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Transient Kinetics in CO Oxidation on Platinum[1]

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Steady state and transient kinetics of CO oxidation on polycrystalline Pt wires at total pressures of ~1 Torr are examined for temperatures up to 1500°K. Following step changes in wire temperature in times less than 1 sec, rates of CO_2 production versus time are measured using an on-line mass spectrometer system with a time response of several seconds. Transients with time constants up to several hundred seconds are observed which suggest that at low temperatures the Pt surface contains a multilayer film on which the reaction rate is different than on the "clean" surface obtained at high temperatures. Activation energies and orders of the transient reaction are obtained from measurements at different temperatures, and the rate of film formation is shown to agree with a model of diffusion limitation.

INTRODUCTION

Measurement of transient reaction kinetics has been recognized for some time to be a potentially revealing way to examine mechanisms of catalytic reactions and to investigate the nature of adsorbed complexes (*1,2*). However, to our knowledge there have been no reports of experiments with system time constants less than 1 min, and on this time scale one is more concerned with what are usually termed activation and deactivation processes (effects of poisons and promotors) rather than reaction rate changes following step changes in catalyst temperature or pressure (*3*). An exception to this is in experiments in ultrahigh vacuum where transient kinetics on a time scale of seconds have been measured (*4,5*), although at low pressure only events which have very high probabilities can be measured in times sufficiently short to avoid contamination.

In this study we examined steady state and transient rates of CO oxidation on polycrystalline Pt wires. This is a much studied reaction system dating back to the classic work of Langmuir (*6–12*). However because of different forms of catalysts (wires, foils, films, and supported) and narrow temperature and pressure ranges (frequently rather low temperatures and high pressures), there is little consensus in the literature as to steady state rates and little mention of reaction transients.

This study is very similar to our earlier studies of NH_3 oxidation (*13*). We have shown that steady state rates of the four reactions in that system could be fit quite well by simple Langmuir–Hinshelwood (LH) type rate expressions between room temperature and 1500°C for all reactant compositions. We also observed that steady state rates were attained within 1 sec following step changes in temperature or reactant partial pressures (*14*). A key conclusion from these experiments is that steady state reaction rates appear to be unique and reproducible and that these rates are explainable in terms of LH kinetics. We also have shown from rate measurements and from surface analysis by Auger electron spectroscopy (AES) that

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these surfaces are in most situations free of contaminants such as carbon and sulfur because of their continual removal as volatile oxides in the presence of oxygen (*15*). Thus these surfaces appear to be essentially "clean," that is, free of contaminants and having only submonolayer densities of species derived from gaseous reactants.

Let us first examine the information to be expected from a transient experiment of this type. For a first order irreversible surface reaction A → B in a reactor of uniform gas composition with only A adsorbed, the mass balance equations on the surface density θ_A (fraction of the saturation density) and gas partial pressure P_A in simplest form are

$$\frac{d\theta_A}{dt} = \frac{S_0(1-\theta_A)}{(2\pi MRT)^{1/2}} P_A - k_d\theta_A - k_R\theta_A \quad (1)$$

and

$$\frac{dP_A}{dt} = AKk_d\theta_A - \frac{AKS_0(1-\theta_A)}{2\pi MRT)^{1/2}} P_A - \frac{P_A}{\tau_s} + F_A, \quad (2)$$

where k_d and k_R are rate parameters for desorption and reaction, respectively; S_0 is the initial sticking coefficient; A, the surface area; K, a constant relating pressure and density; F_A, the inlet flow rate of reactant A; and τ_s the system residence time or pumping time constant.

To obtain the surface reaction rate $k_R\theta_A$ or P_A versus time following a discontinuous variation of T or P_A, one must solve these equations simultaneously with specified initial conditions. However the rate of adsorption term in Eq. (1),

$$r_a = \frac{s_0(1-\theta_A)}{(2\pi MRT)^{1/2}} P_A, \quad (3)$$

is ~10^6 monolayers/sec at $P_A = 1$ Torr and ~10^9 monolayers/sec at 1 atm for $s_0 = 1$ and θ small. Therefore it is easy to show (*14*) that, except for exceptional cases, θ_A and therefore P_A should approach *steady state values* very quickly because θ_A must be less than 1.0 and a term on the right side of Eq. (1) is very large. The exceptions would be very small s_0 ($<10^{-6}$ at 1 Torr and for a 1 sec time constant), very high θ_A at all times, or cancellation of large terms on the right side of Eq. (1). For the latter one would expect that if rates of adsorption and desorption are large compared to the rate of reaction, then θ_A is given by an adsorption isotherm, and again $P_A(t)$ would contain no useful information on $k_R\theta_A$.

We conclude from these arguments and from direct solution of these equations that in this simple example transient experiments should be expected to yield little information on reaction rates except at very low pressures where the adsorption term becomes small. Steady state should be attained in very short times for reasonable values of parameters.

Long time transients would be expected at high pressures if rate constants such as s_0, k_d, and k_R are time dependent. This could occur if these parameters depended on coverages of surface species or complexes which adsorb and desorb (or form and decompose) much more slowly than do the major gas species.

We shall consider a simple example to show that transients experiments should yield information on surface complexes which affect reaction or adsorption parameters. We assume that the reaction rate constant k_R depends on the coverage θ_c of a complex C as

$$k_R = k_{R_0} + \alpha\theta_c, \quad (4)$$

where k_{R_0} is the rate constant in the absence of C and α is a constant. Following a step increase in temperature, C is assumed to decompose with a rate

$$\frac{d\theta_c}{dt} = -k_{d_c}\theta_c$$

so that

$$\theta_c(t) = \theta_{c_0}e^{-k_{d_c}t}. \quad (5)$$

The coverage of A versus time is obtained from Eq. (1), and if P_A is constant and k_a and k_d are much greater than k_R, one obtains

$$\theta_A(t) = \theta_{A_0}e^{-(k_a+k_d)t} + \theta_{A_s}[1 - e^{-(k_a+k_d)t}],$$

where $\theta_{A_s} = k_a/(k_a + k_d)$ is the steady state coverage of A and $k_a \equiv s_0 P_A(2\pi MRT)^{-1/2}$.

