ANALYSIS OF GAS-SURFACE REACTIONS BY SURFACE TEMPERATURE MODULATION: EXPERIMENTAL APPLICATIONS TO THE ADSORPTION AND OXIDATION OF CARBON MONOXIDE ON THE Pt(110)-(1 × 2) SURFACE

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Surface temperature modulation has been employed to investigate the adsorption, desorption and oxidation of CO on the $Pt(110)-(1 \times 2)$ surface. Examination of the adsorption-desorption equilibrium allows a determination of the kinetic parameters describing the desorption reaction. In the limit of zero coverage, the activation energy of desorption is 36 ± 1.5 kcal mol⁻¹ with a first-order preexponential factor of 3×10^{14} s⁻¹. As the coverage of CO increases, both parameters decrease in magnitude. The oxidation of CO has been studied with an emphasis on examining the kinetics of the elementary "bimolecular" surface reaction $CO(a) + O(a) \rightarrow CO_2(g)$. By varying both the reactant partial pressure ratio and the steady-state temperature of the surface, the reaction rate parameters have been evaluated for a variety of combinations of adsorbate concentrations occurring at steady state. The magnitudes of both the activation energy and the preexponential factor of the reaction rate coefficient have been found to correlate well with the oxygen adatom concentration. In the low-coverage limit, the activation energy is 22 ± 1 kcal mol⁻¹, and the preexponential factor is 3×10^{-3} cm² s⁻¹. As the oxygen adatom concentration increases beyond a fractional coverage of approximately 0.15, the magnitudes of both parameters drop precipitously to values given, respectively, by 8 ± 1 kcal mol⁻¹ and 10^{-10} cm² s⁻¹. The decrease in the activation energy at high oxygen coverages is explained best by a decrease in the binding energies of the adsorbed reactants. The apparent decrease in the preexponential factor could well be due to the local configuration of the reactants that occurs at high oxygen coverages.

1. Introduction

The adsorption and the oxidation of CO on transition metal surfaces have attracted particular attention both as model systems of fundamental gas-surface interactions and due to their technological importance. On many late transition metal surfaces, the adsorption of CO has been found to be nondissociative and characterized by a high probability of adsorption [1]. The binding energy is typically on the order of 30 kcal mol⁻¹, indicative of rather

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0039-6028/88/\$03.50 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division) strong chemisorption. Experimental studies employing both electronic and vibrational spectroscopies, coupled with theoretical calculations, have resulted in a thorough understanding of the nature of the chemical bond between the CO molecule and the metal surface [2]. The oxidation of CO on transition metal surfaces, especially platinum, has been studied extensively [1,3] (dating to the time of Langmuir [4]), since the reaction probability is high and the CO₂ product molecule interacts "weakly" with the surface. Studies of the distribution of energy in the translational and internal modes of the gas phase CO₂ product have led to a more complete description of the potential energy surface of the elementary bimolecular surface reaction between the adsorbed reactants [5–7]. Of considerable interest is a determination of the influence that the adlayer composition has on the reaction dynamics. A better understanding of the dynamics will be aided tremendously by independent knowledge of the integral rate parameters, i.e. the activation energy and the preexponential factor of the reaction rate coefficient.

We have employed the technique of surface temperature mcdulation [8,9] to examine both the adsorption and the oxidation of CO on the Pt(110)- (1×2) surface. This technique permits a straightforward analysis of the energetics of *elementary* surface reactions, even for cases in which a number of elementary reactions contribute to the overall, apparent reaction energetics. In addition, the presence of coverage-dependent rate parameters does not preclude a direct determination of the activation energy, i.e. the activation energy can be evaluated for a range of reactant surface concentrations. The surface temperature modulation technique [8,9] may be summarized as follows:

(i) Impose a small periodic (e.g. sinusoidal) temperature profile on a solid surface during a steady-state gas-surface reaction.

(ii) Monitor simultaneously the surface temperature and the desorbing reaction product(s) flux. For a continuously pumped reaction chamber, the average partial pressure of the reaction product(s) is detected.

(iii) Fourier analyze the input (surface temperature) and output (product partial pressure or desorbing flux) waveforms to evaluate the system transfer function.

Although the surface temperature modulation technique possesses conceptual similarities to other frequency response techniques such as modulated molecular beam reactive scattering (MMBRS), activation energies are not evaluated by constructing Arrhenius plots of apparent rate coefficients versus the reciprocal temperature. Rather, the absolute magnitude of the amplitude ratio AR of the input and output waveforms can be used to directly calculate the activation energy E_r of a single elementary reaction; e.g.

$$AR(\omega) \equiv \frac{P^{\dagger}(\omega)\sqrt{(\tau\omega)^{2}+1}}{T^{\dagger}(\omega)} = \frac{(E_{\rm r}/k_{\rm B}T_{\rm s})}{\sqrt{(\nu/\omega)^{2}+1}},$$

where $P^{\dagger}(\omega) \equiv P(\omega)/P_{\rm s} - 1$ is the dimensionless deviation of the product partial pressure from the steady-state value $(P_{\rm s})$, $T^{\dagger}(\omega)$ is the dimensionless deviation of the surface temperature, τ is the pumping time constant of the reactor, ω is the modulation frequency, $k_{\rm B}$ is Boltzmann's constant, $T_{\rm s}$ is the steady-state surface temperature and ν is an apparent rate coefficient. Thus, unlike most frequency response techniques, the frequency is varied in order to "select" (in the frequency domain) a particular reaction such that the amplitude ratio is characteristic of only the reaction that is selected.

The adsorption-desorption equilibration of CO has been examined in order to evaluate the rate parameters that describe the desorption reaction $CO(a) \rightarrow CO(g)$. The oxidation of CO has been examined to investigate explicitly the kinetics of the elementary surface reaction $CO(a) + O(a) \rightarrow CO_2(g)$. We shall emphasize the coverage dependence of the kinetic rate parameters, the results of which represent an important contribution to a more complete understanding of the surface reaction dynamics.

2. Experimental procedures

The experiments described here were performed in an ion-pumped, stainless steel belliar that has been described previously [10]. The base pressure of the belliar is below 1×10^{-10} Torr of reactive gases. Facilities are available for experimental studies involving quadrupole mass spectrometry, low-energy electron diffraction (LEED), photoelectron spectroscopy (XPS and UPS) and Auger electron spectroscopy. The Pt(110) crystal was cut from a single crystalline boule of platinum and polished to within 0.5° of the (110) orientation by using standard metallographic techniques. The crystal was cleaned in situ by argon ion sputtering, heating in 5×10^{-7} Torr of oxygen at temperatures between 600 and 800 K, and high-temperature annealing to 1400 K. Surface cleanliness was verified by Auger electron spectroscopy. Special care was taken to reduce the amount of silicon impurity in the sample to a negligible concentration, since Niehus and Comsa [11] have shown that its presence can be related directly to the formation of a "subsurface oxide" on Pt(111). After cleaning and annealing, the (1×2) LEED pattern characteristic of the clean, reconstructed surface was observed. Structural studies have supported the "missing row" model as the geometrical structure of this reconstructed surface [12,13].

