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Tracer Studies on the Reaction Paths of the CO Oxidation over Platinum

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Transient production of carbon dioxide was monitored by mass spectrometry where a polycrystalline platinum foil covered by given amounts of carbon monoxide was exposed to various gas mixtures of carbon monoxide and oxygen at room temperature. The transient feature depended strongly on the amount of carbon monoxide preadsorbed and the pressure of the dosed gas. When the substrate was covered in advance with carbon monoxide labeled with carbon 13, the initial ratio of $^{13}CO_2$ to $^{12}CO_2$ in the carbon dioxide produced was equal to that of ^{13}CO to ^{12}CO in the carbon monoxide preadsorbed. The equality between them held true for all pressures and the compositions of the dosed gas and for the initial coverages of carbon monoxide studied. Carbon monoxide immediately prior to oxidation was concluded to be in a chemisorption state, i.e., carbon dioxide is produced via a Langmuir–Hinshelwood process, namely $CO(a) + O(a) \rightarrow CO_2$. No contribution from an Eley–Rideal process, namely $CO(g) + O(a) \rightarrow CO_2$, was observed.

INTRODUCTION

Since the study by Langmuir (*1*) numerous investigations have been reported on the carbon monoxide oxidation over single crystal and polycrystalline platinum surfaces (*2–10*). Two reaction paths have been proposed to fit the experimental data under low reactant pressures. The first reaction path (*3–8*) involves a chemisorbed oxygen atom interacting with a carbon monoxide molecule in a physically adsorbed mobil precursor state (Eley–Rideal process, E–R). The kinetics has been studied by monitoring transients in the carbon dioxide production or decays of Auger signal of the surface oxygen, when the oxygen-covered surface is exposed to gaseous carbon monoxide. This interaction was so rapid that the reaction probability of incident carbon monoxide was close to unity. The observed kinetics was quite similar to that of the reaction controlled by the mass transfer process of carbon monoxide. In the second path a carbon monoxide molecule chemisorbed attacks the oxygen adatom (Langmuir–Hinshelwood process, L–H). The kinetics has been studied by various workers (*3, 9, 10*) using a transient technique to study the interactions between gaseous oxygen and carbon monoxide-covered surfaces, or by modulated molecular beam methods. These results showed that there was a significant activation energy and that the rate was controlled in general by the dissociative adsorption of oxygen. Therefore, it is very difficult to isolate either processes purely and to study the kinetics thereof clearly.

Recently certain authors (*11, 12*) have presented their results obtained by molecular beams, in which they made attempts to separate the above two processes (*11*) or

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to rule out one mechanism (*12*). Their kinetic analysis was made on the basis of assumptions that the rates of the E–R and L–H processes were proportional to the product of the collision frequency of carbon monoxide and the coverage of surface oxygen, and that of the coverages of carbon monoxide and oxygen, respectively. These assumptions, however, have not been verified (*7*, *8*, *13*).

In this paper our aims have been to establish a method for separating the above two processes without any assumptions regarding their rate equations. These goals were approached by using a pressure jump method combined with an isotope tracer technique. The results show clearly that carbon monoxide is adsorbed before it is oxidized, i.e., carbon dioxide is produced at room temperature simply through the Langmuir–Hinshelwood process.

METHODS

The system was a bakeable ultrahigh vacuum apparatus with a base pressure of less than 3×10^{-7} Pa (1 Pa = 7.5×10^{-3} Torr), the principal residuals being carbon monoxide and hydrogen. The pressures, total and partial, were monitored with a Bayard–Alpert gauge and a quadrupole mass spectrometer. During the experiments the system was subjected to continuous pumping by an ion pump. The substrate, a polycrystalline platinum foil ($30 \times 4 \times 0.05$ mm), could be heated resistively. Reactant gases, CO, O_2, ^{13}CO, $C^{18}O$ (carbon 12 and oxygen 16 are simply designated as C and O, respectively), and their mixtures were introduced through variable leak valves. Temperatures were monitored with a Pt–Pt/Rh thermocouple spot-welded on to the substrate.