A mass balance on the partial pressure of product B in a mixed reactor yields

$$\begin{aligned}\frac{dP_B}{dt} &= -\frac{P_B}{\tau_s} + k_R\theta_A \\ &= -\frac{P_B}{\tau_s} + (k_{R_0} + \alpha\theta_{c_0}e^{-k_{dc}t}) \\ &\quad \{\theta_{A_0}e^{-(k_a+k_d)t} \\ &\quad + \theta_{A_s}[1 - e^{-(k_a+k_d)t}]\}. \qquad (6)\end{aligned}$$

It has been assumed in this equation that B desorbs immediately upon formation. This equation can be solved analytically for $P_B(t)$. However, if k_{dc} is much smaller than k_a, k_d, and $1/\tau_s$, then the solution for $t > \tau_s$, is

$$P_B(t) = \tau_s\theta_{A_s}(k_{R_0} + \alpha\theta_{c_0}e^{-k_{dc}t}). \qquad (7)$$

Thus, following a temperature step, the product partial pressure should rise to a value $\tau_s(k_{R_0} + \alpha\theta_{c_0})\theta_{A_s}$ with a time constant τ_s, and then approach the steady state value $\tau_s k_{R_0}\theta_{A_s}$ with a time constant of $k_{d_c}^{-1}$.

Expressions similar to Eq. (7) are obtained if the complex alters the adsorption or desorption properties of A rather than the reaction rate constant, Eq. (4). More complicated assumptions on the rates lead to several coupled equations in P_A, P_B, θ_A, θ_B, and θ_c which can only be solved numerically. However, it is clear that a transient experiment should only be expected to yield information on reaction rates when these are controlled by transient processes which occur in times much greater than adsorption, desorption, and system characteristic times.

EXPERIMENTAL METHODS

Our apparatus is similar to that described previously for NH_3 oxidation kinetics (*13*). On-line mass spectrometry is used to measure partial pressures continuously in a Pyrex flow reactor maintained at pressures between 0.1 and 1 Torr. At these pressures the gas composition is uniform and the gas temperature is that of the walls so that the stirred tank reactor equations may be used to obtain reaction rates from partial pressures. Conversions were always below 15% so that the rates were nearly those characteristic of specified feed pressures. The catalyst was a 5 cm length of 0.025 cm diameter high purity polycrystalline Pt wire. Wire temperatures were varied by resistive heating, and temperatures were obtained by measuring the wire resistance with 0.007 cm diameter potential leads. Short segments of 0.007 cm diameter wire were attached between the ends of the wire and the heating leads to provide a nearly constant temperature along the wire length.

Temperatures were controlled by a Kelvin bridge circuit which varies current to match the wire resistance to that of a standard resistor. It was possible to provide a temperature step increase by several hundred degrees within 0.3 sec and to go from room temperature to 1400°C within 1 sec with no overshoot. Cooling times were limited by cooling time constants of the wire and were typically several seconds. The reactor residence time was typically 3–5 sec, and the mass spectrometer response was faster than this. Overall system time constants were therefore a few seconds, and any transients in product or reactant partial pressures slower than this could be measured.

RESULTS

Figure 1 shows steady state rates of CO_2 production versus temperature for a total pressure of 0.9 Torr with percentages of CO in the CO/O_2 mixture as indicated in Fig. 1. Reproducibility was within ±30% on different wires and ±10% on a given wire. Wires were first heated in O_2 at 1 Torr for approximately 1 hr to remove carbon which is initially present in the

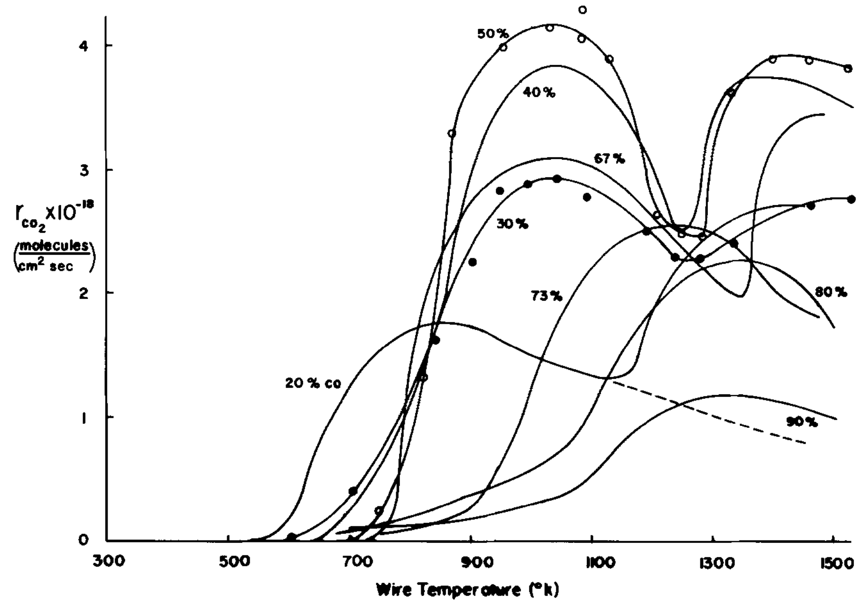

FIG. 1. Steady state rate of CO_2 production versus platinum wire temperature at a total pressure of 0.9 Torr with percentages of CO in the CO_2–O_2 mixture as indicated. Data points are shown for only two of these curves.

wires as discussed previously (*13*). After this procedure the steady states shown in Fig. 1 were uniquely obtained following any temperature–time–composition treatment, although up to several hundred seconds was sometimes required to attain steady state rates at fixed temperature and gas composition.

Transients Upon Heating

A series of experiments was carried out in which the wire was allowed to cool to room temperature in a CO_2/O_2 mixture and then heated to a specified temperature within 1 sec using the temperature controller. Figure 3 shows rates of CO_2 production versus time for final temperatures of 925, 1350, and 1455°K with 20% CO and 80% O_2 at a total pressure of 0.9 Torr. At 925°K the rate of CO_2 production attains a steady state value in ~30 sec. This temperature is near the first steady state maximum of Fig. 2. For all temperatures below 1150°K similar transient behavior was observed. Figure 4 shows a plot of the time τ_1 following the temperature step for the rate to attain 0.9 of its steady state value. This time decreases with increasing T between 600°K (the lowest temperature at which rates could be measured accurately) and 800°K, the approximate temperature of the rate maximum. Between 800 and 900°K the transient time increases to ~40 sec, and above 900°K it decreases again.

Above 1150°K with 20% CO the rate versus time curves first rose to a plateau on which the rate was constant for some time and then, following a fairly sharp break, the rate rose again to the steady state. Figure 4 shows the time τ_2 required for the rate to leave the plateau value, and the time τ_3 for the rate to attain 90% of its steady state value (see insert in Fig. 3). Apparent activation energies are indicated in Fig. 4 for τ_1, τ_2, and τ_3, although the times do not cover a sufficient range to assure that they actually have Arrhenius forms. The rates at the plateau or metastable steady states above 1150°K are plotted in Fig. 2. As shown by the broken line, these rates appear to be an extension of the true steady state rate curve which exists below this temperature.