Isotopic ¹³CO (-90% ¹³C, Merck research grade, 99.99% purity) was utilized to increase the signal-to-noise ratio in the mass spectrometric detection. Research grade oxygen (99.99% purity) was supplied by Matheson. A directional beam doser, consisting of a multichannel array of capillaries [14] was employed to provide a high beam-to-background pressure ratio (which improves the signal-to-noise ratio). Gases were admitted to the dosing line via capillary leaks from identical twin storage bulbs, which permits careful control of reactant partial pressures (which is important for signal averaging). The reaction products in the gas phase were monitored with a quadrupole mass spectrometer (UTI 100C), while the temperature was measured by a thermocouple spot-welded to the back of the crystal.

Accurate temperature control was maintained by the use of an optimal feedback control scheme, described elsewhere [15], which utilizes a laboratory microcomputer as the control element. A complete description of the method used to heat (in this case, resistively) and to cool the crystal is given elsewhere [15]. For a desired output (temperature) wave form, knowledge of the system transfer function which describes the response of the crystal temperature to the applied current produces directly the desired controller forcing function. In particular, if the desired output is given by $T(t) = T_s + T_A \sin(\omega t)$, it can be shown that

$$I'(t) = \frac{T_{\rm A}}{\tau_{\rm c}\rho(T_{\rm s})} \left[\omega\tau_{\rm c}\cos(\omega t) + \sin(\omega t)\right],$$

where $I'(t) \equiv [i(t)]^2 - i_s^2$ is the deviation of the square of the applied current (proportional to the power input) from the value at steady state, τ_c is the thermal time constant of the crystal, $\rho(T_s)$ is proportional to the resistance of the support wires used to heat the crystal and inversely proportional to the heat capacity of the crystal, and ω is the radial frequency. A method for the accurate determination of the two parameters τ_c and $\rho(T)$ is given elsewhere [15].

The temperature control software has also been designed to control and to monitor the mass spectrometer. Thus, one routine provides data acquisition as well as control of the experiment. For each frequency of oscillation, after initial spurious transients have been sufficiently damped, data are collected and summed into a periodic array, increasing the signal-to-noise ratio. Typical periods of data collection for a single frequency and particular set of reaction conditions are 2.5-3 min in duration ($S/N \ge 10$). Once collected, the data are analyzed utilizing standard digital Fourier transform techniques [16]. Since the input (temperature) waveform is nearly sinusoidal, only the results obtained at the fundamental frequency are used in the subsequent analysis.

The pumping time constant can be obtained easily and accurately by creating a step-function change in the rate of the particular surface reaction that affects the product concentration in the gas phase. The exact method that was employed varied for the two reaction systems studied here, as discussed below. An alternate method was also used that involved introducing a pulse of short duration of the gas phase product species into the chamber via a leak line equipped with a solenoid-actuated valve (Allied #3M782). The intensity of the pulse was chosen to be approximately 5–10% of the steady-state intensity of gas phase product species in the reactor (i.e. the perturbation was

linear). The results obtained by the two methods were in good agreement with one another.

A determination of the instrument response function is crucial for any frequency response technique [17]. Utilizing standard techniques employing a function generator and an oscilloscope, distortions of the input (temperature) or output (mass spectrometer ion current) waveforms by the measurement electronics were found to be negligible for the frequency range employed (0.01–1.0 Hz). However, for any system sampling the rate of reaction over the entire surface of the crystal, the desired input waveform is the *spatially averaged temperature* of the surface. Since we employ a spatially inhomogeneous method to heat and cool the crystal [15], this averaged temperature can be expected to differ from the temperature measured by the thermocouple at sufficiently high frequencies. A detailed analysis, presented elsewhere [18], shows that the power input (the square of the applied current) and the spatially averaged temperature can be related simply to one another. Thus, the microcomputer controlling the crystal temperature can be used to determine



Fig. 1. Amplitude ratio (AR) and phase difference of the function $T'_m(p)/T'_{av}(p)$, where T'_m is the deviation of the measured temperature from its steady-state value, T'_{av} is the deviation of the spatially averaged temperature, and $p = i\omega$. (Note that $T_{m,s} = T_{av,s}$.) The circles represent the measured response, and the solid lines represent the predicted theoretical response utilizing a radial thermal time constant of $\tau_r = 1.27$ s.

the frequency response of the *measured* temperature as a function of the *spatially averaged* temperature via the power input. The measured response was found to be linear for the amplitude of the temperature forcing functions used here, with the phase difference becoming significant at high frequencies, while the amplitude ratio was nearly unity for all frequencies. Independent measurements indicated that these effects were not related to spurious EMF signals due to IR drop or capacitive coupling caused by the heating current passing through the sample [19].

The measured response, taking the measured temperature as the output variable, is shown in fig. 1. This result can be compared to that predicted theoretically from a solution of the time-dependent two-dimensional heat conduction equation with the appropriate crystal geometry and boundary conditions. The solution, given elsewhere [18], predicts a linear response between the measured and spatially averaged temperatures. Thus, utilizing a value for the radial thermal time constant of the crystal of 1.27 s ($\tau_r = r^2/\kappa_c$, where r is the radius and κ_c is the thermal diffusivity of the crystal), the theoretical response was calculated and is shown also in fig. 1. The agreement between the measured response and the theoretically predicted response is excellent. Consequently, in the analysis below, the measured input wave form (temperature) has been adjusted accordingly to represent the spatially averaged temperature by utilizing the data displayed in fig. 1.

3. Results and discussion

3.1. CO adsorption-desorption equilibrium on Pt(110)- (1×2)

The interaction of CO with the (110)- (1×2) surface of platinum has been examined for a gas phase pressure of approximately 6.5×10^{-8} Torr ^{#1} and surface temperatures between 500 and 525 K. These experimental conditions were chosen on the basis of the range of realizable temperature forcing function frequencies. Essential to the application of the surface temperature modulation technique employed here is the experimental verification of the linearity assumption. A sufficient demonstration of linearity can be provided by examining the response of the gas phase product signal as the amplitude of the temperature forcing function is varied at constant frequency. The amplitude of the gas phase signal should vary linearly with the amplitude of the temperature, whereas the phase difference should be constant. Equivalently, the amplitude ratio can be calculated, and, as for the phase, its value should be constant. We choose the latter approach, since the results will also given an

^{#1} Beam doser pressures are calibrated such that the effective flux is calculated by using a gas phase temperature of 300 K.

indication of the uncertainty in the values of the amplitude ratio which is of obvious importance to the application of surface temperature modulation [9].

