. No measurements of translational or internal energies for the reaction on either palladium or rhodium have been reported.

In an attempt to further explore the similarities and differences between the various metals, we have undertaken a detailed investigation of the oxidation of CO on a Rh(111) crystal, employing a variety of molecular beam techniques. Here we report modulated beam relaxation spectrometry (MBRS) results on the reaction kinetics as well as the angular distribution of the product molecules. In general, the results are quite similar with previously reported data for Pt(111). The combination of MBRS with the angular distri-

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bution measurements does, however, lead to a rather different interpretation of the data. Specifically, no direct evidence is seen of the two-channel model proposed by Segner, *et al.*¹⁶ All of the data are consistent with a single pathway to CO₂ formation and desorption. Measurements of product velocity distributions will be presented in a subsequent paper.¹⁹

EXPERIMENTAL

The molecular beam scattering apparatus has been described previously.¹² Key features for the present experiments will be outlined here briefly.

The main UHV chamber is equipped with a rotatable quadrupole mass spectrometer, an Auger electron spectrometer, and an ion gun for sputtering. Base pressures in this chamber were $< 10^{-10}$ Torr, as measured by a nude ion gauge. Both the crystal manipulator and the mass spectrometer are mounted on differentially pumped rotating platforms, so that the angles of incidence and detection for the molecular beams can be independently varied.

A nonbakeable source chamber attached to the main chamber provides two molecular beams coincident on the crystal surface. Each beam is produced by a continuous supersonic expansion, skimmed, and triply differentially pumped before entering the main chamber. The center beam, CO in the present experiments, is modulated by a rotating chopper wheel to provide a periodic reactant flux. For the experiments described here a 50% duty cycle chopper at speeds of 20–600 Hz was used. The center line of the CO beam and the crystal normal define the scattering plane in which the detector rotates. The O₂ beam is at a 15° angle from the center beam in a plane perpendicular to the scattering plane, and was not modulated. Each beam could be blocked from entering the main chamber by an electro-mechanical shutter. Collimating aperture sizes were chosen so that the CO beam spot lies completely within both the O₂ spot and the detector viewing area.

The desorbing product molecules were detected using the rotatable quadrupole mass spectrometer. The detector is doubly differentially pumped. In an effort to minimize background, a 50 ℓ /s turbomolecular pump was added to the ionizer region, in addition to the 60 ℓ /s ion pump which had previously been used. The flight path from crystal to ionizer is 14.45 cm. Output current from the electron multiplier is amplified and digitized, and the subsequent pulses are counted using a multichannel scaler to record the time of arrival waveform. For angular distribution measurements, the MCS was replaced by a dual scaler gated to collect signal and background counts.

All data collection operations and detector positioning are controlled by an LSI-11 compatible minicomputer which is interfaced to the apparatus through CAMAC modules.

The Rh(111) single crystal was cut and polished in accordance with standard metallographic techniques. Laue x-ray diffraction measurements performed prior to mounting the crystal in the UHV chamber showed that the surface was oriented within 1/2° of the (111) plane. Auger electron spectroscopy originally revealed substantial carbon contamination, with smaller amounts of sulfur and boron also present. These impurities were removed by a combination of argon

ion bombardment and heating in oxygen, following a procedure described by DeLouise *et al.*²⁰ Once the crystal had been cleaned in this way, it generally remained free of contamination during the course of experiments as the continuous flux of oxygen to the surface prevented the accumulation of any impurities from the background gas. Specular helium scattering was occasionally used to check the surface condition and to optimize the crystal position with respect to the beams and detector.

The crystal was heated resistively. A chromel–alumel thermocouple was spot-welded to the back of the crystal to monitor the temperature, and a feedback controller maintained temperatures constant within ± 2 K.