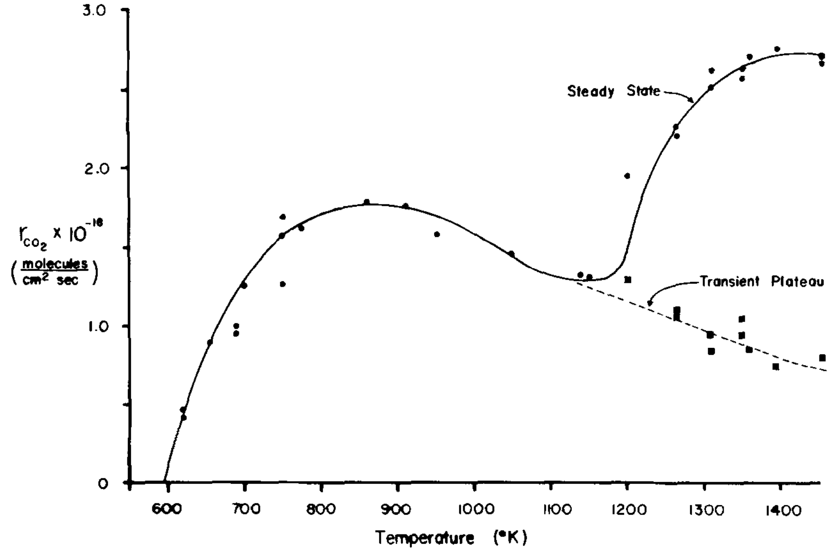

FIG. 2. Rates of CO_2 production versus temperature at 0.9 Torr for 20% CO. Above 1150°K (—) indicates the steady state rate and (--) the rate at the plateaus as shown in Fig. 3.

In 40% CO the rate exhibited a slight maximum at some temperatures as shown in Fig. 5. Above 1250°K, [the minimum temperature in a steady state rate (Fig. 1)], an inflection in the rate versus time was observed, but the rate did not attain a plateau which was sufficiently defined to determine time constants. With 40% CO or higher no plateaus or inflections were observed. Figure 6 shows the time required to attain 90% of the steady state rate versus $1/T$. Above 1250°K, the steady state rate minimum at this composition, the steady state is attained in less than 10 sec, and the system time response was inadequate to resolve time dependent structure in these rates.

With more than 20% and up to 80% CO

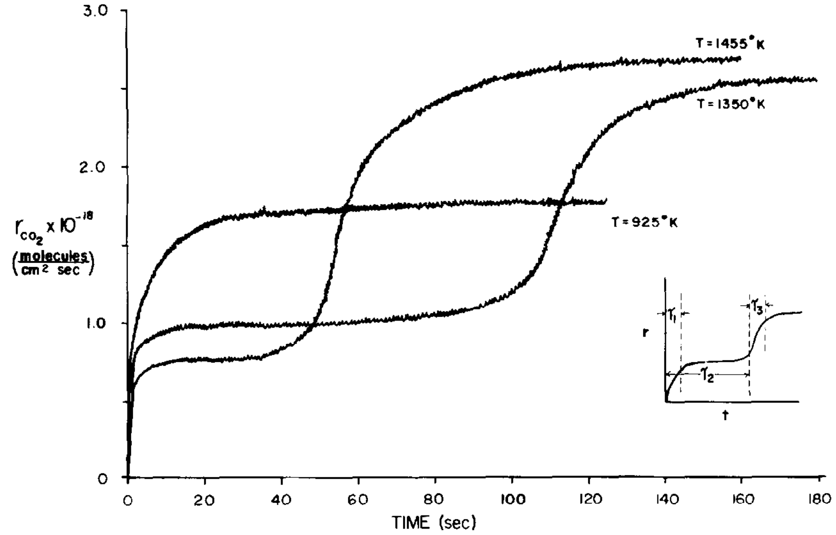

FIG. 3. Rate of CO_2 production versus time in 20% CO following step increases of the wire temperature from 300°K to the temperatures indicated. Above 1150°K the rate passes through a plateau before approaching the true steady state. The insert shows the definitions of times τ_1, τ_2, and τ_3 for these curves.

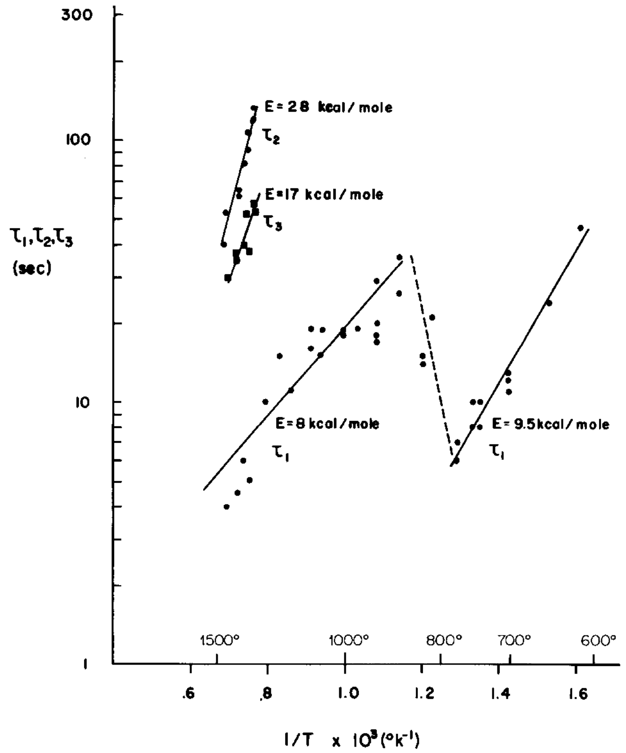

FIG. 4. Plot of τ_1, τ_2, and τ_3 versus $1/T$ from data similar to that of Fig. 3 for 20% CO. Apparent activation energies obtained from the slopes of the straight line segments are shown.

the approach to the steady state for temperatures below the steady state minimum was accompanied by a visible darkening of the wire from its initial metallic appearance to a brown or gray color. For the curve shown in Fig. 5 darkening occurred at ~20 sec where the rate of CO_2 production was at a maximum. In pure CO or pure O_2 the wires remained shiny and metallic in appearance. When wires which had become darkened by heating in a CO/O_2 mixture were heated to higher tem-

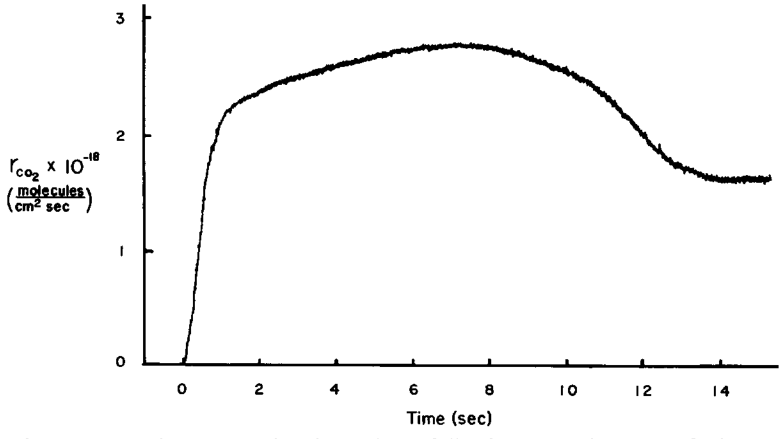

FIG. 5. Rate of CO_2 production versus time in 40% CO following a step increase of wire temperature from 300 to 820°K.