The amplitude ratio (AR) and phase difference of the gas phase signal $(N_g^{\dagger}(t) \equiv [N_g(t) - N_{g,s}]/N_{g,s})$, i.e. the dimensionless deviation of the product partial pressure from its steady-state value, where N_g is proportional to the product partial pressure, and the subscript s refers to the steady-state value) that is detected by the mass spectrometer and corrected for the pumping term (i.e. $\tau p + 1$, where τ is the pumping time constant and $p = i\omega$ is the complex modulation frequency; see below) are plotted in fig. 2 as a function of the (first Fourier coefficient) amplitude of the temperature forcing function (T_A) . Both the amplitude ratio and the phase difference are independent of the amplitude of the temperature modulation, providing experimental proof of the linearity of the response. The two cases shown in fig. 2 represent the lowest and highest frequencies employed in this particular study. The temperature



Fig. 2. Amplitude ratio (AR) and phase difference data representing the system transfer function for the reaction $CO(g) \Leftrightarrow CO(a)$. The insensitivity of the response with respect to the amplitude of the temperature forcing function demonstrates the validity of the linearity assumption. Note the two different temperature scales.

amplitudes for these two frequencies utilized in the data that appear below are given by the median values shown in fig. 2. These values bracket the amplitudes employed at intermediate frequencies.

A quantitative interpretation of the data presented here for the case of the adsorption-desorption equilibrium of CO in terms of kinetic parameters is dependent upon an evaluation of the product $S_s \eta$ (where S_s is the probability of adsorption at steady state, and η is the fraction of molecules in the beam which strike the crystal) and the pumping time constant τ of the chamber. A determination of S_{n} permits a subtraction of the constant fraction of the signal that is due to molecules that neither adsorb nor strike the crystal. Both parameters can be obtained by producing a step-function change in the rate of adsorption. Our measurements of the kinetics of adsorption of CO on the Pt(110)-(1 \times 2) surface show that the probability of adsorption is essentially independent of coverage for fractional coverages below approximately 0.3, in agreement with previous investigations [20-23]. Fair and Madix [20] have also found that the absolute value of the probability of adsorption of CO on Pt(110)-(1 \times 2) is independent of temperature between 200 and 600 K. This coverage- and temperature-independence of the adsorption kinetics will be exploited to produce the desired step-function change in the rate of adsorption.

The specific procedure is as follows. The crystal, rotated out of line-of-sight of the beam doser, is flashed to desorb any molecules present on the surface due to adsorption from the background. Once the crystal has cooled to a temperature below 400 K, it is rotated quickly to be in line-of-sight of the beam doser, producing a step-function change in the rate of adsorption $^{#2}$ (i.e. $r_a(t) = S_s \eta u(t)$, where u(t) is the Heaviside unit step function). For sufficiently low reactant partial pressures (the impingement rates utilized here were approximately 0.03 site⁻¹ s⁻¹), the rate of adsorption will be constant for a significant period of time with respect to the pumping time constant of the chamber. During this period of time the partial pressure of the reactant

^{#2} For precursor-mediated adsorption, an exact step-function change in the rate of irreversible adsorption or "uptake" cannot be obtained due to the presence of the precursor state. Utilizing the specific forms for the rate expressions consistent with eq. (1) and assuming that adsorption into the chemisorbed state is irreversible whereas adsorption into the precursor state is reversible, we find that for a step-function change in the reactant flux the resulting response in the rate of irreversible adsorption is proportional to $u(t)\{1 + [(1 - \alpha)/\alpha] \exp(-a_{22}t)\}$, where α is the probability of chemisorption from the precursor state, and $a_{22} = 1/\tau_2$ is the reciprocal of the average residence time in the precursor state. Thus, if $a_{22} \gg 1/\tau$ or $\alpha \cong 1$, the response of the rate of irreversible adsorption approximates a step-function change with respect to the pumping time constant, the rate of irreversible adsorption will approximate a step-function change.

(proportional to N_g) is given by

$$N_{\rm g}(t)/N_{\rm g,s} = 1 - S_{\rm s}\eta [1 - \exp(-t/\tau)].$$

Thus, the concentration of the reactant in the gas phase will decay exponentially, characterized by the pumping time constant of the reactor, to a new value given by $N_g = N_{g,s}(1 - S_s \eta)$. Provided the rate of adsorption is constant for a period of time such that $t \gg \tau$, both the pumping time constant τ and the product $S_s \eta$ can be obtained. We note that this procedure for obtaining an apparent probability of adsorption (i.e. $S_s \eta$) is essentially equivalent to that proposed previously by King and Wells [24]. In practice, the determination of the product $S_s \eta$ was quite reproducible utilizing this procedure $(\pm 5\%)$. The determination of the pumping time constant compared well with the results obtained independently by employing the pulse-testing method utilizing the solenoid-activated value, as described in section 2. The more reproducible values for the pumping time constant obtained via the pulse-testing method are used in the analysis below.

The fact that the probability of adsorption of CO on $Pt(110)-(1 \times 2)$ is essentially independent of coverage at fractional coverages below approximately 0.3 is indicative of precursor-mediated adsorption kinetics. Since the residence time of CO in the precursor state is much less than both the residence time in the chemisorbed state and the reciprocal of the modulation frequency, an approximate form of the system transfer function, derived elsewhere, is appropriate. This approximate form, which does not distinguish between "intrinsic" and "extrinsic" precursor states [26], is given by

$$(\tau p+1)N_{\rm g}^{\dagger}(p) = S_{\rm s}\eta \left[\frac{p/\nu_{\rm d}^{\ast}}{1+p/\nu_{\rm d}^{\ast}}\right] (\Delta\epsilon_{\rm h}^{\ast})_{\rm s}T^{\dagger}(p), \qquad (1)$$

and

$$\nu_{\rm d}^* = (1-\alpha)k_{\rm d,s} \Big(1 + \theta_{\rm s} \frac{\partial}{\partial \theta} \Big[\ln(k_{\rm d}^{(1)}) - \Delta \epsilon_{\rm h}^* \Big]_{\rm s} \Big), \qquad (2)$$

where $p = i\omega$ is the complex radial frequency $S_s \equiv S^*\alpha$, S^* is the trapping probability into the precursor state from the gas phase, α is the probability that a molecule in the precursor state will be chemisorbed, ν_d^* is the apparent reaction rate coefficient, $\Delta \epsilon_h^* \equiv (E_d - E_a + E_d^*)/k_B T$ is a dimensionless combination of activation energies, k_d ($k_d^{(1)}$) is the reaction rate coefficient (preexponential factor) for desorption from the chemisorbed state into the precursor state, $T^{\dagger}(t) \equiv [T(t) - T_s]/T_s$, and θ is the fractional coverage in the chemisorbed state. The subscript s refers to the values occurring at steady state. Note we have assumed that the rate of adsorption is independent of coverage and the rate of desorption is first-order in coverage. The reaction