Prior to the experiments the substrate was exposed to oxygen at a pressure of 1×10^{-4} Pa and a temperature of 1500 K for several hours and then flashed to 1700 K under vacuum for a few tens of minutes. Several repetitions of this treatment were sufficient for the establishment of stable catalyst behavior such as the highest activity for the oxidation and the stable adsorption–desorption phenomena of carbon monoxide and oxygen. During a series of measurements, the substrate was heated to 1700 K for about 5 min prior to each experiment. The above oxygen treatment was applied even in a series of measurements whenever the stable catalyst behavior was not observed.

All of these experiments utilize a hot filament electron supply in the mass spectrometer. The ionization gauge was used only for calibration of the mass spectrometer sensitivity. There is some background reaction on the filament which, being independent of the substrate temperature, was determined separately with the substrate covered fully by carbon monoxide at room temperature and subtracted from measurements made under the same gas phase compositions. Since the background reaction reached a steady state very rapidly, the carbon dioxide background level was readily estimated from the gas compositions at operating conditions.

RESULTS

In order to estimate ambiguities in the tracer experiments, the isotopic mixing in carbon monoxide and the replacement of carbon monoxide adsorbed by another were first examined.

1. *Isotopic Mixing in Carbon Monoxide*

$^{12}C^{18}O$ and $^{13}C^{16}O$ were adsorbed together onto the substrate at room temperature and after 1 hr evacuation, the substrate was heated slowly (about 10 K/sec) to 800 K. The mass 31 peak due to the production of $^{13}C^{18}O$ did not increase during the heating over the background level which was about 2% of the total carbon monoxide peak.

Another possibility of the isotopic mixing was tested. An isotopic mixture gas ($^{12}C^{16}O$: 42.9%, $^{13}C^{16}O$: 28.6%, and $^{12}C^{18}O$: 28.5%) was allowed to flow at a pressure of 1.2×10^{-5} Pa and the substrate was heated stepwise from 300 to 1200 K. The mass 31 peak ($^{13}C^{18}O$) showed no increase over the temperature range studied. Therefore, the isotopic mixing in carbon monoxide may be negligible on the platinum surface in this reaction system.

2. Replacement of $^{12}C^{18}O$ or $^{13}C^{16}O$ Preadsorbed on Platinum by Gaseous $^{12}C^{16}O$

The replacement of carbon monoxide preadsorbed by another was studied under various carbon monoxide pressures at room temperature. In this experiment the substrate was flashed to 800 K where carbon monoxide was not adsorbed, in carbon monoxide gas containing $^{12}C^{18}O$ or $^{13}C^{16}O$ and then cooled down to room temperature. After the pressure reached a steady state, the isotope gas flow was stopped and pure $^{12}C^{16}O$ was introduced quickly at the same pressure as before. The partial pressure of $^{12}C^{18}O$ or $^{13}C^{16}O$ decreased immediately to less than 5% of the total carbon monoxide pressure. After desired intervals the substrate was flashed to 800 K while the partial pressure of $^{12}C^{18}O$ or $^{13}C^{16}O$ was recorded and the amount of the remaining $^{12}C^{18}O(a)$ or $^{13}C^{16}O(a)$ was determined from the peak area. The amount decreased exponentially with the replacement time. The half-life was about 120 min in length, independent of the carbon monoxide pressure. The replacement was so slow that the isotopic compositions in carbon monoxide adsorbed may hold up the time of initiation of the transient experiments described below.

3. Transient Carbon Dioxide Production by Dosing a Mixture Gas ($^{12}CO + O_2$) to the Substrate Partially Precovered by ^{12}CO.

In order to study experimental conditions available for a transient isotope tracer technique, the general features of the transient production of carbon dioxide were studied at room temperature as a function of the coverage of carbon monoxide preadsorbed, θ_0. A negligible amount of carbon dioxide was produced on platinum fully covered by carbon monoxide (*15*). It was shown that the transient production should be started within some limited range of θ_0.

