JOURNAL OF CATALYSIS 36, 185-198 (1975)

On the Oxidation of Carbon Monoxide Catalyzed by Palladium

JOHN S. CLOSE[1] AND JOHN M. WHITE

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Received July 15, 1974

We report here experimental data pertaining to the oxidation of CO when CO-O_2 mixtures are exposed to Pd substrates. The substrates were prepared by exposure to O_2 at high temperatures for extended periods of time. The rate of CO_2 production was measured in the region 300-975 K and reaction orders and apparent activation energies have been derived from the data. At temperatures below 450 K the rate is very low and is inhibited by CO. Above 475 K the rate proceeds readily and involves an Eley-Rideal type reaction between chemisorbed oxygen atoms and gas phase CO. The rapid increase of the rate between 450 and 475 K is attributed to the desorption of CO which then allows the chemisorption of O_2. Above 500 K the rate falls off slowly due to the decreasing residence time of CO and decreasing amounts of chemisorbed oxygen atoms available at the surface. The qualitative features of the temperature dependence of the rate are very similar to those observed on clean single-crystal substrates. Near 475 K the reaction orders with respect to O_2 and CO are the same as those observed on clean single-crystal substrates.

I. INTRODUCTION

In this paper we present kinetic data on the oxidation of carbon monoxide catalyzed by a polycrystalline palladium foil which was prepared by exposure for several hours to oxygen at high temperature. Kinetic orders and activation energies are presented and mechanisms commensurate with these kinetic parameters are discussed.

Considerable experimental attention has been given to the oxidation of CO over the transition metal group—nickel, palladium and platinum (*1–19*), but the oxides of this group have received little attention. The physical properties of these oxides are quite different. At about one bar oxygen nickel oxide is stable at temperatures up to 2200 K, palladium oxide is stable only up to about 1150 K, and platinum oxide becomes unstable at about 850 K. As a result of these relative stabilities, only the oxide of nickel has received much attention. Several studies of the oxidation of CO over NiO have been reported (*20–30*) while the early work of McKinney (*31,32*) is the only study of CO oxidation over PdO. To our knowledge this reaction has not been investigated using platinum oxide. A perusal of the work on nickel oxide reveals several discrepancies from one laboratory to another, these disparities being generally attributable to procedural variations in either the catalyst preparation or the experimental approach. Krylov (*33*), after reviewing the work on these oxides, concluded only that the oxidation proceeds with low activation energy at low temperature and sustains a substantial change in mechanism in the 473–673 K region as substrate oxygen atoms begin to participate in the reaction.

Our purpose in the experiments reported here has been to study the properties of an oxygen-exposed palladium target as it par-

---

[1] Present address: Western Christian College, North Weyburn, Saskatchewan, Canada SOC IXO.

ticipates in the low-pressure production of CO_2 from carbon monoxide–oxygen mixtures. We wish to draw a distinction between oxygen-exposed palladium and palladium oxide since under many of our experimental conditions bulk palladium oxide is thermodynamically unstable. Nevertheless, as discussed below, there is considerable evidence that Pd will incorporate O_2 under conditions where the bulk oxide is unstable.

II. EXPERIMENTAL

All experiments were carried out in a bakeable ultra-high vacuum apparatus built of stainless steel, Pyrex, and fused silica. Pumpdown was achieved using a sorption pump followed by activation of a 4-in. electrostatic ion pump. Each pump was isolatable with a one-inch, gold seal valve. The reaction vessel (5 cm diameter × 20 cm length) was constructed of Pyrex with a fused silica window. Six Pyrex-covered tungsten feed-throughs were provided to mount the catalyst foil, a pair of nickel electrodes and a thermocouple. The substrate consisted of a 20 mm diameter × 0.13 mm thick disc of 99.97% pure palladium. An iron-constantan thermocouple was spot-welded to one side of the substrate. Two nickel electrodes were mounted near the foil to provide for argon-ion bombardment.

Total pressures were measured with a Bayard–Alpert type ionization gauge (BAG) while partial pressures were determined using a small magnetic sector residual gas analyzer (RGA) equipped with an electron multiplier. All pressures reported here make use of the sensitivity of the ionization gauge for nitrogen and relative sensitivities for other gases with respect to nitrogen. The sensitivity of the partial pressure analyzer with respect to the ionization gauge was determined experimentally. Measured pressures were adjusted for conductance and pumping speed effects in order to determine the total and partial pressures within the reaction vessel. Reactants were introduced from a high pressure (ca. 1 atm) storage vessel through a continuously-variable leak.

The catalyst temperature, monitored with the iron-constantan thermocouple, was controlled with a series connection of two 8-A variable autotransformers. With this arrangement it was possible to control the steady-state temperature to within 2 K and, in the desorption experiments, to produce linear heating schedules by increasing the transformer setting manually while recording the temperature.

The system was pumped down and baked, with the exception of the electron multiplier, at 675–725 K for several days. During the final 12 h the electron multiplier was baked at 525 K. After cooling slowly a base pressure of 7×10^{-8} Pa[2] was reached. Under working conditions with both the ionization gauge and residual gas analyzer filaments on, the base pressure was routinely 3–5 $\times 10^{-7}$ Pa.

The substrate, whose stability was defined by the reproducibility of the oxidation reactions it catalyzed, was prepared by the *in situ*, high temperature exposure of the substrate to oxygen. After establishing a steady-state oxygen flow in the 10^{-4} Pa region, the substrate was heated to 900 K until its condition was adequate as judged by the above criterion.

Two kinds of experiments were performed using this substrate-steady state and non-steady state. In the latter a constant leak rate of reactants was established at room temperature and the partial pressures of each reactant were allowed to stabilize. Then while recording 1) the total pressure, 2) the partial pressure of one species, and 3) the temperature, the substrate was heated linearly at 13.1 ± 0.2 $K \cdot s^{-1}$ over a predetermined range after which it was allowed to cool to room temperature. This process was repeated sev-

---

[2] 1 Pa = 1 $N \cdot m^{-2} = 7.5 \times 10^{-3}$ Torr.

eral times while monitoring successively $m/e = 28$, 32, and 44. The data, when corrected for background contributions, sensitivity variations, pumping speed and conductance, furnished the rates for formation of CO_2 and depletion of CO and O_2. In the discussion below this kind of experiment is referred to by the term flash or flashing.