Fig. 3. Experimental data representing the system transfer function given by eq. (1) as a function of frequency in terms of the amplitude ratio (AR) and phase difference. The solid lines represent least-squares fits to eq. (1) where $AR(\omega) = S_s \eta (\Delta \epsilon_h^*)_s / [(\nu_d^*/\omega)^2 + 1]^{1/2}$ and $\phi(\omega) = \tan^{-1}(\nu_d^*/\omega)$.

probabilities, rate coefficients, preexponential factors and activation energies correspond to the following elementary reactions:

 $CO(g) \xrightarrow{S^*} CO^*(a),$ $CO^*(a) \xrightarrow{\alpha, E_a} CO(a),$ $CO(a) \xrightarrow{k_d, k_d^{(1)}, E_d} CO^*(a),$ $CO^*(a) \xrightarrow{(1-\alpha), E_d^*} CO(g),$

where CO^{*}(a) represents the precursor state. Note we have assumed that trapping into the precursor state is not activated (i.e. $E_a^* = 0$).

Amplitude and phase response data representing the system transfer function given by eq. (1) are shown in fig. 3 for a particular set of conditions with the same reactant partial pressure but different steady-state temperatures (and hence different coverages). The experimental data are in quantitative agreement with eqs. (1). In particular, the amplitude ratio approaches a constant value at high frequencies, whereas the phase difference varies from a value of $\pi/2$ to a value of zero as the frequency increases. The data shown in fig. 3 were fit to eq. (1) employing a least-squares functional minimization routine based on a simplex method [26]. The parameters obtained, $S_s\eta(\Delta\epsilon_h^*)_s$ and ν_d^* ^{#3}, can be used to calculate directly the heat of adsorption and, under appropriate conditions, the preexponential factor of the desorption rate coefficient. Examination of eq. (2) indicates that the latter calculation should be justifiable at sufficiently low coverages, i.e. when $\theta_s[\partial(\ln k_d^{(1)} - \Delta\epsilon_h^*)/\partial\theta]_s \ll 1$. (Note that only knowledge of $S_s\eta(\Delta\epsilon_h^*)_s$ is required to evaluate the heat of adsorption.) The fractional surface coverages occurring at steady state were estimated by heating the crystal rapidly while it was in line-of-size of the beam doser. The integrated area (versus time) of the resulting desorption spectrum is proportional to the steady-state fractional surface coverage at 350 K, of which the absolute value has been obtained [21], the absolute surface coverage can be calculated.

The calculated values for the heat of adsorption and the preexponential factor of the desorption rate coefficient (calculated in two different ways; vide infra) are shown in fig. 4 as a function of surface coverage. Since the probability of adsorption is constant between 200 and 600 K [20], the two activation energies E_a and E_d^* of eq. (1) are essentially equal. Thus, in this case, the dimensionless heat of adsorption $\Delta \epsilon_h^* = (E_d - E_a + E_d^*)/k_BT$ is equivalent to the dimensionless activation energy of desorption from the chemisorbed state $\epsilon_d = E_d/k_BT$. The three data points shown represent the same reactant partial pressure but different steady-state temperatures, and are the average values obtained from two separate experiments under identical conditions. For reference purposes, the values obtained by modulated molecular-beam reactive scattering (MMBRS) [20] for the zero-coverage limit are displayed on the left-hand ordinate in fig. 4. We see that the kinetic parameters decrease in magnitude as the coverage increases and display a certain degree of compensatory behavior insofar as the rate of desorption is concerned, as has been observed previously [20-22]. Extrapolating to zero coverage, the results obtained here compare very well with those obtained via MMBRS.

The preexponential factor is calculated using eq. (2), and assuming $\theta_s[\partial(\ln k_d^{(1)} - \Delta \epsilon_h^*)/\partial \theta]_s \ll 1$. The solid line and open circles in fig. 4 pertaining to $k_d^{(1)}$ were calculated by assuming that desorption from the chemisorbed state is "direct" (i.e. $v_d^* = k_{d,s}$) whereas the dashed line was calculated by assuming that the CO which desorbs from the chemisorbed state is trapped in the precursor state $[v_d^* = (1 - \alpha)k_{d,s}]$. The latter utilized a probability of

^{#3} Alternatively, if the pumping time constant τ is considered to be a *parameter* (i.e. a three rather than a two-parameter fit), the values estimated by the least-squares procedure are within approximately 10% of the independently measured values.



Fig. 4. Activation energy E_d and preexponential factor $k_d^{(1)}$ of the desorption rate coefficient of CO from Pt(110) as a function of the surface coverage. $\theta_{CO} = 1$ is equivalent to $9.2 \times 10^{1.1}$ molecules cm⁻². The open circles and solid lines were calculated by assuming that the desorption reaction is direct, whereas the dashed line was calculated by assuming that desorption proceeds through a precursor state (see text). The values displayed on the ordinate were obtained by MMBRS [20].

chemisorption of $\alpha = 0.7$ ($S^* = 1$ and $S^*\alpha = 0.7$ [20]). Note that in this case the preexponential factor describes the elementary reaction CO(a) \rightarrow CO*(a), not CO(a) \rightarrow CO(g). Although this is consistent with the assumptions inherent in the derivation of eq. (2), the possibility exists that the trapping mechanism may not be so efficient for CO that is *desorbed* from the chemisorbed state (at surface temperatures near 500 K) relative to CO that is *adsorbed* from the gas phase (at gas and surface temperatures near 300 K). The actual physical situation may well lie between these two limiting cases, which cannot be distinguished experimentally as may be seen in fig. 4. Unfortunately, the *form* of the experimentally measured response function (cf. fig. 3) also cannot resolve this issue, since the predicted functional forms for the direct and (approximated) precursor-mediated adsorption cases are identical [9] ^{#4}.

^{#4} If sufficiently high-frequency teraperature forcing functions were available, i.e. on the order of the reciprocal of the residence time of a molecule in the precursor state, in principle, direct and precursor-mediated adsorption-desorption could be distinguished experimentally.

3.2. CO oxidation on $Pt(110)-(1 \times 2)$

The oxidation of CO on Pt(110)- (1×2) has been examined for a CO partial pressure of approximately 4×10^{-9} Torr (see footnote #1), O₂-to-CO partial pressure ratios between approximately one and ten, and surface temperatures between 375 and 450 K. The general features of the CO oxidation reaction on the platinum metals have been reviewed by Ertl and Engel [3]. We are concerned with the kinetics of the elementary surface reaction between CO admolecules and oxygen adatoms to produce CO₂. To date, the most reliable investigations of this elementary reaction on platinum surfaces have employed molecular beam techniques [27–29]. The activation barrier has been calculated to be 22–24 kcal mol⁻¹ in the low coverage limit [27,28], while in the presence of high coverages of chemisorbed oxygen adatoms, the barrier has been



Fig. 5. Amplitude ratio (AR) and phase difference data representing the system transfer function $(\tau p + 1)N_3^{\dagger}(p)/T^{\dagger}(p) \equiv \epsilon_r G''(p)$ given by eq. (3) for the reaction $CO(a) + O(a) \rightarrow CO_2(g)$. The insensitivity of the response with respect to the amplitude of the temperature forcing function demonstrates the validity of the linearity assumption. Note the two different temperature scales.

observed to decrease to values between approximately 10 and 12 kcal mol⁻¹ [27,29].