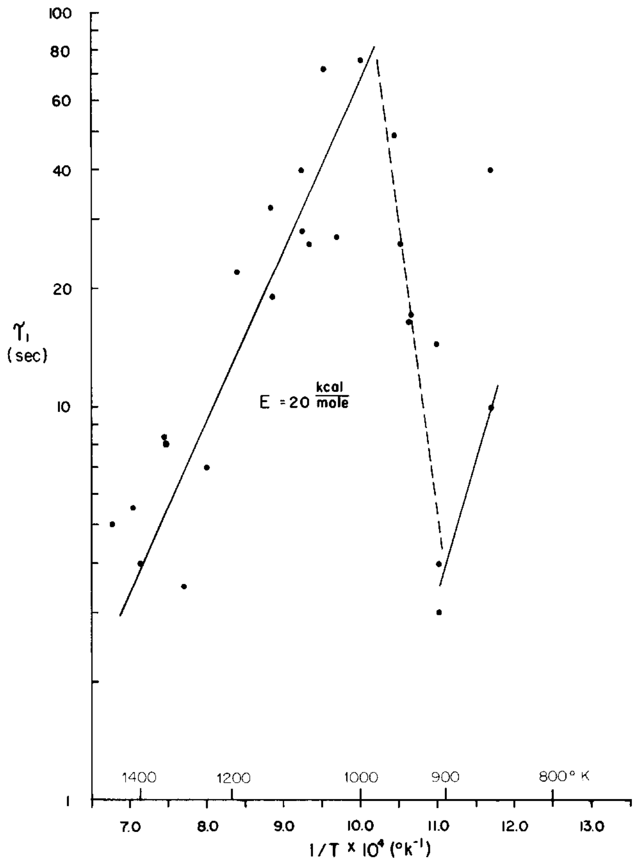

FIG. 6. Plot of transient time constant τ_1 versus $1/T$ in 40% CO at 0.9 Torr.

peratures (above the steady state rate minima in Fig. 1), they became shiny as soon as the reaction rate approached its steady state value.

These surfaces were also examined by scanning electron microscopy. After heating for 20 min in CO/O_2 mixtures at 0.9 Torr the surfaces had become completely roughened with structures ~1000 Å in size, while at temperatures >1000°K these structures were typically 5000 Å. After heating in pure O_2 or CO at any temperatures or in mixtures at very high temperatures, the surfaces were generally smooth except for widely spaced grain boundaries which are characteristic of a thoroughly annealed surface. Elemental composition of several surfaces were analyzed by Auger electron spectroscopy and ion bombardment (*15*). Measurements were not definitive because ribbon specimens used for these experiments had become contaminated with Fe, Ni, and Cr when the Pt wires were rolled into ribbons. After heating in O_2, surfaces were essentially free of carbon as noted previously (*15*), while surfaces heated in CO/O_2 mixtures under conditions where the surfaces appeared brown or grey contained considerable carbon within 10 Å of the original surface. However, because of the possible presence of iron oxides associated with Fe contamination, it was not possible to ascertain whether the low temperature surface complexes may have contained oxygen in addition to carbon.

Transients Upon Cooling

In all experiments in which the wire was first allowed to cool to below ~600°K in a

CO/O_2 mixture and then heated, the rate versus time was similar to the results shown in Figs. 2 and 3: the approach to the steady state was essentially independent of the length of time the wire had been maintained at a low temperature. On the other hand if the wire was heated to high temperatures and then cooled to between 600 and ~ 1200°K, a measurable time was required for the rate to attain its low temperature steady state, and then upon heating again to a higher temperature, the time required to return to the high temperature steady state depended on the time the surface had been held at the lower temperature. Thus experiments of this type can be used to examine the rates of approach to both low and high temperature steady states.

Figure 7 shows rates of CO_2 production versus time in 20% CO at 0.9 Torr for a wire which was heated at 1475°K, allowed to cool to 975°K for a specified period of time, and then heated back to 1475°K. For $t < 0$ the rate is the steady state value at 1475°K, $\sim 2.7 \times 10^{18}$ molecules cm^{-2} sec^{-1}. Upon cooling to 975°K (temperature attained within a few seconds), the rate first rises and then slowly approaches the lower steady state value of $\sim 1.7 \times 10^{18}$ molecules cm^{-2} sec^{-1}. After 80 sec at 975°K (the rate has not yet attained its steady state value), the wire is again heated to 1475°K. The rate falls immediately to $\sim 0.6 \times 10^{-18}$ molecules cm^{-2} sec^{-1} where it remains for ~ 30 sec, after which it returns to the high temperature value. Note that the steady state rates and the metastable rate shown in Fig. 7 are exactly those obtained previously from experiments in which the wire had been allowed to cool to room temperature before being heated to 975 or 1475°K (Figs. 2 and 3). The fact that the plateau rate is identical in the two experiments shows that the rates indicated by the broken curve in Fig. 2 are *independent of the previous low temperature history* of the wire.