RESULTS

Time of arrival waveforms (number density vs time) for the product CO₂ were recorded for a wide range of surface temperatures and modulation frequencies. Figure 1 shows typical data obtained in the temperature range 500–550 K. Each waveform shown corresponds to approximately 15 min of data collection. As is evident in the figure, the signal-to-noise ratio of the data is excellent. For each wave, the zero of time corresponds to the opening of the chopper. The time delay between this opening and the detection of the signal can be broken down into several parts:

- (i) the flight time of the CO molecule from the chopper to the crystal,

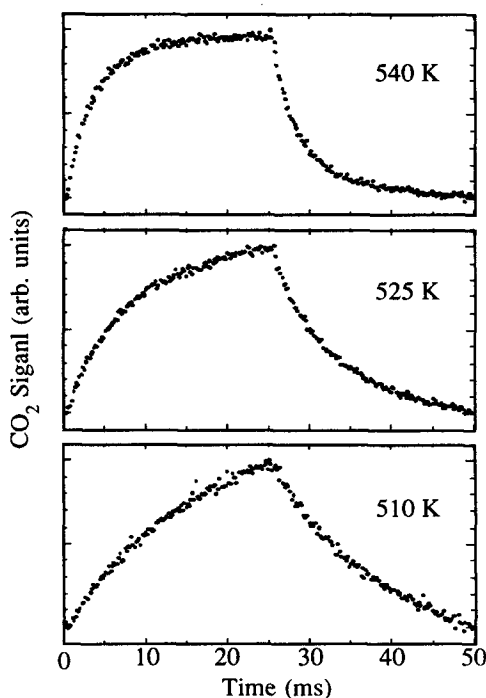


FIG. 1. Time of arrival waveforms for the product CO₂ are shown for the indicated surface temperatures. The chopping frequency was 20 Hz, and the waves shown were obtained in approximately 15 min of data collection time. The decay times for the waves are on the order of several milliseconds, and are very sensitive to the surface temperature, indicating that the shape of the wave is dominated by the surface lifetime of the CO molecule (see the text).

- (ii) the residence time of the CO molecule on the surface prior to reaction,
- (iii) the residence time of the CO₂ product on the surface prior to desorption,
- (iv) the flight time of the desorbed CO₂ product from crystal to ionizer, and
- (v) the drift time of the CO₂⁺ ion from the ionizer to the electron multiplier, as well as any other possible delays involved in detection electronics.

The detected signal represents the convolution of the distribution functions describing these various contributions. In time space, the convolution of two functions $f_1(t)$ and $f_2(t)$ is given by

$$F(t) = \int_{-\infty}^{\infty} f_1(t)f_2(t-\tau)d\tau. \quad (1)$$

By working in frequency space, however, the convolution integral becomes a simple product, and can be written as

$$F(\omega) = f_1(\omega) f_2(\omega), \quad (2)$$

where $f_i(\omega)$ is the Fourier transform of $f_i(t)$. This can readily be expanded to include any number of functions, so that the observed signal can be described by²¹

$$S(\omega) = \prod_{i=1}^5 f_i(\omega), \quad (3)$$

where the $f_i(\omega)$ represent, in frequency space, the five contributions listed above. Any one of the contributing functions can be extracted from the observed signal provided that the other functions are known or can be safely neglected.

For the present work, it is the CO residence time which is actually of interest, as this is the inverse of the rate constant for the surface reaction. In order to properly extract this from the data, the remaining delays must be measured or approximated. The first contribution, due to incident beam flight time, can be measured directly in our apparatus by rotating the detector into the path of the incident beam and obtaining the velocity distribution. The final contribution, due to detection times after ionization, can also be accurately determined. Possible residence time of the CO₂ will be neglected, as the low binding energy and relatively high temperatures involved should guarantee that it will be several orders of magnitude smaller than the CO lifetime. This leaves contributions due to CO residence time and CO₂ flight time to determine the shape of the observed wave. Temperatures have been chosen at which the observed decay times are on the order of several milliseconds (see Fig. 1). This is far in excess of what could be expected for flight time effects over the 14.45 cm crystal to ionizer distance, and hence must be due primarily to the CO residence time. Still, the CO₂ flight time effects are not negligible. For the present discussion we have elected to assume that the desorbing molecules have a Maxwell-Boltzmann velocity distribution at the surface temperature. Results of Becker *et al.*¹² for the same reaction on platinum indicate that this assumption may well be a poor one, and that the actual translational energy of the product CO₂ may be considerably higher than that corresponding to the surface temperature. Using the same apparatus, Becker measured an average flight time from crystal to detector of approximately 100 μ s. For the temperature range