The linearity of the response function was again verified experimentally by varying the amplitude of the temperature forcing function at fixed frequencies. The amplitude ratio and phase difference of the gas phase CO_2 product signal $[N_3^{\dagger} \equiv (N_3(t) - N_{3,s})/N_{3,s}]$, where the '3' denotes the product CO_2], corrected for the pumping term is shown in fig. 5 as a function of the temperature amplitude. The linearity of the response function is evidenced by the independence of the amplitude ratio and phase difference with respect to the amplitude of the temperature modulation.

The pumping time constant of the chamber was evaluated by imposing a step-function change in the rate of the surface reaction that produces CO_2 . If the CO partial pressure is reduced suddenly at sufficiently high temperatures (≥ 650 K), the rate of the overall reaction will be reduced correspondingly (since the rate is approximately first-order in the CO partial pressure at these temperatures). The time constant of the decay in the production of CO_2 will be less than the residence time of the adsorbed CO molecules in the absence of reaction. For temperatures above 650 K, we estimate a residence time for adsorbed CO on the clean surface that is below 0.01 s. Thus, the resulting exponential decay of the gas phase product signal will reflect the pumping time constant of the chamber, since, in this case, it is much greater than the "reaction response time".

In actual practice, the CO and O₂ partial pressures are reduced suddenly by rotating the crystal quickly out of line-of-sight of the beam doser at high temperatures (≥ 650 K). The values obtained by this procedure ($\tau \geq 0.3$ s) were very reproducible and compared well with results obtained independently from the pulse-testing method utilizing the solenoid valve. The value of the pumping time constant was measured periodically during the course of an experiment and was found to vary by less than $\pm 5\%$.

Amplitude and phase response data representing the system transfer function $\epsilon_r G''(p)$ (vide infra) for a particular set of reaction conditions with the same reactant partial pressures but different steady-state temperatures are shown in fig. 6. Due to both the limited frequency bandwidth of the temperature forcing functions and the advantages discussed both elsewhere [9] and below, reaction conditions were chosen such that an approximate form of the system transfer function could be employed. This approximate form, for which a complete derivation is given elsewhere [9], involves the following assumptions: (1) the reaction probability upon adsorption of both reactants (i.e. CO and O₂) is nearly unity; (2) the adsorption reactions are essentially independent of surface temperature; (3) adsorbate coverages are not near saturation levels; and (4) the product (CO₂) molecule is not trapped on the surface upon formation, but rather it desorbs "immediately". Under these conditions the system transfer function (rigorously specified by seven parameters) is



Fig. 6. Experimental data representing the system transfer function $\epsilon_r G''(p)$ given by eq. (3) as a function of frequency in terms of the amplitude ratio (AR) and phase difference. The solid lines represent least-squares fits to eq. (3), i.e. $AR(\omega) = \epsilon_r [(v_r^{(2)}/\omega)^2 + 1]^{1/2}$ and $\phi(\omega) = \tan^{-1}(v_r^{(2)}/\omega)$.

dominated by the linearized rate coefficients $(\chi_j, \text{ vide infra})$ of the elementary bimolecular surface reaction $CO(a) + O(a) \rightarrow CO_2(g)$ and may be approximated by

$$(\tau p+1)N_3^{\dagger}(p)/T^{\dagger}(p) = \epsilon_r G''(p) \cong \epsilon_r \left(\frac{p/\nu^{(2)}}{1+p/\nu_r^{(2)}}\right), \tag{3}$$

where $\epsilon_r \equiv (E_r/k_B/T)_s$ is the dimensionless activation energy of the bimolecular surface reaction at the steady state, and $\nu_r^{(2)} = \chi_1 + \chi_2$ is the apparent reaction rate coefficient [the subscript "1" represents O(a) and "2" represents CO(a)]. Note that eq. (3) predicts that the apparent activation energy [i.e. $E_rG''(0)$] will be nearly zero with respect to the actual activation energy of the bimolecular surface reaction (E_r) . Thus, the experimental observation of both high reaction probabilities and low apparent activation energies (relative to E_r) will virtually ensure the applicability of eq. (3). The coefficients χ_j are defined as $\chi_j \equiv [\partial(xk_r)/\partial\theta_j]_s$, where $x(\theta_1, \theta_2)$ is the implicit coverage dependence of the bimolecular surface reaction, $k_r = n_s k_r^{(2)} \exp(-E_r/k_BT)$ is the reaction rate coefficient, and n_s is the density of surface sites. If the adsorbed

reactants are uniformly dispersed on the surface, $x(\theta_1, \theta_2) = \theta_1 \theta_2$, and the apparent rate coefficient is given by

$$\nu_{\rm r}^{(2)} = \chi_1 + \chi_2 = (\theta_1^* + \theta_2^*) k_{\rm r,s}, \tag{4}$$

where

$$\boldsymbol{\theta}_{i}^{*} = \boldsymbol{\theta}_{i,s} \left(1 + \boldsymbol{\theta}_{j,s} \frac{\partial}{\partial \boldsymbol{\theta}_{j}} \left(\ln k_{r}^{(2)} - E_{r} / k_{B} T \right)_{s} \right),$$
(5)

and (i, j) = (1, 2) and (2, 1). Note the similarities between the apparent rate coefficient for the adsorption-desorption equilibrium [eq. (2)] and that for the bimolecular surface reaction [eqs. (4) and (5)].

The advantages of using the "high-reaction-probability" approximate form given by eq. (3) are evident: the simplicity of a two-parameter transfer function (which permits use of the entire data set in the analysis) and the possibility of evaluating the preexponential factor via the apparent rate coefficient $v_r^{(2)}$ [cf. eqs. (4) and (5)]. Concerning the restrictions placed on the use of this approximate form, the reaction probability of CO upon adsorption was measured to be greater than 0.9, whereas that for the adsorbed oxygen adatoms was unity for all reaction conditions considered. In addition, for these experimental conditions both the adsorption of CO [20] and the dissociative adsorption of oxygen [30,31] are essentially independent of the surface temperature. Finally, the observed apparent activation energies were such that $|G''(0)| \leq 0.05$. Based on these experimental observations, the measures response should be described well by the approximate form of eq. (3) for a wide range of frequencies. Curves representing eq. (3), with the parameters ϵ_r and $v_r^{(2)}$ determined by the least-squares routine employed above [26] are displayed in fig. 6. We see that the functional agreement of both the amplitude and the phase is excellent, which lends further support to the use of eq. (3) for these reaction conditions. An analysis of the data shown in fig. 6 leads to a direct determination of the activation energy of the elementary surface reaction via the parameter ϵ_r (i.e., $E_r \equiv k_B T_s \epsilon_r$). For the two conditions shown, we find activation energies of approximately 21 and 17.5 kcal mol^{-1} at 375 and 400 K.