However, the time required to leave the plateau and return to the true steady state at 1475°K depends on the time the wire had been maintained at 975°K. The lower curve in Fig. 7 shows the corresponding rate versus time after heating back to 1475°K following exposure to the gas mixture for 120 sec rather than the 80 sec for

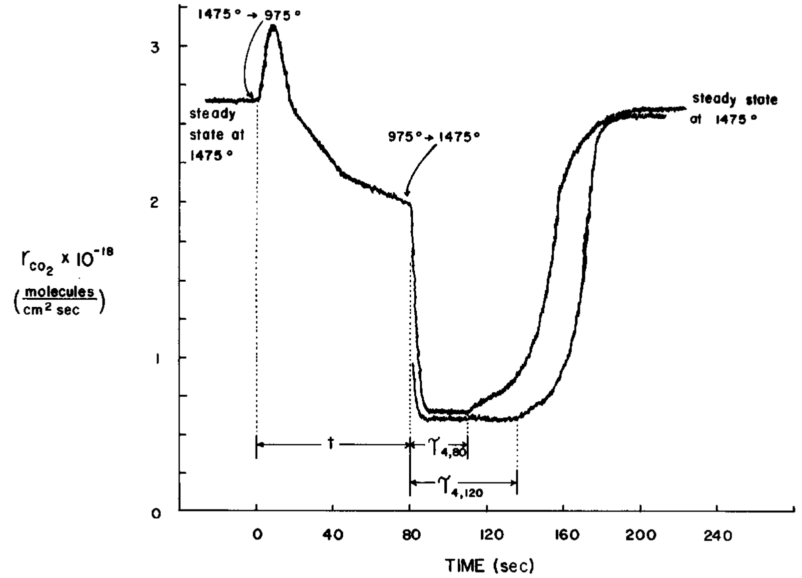

FIG. 7. Rate of CO_2 production versus time when the wire is cooled from its steady state at 1475 to 975°K for a specified time and is then heated back to 1475°K. The time τ_4 at the lower rate at 1475°K depends on the time interval of heating at 975°K, 80 to 120 sec for the curves shown here.

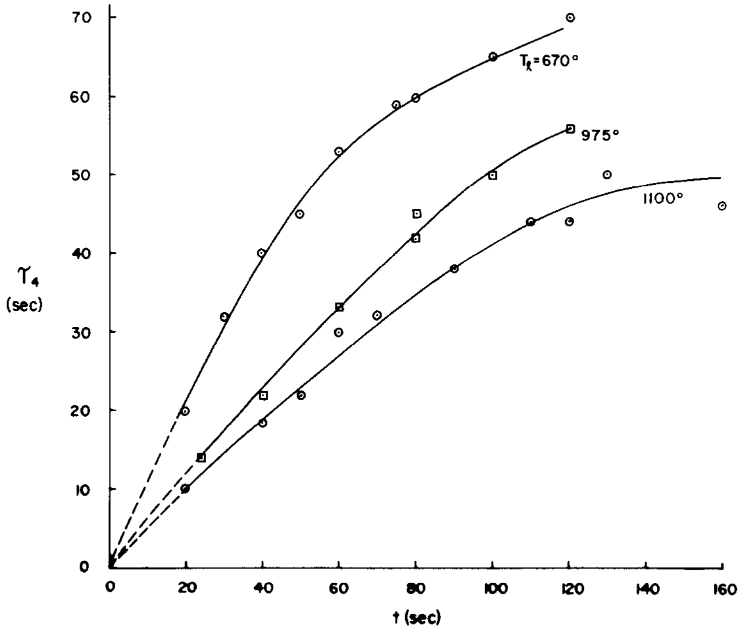

FIG. 8. Plot of time τ_4 from Fig. 7 versus the time of previous heating at lower temperatures of 670, 975, and 1100°K.

the upper curve. Following the temperature increase to 1475°K, the rate is precisely constant for 30 and 55 sec in the two curves, then exhibits a well-defined break, and rises to the steady state in ~50 sec. This rise time was approximately the same for any previous time and temperature treatment.

Figure 8 shows a plot of the time τ_4 versus the time t during which the wire had previously been maintained at the low temperature. Data shown are for low temperatures of 670, 975, and 1100°K and an upper temperature of 1475°K.

DISCUSSION

Our results indicate that steady state rates of CO oxidation are attained very slowly under most conditions. Further, the shapes of the rate versus time curves and the time constants versus temperature exhibit characteristic plateaus and maxima under certain conditions.

We maintain that all of these results can be interpreted quite simply in terms of processes involving formation of monolayer and multilayer complexes on the surface for temperatures below the steady state minimum and the decomposition of these complexes to form a "clean" surface above these temperatures. Our discussion will be concerned with analysis of the steady state and transient kinetics to try to quantify this contention.

We have no direct information as to the nature of the surface complexes. They are stable below ~1200°K (depending on CO and O_2 pressures) and are in some cases accompanied by a visible discoloration of the wire and a roughening of the surface to produce structures whose dimensions are 1000 to 5000 Å. Auger electron spectroscopy suggests that these surfaces may contain carbon, but Fe contamination during preparation of ribbons suitable for AES prevented a quantitative determination of surface concentrations of other species, particularly oxygen.

Among the likely surface complexes (*3*) on Pt—carbon, oxygen and carbon–oxygen mixtures (such as carbonate species)—we believe that a platinum–carbon film appears to explain the experimental results most consistently. The temperature at which the low temperature complex decomposes (i.e., the temperature at which the minimum occurs in Fig. 1) increases with increasing CO partial pressure and this suggests that carbon may form by the disproportionation reaction

$$2CO(g) + Pt(s) \rightleftarrows PtC(s) + CO_2(g). \quad (8)$$

Carbon would probably be removed by reaction with oxygen such as

$$O_2(g) + PtC(s) \rightarrow CO_2(g) + Pt(s), \quad (9)$$

but of course there are several possible reactions in this system and one can only speculate on their relative importances.

Since platinum oxides are stable (*16*) at or near the temperatures and O_2 pressures where the complexes are observed, the surface complexes responsible for the transient CO oxidation rates could be monolayer or multilayer films of PtO_2. However the decomposition temperature *increases* with decreasing O_2 pressure (Fig. 1). Further, in NH_3 oxidation and in reactions involving NO decomposition, *no transients were observed* for measured times down to 1 sec for any temperatures or gas compositions, and AES showed that even after heating Pt in pure O_2, oxygen was only observed within a few angstroms of the surface.

Roughening of the surface must be accompanied by an increased rate due to the increase in surface area. However, the reaction rate under conditions where a roughened surface was observed by SEM was always *lower* than the rate on the complex free surface (Figs. 3 and 7). Thus, on the complex there appears to be a reduced activity per unit area which more than compensates for the increased area due to roughening.

Steady State Kinetics

For temperatures below the second rise in Figs. 1 and 2, the steady state process appears to be occurring on a surface covered by a complex, while at higher temperatures the surface appears to be "clean." For high CO pressures the temperature of the second rate increase shifts to successively higher temperatures, suggesting that at lower O_2 pressures the temperatures sufficiently high to destroy the surface complex cannot be attained in our experiments. Even though transient results and wire morphologies at low temperatures suggest that complicated changes may be occurring on the surface (for example the roughening produces an increase in total surface area), we shall analyze these results in terms of the simple LH reaction model using steady state reaction rate data below the steady state minimum. Qualitative examination of the curves in Fig. 1 shows that CO inhibits the reaction at low temperatures because the rate is highest at low CO partial pressures and the rate maximum shifts to higher temperatures as P_{CO} increases.