considered here (500–550 K), the assumption of a Maxwellian distribution predicts a mean flight time on the order of 200 μ s. This means that if the correct velocity distribution were similar to that found on platinum, then we would be underestimating the surface lifetime by roughly 100 μ s. Since the measured residence times reported here are all >2 ms, the error introduced by assuming a thermal velocity distribution should not exceed 5%. The correct velocity distributions for the CO₂ product can be measured at higher temperatures, and will be presented in detail in a future paper.¹⁹

Within these approximations, the frequency space representation of the surface transfer function can be written as

$$F_s(\omega) = f_3(\omega) = \frac{S(\omega)}{f_1(\omega)f_2(\omega)f_4(\omega)f_5(\omega)}. \quad (4)$$

In principle it is possible to simply take the inverse Fourier transform of Eq. (4) to obtain directly the distribution of surface lifetimes. This procedure is generally unsuccessful, however, because it is extremely sensitive to small errors in the deconvolution as well as noise in the original experimental data. Much more reliable information has been obtained by examining the surface transfer function directly in frequency space. A particularly useful way of doing this is to plot the real part of the transfer function vs the imaginary part. It has been well established that such a plot is quite sensitive to qualitative features of the reaction mechanism.^{22,23} Various types of mechanisms, such as simple first-order reactions, parallel or sequential reaction networks, higher-order kinetics, or diffusion controlled reactions, have all been shown to produce a distinctive pattern in the transfer function.²³

Figure 2(a) shows the transfer function obtained from a single waveform taken at a surface temperature of 525 K and a modulation frequency of 20 Hz. The data points correspond to the first 15 odd harmonics of the chopping frequency, and the solid line shows the form expected for a single first-order reaction. Clearly the data are entirely consistent with such a mechanism. Although the actual surface reaction must be bimolecular, involving the combination of an adsorbed CO molecule and an adsorbed oxygen atom, pseudo-first-order kinetics are obtained because the continuous flux of oxygen to the surface is much greater than the modulated CO flux. This results in constant oxygen coverage at the surface throughout a CO modulation cycle. Because these experiments were conducted well below the oxygen desorption temperature, nearly a full monolayer of oxygen adatoms were adsorbed. Variation of the backing pressure of the CO molecular beam by a factor of 5 produced no change in the shape of the CO₂ product waveform and a linear variation in amplitude, consistent with pseudo-first-order behavior. The transfer function never contained any nonzero even harmonics of the chopping frequency, confirming that there are no nonlinear steps in the reaction sequence. Since the reaction sequence consists only of linear steps, it is possible to combine the results of several experiments at different modulation frequencies and temperatures to create a single transfer function.²² Figure 2(b) shows the transfer function obtained in this manner for a range of temperatures from 510 to 540 K and chopping frequencies of 20 and 50 Hz. Again