To determine the effect of the composition of the adlayer on the kinetics of the surface reaction, a series of experiments were carried out at a constant CO partial pressure $(3.8 \times 10^{-9} \text{ Torr})$ and a varying oxygen partial pressure (between 6.8×10^{-9} and 3.4×10^{-8} Torr). Results similar to those presented in fig. 6 were obtained, and the activation energy of the surface reaction was evaluated for these various experimental conditions. These results are displayed in fig. 7^{#5}. For small values of P_{O_2}/P_{CO} , the activation energy is

^{#5} The data given by partial pressure ratios of $P_{O_2}/P_{CO} = 3.2$ and 5.5 represent the average values of two different experiments carried out under identical conditions. The values obtained for the activation energies were within approximately ± 1 kcal mol⁻¹ of the resulting mean values.



Fig. 7. Activation energy for the surface reaction $CO(a) + O(a) \rightarrow CO_2(g)$ as a function of the surface temperature. $P_{CO} = 3.8 \times 10^{-9}$ Torr (see also footnote #1).

virtually independent of the adlayer composition of which the latter is dictated by the surface temperature. The measured value of approximately 22 kcal mol⁻¹ is in excellent agreement with previous results in the low-coverage limit on other platinum surfaces [27,28]. Note that the *difference* between the activation energies for the desorption and the oxidation of CO was measured in this previous work to determine the low-coverage value of the activation energy to reaction [27,28]. For larger values of P_{O_2}/P_{CO} , the activation energy decreases markedly as the surface temperature is increased, as may be seen in fig. 7.

To determine if this effect is related to structural changes in overlayer, as has been postulated previously [32], the surface was monitored using LEED during all of the reaction conditions displayed in fig. 7. In agreement with previous work [21], we observed a (1×1) LEED pattern at $\theta_{CO} = 0.5$ and a plg1(2 × 1) pattern at $\theta_{CO} = 1$ in the presence of pure CO. On the other hand, in the presence of pure O₂, no ordered oxygen superstructures were observed for any coverage of oxygen adatoms which is in agreement with previous experimental observations [30]. Of most importance here, no ordered superstructures were observed during any reaction conditions; the (1×2) LEED pattern of the reconstructed surface was always maintained. However, upon reducing the temperature below approximately 375 K, (reaction conditions that are not represented in fig. 7), the exact temperature depending on the partial pressure ratio P_{O_2}/P_{CO} , a (1 × 1) LEED pattern was observed concomitant with a complete extinguishing of the rate of production of CO₂. This observation suggests that a coverage of CO of $\theta_{CO} = 0.5$ is sufficient to block completely the dissociative chemisorption of oxygen and, hence, the rate of oxidation of CO. Although separate disordered domains of CO(a) and O(a) remain a possibility (a remote possibility since adsorbate ordering is the major driving force for domain formation), a (long-range) structural rearrangement of the overlayer seems unlikely as the cause of the observed behavior. An alternate, more reasonable explanation for the observed variation in the activation energy can be put forward. As stated earlier, high coverages of oxygen adatoms have been observed to have a profound effect on the activation barrier for the reaction, the observed large decrease having been attributed to a decrease in the binding energies of the adsorbed reactants [27]. Although fixing the level representing the transition state obviously results in a decrease in the barrier height, we believe a more plausible argument includes a differential shift in both the reactants and the transition state, the reactants shifting up more than the transition state [33].

Utilizing reaction rate measurements and the expressions for the rates of adsorption (both CO and O_2) and desorption (CO only) of the reactants determined from independent measurements [18], the adsorbate concentrations were calculated for the conditions shown in fig. 7. The form of the calculated values as a function of temperature is in agreement with experimental measurements [34,35], i.e. there is a decrease in the CO coverage and a concomitant increase in the oxygen coverage as the temperature increases. As may be seen in fig. 8, the variation of the activation energy of the surface reaction correlates well with fractional coverage of oxygen adatoms. Indeed, this is the *only* functional dependence of the adlayer that shows a consistent trend. Variation of the parameters used in the numerical model was found to result in differing absolute values for the coverage of oxygen (~ $\pm 20\%$), while the *form* of the curve shown in fig. 8 remained the same.

The variation of the activation energy with oxygen coverage is obviously quite nonlinear. In particular, the precipitous drop in the activation energy above $\theta_0 \approx 0.15$ suggests that configurational effects may be important. (Note that $\theta_0 = 0.4$ represents saturation [30,31].) In this picture, for $\theta_0 \leq 0.15$, CO admolecules are reacting with nearly independent oxygen adatoms, which are essentially equivalent to one another and isolated. However, for $\theta_0 > 0.15$ the adsorbed CO reacts in regions of higher (local) oxygen adatom concentration. This configuration of reactants serves to decrease the bond energy of the adsorbed reactants [3,36-39].



Fig. 8. Activation energy and second-order preexponential factor for the surface reaction CO(a) + O(a) \rightarrow CO₂(g) as a function of the calculated coverage of oxygen adatoms C_0 , where $C_0 \rightarrow 0.4$ is saturation.

Examination of eqs. (4) and (5) shows that if coverage-dependent effects on the kinetic parameters are small and/or compensatory, the preexponential factor of the surface reaction rate coefficients can be calculated via the parameter $\nu_r^{(2)}$, provided the adsorbate coverages are known. We submit that this use of the parameter $\nu_r^{(2)}$ is valid for the reaction conditions represented in fig. 8 if $\theta_0 \leq 0.15$. Due to the relatively low coverages of both reactants under these conditions (calculations indicate that $\theta_{CO} \leq 0.25$) [18]), adsorbate domain formation is unlikely. Since the temperature of reaction is relatively high, surface diffusion of CO is rapid, and the elementary surface reaction is certainly first-order in the CO coverage. However, under these same conditions, the oxygen adatoms are relatively immobile [40]. Nonetheless, provided all of the oxygen adatoms arc equivalent and equally "accessible" which, in general, is valid at low coverages (where the adatoms are isolated), the surface reaction will also be first-order in the oxygen adatom coverage. Thus, since the activation energy is virtually independent of the adlayer composition below oxygen adatom coverages of approximately 0.15, we may assume that θ_{CO}^* + $\theta_0^* = \theta_{CO} + \theta_0$ [see eq. (5)], and it follows directly that $k_r^{(2)} =$ $v_{\rm r}^{(2)} \exp(\epsilon_{\rm r})/n_{\rm s}(\theta_{\rm CO}+\theta_{\rm O}).$