In the steady state experiments a similar procedure was followed except the substrate temperature was increased in steps and a full gas-phase analysis was performed using a repetitious set of partial pressure measurements. In the analysis the major difference between the two kinds of experiment was the absence of time-dependent partial pressure terms in the steady-state experiments. In some experiments surface coverages were calculated in the usual way by integrating pressure versus time curves.

III. RESULTS AND DISCUSSION

1. *Surface Conditioning Experiments*

During the course of our experiments we dealt with three general Pd surface conditions. For reference purposes we designated these as follows: "initial," meaning that surface condition generated by the bakeout, "intermediate," referring to the surface exposed to a limited amount of O_2, and "stable," that final surface, extensively exposed to O_2, on which reproducible CO oxidation experiments could be performed. Quantitative analysis of the rates of these oxidation reactions was possible only when it was clear that no changes were occurring in the catalytic activity of that "stable" surface. Therefore the non-steady state (non-SS) reactions, which were both rapid and sensitive, were utilized as a chemical probe to monitor the surface activity and thus eliminate this potential difficulty.

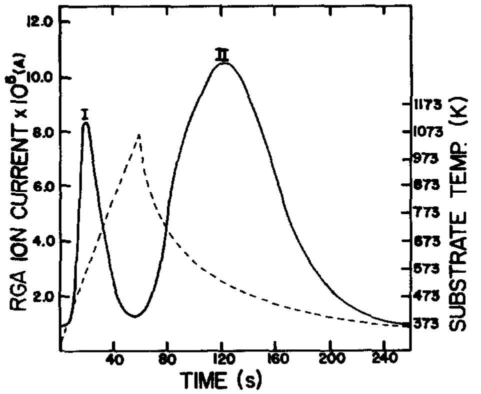

FIG. 1. Variation of CO_2 pressure with time during the flash of a palladium substrate preexposed to oxygen at high temperatures. The total pressure was about 10^{-4} Pa and $O_2/CO \simeq 1.5$. The dashed line shows the temperature variation and the solid line the CO_2 pressure.

Figure 1 illustrates a typical non-SS experiment in which the $m/e = 44$ RGA ion current was recorded as the substrate was flashed in a mixture of $CO + O_2$ flowing at a constant leak rate. After a rapid series of these flashes, the maxima of the CO_2 peaks (denoted I, for $dT/dt > 0$, and II for $dT/dt < 0$) were plotted as in Fig. 2 to expose any changing surface activity. The first three segments of this figure involve the "intermediate" substrate and indicate that catalytic activity is dependent both on the number of flashes and on the maximum flashing temperature. The fourth segment is for the "stable" substrate; its activity shows no dependence on

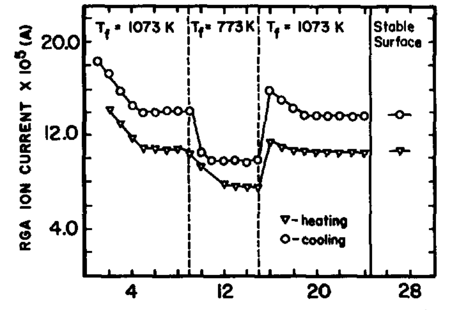

FIG. 2. Variation of maximum rate of CO_2 production with number of flashes. The total pressure was 1.08×10^{-4} torr and $O_2/CO \simeq 1.5$. The substrate was heated (▽) to T_f in each case and then allowed to cool (○) to room temperature. The first three panels are for a substrate in the intermediate condition.

number of flashes and on flashing temperature between 700 and 1100 K. During the preparation of a stable substrate the ambient conditions were monitored using the BAG and RGA. From an analysis of the oxygen pressure as a function of time and the pumping speed characteristics of the system the amount of oxygen gained or lost by the substrate could be estimated. As many as 5×10^{16} molecules cm^{-2} were adsorbed according to this calculation. In view of the thermodynamic instability of bulk PdO under our conditions (*34*), this is a surprisingly large amount of incorporated oxygen.

Of central importance here is the qualitative observation that when the target was heated to 900 K, after establishing a steady-state oxygen flow, the pressure of oxygen, as indicated by both the BAG and the RGA, dropped. The magnitude of this drop was not reproducible and definitely depended on the previous history of the substrate. On a substrate not previously exposed to oxygen the initial rate of oxygen incorporation was rapid but after about five minutes the rate decreased to a slow and roughly constant value that persisted over periods as long as 14 h. On cooling the oxygen pressure rose to a value slightly less than the original pressure. Typically when the initial oxygen pressure was 10^{-4} Pa the pressure drop observed after 5 min of heating was 1.7×10^{-5} Pa and on cooling after 14 h a pressure increase of 0.9×10^{-5} Pa was noted. After exposure some oxygen could be desorbed by flashing in vacuo to 900 K. Even after accounting for oxygen pumping by the RGA and the BAG, the amount desorbed was at most only a few percent of the amount previously taken up. Recently Ertl and Koch (*35*) have reported the chemisorption of oxygen on Pd(111) finding that oxygen chemisorbed at room temperature diffused into the bulk at moderate temperatures near 525 K. Some desorption of O_2 occurred at higher temperatures near 675 K. This observation tends to confirm our conclusion that some O_2 is incorporated into Pd, not to form bulk oxide which is unstable but more likely a nonstoichiometric solid phase.

On each of the three general surfaces, two distinct surface states of adsorbed CO were observed by thermal desorption (Fig. 3)—a low temperature α state and a high temperature β state. When the substrate was flashed, the α-CO exhibited a pressure maximum in the range 375–440 K, while the β-CO displayed its maximum between 615 and 675 K.

The α-CO was always present to the extent of ca. 10^{11}–10^{12} cm^{-2} after the substrate had been exposed to CO and the system pumped back down to p_∞, the base pressure. Though this was only about 0.01–0.1% of a monolayer, it was not surprisingly low since we were never dealing with an atomically clean Pd surface. After baking several days at 725 K one would expect the substrate surface to be heavily contaminated with carbon and possibly sulfur which had diffused there from the bulk (*36*). During the various stages of substrate preparation, and following the oxidation experiments, the original Pd substrate was clearly perturbed by the incorporated oxygen. Very likely this surface is relatively passive to CO adsorption (*32*).