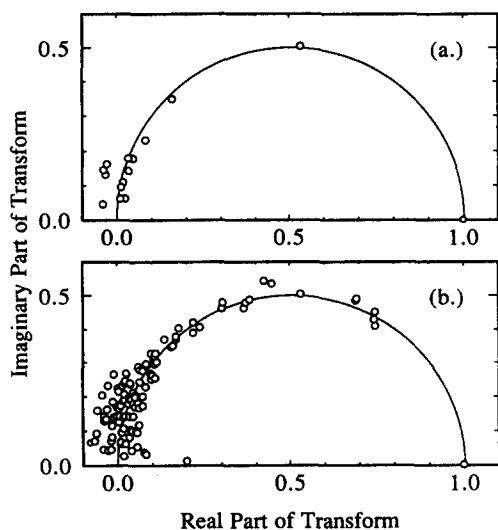


FIG. 2. (a) The surface transfer function obtained from a single time of arrival waveform at a crystal temperature of 525 K and a modulation frequency of 20 Hz is shown. The solid line represents the shape of the transfer function expected for an ideal first order reaction process. Clearly the data are consistent with such a mechanism, and do not show any of the features expected for parallel or sequential reaction networks (Ref. 22) (b) Because the reaction mechanism is linear, the transfer function can be constructed by combining results from a series of waveforms obtained at different temperatures and chopping frequencies (Ref. 22). The data points shown were obtained at surface temperatures between 510 and 540 K and at chopping frequencies of 20 and 50 Hz. As in (a), the solid line is the transfer function expected for an ideal first-order process, and the data are in good agreement with this model.

the data are entirely consistent with a single pseudo-first-order reaction.

A surface residence time τ for the CO molecule prior to reaction can readily be obtained from the surface transfer function. For a first-order reaction, the residence time is given by²¹

$$\tau = \frac{1}{k} = \frac{\tan \varphi}{\omega} \quad (5)$$

$$= \frac{\text{Im } F_s(\omega)}{\text{Re } F_s(\omega)} \frac{1}{\omega} \quad (6)$$

This relationship also holds for the pseudo-first-order case considered here. Figure 3 shows an Arrhenius plot of residence time vs $1/T_s$, obtained in this fashion. From this plot an activation energy of 24.5 ± 0.4 kcal/mol was obtained, with an apparent preexponential factor of $2 \pm 1 \times 10^{12} \text{ s}^{-1}$ for the pseudo-first-order reaction. The meaning of these values in terms of the actual rate constants for the reaction will be considered in the next section.

All of the data points shown in Fig. 3 were obtained from the phase shift of the first harmonic for a given waveform, as this is the most accurate frequency in the data. The signal-to-noise ratio obtained in these experiments, however, should allow the use of higher frequencies present in the data as well. In order to fully utilize the information present in the waveforms, a fitting approach is useful. As outlined above,

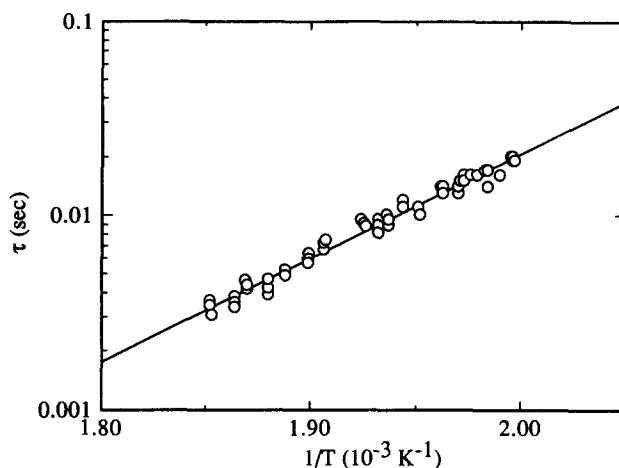


FIG. 3. Arrhenius plot of the surface residence time τ vs $1/T_s$. Residence times have been obtained from the phase shift of the time of arrival waveforms as explained in the text. The solid line is a least squares fit to the data, and corresponds to an activation energy of 24.5 ± 0.4 kcal/mol and an apparent pre-exponential factor of $2 \pm 1 \times 10^{12} \text{ s}^{-1}$.

the shape of the measured waveform should be given by Eq. (3). Since we have either accurate measurements or reasonable approximations for all of the other terms, we should be able to evaluate the distribution of surface lifetimes, $f_s(t)$, by fitting the data. This has been done by assuming that the residence time distribution can be described by a simple exponential,

$$f_s(t) = N \exp(-t/\tau), \quad (7)$$

where N is a normalization constant and t is the surface lifetime. Equation (3) is then evaluated to obtain the resulting signal for trial values of τ . Deviations between the resulting waveform and the data were minimized using a nonlinear least squares routine, resulting in a best-fit value for τ .