Figure 1 shows a transient carbon dioxide production, which was induced by dosing a mixture gas of carbon monoxide and oxygen ($^{12}CO/O_2 = 0.24$) at a pressure of 1×10^{-4} Pa to a clean platinum surface ($\theta_0 < 0.01$), as well as variations in the carbon monoxide and oxygen partial pressures. During the transient experiment the apparent total pressure was kept constant, by monitoring the ion current of the ion pump. In the first experiment the carbon dioxide peak was monitored. Later the system was returned to the same condition and the carbon monoxide and oxygen peaks were recorded during a second experiment. The features of the transient production were well reproduced. It should be noted that the carbon dioxide production was maximized approximately 50 sec after the mixture gas was dosed, but not at the initial part, and that it decreased rapidly to the background level, showing a small shoulder around 350 sec. The oxygen pressure increased slightly at 150 sec. This was attributed to the completion of carbon dioxide production. The partial pressure of carbon monoxide remained less than half of the final pressure up to 250 sec. This was caused by the consumption via oxidation to carbon dioxide and the adsorption onto the surface. The amounts of CO(a) and O(a) during the transient experiment were determined by flash desorption and titration by carbon monoxide (*3, 14*). Until the first peak around 50 sec, both amounts increased with the time up to the coverages around 0.2 (*16*). The amount of O(a) decreased to a very small value after the peak, while the other continued to increase.

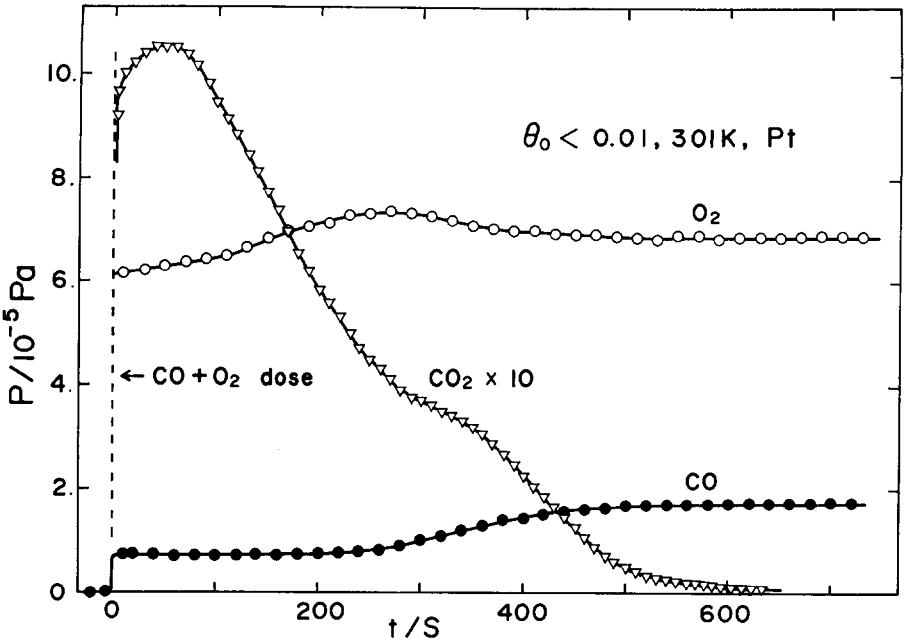

FIG. 1. Application of ($^{12}CO + O_2$) pressure jump to induce transients in carbon dioxide production at 301 K. Variation of ^{12}CO, O_2, and $^{12}CO_2$ partial pressures was shown during a mixture gas ($^{12}CO + O_2$) dosed onto a clean platinum surface. The apparent total pressure was kept constant at 1×10^{-4} Pa.