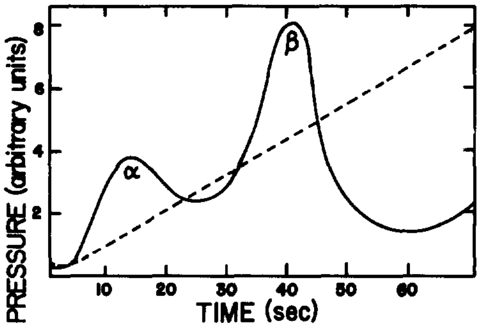

FIG. 3. Variation of CO pressure with time during flashing of a palladium target in the initial condition. The dotted line is the temperature variation from 300 to 1075 K. Two distinct binding states of CO are resolved.

The β-CO only appeared under certain conditions—all of which are consistent with the view that this β-CO is the product of the oxidation of surface carbon. After the initial bakeout, the first flash produced a very large β-CO peak. Though it was not measured accurately the coverage was obviously at least an order of magnitude larger than the 10^{11}–10^{12} cm^{-2} subsequently found on the intermediate and stable surfaces. As suggested above, the bakeout presumably led to considerable surface carbon on the substrate surface and though the partial pressure of oxygen was very low during the bakeout ($< 10^{-8}$ Pa), the ambient pressure of H_2O could possibly have produced this β-CO by the common water-gas reaction, $C_\sigma \times H_2O - CO_\sigma + H_2$. This reaction has been observed to occur rapidly with graphite and a metal oxide catalyst (e.g., CuO, NiO, FeO) at temperatures as low as 850 K (*37*). With the exception of this initial flash, the β-CO was found only after heating the substrate in the presence of a significant partial pressure of oxygen (e.g., 10^{-5}–10^{-4} Pa) and then only when carbon could reasonably be expected to be present on the surface. With the "intermediate" surface condition the carbon was apparently able to diffuse to the surface. However, following repeated flashes in O_2, the carbon impurity was apparently depleted near the surface and the β-CO peak became smaller and smaller until on the stable surface it disappeared altogether. This stable surface, which contained considerable oxygen, was apparently an effective barrier to the carbon diffusion process. The β-CO peak was regenerated from a stable substrate in two ways. First, after heating a stable substrate in vacuum for 24 h at 1050 K, the catalytic activity dropped and the β-CO peak reappeared on flashing. Second, by Ar^+ bombardment the stable substrate was destroyed and the characteristics of the "initial" substrate reappeared including the β-CO peak.

The β-CO peak reappeared under one other set of conditions, namely after prolonged oxidation of a CO–O_2 mixture at high temperatures near 1000 K. This suggests that a small amount of dissociation or disproportionation of CO occurs at these temperatures and leaves behind the surface carbon precursor to β-CO. In this context it should be noted that Madden and Ertl (*38*) interpreted the β-CO which they observed on Ni (110) as arising from surface carbon produced by the dissociation of CO. The oxidation of such surface carbon is not an unusual phenomenon having been observed on Ni in several laboratories (*38–41*). Furthermore, McAllister and White (*41*) demonstrated that the oxidation of surface carbon on polycrystalline Ni always resulted in a high temperature sorbed state similar to the state we have called β-CO.

2. *Non-Steady State Oxidation Experiments*

Though the non-SS CO oxidation experiments were principally utilized to explore the relative surface activity of the catalyst, they revealed two other important aspects of the reaction: the surface concentration of adsorbed CO and the continuing oxygen uptake of the substrate. Once a stable surface had been achieved, repeated non-SS experiments were found to be consistently reproducible. Therefore by monitoring $m/e = 28$, 32, and 44 on successive flashes, the course of the reaction could be observed with respect to each of the reactant and product species. For example, assuming that the only sink for CO, aside from the pump, is its conversion to CO_2, and the only source of CO_2 is CO, it is clear from stoichiometry that the rates of reaction of CO and CO_2 should be equal in magnitude and opposite in sign. Thus having calculated the rate of formation of CO_2 at any temperature, it should be possible to anticipate the CO pressure at this same temperature.

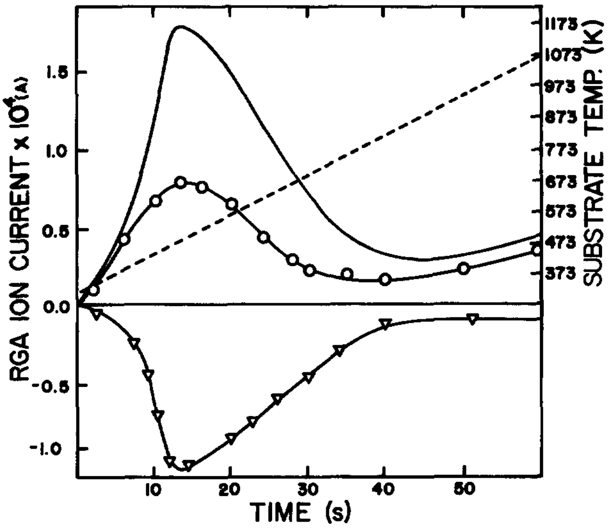

FIG. 4. Non-steady state variation of CO on flashing a stable substrate. The initial $O_2/CO = 1.5$. The origin of the ordinate is defined as the CO pressure recorded at room temperature. The curves are denoted as follows: ○, observed CO, ▽, calculated on the basis of CO_2 production, —, difference between observed and calculated, and ---, temperature.

In Fig. 4 we can see the result of this analysis. The bottom curve is the anticipated $m/e = 28$ RGA ion current calculated from the measured rate of formation of CO_2, while the middle curve is the ion current actually observed. Obviously any explanation of the discrepancy must assume a source of CO other than the constant leak of the $CO + O_2$ mixture. It was also noted that as the substrate cooled to room temperature, the observed CO pressure was temporarily much lower than could be explained by its conversion to CO_2. Since the source and the sink were observed each time the substrate was heated and cooled, it is plain that we were observing the desorption and readsorption of CO at the substrate surface. Therefore it was possible to treat the difference curve (observed CO − calculated CO) just like a thermal desorption spectrum from which the surface coverage of CO could be calculated. Table 1 displays the results of these calculations at various total pressures. Also shown are the SS partial pressures of the two major constituents of the ambient prior to (and following) the non-SS experiments. It should be noted that the ratio P_{32}/P_{28} is approximately constant and equal to 1.5 at all three total pressures.