If CO_2 is produced by a surface reaction between adsorbed CO molecules and adsorbed atomic oxygen with a rate

$$r_R = k_R\theta_{CO}\theta_O, \quad (10)$$

then, assuming competitive adsorption between CO and O atoms, one obtains (*4*)

$$r_R = \frac{k_R K_{CO} K_{O_2}^{1/2} P_{CO} P_{O_2}^{1/2}}{(1 + K_{CO}P_{CO} + K_{O_2}^{1/2}P_{O_2}^{1/2})^2}. \quad (11)$$

The parameters K_{CO} and K_{O_2} are obtained by assuming Langmuir isotherms to write Eq. (10) in terms of partial pressures. These parameters are of the form

$$K_{O_2} = K_{0,O_2} \exp (E_{O_2}/RT), \quad (12)$$

where E_{O_2} is the heat of adsorption of O_2.

Figure 9 shows computed curves of $r_R(T)$ using an equation of the form of Eq. (11) to fit the steady state rates of Figs. 1 and 2. The expression used to generate curves in Fig. 9 was

$$r_R = \frac{6.23 \times 10^{18} \exp (7000/RT) P_{CO} P_{O_2}^{1/2}}{(1 + 3.38 \times 10^{-6} \exp (16{,}000/RT) P_{CO})^2}. \quad (13)$$

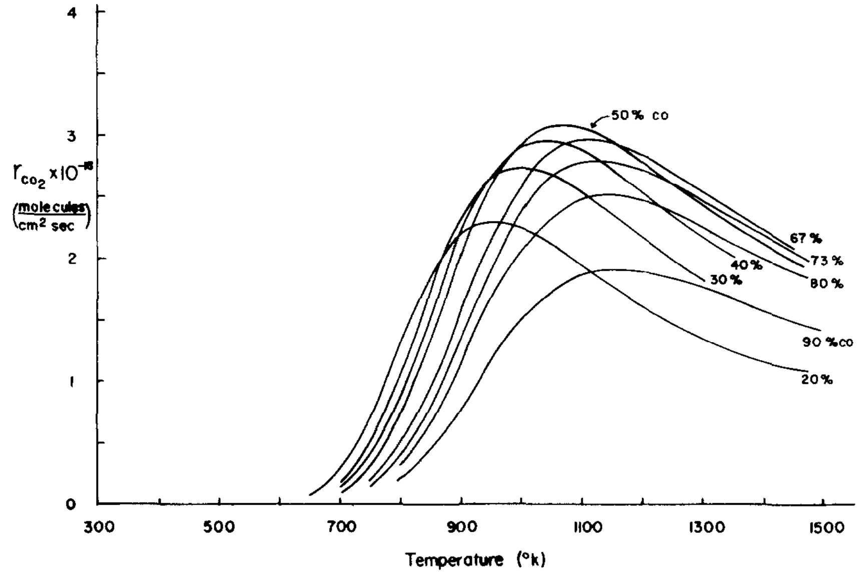

FIG. 9. Calculated rates of CO_2 production versus temperature according to Langmuir–Hinshelwood kinetics, Eqs. (11) and (13). Parameters were chosen to fit the steady state data of Fig. 1 for temperatures below those of the rate minimum. Peak shapes and shifts with composition are qualitatively the same as Fig. 1.

It was assumed that CO adsorption was much stronger than O_2 adsorption ($K_{CO}P_{CO} \gg K_O P_{O_2}$) in agreement with all studies of CO oxidation on Pt. These curves qualitatively reproduce the experimental curves up to the temperature of the rate minimum, but do not give the observed large shifts in the peaks with composition or the rapid falloff with temperature near 50% CO. Nevertheless the temperature and composition dependences of the reaction rate are qualitatively correct.

It is possible to reproduce the temperatures of the rate maxima by an expression of the form of Eq. (11) by using a lower heat of adsorption of CO, as shown in Fig. 10. These curves were obtained assuming

$$r = \frac{4.38 \times 10^{18} \exp{(3000/RT)} P_{CO} P_{O_2}^{1/2}}{(1 + 0.040 \exp{(6000/RT)} P_{CO})^2}. \tag{14}$$

However, the general shapes of these curves do not reproduce the experimental data as well as does Eq. (13).

We conclude that steady state rates of CO oxidation in the temperature range where a surface complex exists can be fit qualitatively by an expression of the form of Eq. (11) for all temperatures and compositions, but details of the curves do not agree with this simple equation. Agreement would not necessarily imply that the simple reaction mechanism of Eqs. (10) and (11) (the surface is assumed to be identical except for adsorbed CO and oxygen up to ~1300°K) is operative, although it does indicate that CO inhibits the reaction at low temperatures and that the effective activation energy is negative over a temperature range of several hundred degrees.

Transient Kinetics

The variation of the rates with time (τ_1, τ_2, τ_3 and τ_4 in Figs. 3 and 7) may permit one to decide on the mechanisms of the processes leading to surface complex formation and decomposition.

We assume according to the arguments used in deriving Eq. (7) that, in the absence of surface complexes, transients in this system should be very short and would be limited either by shifts in adsorption–desorption equilibrium or, more

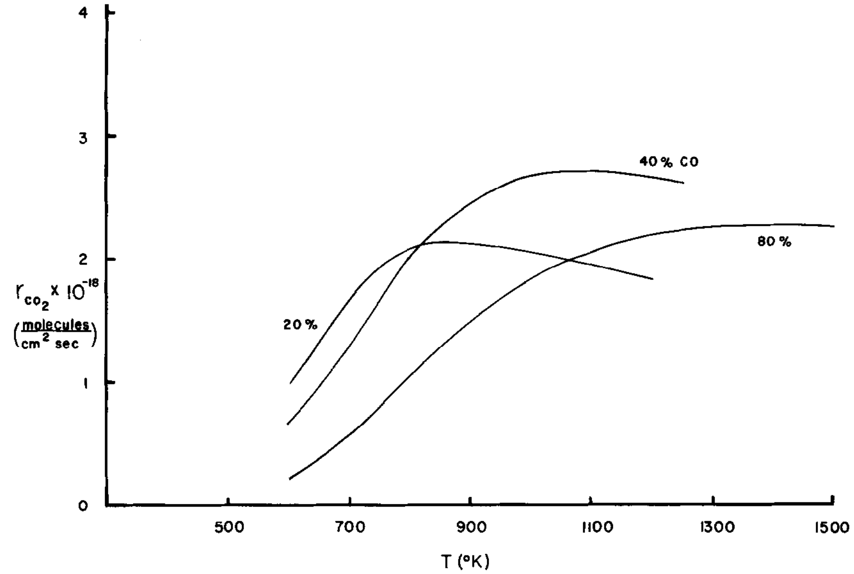

FIG. 10. Calculated rate of CO_2 production versus temperature according to Eq. (11) obtained by making peak shifts with composition agree with data of Fig. 1. Parameters of Eq. (14) do not reproduce overall shapes of curves as well as those of Eq. (13).

likely, by the system pumping time constant τ_s. Thus the exact forms of the adsorption, desorption, and reaction terms in Eqs. (1) and (2) are not important in this analysis, and transients in CO_2 production should be determined solely by the rates of formation or decomposition of surface complexes.