Figure 4 shows a sample data set and fit obtained in this fashion. Results obtained by fitting waveforms were identi-

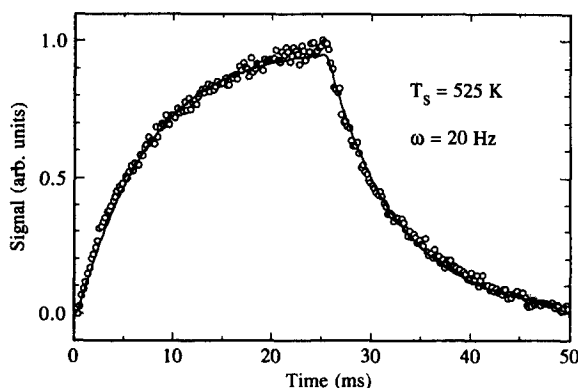


FIG. 4. The time of arrival waveform obtained at $T_s = 525$ K and a modulation frequency of 20 Hz is shown together with the curve obtained by a least squares fit of Eq. (3) to the data. A value of $\tau = 6.9$ ms was obtained from the fitting procedure, in reasonable agreement with the value of 6.4 ms obtained from the phase shift method used for the data in Fig. 4.

cal with those obtained using the phase-shift method described above.

It is also possible in principle to obtain residence times from the amplitude of the transfer function as well as the phase.²¹ This has not been done here because of the complicated angular distribution of the product CO₂. To correctly use the amplitude data, it would be necessary to integrate over the angular distribution. The transfer functions presented here have been arbitrarily normalized to an amplitude of 1.0 at zero frequency.

All of the waveforms used in the above analysis were obtained with the detector along the surface normal, since this provides the highest possible signal levels. By rotating the detector away from the normal, product angular distributions can be measured. Figure 5 shows the angular distribution of CO₂ measured for a surface temperature of 550 K at a chopping frequency of 20 Hz. As above, the situation corresponds to full oxygen coverage and near zero CO coverage. The data are plotted as number density vs desorption angle. For the temperature range considered here, the shape of the observed waveform is dominated by the surface residence time, and the product velocity distribution can not be accurately determined, so it is not possible to convert from number density to flux. The distribution is clearly much sharper than cosine, and could not be fit with a single function of the form $\cos^n \theta$ as has often been used to describe sharply peaked angular distributions. Segner *et al.*¹⁶ observed similar distributions for the same reaction on Pt(111), and fit them with a two term expression of the form

$$I(\theta) = \alpha \cos^n \theta + (1 - \alpha) \cos \theta. \quad (8)$$

Such a form was able to fit our angular distributions reasonably well. The best fit obtained for the data in Fig. 5 corre-

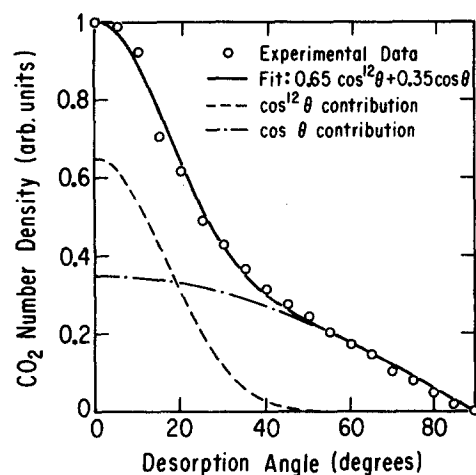


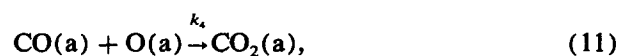
FIG. 5. The angular distribution of the product CO₂ number density is shown for a surface temperature of 550 K. The solid line is the best fit of Eq. (8) to the data, and the dashed lines show the contributions of the two terms to the distribution. Note that along the surface normal ($\theta = 0^\circ$) the distribution is dominated by the sharply peaked $\cos^{12} \theta$ term, while at $\theta = 60^\circ$ only the cosine term contributes appreciably.