Thus the rate of the carbon dioxide production after the first peak may be controlled in general by the oxygen adsorption. The mixture gas flow was terminated after 800 sec and the substrate was heated to 800 K while the carbon monoxide and carbon dioxide peaks were monitored. The amount of carbon dioxide desorbed was less than 5% of that of carbon monoxide. The latter amount showed that the substrate was almost fully covered by carbon monoxide. Oxygen was not desorbed.

The feature of the transient carbon dioxide production depended strongly on the initial coverage of carbon monoxide. Typical examples are shown in Fig. 2. The initial coverage of carbon monoxide was estimated by flash desorption; carbon monoxide was introduced at a desired pressure for 120 sec immediately after the substrate was cooled down to room temperature from 800 K and the amount of carbon monoxide adsorbed during this period was determined by a flash desorption technique. Afterwards the substrate was cooled down and exposed to carbon monoxide in the same manner as before, but in this case the mixture gas was introduced after the leak valve of carbon monoxide was closed, while the carbon dioxide or carbon monoxide and oxygen peaks were recorded. The coverage was defined as the peak area of the carbon monoxide relative to the maximum area which was obtained by flashing from the steady state of carbon monoxide flow at room temperature. Below $\theta_0 = 0.03$ carbon dioxide was produced in a manner similar to that of $\theta_0 < 0.01$, i.e., it maximized at a certain interval after the mixture gas was dosed and showed a small shoulder after 200 sec. From $\theta_0 = 0.06$ it did not show such a maximum but decreased monotonously. Further, from $\theta_0 = 0.13$–0.19 it decreased very rapidly and the shoulder became clear. The transient carbon dioxide production from $\theta_0 > 0.5$

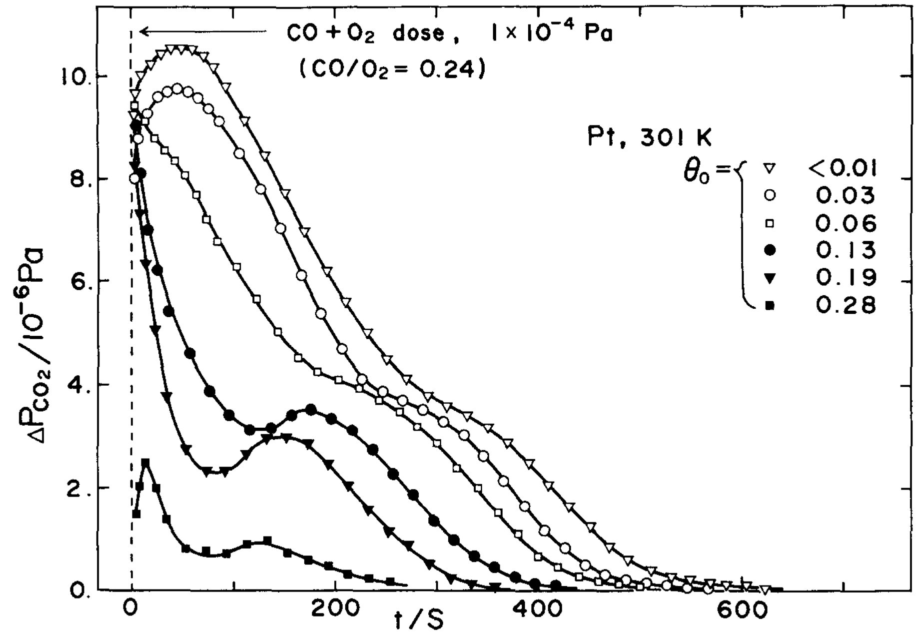

FIG. 2. Variation of transient $^{12}CO_2$ production with initial ^{12}CO coverages, θ_0.

was diminished in the background. Therefore, the transient isotope tracer technique can be applied on the surface precovered by carbon monoxide in a range of $\theta_0 = 0.02$–0.3. The kinetic behavior of the transient carbon dioxide production will be discussed in detail elsewhere (*16*).