To analyze the transients observed upon heating from room temperature to a particular final temperature, Fig. 3, we assume that the rate of complex formation is some function of surface and/or gas phase concentrations. For a first order removal of species C, Eq. (5), the pressure of product should vary with time according to Eq. (7). Transient rate data at 750, 950 and 1390°K were analyzed using this equation, and Fig. 11 shows that at all three temperatures data exhibit definite curvature, showing that kinetics do not fit the τ_1 transient data. If the complex decomposed following second order kinetics,

$$\frac{d\theta_c}{dt} = -k_{dc}\theta_c{}^2,$$

then integration yields

$$\frac{1}{\theta(t)} = \frac{1}{\theta_0} - k_{dc}t, \qquad (15)$$

so that $[P_{CO_2,s} - P_{CO_2}(t)]^{-1}$ should be proportional to time. Figure 12 shows that when the data of Fig. 11 are plotted in this fashion a straight line is obtained at all three temperatures.

Figure 13 shows that a plot of $\log[(r_\infty - r)/(r_\infty - r_p)]$ vs τ_2 gives a straight line at 1350°K. The transient involved in the approach to the high temperature steady state τ_2 appears to follow first order kinetics, Eqs. (4) and (5). This transient involves removal of the last monolayer of the surface complex (which we suggest consists of a Pt and carbon film) and therefore the model used in Eqs. (4)–(7) should describe this process. Although the actual process would be the oxidation of carbon [perhaps by Eq. (9)], if P_{O_2} and θ_0 attained their steady state values rapidly, the rate would appear to be first order in θ_c.

The apparent agreement of the data with this model does not demonstrate that either of these simple mechanisms involves

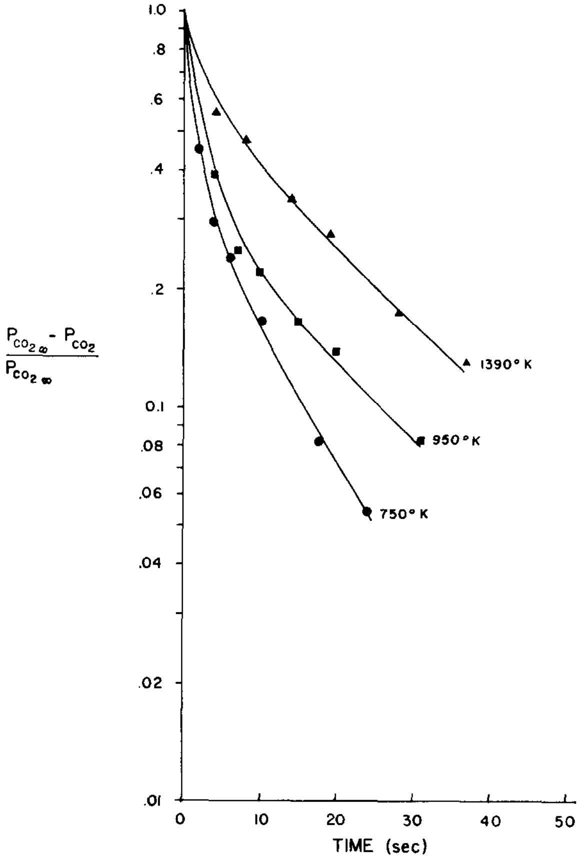

FIG. 11. Plot of transient rates versus time in 20% CO assuming a first order approach to the plateau rate, Eqs. (5) and (7).

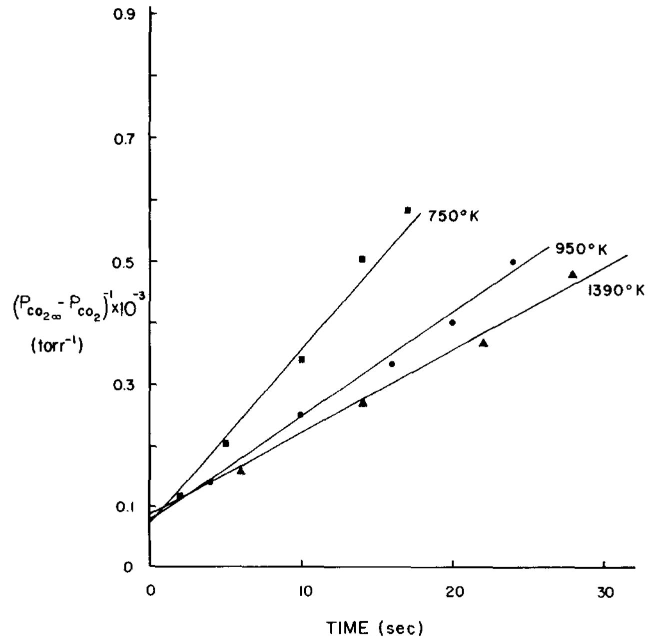

FIG. 12. Plot of transient rates versus time in 20% CO assuming a second order approach to the plateau rate, Eq. (15).