The values of the parameter $v_r^{(2)}$, corresponding to the reaction conditions of fig. 7 and obtained via an analysis of data similar to those shown in fig. 6,



Fig. 9. Apparent rate coefficient $[\nu_r^{(2)} \text{ of eq. (4)}]$ of the surface reaction CO(a) + O(a) \rightarrow CO₂(g) for the reaction conditions corresponding to the data given in fig. 7. $P_{CO} = 3.8 \times 10^{-9}$ Torr (see also footnote #1).

are displayed in fig. 9. Utilizing these values, the measured values for the activation energies, and the calculated values for the adsorbate concentrations, we can calculate the corresponding values for the second-order preexponential factor of the reaction rate coefficient. These values of the preexponential factor are displayed in fig. 8 as a function of the oxygen adatom concentration ^{#6}. Within experimental error, the preexponential factor is nearly independent of the adlayer composition below oxygen adatom coverages of approximately 0.15. In the limit of low coverages, the preexponential factor approaches a value of approximately 3×10^{-3} cm² s⁻¹, accurate to within a factor of approximately five. This value for the low-coverage limit of the preexponential factor is in excellent agreement with previous results on various surfaces of platinum [27], palladium [32] and rhodium [41], as well as the "normal" value of $10^{-2}-10^{-3}$ cm² s⁻¹ predicted by transition state theory.

^{#6} The ordinate axes in fig. 8 have been scaled to correspond to an "isokinetic temperature" of $T_{iso} = 437$ K. If the parameters compensate exactly for one another, then a differential change in the coverage (of oxygen in this case) will result in no change in the value of the reaction rate coefficient, i.e. by definition $\partial (k_B T_{iso} \ln k_r^{(2)} - E_r)/\partial \theta = 0$.

The preexponential factor has also been evaluated for oxygen adatom coverages above approximately 0.15 (cf. fig. 8). As the oxygen concentration increases beyond $\theta_{\rm O} \cong 0.15$, the magnitude of the preexponential factor drops precipitously in concert with the activation energy. Errors in the calculation of the preexponential factor for $\theta_0 \ge 0.15$ can arise from both coverage-dependent rate parameters, and the assumption of an incorrect implicit coverage dependence, i.e. $x(\theta_{CO}, \theta_{O}) \neq \theta_{CO}\theta_{O}$. Concerning the former, if the rate parameters compensate sufficiently for one another such that the rate coefficient is essentially independent of coverage, the calculation is valid. If the preexponential factors in fig. 8 are the true values, it appears that significant compensation is indeed occurring. However, if the true preexponential factor is essentially constant, we find from the data in fig. 8 that for $\theta_0 \approx 0.2$, $\{\theta_0\partial[E_r(\theta_0)/k_BT]/\partial\theta_0\}_s = -40$. Clearly, this value cannot totally account for the deviation of the preexponential factor by 10⁷. Thus, if errors have been made in the calculation, the latter explanation is probably the major contributor, e.g. $x(\theta_{\rm CO}, \theta_{\rm O}) = \theta_{\rm CO} f(\theta_{\rm O})$, where $f(\theta_{\rm O}) \ll \theta_{\rm O}$.

Explanations for anomalously low apparent preexponential factors, such as those observed here at high oxygen adatom coverages have usually involved the following plausibility arguments: (1) effects due to adsorbate phase separation [42]; and/or (2) abnormally high partition functions for the reactants resulting from the presence of "softened" vibrational modes for the adsorbed reactants (especially CO) [27]. Concerning the latter, it is unlikely that an argument involving transition state theory and abnormally large vibrational partition functions for the reactants could reasonably explain the apparent deviation of the preexponential factor by more than seven orders of magnitude. Concerning the former, the presence of oxygen adatom islands acts to limit the number of oxygen adatoms "accessible" for reaction with CO to those at the perimeter of islands $(x(\theta_{CO}, \theta_O) \neq \theta_{CO}\theta_O^{\#7})$. This argument presupposes that the adsorption and/or reaction probability of CO is negligible within an oxygen adatom domain. If we assume that the islands are composed of a locally saturated oxygen adlayer (i.e. $\theta_0 = 0.4$), in order to account for the factor of 10⁷ deviation of the preexponential factor the island diameter must be on the order of one cm! Obviously, this size for a "static" oxygen adatom island is very unlikely.

An alternate explanation for the apparently anomalously low preexponential factors can be put forward. We have argued that the decrease in the activation energy for $\theta_0 \ge 0.15$ can be explained by a decrease in the binding energy of the reactants due to their local configuration. It is probable that this configuration of reactants occurs with a very low probability (i.e. on the order of 10^{-7}). If the reaction probability (or "cross-section") of a diffusing CO

^{#7} For examples of model rate expressions that describe bimolecular surface reactions in which adsorbate domain formation occurs, see, for example, ref. [43].

admolecules with this configuration of oxygen adatoms is much greater than that of isolated oxygen adatoms (e.g. due to a decrease in the binding energy of the oxygen adatoms in this configuration), this proposal would account for both an anomalously low preexponential factor and a lower activation energy of reaction, and it is consistent with other experimental observations (e.g. since the probability of reaction with isolated adatoms is already nearly unity, there is no marked deviation in overall rate. It is important to note that the activation energy displayed in fig. 8 is represented solely as a function of θ_0 , i.e. it is independent of surface temperature. This result implies that this configuration of reactants is not intrinsically a function of surface temperature, which tends to rule out, for example, an equilibrium in the oxygen adlayer between low- and high-concentration adatom phases. Since the residence time of the oxygen adatoms τ_0 is reduced due to reaction with CO $(\tau_0 \sim 1/\nu_r^{(2)} \sim 1$ s), a metastable configuration of the adlayer could easily exist under reaction conditions [40].

The dominance of the Langmuir-Hinshelwood mechanism in describing the oxidation of CO has been demonstrated clearly by Ertl and coworkers [27,32] on surfaces of platinum and palladium, and by Egelhoff and coworkers [35,42] on the (111) surface of iridium. We shall show next that our experimental data employing surface temperature modulation support these conclusions. By definition, the Langmuir-Hinshelwood mechanism involves a surface reaction between chemisorbed reactants, whereas the Eley-Rideal mechanism involves reaction between a chemisorbed reactant and a gas phase species (CO in this case) via a direct collision or after adsorption into a weakly bound precursor state. For reaction via a direct collision, the rate may be expressed as $r_r = (F_{CO}/n_s)\theta_O k_r^{ER}(\theta_O, T)$, where F_{CO} is the incident flux of CC(g). Thus, utilizing the expression $\nu_r^{(2)} = \chi_O = r_r/\theta_O$, the measured rate of reaction and the calculated coverages of oxygen ^{#8}, we find that the estimated values for the parameter $\nu_r^{(2)}$ are more than an order of magnitude smaller than those actually observed, which are shown in fig. 9. Hence, we can rule out any significant rate of reaction via the direct collision of gas phase CO with oxygen adatoms.