A similar analysis was conducted on oxygen. Again the predicted $m/e = 32$ RGA ion current was plotted (assuming $R_{32} = -\frac{1}{2}R_{44}$) along with the observed ion current. As shown in Fig. 5 a wide divergence was once more evident. In this case the difference curve implied the existence of a sink for oxygen which became more important as the substrate temperature was raised. This suggests a continuing incorporation of oxygen by the substrate during the course of the catalysis experi-

TABLE 1

CONCENTRATION OF ADSORBED CO AS A FUNCTION OF AMBIENT PRESSURE

Cell pressures			
P_T (Pa)	P_{28} (Pa)	P_{32} (Pa)	N_{28} (cm^{-2})
1.43×10^{-4}	5.80×10^{-5}	8.03×10^{-5}	8.46×10^{13}
2.95×10^{-4}	1.16×10^{-4}	1.72×10^{-4}	1.32×10^{14}
5.77×10^{-4}	2.25×10^{-4}	3.36×10^{-4}	1.76×10^{14}

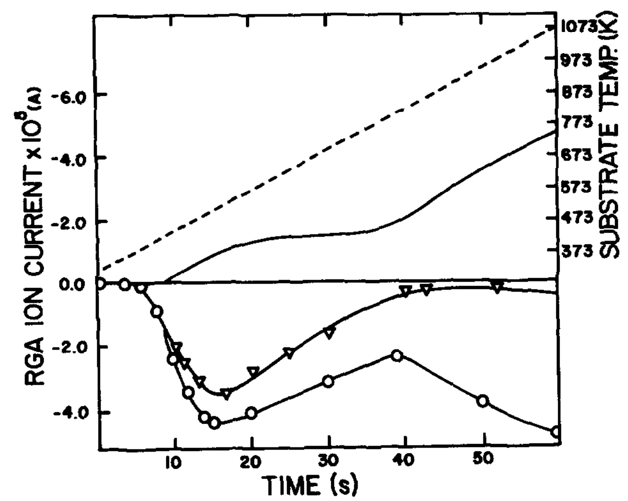

FIG. 5. Non-steady state variation of O_2 pressure with time during the flashing of a stable substrate. Symbols and conditions are identical to those of Fig. 4.

ments since no oxygen containing species (above background) other than O_2, CO, and CO_2 were found.

3. *Steady-State Oxidation Experiments*

The results of a typical SS experiment are shown in Fig. 6. It is apparent that, within experimental error, the SS rates of reaction of CO_2 and CO are equal in magnitude. Furthermore, just as with the non-SS experiments, the SS reactions disclose a large oxygen sink that increases with substrate temperature and is attributable to the uptake of oxygen by the substrate.

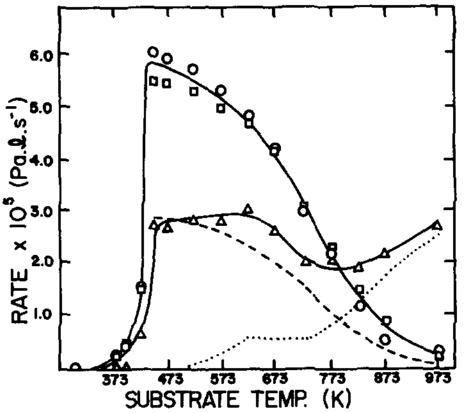

FIG. 6. Steady state variation of production rates with temperature using a stable substrate. Total pressure ≈ 10^{-4} Pa and $O_2/CO = 1.5$. Symbols are defined as follows: ○, CO_2 production rate, □, negative of CO production rate, △, negative of O_2 production rate, · · ·, one half the CO_2 production rate plus the O_2 production rate, and ---, one half the CO_2 production rate. The ordinate can be roughly converted to units of molecules per second per square centimeter of substrate by multiplying by 2.6×10^{16}. Thus the rate of CO_2 production at the maximum is about 1.6×10^{12} molecules · cm^{-2} · s^{-1}.

One of the most interesting aspects of this study was the observation that the oxidation of CO by O_2 in the presence of the stable catalyst obeyed three distinct rate laws, depending on the temperature of that catalyst. Compiled in Table 2 and diagrammatically displayed in Fig. 7 are the orders of the reaction with respect to CO and O_2 over the entire range of temperatures from

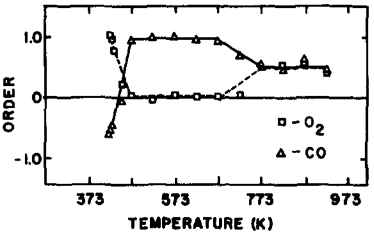

FIG. 7. Variation of reaction order with temperature in the oxidation of CO catalyzed by a stable substrate. The total pressures were about 10^{-4} Pa and $1.0 \leq O_2/CO \leq 3.0$. The symbols are defined as: □, order with respect to O_2 and △, order with respect to CO.

TABLE 2

Rate Law Orders with Respect to O_2 and CO as a Function of Catalyst Temperature

Region	T (K)	Order wrt CO	Order wrt O_2
I	423	−0.61	1.02 ± 0.02
	425	−0.52	0.98 ± 0.02
	433	−0.45	0.78 ± 0.02
	453	−0.05 ± 0.21	0.23
II	473	0.95 ± 0.17	0.02 ± 0.12
	523	0.98 ± 0.20	−0.02
	573	1.01 ± 0.14	0.04
	623	0.96 ± 0.08	0.01
	673	0.91 ± 0.12	0.02
	723	0.65 ± 0.02	0.08
III	773	0.54	0.53 ± 0.02
	823	0.45	0.55
	873	0.68 ± 0.13	0.59 ± 0.10
	923	0.44	0.42

273–973 K. Total pressures were in the low 10^{-4} Pa range and P_{32}/P_{28} varied from 1 to 3. The uncertainties stated in the table are one standard deviation, while those results with no expressed uncertainty are the outcome of a single determination. The experimental orders defining the rate laws in each temperature region were taken to be the averages of all the tabulated values for that region.