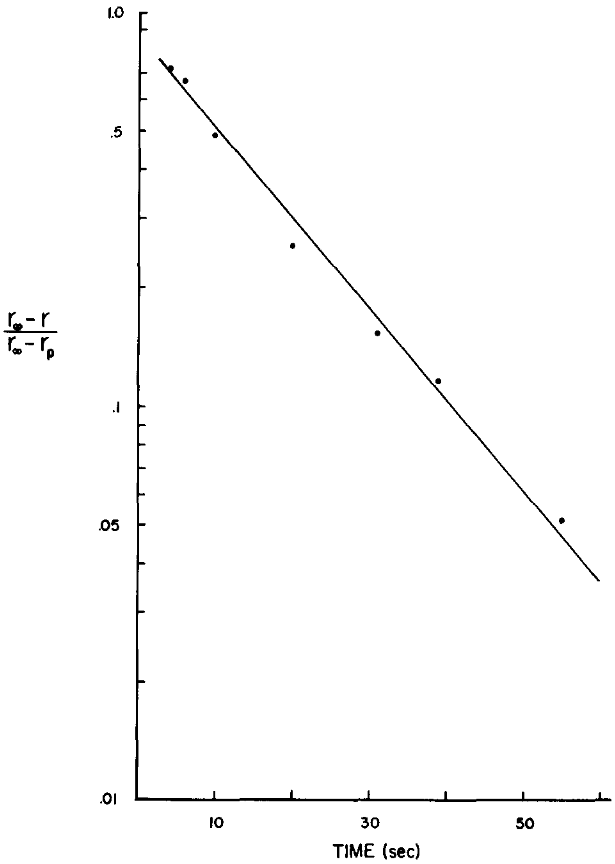

FIG. 13. Plot of transient rates versus time in 20% CO assuming a first order approach to the true steady state, Eqs. (5) and (7).

only the steps implied by Eqs. (5) and (15). However, the kinetics of these processes do appear to be described well by first or second order kinetics and the rate limiting step may be those indicated.

Rate of Film Formation

The constant plateau rates of Fig. 2 and the constant rate in Fig. 8 suggest that under these non-steady state conditions, the rate for some time is independent of changes which probably occur in the decomposing surface complex. This would be expected with a *multilayer* film at the surface, for example, in a platinum–carbon complex. Upon heating, the carbon is slowly oxidized by oxygen to form CO or CO_2, and if carbon is mobile, this film will merely become thinner as decomposition proceeds. However, the rate of CO oxidation on this surface should be *independent of film thickness* down to one monolayer, after which the rate approaches the clean surface value, perhaps with a rate constant of the form of Eq. (7). This interpretation of the constant rate regions observed in the transient experiments is a reasonable one, is consistent with film decomposition kinetics to be described below, and is the only mechanism we have devised which gives a region of constant rate in the transient experiments.

The rate of film formation appears to agree with a film diffusion model. Assume that there is a reaction such as disproportionation of CO, Eq. (8), which produces carbon in a compound with Pt and as PtC. The net rate of accumulation of this compound may be limited by the diffusion of carbon through the compound film to form

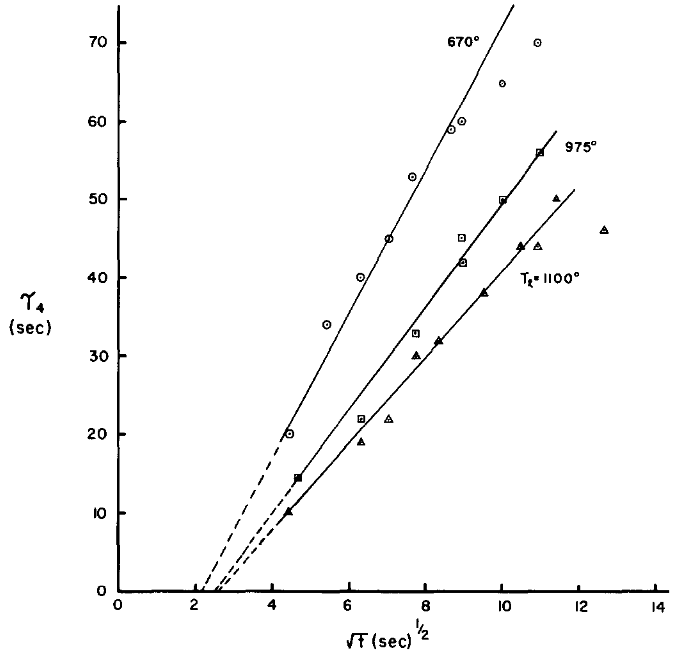

FIG. 14. Film formation kinetics. Plot of time τ_4, versus $t^{1/2}$ for data of Fig. 8. As indicated in the text, a straight line suggests that film formation is occurring at a rate given by Eq. (7).

PtC at the interface with Pt. If this is so, the film thickness should increase with time as

$$d \simeq (Dt)^{1/2} \qquad (16)$$

if the activity of carbon produced at the external surface is fixed.

Next we assume that carbon removal at high temperatures occurs at a constant rate (because of a constant pressure of O_2) so that the time required for complete removal of the film of PtC should be proportional to d. According to this model the time required to remove the film (τ_4 in Figs. 7 and 8) should be proportional to the square root of the time allowed for its formation (τ_4 in Figs. 7 and 8). Figure 14 shows that a plot of τ_4 versus $t^{1/2}$ yields straight lines for the three temperatures shown. τ_4 approaches zero for $t \simeq 5$ sec, and this is probably due to the fact that the film does not begin to form until it has cooled several hundred degrees below its initial temperature.

This analysis suggests that multilayer film growth is controlled by diffusion of carbon through the Pt–C film. While many properties of this film are unknown, this simple model gives a consistent and reasonable interpretation of the metastable constant rates and of the kinetics of growth and removal of films.

SUMMARY

The objectives of this paper are first, to demonstrate the utility of transient kinetics to study catalytic reactions, and second, to examine steady state and transient kinetics of CO oxidation on Pt.

Our apparatus is capable of following transients with a system response time ~1 sec. This time can easily be reduced to <0.1 sec using faster pumps, although gas equilibration times limit analysis of transients except for lower pressures. We have shown that there are no transients with times 0.5 sec in the NH_3, O_2, NO reactions on Pt, while long transients exist in CO oxidation on Pt. The difference between these systems in identical apparatuses shows that transients are only observed in certain situations, namely when reaction rates change due to changes in surface complexes which occur much more slowly than system or adsorption time constants.

Carbon monoxide oxidation on Pt appears to occur on a surface containing a multilayer film of some complex with Pt for pressures ~1 Torr and temperatures <1200°K. This conclusion seems to be consistent with previous high pressure studies of this system because all previous experiments employed very long measuring time constants and thus should have observed *only* steady state behavior.

The reactions responsible for measured transients (suggested to be disproportionation of CO and carbon oxidation) have rates in our measurements of $< 10^{-5}$ of the rate of the major CO oxidation reaction which has a maximum probability of $< 10^{-2}$. This emphasizes the fact that very slow rate processes which alter the surface can dominate catalytic reaction rates and yet be completely undetectable in experiments at high pressures unless the system is capable of following rapid transients. For a process involving alteration of the surface by the reactant to have a time constant of 1 sec, the reaction probability (fraction of reactant flux which reacts) must be $\sim 10^{-6}$ at 1 Torr and $\sim 10^{-9}$ at 1 atm. The only means of detecting such changes is by lowering the pressure and/or by using systems capable of following even more rapid transients.

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