Reaction via a weekly bound precursor state of CO can also be precluded by the following argument. When the oxygen coverage is moderately high (i.e. $\theta_0 \ge 0.10$) and the CO coverage is low ($\theta_{CO} \ll 1$), the partial derivative term with respect to θ_{CO} provides the dominant contribution to the parameter $\nu_r^{(2)}$ [cf. eqs. (4) and (5)]. In addition, since the approximations inherent in the construction of eq. (3) are satisfied for the reaction conditions examined here (verified by the experimentally measured system transfer function), we must have $\nu_r^{(2)} \cong \chi_{CO} = \theta_0 k_r \gg k_d$, where k_d is the desorption rate coefficient of

^{#8} Note that the coverages are calculated without the need to invoke a mechanism for the bimolecular surface reaction.

CO. This inequality becomes obvious if one realizes that the reaction probability of CO is given by $\theta_0 k_r / (\theta_0 k_r + k_d)$, and this quantity is near unity. Consequently, $v_r^{(2)}$ can be used to specify a maximum desorption rate coefficient. Equivalently, if we assume a reasonable value for the preexponential factor of the desorption rate coefficient, we can obtain a *minimum* value for the activation energy of desorption of CO under reaction conditions. For example, utilizing $v_r^{(2)} = 1.5 \text{ s}^{-1}$ (i.e. $P_{O_2}/P_{CO} = 8.9 \text{ and } T_s = 400 \text{ K in fig. 9}$) and $k_d^{(1)} = 10^{13} \text{ s}^{-1}$, we find $E_{d,min} \cong 23 \text{ kcal mol}^{-1}$. This value for the desorption energy is beyond any reasonable value appropriate for a precursor state and obviously represents chemisorbed CO. Thus, the Langmuir-Hinshelwood mechanism is the only viable explanation for the experimental results.

4. Conclusions

Surface temperature modulation [8,9] has been employed to investigate the interaction of CO with the Pt(110)-(1 × 2) surface and the oxidation of CO by oxygen on this surface. The adsorption-desorption equilibrium of CO was studied to determine the kinetic parameters describing the desorption reaction. These kinetic parameters were found to vary in sympathy with coverage, decreasing in magnitude as the coverage increases. Extrapolating to zero coverage, we find values for the activation energy of $E_d = 36 \pm 1.5$ kcal mol⁻¹ and for the preexponential factor of $k_d^{(1)} = 3 \times 10^{14}$ s⁻¹. By including trapping effects due to the presence of a precursor state, the value of the preexponential factor associated with the elementary reaction CO(a) \rightarrow CO*(a) may be as large as 1×10^{15} s⁻¹ in the zero-coverage limit.

The oxidation of CO on Pt(110) was studied with particular emphasis on an examination of the elementary bimolecular surface reaction $CO(a) + O(a) \rightarrow CO_2(g)$. Despite the large number of fundamental studies directed at examining this surface reaction [3], surprisingly little quantitative information has been obtained concerning the variation of the kinetic parameters with surface coverage. Typically, measurements have been made under nonsteady-state conditions and/or only for limiting cases representing extremes in the composition of the adlayer (i.e. low coverages of both species, or relatively high oxygen adatom coverages).

The activation barrier for the elementary bimolecular surface reaction has been evaluated here in a direct fashion at a variety of steady-state conditions. The observed activation energy ranges between approximately 22 and 8 kcal mol^{-1} . Calculations show that the coverages of both adsorbed reactants very considerably for the conditions studied here. A strong correlation was found between the magnitude of the activation barrier and the coverage of oxygen adatoms. A precipitous drop in the magnitude of the activation barrier was observed as the fractional coverage of oxygen adatoms increased above approximately 0.15, the variation in the magnitude of the activation energy with oxygen coverage being quite nonlinear. This result is interpreted qualitatively as a manifestation of the crucial role that the local configuration of the reactants plays in determining the surface reaction dynamics. At relatively high oxygen coverages ($\theta_0 \ge 0.15$), adsorbed CO reacts in regions of high local oxygen adatom concentration. In these regions of the surface, the adsorbed reactants have reduced binding energies that lead directly to a decrease in the activation energy for the production of CO₂.

The preexponential factor for the elementary bimolecular surface reaction has been evaluated also for these reaction conditions. A value of $k^{(2)} = 3 \times 10^{-3}$ cm² s⁻¹ was found for the low coverage limit, whereas concomitant with the variation of the activation energy, the magnitude of the preexponential factor drops precipitously as the oxygen coverage increases ($\theta_0 \ge 0.15$), to an apparent value as low as 10^{-10} cm² s⁻¹ at $\theta_0 \cong 0.25$. The major factor contributing to this marked decrease in the preexponential factor is probably associated with the probability of occurrence (i.e. the concentration) of oxygen adatoms of high local density, not with the formation of separate adsorbate domains. Finally, knowledge of the approximate residence time of the adsorbed CO ($\tau_{CO} \cong 1/\nu_r^{(2)}$) has demonstrated clearly that the CO oxidation reaction proceeds via the reaction of chemisorbed CO with oxygen adatoms, i.e. the Langmuir-Hinshelwood mechanism dominates.

A number of extensions of this surface temperature modulation technique are obvious. For the modulation frequencies used here, the technique can be coupled with time-resolved surface spectroscopies [44–47] or diffraction techniques [48] in order to provide direct complementary information concerning the composition and configuration of the adlayer. Time-resolved measurements of the fractional coverages of the adsorbed reactants could identify explicitly the adsorbate transfer functions [9] which, in principle, could be used to deduce the form of the implicit coverage dependence of a particular surface reaction. Alternatively, the energetics of (reversible) interconversion between stable surface species could be examined by the use of an appropriate surface spectroscopy coupled with a modulation in surface temperature. In this case, the formalism developed previously for homogeneous chemical kinetics should be sufficient [49].

Finally, the combined use of conventional, line-of-sight, differentially pumped mass spectrometric detection and localized surface heating techniques (e.g. laser heating [50]) would provide higher frequencies of the temperature forcing function. This would extend considerably the frequency bandwidth of the technique. Since direct measurement of the time evolution of the surface temperature produced by rapid laser heating would be difficult ^{#9} a calibra-

^{#9} Currently available commercial optical and infrared pyrometers have response times on the order of 10 ms.

tion procedure might have to be implemented, e.g. by considering a system for which the amplitude and phase response could be predicted by independent measurements. The adsorption-desorption equilibrium of CO described here should provide an ideal system for calibration purposes.

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