sponds to $\alpha = 0.65$ and $n = 12$, and is shown by the solid line in the figure. The exact shape of the angular distribution as a function of surface temperature and reaction coverages will be discussed in a separate paper.²⁴

The presence of the $\cos \theta$ term in the angular distribution suggests the possibility that a fraction of the molecules may become accommodated in the CO₂ physisorption well prior to desorption, while the remaining molecules ($\cos^n \theta$ term) desorb more directly without accommodation.¹⁶ Figure 6 shows the product time of arrival waveforms obtained at 550 K for two desorption angles. At $\theta = 0^\circ$, the angular distribution contains significant contributions from both the cosine and peaked terms, while at $\theta = 60^\circ$ only the cosine term contributes appreciably. As seen in Fig. 6, the time of arrival distributions for the two angles are indistinguishable. No evidence is seen to suggest that any difference in reaction mechanism exists between the two desorption angles, implying that the separation of the angular distribution into two terms may be artificial.

DISCUSSION

The Langmuir-Hinshelwood (LH) reaction mechanism for CO oxidation on noble metal surfaces can be written as follows:



As indicated earlier, CO₂ interacts only weakly with the Rh(111) surface, so that the lifetime of any adsorbed CO₂ species can reasonably be neglected. This is equivalent to

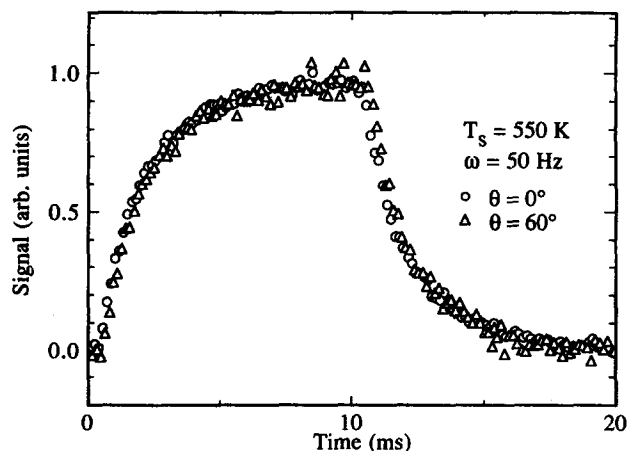
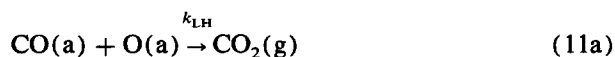


FIG. 6. Product time of arrival waveforms obtained at $\theta = 0^\circ$ and $\theta = 60^\circ$ show no detectable differences. This suggests that the separation of the angular distribution into two terms may be artificial.

saying that reaction (12) is much faster than the actual LH reaction step, reaction (11), and suggests that we might write



in order to show explicitly the relatively direct desorption of the product CO_2 molecule. Within this assumption, we can write the rate of CO_2 production (as observed in the gas phase) as

$$\text{rate} = \frac{d[\text{CO}_2]}{dt} = k_{\text{LH}} \theta_{\text{O}} \theta_{\text{CO}}, \quad (13)$$

where k_{LH} is the rate constant for the bimolecular surface reaction and θ_{CO} and θ_{O} are the surface coverages of the two reactants. If the coverages are expressed in adsorbate particles per cm^2 , and the rate is in CO_2 molecules per cm^2 per second, then k_{LH} will have units of $\text{cm}^2 \text{s}^{-1}$. All of the experiments reported here were carried out under conditions which provide a large constant coverage of oxygen. The appropriate kinetic equations for this case have been considered by Engel and Ertl in a study of CO oxidation on Pd(111).¹⁰ The rate of CO_2 production is given by