4. *Transient Isotopic Carbon Dioxide Production when the Substrate Partially Covered by ^{13}CO and ^{12}CO was Exposed to a Mixture Gas, $^{12}CO + O_2$*

Figure 3 shows variations of the partial pressures of $^{13}CO_2$, $^{12}CO_2$, O_2, ^{12}CO and ^{13}CO during a typical transient isotopic carbon dioxide production. This was induced by dosing with a mixture gas of ^{12}CO and O_2 ($^{12}CO/O_2 = 0.24$) at a pressure of 1×10^{-4} Pa to the surface which was precovered by isotopic carbon monoxide at a ratio $^{13}CO(a)/^{12}CO(a) = 1.9$ and $\theta_0 = 0.13$. The ratio of $^{13}CO(a)$ to $^{12}CO(a)$ was estimated in the following two methods; (a) the ratio of the partial pressures of ^{13}CO and ^{12}CO in carbon monoxide dosed was determined, and (b) after 120 sec exposure of isotopic carbon monoxide, the substrate was flashed to 800 K and the ^{13}CO and ^{12}CO peaks were monitored. There was a good agreement in the ratios determined by these two methods. During the transient experiments gaseous ^{13}CO was observed appreciably, but it was less than 10% of ^{12}CO.

A significant production of $^{13}CO_2$ was observed as well as that of $^{12}CO_2$. $^{13}CO_2$ decreased rapidly, on the other hand $^{12}CO_2$ remained at the initial level for a while and decreased to the background level. The $^{13}CO_2 + {}^{12}CO_2$ sum agreed well with the transient carbon dioxide production from $\theta_0 = 0.13$ as shown in Fig. 2. The long and short dashed curve in Fig. 3 indicates the amount of $^{12}CO_2$ estimated to be produced from only $^{12}CO(a)$ preadsorbed; this was 52.6% of the $^{13}CO_2$ since the initial isotope ratio $^{13}CO(a)/^{12}CO(a)$ was 1.9. The difference between the observed $^{12}CO_2$ and the calculated value was a contribution from gaseous $^{12}CO_2$. $^{13}CO_2$ was produced by the oxidation of $^{13}CO(a)$ preadsorbed on the surface since gaseous ^{13}CO was much less than ^{12}CO and its contribution was negligible. In order to estimate the ratio of $^{13}CO_2$ to $^{12}CO_2$ at the dose time $t = 0$, logarithm of the partial pressure of $^{13}CO_2$ was plotted against the dose time and extrapolated to $t = 0$. The initial ratio determined in this manner was equal to that of $^{13}CO(a)$ to $^{12}CO(a)$ in carbon monoxide preadsorbed within the margin of experimental errors. The results are summarized in Table 1. The errors listed in the fourth column of Table 1 were estimated as follows. The mass of $^{13}CO_2$ or $^{12}CO_2$ was recorded *continuously* under the same transient conditions as those in Table 1 and then extrapolated to $t = 0$ in the same manner as shown above. The extrapolated values obtained in this manner were not different by more than 5% from the values actually observed in the very early stages of the transient carbon dioxide production and showed an agreement with the values in Table 1 within the margin of errors listed.

Figure 4 shows other transient isotopic carbon dioxide production induced at $\theta_0 = 0.04$ and the isotope ratio, $^{13}CO(a)/^{12}CO(a) = 1.0$. Since the initial coverage was small, the $^{13}CO_2 + {}^{12}CO_2$ sum remained at the initial level for a while and decreased rapidly to the background, and a contribution from gaseous ^{12}CO was relatively large. The initial ratio of $^{13}CO_2$ to $^{12}CO_2$, however, was equal to that of $^{13}CO(a)$ to $^{12}CO(a)$ in carbon monoxide adsorbed in advance. The equality between the ratio of $^{13}CO_2$ to $^{12}CO_2$ in carbon dioxide at $t = 0$ and that of $^{13}CO(a)$ to $^{12}CO(a)$ in carbon monoxide preadsorbed was confirmed over the coverage range $\theta_0 = 0.02$–0.3 and various isotope ratios. In all cases all of the carbon monoxide molecules oxidized to carbon dioxide were concluded to be derived from the chemisorption state, but not from the gas phase.