4. *Mechanistic Considerations*

The stable catalyst surface, consisting of Pd with incorporated oxygen and presumably devoid of surface carbon, readily catalyzes the oxidation of CO to CO_2. As shown in Fig. 6, the rate of CO_2 production shows a sharp onset near 450 K at just the point where a distinct change in the reaction mechanism is taking place as indicated by the reaction orders. At higher temperatures, following the sharp maximum near 460 K, the rate of CO_2 production falls off slowly. The general behavior we observed is reminiscent of that observed by Ertl and co-workers on Pd(100), Pd(110) and Pd(111) (*13,14,35*). For all practical purposes the rate of CO_2 production shows the same temperature dependence on all of these surfaces and shows a sharp onset rising to a maximum slightly above 475 K followed by a slow decline. Although they do not report detailed investigation of the oxygen uptake phenomena, they observed it only on Pd(111). We suspect that their kinetic results like ours were influenced by oxygen uptake especially at higher temperatures. The Auger spectra of Ertl and Koch (*35*) suggest however that the oxygen uptake left a Pd-rich surface behind. One qualitative model that suggests itself involves a Pd-rich surface layer beneath which lies a nonstoichiometric oxygen-palladium layer. While this is appealing, it ignores one basic distinction between the substrates used by Ertl and co-workers and those we used; namely, our substrate will only chemisorb about 0.01 monolayer of CO whereas the argon-bombarded surfaces used by Ertl and co-workers will chemisorb close to a full monolayer of CO at room temperature. While this distinction may be of degree rather than kind insofar as the substrate properties are concerned, it is nonetheless important to recognize. Unfortunately we are not able to compare absolute rates, so while the temperature variations are similar the absolute activities may have been quite different. Quite possibly our substrates were partially covered with sulfur; a preliminary Auger analysis suggests this (*42*). It is not yet clear just how much of this sulfur is removed by high temperature exposure to oxygen. Sulfur is known to severely inhibit the oxidation of CO over Pt (*43*) and on this basis we might expect a similar inhibition on Pd. This remains to be demonstrated. With these qualifications in mind we will now discuss our kinetic results as though sulfur played no qualitative role in the mechanism of the CO oxidation. We shall assume on the basis of our own experiments that both CO and O_2

can be chemisorbed and that O_2 is incorporated into the target in some fashion. Listed below are some elementary reactions which could be important in the range 273–973 K:

$$CO + 2\sigma \rightarrow (CO)_{2\sigma}, \quad (1)$$

$$(CO)_{2\sigma} \rightarrow CO + 2\sigma, \quad (2)$$

$$CO + \sigma \rightarrow CO_\sigma, \quad (3)$$

$$CO_\sigma \rightarrow CO + \sigma, \quad (4)$$

$$O_2 + 2\sigma \rightarrow 2\ O_\sigma, \quad (5)$$

$$O_2 + \sigma \rightarrow (O_2)_\sigma, \quad (6)$$

$$O_\sigma \rightarrow Pd/O + \sigma, \quad (7)$$

$$CO + O_\sigma \rightarrow CO_2 + \sigma, \quad (8)$$

$$CO + O_\sigma \rightarrow (CO_2)_\sigma, \quad (9)$$

$$(CO_2)_\sigma \rightarrow CO_2 + \sigma, \quad (10)$$

$$CO \rightarrow C_\sigma + O_\sigma, \quad (11)$$

$$2\ CO \rightarrow C_\sigma + CO_2, \quad (12)$$

$$C_\sigma + O_\sigma \rightarrow CO + 2\sigma. \quad (13)$$

In these reactions σ represents an adsorption site. There are a variety of these on an energetic basis but for a tractable mechanistic treatment we lump them all under a single symbol. Reaction (7) represents the incorporation of a surface oxygen into the substrate and Pd/O represents a nonstoichiometric palladium–oxygen species.

We now turn to the task of finding a mechanism for each of the distinct temperature regions which is compatible with the observed rate law. In temperature region I the rate of CO_2 production, R_{44}, is

$$R_{44} = k_I p_{28}^{-0.53} p_{32}^{0.93}\ Pa \cdot s^{-1}. \quad (16)$$

As discussed below there are at least two mechanistic schemes furnishing such a rate law. The first, and favored, mechanism for temperature region I involves reactions (1), (2), (5), (9), and (10): the dual-site adsorption-desorption of CO, the dissociative adsorption of gas phase O_2 and the Eley–Rideal (ER) mechanism for the production of CO_2 (i.e., the interaction between a gas phase CO molecule and an absorbed oxygen atom to produce an adsorbed CO_2 molecule which then desorbs):

Mechanism I-A

$$CO + 2\sigma \rightarrow (CO)_{2\sigma}, \quad (1)$$

$$(CO)_{2\sigma} \rightarrow CO + 2\sigma, \quad (2)$$

$$O_2 + 2\sigma \rightarrow 2O_\sigma, \quad (5)$$

$$CO + O_\sigma \rightarrow (CO_2)_\sigma, \quad (9)$$

$$(CO_2)_\sigma \rightarrow CO_2 + \sigma. \quad (10)$$

The bridged (dual-site), carbonyl-like CO adsorption has been postulated previously to explain ir studies by Eischens, *et al.* (*44,45*) and LEED results by Park and Madden (*46*) for Pd metal surfaces. Blyholder (*47,48*) however questioned the interpretation of Eischens *et al.* preferring to explain the observed low frequency bands as being due to linear CO bonding at high energy sites on the dislocations (edges, corners, kinks) of a heterogeneous surface.

The ER mechanism is generally postulated for CO oxidation by O_2 over Ni (*49*), Pd (*12–14*) and Pt (*50,51*), and we also find it consistent with our results over Pd/O. However, the choice between reaction (8) and reactions (9) and (10) is not as clear-cut as the writing of those equations implies. Obviously the CO_2 will have some finite residence time on the surface, so the real question is whether or not, at a given pressure of CO_2, the lifetime of $(CO_2)_\sigma$ is long enough to block a large number of adsorption sites and become an important consideration in the overall kinetics. It should be observed that as long as reaction (10) was not the rate-limiting step, the two mechanisms for producing gas phase CO_2 would be kinetically equivalent, leading to identical rate laws. However in view of McKinney's observation (*32*) that CO_2 was adsorbed on PdO and considering that the pressure of CO_2 at times reached

25–30% of the ambient in our experiments, reactions (9) and (10) are felt to more accurately reflect the actual mechanism. But keeping in mind that McKinney also observed that the CO_2 adsorption on PdO was weak and reversible, and adding our own observations following the pump down after the SS experiments which demonstrated that the only surface species observable via thermal desorption was CO (confirming McKinney's observation), it seems unlikely that reaction (10) would be rate limiting. Speculation about this aspect of the mechanism could be eliminated by conducting future experiments with varying amounts of CO_2 added to the reactant mixture and observing its effect on the rate of reaction.