$$\frac{d[\text{CO}_2]}{dt} = k_{\text{LH}} \theta_{\text{O}} \left[\frac{k_1 \alpha e^{i(\omega t - \varphi)}}{\{(k_2 + k_{\text{LH}} \theta_{\text{O}})^2 + \omega^2\}^{1/2}} \right] \quad (14)$$

and the observed temperature dependent phase lag for the CO_2 signal is given by

$$\tan \varphi = \frac{\omega}{k_2 + k_{\text{LH}} \theta_{\text{O}}}. \quad (15)$$

For the temperature range considered here, $k_{\text{LH}} \theta_{\text{O}} \gg k_2$, so that reaction to form CO_2 is fast compared with CO desorption. This means that the observed relaxation times are related to k_{LH} by

$$\tau = \frac{\tan \varphi}{\omega} = \frac{1}{k_{\text{LH}} \theta_{\text{O}}}. \quad (16)$$

It follows from this that a plot of $\ln \tau$ vs $1/T$ (Fig. 3) yields a straight line with a slope of E_{LH}/kT and an intercept of the apparent preexponential factor, $\nu_{\text{app}} = \nu_{\text{LH}} \theta_{\text{O}}$. The values obtained from a least squares fit to the data in Fig. 4 are $E_{\text{LH}} = 24.5 \pm 0.4$ kcal/mol and $\nu_{\text{app}} = 2 \pm 1 \times 10^{12} \text{ s}^{-1}$. Assuming a saturation oxygen coverage²⁵ of $1.3 \times 10^{15} \text{ cm}^{-2}$, this corresponds to a value of $2 \pm 1 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ for the true preexponential, ν_{LH} . These values are in reasonable agreement with those which have been reported in the literature for CO oxidation on rhodium,^{6,9} as well as on palladium¹⁰ and platinum²⁶ surfaces. The observed preexponential also lies well within the range predicted by transition state theory for second order surface reactions.²⁶ As has been pointed out by Engel and Ertl,¹⁰ it is not generally possible to define a rate constant which is independent of conditions, so that the values determined here may well be specific to the surface coverage prevalent in these experiments. This will be explored in a future paper.²⁴

As shown in Fig. 6, the angular distribution of the CO_2 product is much sharper than the cosine distribution which would be expected for molecules leaving a surface at equilib-

rium. Sharp angular distributions have been reported previously in molecular beam scattering investigations of CO oxidation on platinum surfaces,^{12,16,28} and also in angularly resolved thermal desorption experiments on both platinum²⁹ and rhodium⁷ surfaces. For primarily historical reasons,³⁰ these distributions have generally been described by an expression of the form $\cos^n \theta$, with the exponent n being fit to the experimental data. Values of n ranging from 2–7 have been reported for platinum in scattering experiments,^{12,28} while Matsushima found $n = 4$ –15 in TPD measurements on Rh(111).⁷ The present data clearly cannot be fit satisfactorily with a single $\cos^n \theta$ term.

Segner *et al.*¹⁶ performed the most detailed measurements of angular distributions reported to date for CO oxidation on Pt(111), and also found that a single expression of this form could not adequately fit the observed data. Instead they used a two term model involving a sum of two cosine terms [Eq. (8)], and found that their results were fit well with $n = 7$. The branching fraction α was a function of experimental conditions such as temperature and coverage. We have applied the same form to the current data, and obtained a reasonable fit for $n = 12$ and $\alpha = 0.65$, as shown in Fig. 5. Variations in the exact shape of the angular distribution with temperature and coverage have also been observed, and will be described in a subsequent paper²⁴.