A steady-state analysis of mechanism I-A leads to

$$R_{44} = \frac{k_2 k_5}{k_1} [(CO)_{2\sigma}] \frac{P_{32}}{P_{28}}. \qquad (17)$$

This expression becomes compatible with the observed rate law if the concentration of adsorbed CO is given by a Freundlich isotherm (*52*)

$$[(CO)_{2\sigma}] = C P_{28}{}^{x}, \qquad (18)$$

with $x = \frac{1}{2}$ and where C is a constant. Such adsorption behavior has been observed by Horgan and King (*49*) who pointed out that in their study of the $CO + O_2$ reaction over clean Ni surfaces, the surface CO indeed followed a Freundlich isotherm with $x = \frac{1}{3}$. Finally, it is apparent that if the CO adsorption process in our reactions is consistent with the Freundlich isotherm, a plot of ln p_{28} vs ln $[(CO)_{2\sigma}]$ should yield a straight line. From Table 1 we can get three points for such a plot and they yield a reasonably good straight line with a least-squares slope of 0.54. Thus though the paucity of data prohibits any unequivocal statement about the $(CO)_{2\sigma}$ isotherm, the data available is compatible with Eq. (18) with $x = \frac{1}{2}$.

Using the Freundlich isotherm in Eq. (17) and making the definition

$$k_I = C k_2 k_5 / k_1, \qquad (19)$$

the derived rate law becomes

$$\frac{dP_{44}}{dt} = k_I P_{28}{}^{-1/2} P_{32}. \qquad (20)$$

A plot of the logarithm of the experimental rate coefficient versus T^{-1} then allows us to determine the Arrhenius parameters, which are $E_a = 47.8 \pm 3.3$ kJ · mole^{-1} and $A = 1.92 \pm 0.09 \times 10^2$ Pa$^{1/2}$ · liter · s^{-1}. It should be noted that the A-factor includes system dependent factors such as surface area and system volume. According to Eq. (19), the observed activation energy should be related to the energetics of reactions (1), (2), and (5). On Pd (111), Ertl and Koch (*35*) found the isoteric heat of adsorption of CO to vary between 142 and 92 kJ · mole^{-1} as the coverage varied from 0.0 to 0.5 monolayers. The adsorption energy for oxygen was in the vicinity of 230 kJ · mole on the same substrate. These figures are, of course, insufficient to determine the activation energy of the overall reaction. However, on the basis of the arguments made in this paper, region I is strongly influenced by the desorption of CO so the activation energy should be in the range of 90 kJ · mole^{-1} if we use the data of Ertl and Koch (*35*). It is not surprising that our results differ considerably since our surfaces were preexposed to large amounts of oxygen at high temperatures, may have been partially covered with sulfur, and would chemisorb only about 0.01 monolayer of CO.

It should be observed at this point that it is possible to arrive at the same rate law through a somewhat different mechanism:

Mechanism I-B

$$CO + \sigma \xrightarrow{k_3} CO_\sigma, \qquad (3)$$

$$CO_\sigma \xrightarrow{k_4} CO + \sigma, \qquad (4)$$

$$O_2 + \sigma \xrightarrow{k_8} (O_2)_\sigma, \qquad (6)$$

$$CO + (O_2)_\sigma \xrightarrow{k_{14}} CO_2 + O_\sigma, \qquad (11)$$

$$CO + O_\sigma \xrightarrow{k_{12}} (CO_2)_\sigma, \qquad (9)$$

$$(CO_2)_\sigma \xrightarrow{k_{13}} CO_2 + \sigma. \qquad (10)$$

A kinetic treatment of this mechanism, including application of the SS hypothesis to the surface species $(CO_2)_\sigma$, $(O_2)_\sigma$, O_σ and CO_σ yields the rate law

$$\frac{dP_{44}}{dt} = \frac{2Ck_4k_8}{k_3} \frac{P_{32}}{P_{28}^{1/2}}, \qquad (21)$$

if the $[CO_\sigma]$ is again assumed to follow the Freundlich isotherm. The principal difference between mechanisms I-A and I-B is that while the former specifies dual-site CO adsorption and dissociative oxygen adsorption, the latter stipulates single-site CO adsorption and nondissociative oxygen adsorption. It is important to recognize that the nature of the CO adsorption and the dissociative or nondissociative character of the oxygen adsorption are mechanistically interdependent. For example, in order to achieve the experimental rate law the single site CO adsorption would not be compatible with a dissociative oxygen adsorption.

While mechanisms I-A and I-B cannot be unequivocally distinguished, previous work on metal–oxygen and metal oxide–oxygen systems tends to support dissociative adsorption and thus mechanism I-A (*2,13,50,53,54*). We, therefore, conclude that mechanism I-A probably predominates.

Turning now to temperature region II ($473\ K < T < 673\ K$) the rate expression for CO_2 production is

$$R_{44} = k_{II} p_{28}{}^{0.96} p_{32}{}^{0.01}. \qquad (22)$$

In this temperature region we again propose to use mechanism I-A; however, the surface concentration of CO is low enough to be ignored, and if we assume that $(CO_2)_\sigma$ is weakly bound, the kinetic features are determined by reactions (5) and (8). At SS conditions these two reactions furnish the rate law

$$R_{44} = k_{II}\, \theta\, p_{28}. \qquad (23)$$

Since we observe no oxygen pressure dependence in this region, the coverage of oxygen, θ, in the above expression must be taken as essentially constant if our proposed mechanism is to fit the experimental observations. This result is in accord with Ertl and Rau (*13*) who found at 473 K that the CO_2 production rate was first order in CO and zero order in O_2 when O_2 exceeded CO as it did in most of our experiments. The temperature dependence of the rate in this region furnishes an apparent Arrhenius activation energy of -8.84 ± 0.08 kJ · mole^{-1} and a preexponential factor of 0.47 ± 0.09 s^{-1}. The negative activation energy reflects the fact that the rate at a given gas phase pressure and thus the rate coefficient decline slowly with increasing target temperature in this region. In terms of the mechanism we have proposed this is partially attributable to the declining time which the CO reactant spends at the surface as the temperature increases. Assuming the reactants striking the surface are near room temperature regardless of the substrate temperature, then the collision frequency at a given pressure is constant as the substrate temperature varies. Once at the surface, however, the time spent there is smaller when the substrate temperature is higher. Toward the higher temperature part of this region a decline in the extent of oxygen chemisorption may also contribute to the apparent negative activation energy. Combining the data from both regions I and II suggests, as previously discussed by Ertl and Rau (*13*), that the rapid onset of the reaction is a consequence of the slowness of the rate of CO_2 production when CO_σ and O_σ are involved. Once the CO surface concentration reaches a very low value the reaction can proceed readily.