As has been pointed out by Comsa,³⁰ there is no *a priori* reason why the angular distribution should necessarily be described by a cosine to some power. Similarly, the two channel form of Eq. (8) arose simply as an empirical fit to experimental data. By definition, the reactants in a Langmuir-Hinshelwood mechanism must be adsorbed to the surface, and therefore must have no memory of their incident angles and energies. This leads to the requirement that the angular distribution must be symmetric about the surface normal. (More specifically, the distribution must be symmetric with respect to reflection planes containing the surface normal.) In general it will always be possible to fit any such observed distribution with a sum of cosine terms. Still, the success of Segner *et al.* in fitting their data with the two term expression was quite good, as variation of a single parameter was able to describe the distributions over a wide range of conditions. This success implied that the two terms used to fit the distributions might correspond to two distinct reaction pathways. In particular, the appearance of the $\cos \theta$ term suggested the possibility that a fraction $(1-\alpha)$ of the molecules was actually equilibrating in the CO_2 physisorption well prior to desorption while the remaining fraction desorbed more directly.¹⁶

In the present experiments, the ability to perform MBRS waveform analysis provides the capability to examine the possibility of dual pathways in two ways. First the transfer function plots shown in Fig. 2 are quite sensitive to branching in reaction networks, and no evidence of such behavior is seen. From the angular distribution, the signal at the surface normal where the data for these plots was obtained should consist of both branches in a ratio of roughly 2:1. This branching would be readily visible in the transfer function, provided that the rate constants for the two channels were appreciably different. D'Evelyn and Madix²² have

suggested that branching would be very clearly evident in the transfer function provided that the rate constants for the two branches differ by a factor of 5. A more direct means of checking for measurable differences in the reaction mechanisms for the two terms of the distribution is the measurement of waveforms as a function of angle. At the surface normal the angular distribution is dominated by the $\cos^{12} \theta$ term, while at 60° only the $\cos \theta$ term can contribute appreciably (see Fig. 5). Figure 6 shows that the waveforms obtained at these two angles are indistinguishable, again providing no evidence to support a branched mechanism. This suggests that the separation of the angular distribution into two terms might be artificial. A single mechanistic pathway which produces a peaked angular distribution is completely consistent with all of the observed data.

The present data do not suffice, however, to rule out a branched mechanism entirely. In the limit of two branches with identical rate constants, it would clearly be impossible to distinguish between them. Since relaxation at the surface may proceed on a very short time scale, the difference in surface lifetime between molecules which equilibrated and those which desorb directly might be smaller than the detection limit ($\approx 10^{-4}$ s for the chopping frequencies used here). Further evidence for a single mechanism has been found in measurements of the velocity distributions in the product CO_2 molecules. Even at an angle of 60° from the surface normal, nonthermal velocity distributions with translational energies in excess of those corresponding to the surface temperature were obtained, indicating that the molecules desorb without equilibrating in the CO_2 adsorption well. Furthermore, no evidence was seen for a bimodal velocity distribution, as would be expected to arise from the sort of two-channel mechanism suggested by Segner *et al.*¹⁶ These results will be presented in detail in a subsequent paper.¹⁹

CONCLUSION

Modulated molecular beam scattering experiments have been used to investigate the kinetics and mechanism of the oxidation of carbon monoxide on a Rh(111) surface. Experiments reported here were performed under conditions where the oxygen atom coverage is high and the CO coverage is near zero. Under these conditions pseudo-first-order kinetics were observed. An activation energy of 24.5 kcal/mol and a preexponential factor of $1.9 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ were determined. The angular distribution of the product CO_2 was sharply peaked about the surface normal, in a manner similar to that reported previously on Pt(111). Although the angular distribution was fit with a two term expression, no evidence for a branched mechanism was seen in Fourier analysis of the product waveforms, and waveforms obtained at different desorption angles from the sur-

face normal were indistinguishable. All of the data are consistent with a single mechanism producing a peaked angular distribution.

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