In the highest temperature region which we studied (773–973 K), the rate law is

$$R_{44} = k_{\text{III}}\, p_{28}{}^{0.53}\, p_{32}{}^{0.53}. \qquad (24)$$

While these orders with respect to CO and O_2 seem well-defined in this region and an Arrhenius plot was linear over the region, no simple mechanism could be found which would give this dependence. The Arrhenius plot gave an apparent activation energy of -54.0 ± 3.9 kJ · mole^{-1} with a preexponential factor of $1.1 \pm 0.8 \times 10^4$ s^{-1}. Some observations can, however, be made about various reactions which might be important in this temperature region. First of all, it is expected that for substrate temperatures between 773 and 973 K, the concentration of the absorbed species of CO and O_2 would be rapidly decreasing—to possibly orders of magnitude less than in temperature region I. This would no doubt compensate for and even completely dominate the anticipated increases with temperature of such rate coefficients as k_5. Yet this reaction probably continues to contribute significantly to the overall mechanism because the concept of the reaction of an "adsorbed" species is really related to its lifetime in the vicinity of the surface and the probability of reaction during that time. Thus considering even the most unfavorable circumstances for a gas-surface interaction (e.g., normal incidence trajectory, root mean square velocity consistent with a substrate temperature of 1000 K, and limiting the gas-surface distance of strong interaction to 0.5 nm) the gas phase CO and O_2 would be within this region of strong interaction for a time period of at least 10 molecular vibrations. This could easily be sufficient for reactions (3) and (5) to remain viable contributors to the mechanism at pressures of 10^{-5}–10^{-4} Pa where collision frequencies with the surface are 10^{14}–10^{15} cm^{-2} s^{-1}.

Secondly, it is clear from Figs. 5 and 6 that as the temperature increases, so does the relative importance of reaction (7). Furthermore, the mechanism is probably becoming increasingly complicated by such reactions as (11)–(13). The dissociation process of reaction (11) has been observed on Pt by Tucker (*55*) and on Ni by Madden and Ertl (*38*). Reaction (12) has been postulated (*56*) at temperatures as low as 463 K on Ni (*57*) and was determined to be the principal reaction over Ni between 550 and 1000 K by Gregg and Leach (*58*). In addition, our own results in which β-CO was discovered on the surface after high temperature oxidation experiments, requires participation of either reaction (11) or (12) coupled with (17).

Briefly, then, aside from the complicating aspects discussed in the previous paragraph it is plausible to conjecture that the rapidly decreasing R_{44} is partly due to the increasing competition for O_σ that reaction (8) is feeling from reaction (7).

IV. SUMMARY AND CONCLUSIONS

A summary of the experimentally determined parameters determined from the SS experiments is displayed in Table 3. The dominant feature of the reaction below 450 K is the inefficient formation of CO_2 through an Eley–Rideal mechanism, the inefficiency being apparently controlled by chemisorbed CO. In this region the rate of production of CO_2 is first order in O_2, negative one-half order in CO, and proceeds with an activation energy of 47.8 ± 3.3 kJ · mole^{-1}.

In region II, between 473 and 673 K, the amount of chemisorbed CO is very small, oxygen chemisorption is no longer inhibited and the production of CO_2 proceeds readily. In this region we find the rate to be first order in CO, zero order in O_2 and proceeding with an apparent activation energy of -8.84 ± 0.08 kJ ·

TABLE 3

SUMMARY OF ARRHENIUS PARAMETERS AND ORDERS OF CO AND O_2 DEFINING THE RATE LAWS IN THE THREE TEMPERATURE REGIONS

Temperature region	Arrhenius parameters		Order	
	A	E_a (kJ · mole^{-1})	wrt CO	wrt O_2
I	$1.92 \pm 0.09 \times 10^2$	47.8 ± 3.3	-0.53 ± 0.08	0.93 ± 0.13
II	0.47 ± 0.09	-8.84 ± 0.08	0.96 ± 0.04	0.01 ± 0.02
III	$1.1 \pm 0.8 \times 10^{-4}$	-54.0 ± 3.9	0.53 ± 0.11	0.52 ± 0.07

mole^{-1}. The negative activation energy is attributable to variations in the residence time of CO near the surface and to variations in the availability of oxygen at the surface. The orders we have determined are in close agreement with previous work (*13,14,35*). The qualitative features of the variation of the rate of CO_2 production with temperature also agree closely with this same work. From these observations we conclude that polycrystalline substrates, preexposed to large amounts of oxygen, and not cleaned by Ar^+ bombardment catalyze the oxidation of CO by essentially the same mechanism and with the same temperature dependence as do cleaned single crystal substrates. Especially in the region 473–673 K it will be interesting to study the rate of CO_2 production as a function of relative composition and total pressure. Ertl and co-workers (*13,14,35*) found a change in order with respect to O_2; the order changed from one to zero as the oxygen pressure was increased. Our apparatus has been modified to allow separate introduction of CO and O_2 and these experiments are underway.

In the highest temperature region, 773–973 K, the rate of CO_2 production is half order in both CO and O_2 and proceeds with an apparent activation energy of -54.0 ± 3.9 kJ · mole^{-1}. No suitable simple mechanism was found to describe this region, however, it should be noted that oxygen is being taken up by the substrate in this region, the surface concentration of chemisorbed oxygen is apparently very small, and the residence time of CO is very small. Each of these factors may contribute to the decline in the rate of CO_2 production. Other mechanistic features including dissociation and disproportionation of CO also seem to be implicated.

ACKNOWLEDGMENTS

The assistance of Deborah Wales and David Almy with certain of the experiments is appreciated. The stimulating counsel of Dr. J. W. McAllister is gratefully acknowledged. This work was supported in part by the National Science Foundation under Grants Nos. GP-37974 and GP-20370.

REFERENCES

1. ALEXANDER, E. G., AND RUSSEL, W. W., *J. Phys. Chem.* **68**, 1614 (1964).
2. HORGAN, A. M., AND KING, D. A., *Trans. Faraday Soc.* **67**, 2145 (1971).
3. PARK, R. L., AND FARNSWORTH, H. E., *J. Chem. Phys.* **40**, 2354 (1964); *J. Chem. Phys.* **43**, 2351 (1965).
4. ONCHI, M., AND FARNSWORTH, H. E., *Surface Sci.* **11**, 203 (1968).
5. ELEY, D. D., AND RIDEAL, E. K., *Nature (London)* **146**, 401 (1940); *Proc. Roy. Soc. London Ser. A* **178**, 429 (1941).
6. STEPHENS, S. J., *J. Phys. Chem.* **63**, 188 (1959).
7. KAWASAKI, K., SUGITA, T., AND EBISAWA, S., *J. Chem. Phys.* **44**, 2313 (1966); *Surface Sci.* **8**, 485 (1967).
8. PARK, R. L., "Fundamentals of Gas-Surface Interactions" (H. Saltsburg, J. N. Smith, Jr., and M. Rogers, Eds.), p. 295. Academic Press, New York, 1967.
9. LANGMUIR, I., *Trans. Faraday Soc.* **17**, 607 (1922).

10. Hinshelwood, C. N., *Annu. Rep. Chem. Soc. London* **24**, 335 (1928).

11. Baddour, R. F., Modell, M., and Heusser, U. K., *J. Phys. Chem.* **72**, 3621 (1968).

12. Baddour, R. F., Modell, M., and Goldsmith, R. L., *J. Phys. Chem.* **74**, 1787 (1970).

13. Ertl, G., and Rau, P., *Surface Sci.* **15**, 443 (1969).

14. Ertl, G., and Koch, J., *Z. Phys. Chem. Neue Folge* **69**, 323 (1970).

15. Heyne, H., and Tompkins, F. C., *Proc. Roy. Soc. London Ser. A* **292**, 460 (1966).

16. Langmuir, I., *Trans. Faraday Soc.* **17**, 621 (1922).

17. Skylarov, A. V., Tret'yakov, I. I., Shub, R. R., and Roginskii, S. Z., *Dokl. Akad. Nauk SSSR* **189**, 1302 (1969).

18. Bonzel, H. P., and Ku, R., *J. Vac. Sci. Technol.* **9**, 664 (1972); *Surface Sci.* **33**, 91 (1972).

19. Winterbottom, W. L., *Surface Sci.* **36**, 205 (1973).

20. Engelder, C. J., and Blumer, M., *J. Phys. Chem.* **36**, 1353 (1962).

21. Winter, E. R. S., *Adv. Catal.* **10**, 196 (1958).

22. Schwab, G. M., and Block, J., *J. Chim. Phys.* **51**, 664 (1954); *Z. Phys. Chim.* **1**, 42 (1954).

23. Parravano, G., *J. Amer. Chem. Soc.* **75**, 1148, 1152 (1953).

24. Dell, R. M., and Stone, F. S., *Trans. Faraday Soc.* **50**, 501 (1954).

25. Eischens, R. P., and Pliskin, W. A., *Adv. Catal.* **9**, 662 (1957).

26. Coue, J., Gravell, P. C., Ranc, R. E., Rue, P., and Teichner, S. J., *Proc. Int. Congr. Catal., 3rd, 1964* p. 748 (1965).

27. Schlosser, E. G., and Herzog, W., *Proc. Int. Congr. Catal., 4th, 1968* p. 128 (1971).

28. Gosšel, H., *Ber. Bunsenges Phys. Chem.* **65**, 98 (1961).

29. Bielanski, A., "Catalysis and Chemical Kinetics," p. 118. Academic Press, New York, 1964.

30. Yao, Y. Y., and Kummer, J. T., *J. Catal.* **28**, 124 (1973).

31. McKinney, P. V., *J. Amer. Chem. Soc.* **54**, 4498 (1932).

32. McKinney, P. V., *J. Amer. Chem. Soc.* **55**, 3626 (1933).

33. Krylov, O. V., "Catalysis by Nonmetals," p. 168. Academic Press, New York, 1970.

34. Sandler, Y. L., and Durigon, D. D., *J. Phys. Chem.* **73**, 2392 (1969).

35. Ertl, G., and Koch, J., "Adsorption–Desorption Phenomena," (F. Ricca, Ed.), p. 345. Academic Press, New York, 1972.

36. Sikafus, E. N., *Surface Sci.* **19**, 181 (1970).

37. Berkman, S., Morrell, J. C., and Egloff, G., "Catalysis: Inorganic and Organic," p. 775. Rheinhold, New York, 1940.

38. Madden, H. H., and Ertl, G., *Surface Sci.* **35**, 211 (1973).

39. MacRae, A. U., *Science* **139**, 379 (1963).

40. Onchi, M., and Farnsworth, H. E., *Surface Sci.* **11**, 203 (1968).

41. McAllister, J. W., and White, J. M., *J. Phys. Chem.* **76**, 968 (1972).

42. Ellis, W. P., Rusch, T. W., and White, J. M., unpublished results.

43. Bonzel, H. P., and Ku, R., *J. Chem. Phys.* **59**, 1641 (1973).

44. Eischens, R. P., and Pliskin, W. A., *Adv. Catal.* **10**, 1 (1958).

45. Eischens, R. P., Pliskin, W. A., and Francis, S. A., *J. Phys. Chem.* **60**, 194 (1956).

46. Park, R. L., and Madden, H. H., *Surface Sci.* **11**, 188 (1968).

47. Blyholder, G., *J. Phys. Chem.* **68**, 2772 (1964);

48. Blyholder, G., *Proc. Int. Congr. Catal., 3rd, 1964* p. 657 (1965).

49. Horgan, A. M., and King, D. A., *Trans. Faraday Soc.* **67**, 2145 (1971).

50. Bonzel, H. P., and Ku, R., *J. Vac. Sci. Technol.* **9**, 663 (1971).

51. Bonzel, H. P., and Ku, R., *Surface Sci.* **33**, 91 (1972).

52. Freundlich, H., "Colloid and Capillary Chemistry." Methuen, London, 1926.

53. Robert, T., Bartel, M., and Offergeld, G., *Surface Sci.* **33**, 123 (1972).

54. Bielanski, A., and Najbar, M., *J. Catal.* **25**, 398 (1972).

55. Tucker, C. W., *Surface Sci.* **2**, 516 (1964).

56. Edmonds, T., and Pitkethly, R. C., *Surface Sci.* **15**, 137 (1969).

57. McBaker, M., and Rideal, E. K., *Trans. Faraday Soc.* **51**, 1597 (1955).

58. Gregg, S. J., and Leach, H. F., *J. Catal.* **6**, 308 (1966).