If some carbon monoxide could be

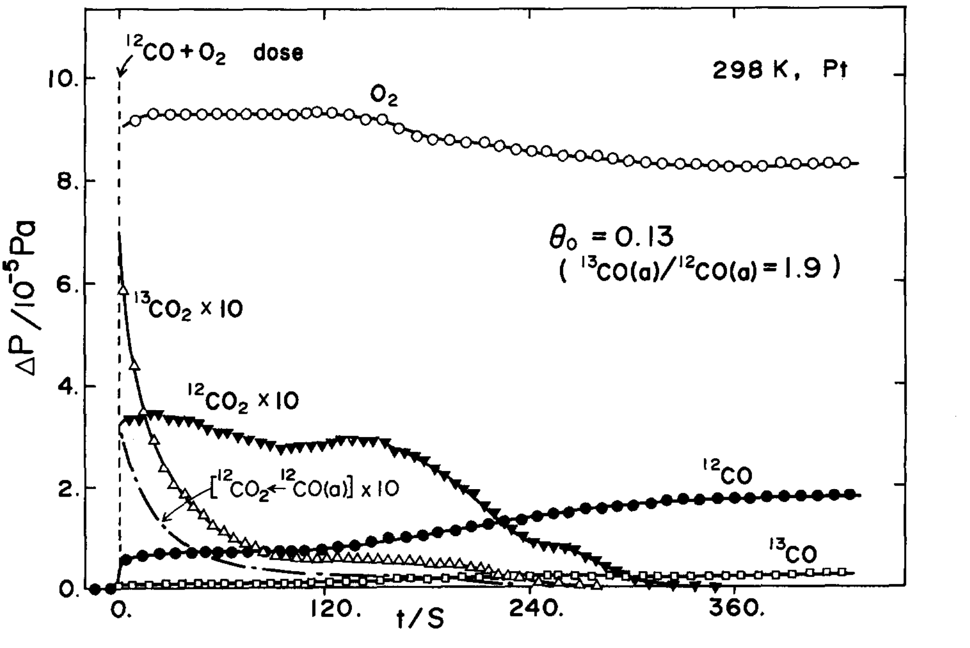

FIG. 3. Variation of ^{12}CO, ^{13}CO, O_2, $^{13}CO_2$, and $^{12}CO_2$ partial pressures during a mixture gas ($^{12}CO + O_2$) dosing to a surface covered by carbon monoxide involving $^{13}CO(a)$. The apparent total pressure was kept constant at 1×10^{-4} Pa.

TABLE 1

The Results of the Transient Isotopic Carbon Dioxide Production Induced by Dosing the Mixture Gas at Various Pressures to the Surface Covered with Carbon Monoxide at the Coverage 0.12 ± 0.1[a]

No.	Mixture gas dosed (Pa)[b]		Initial rate of CO_2 (Pa)	Initial isotope ratio in CO_2: $^{13}CO_2/^{12}CO_2$	Total amount of CO_2 (arb. units)	Isotope ratio in whole CO_2: $^{13}CO_2/^{12}CO_2$
	^{12}CO	O_2				
1	3.2×10^{-5}	4.3×10^{-4}	4.4×10^{-5}	2.3 ± 0.4	1.2	0.49
2	0.67	0.93	1.1	2.1 ± 0.1	1.0[c]	0.41
3	1.4	1.5	1.7	2.2 ± 0.2	1.1	0.35
4	0.62	0.58	0.78	2.3 ± 0.3	0.94	0.45
5	0.45	0.37	0.73	2.1 ± 0.1	1.1	0.38
6	0.25	0.15	0.36	1.9 ± 0.2	0.76	0.41
7	0.38	0.31	0.73	2.0 ± 0.2	1.1	0.33

[a] The carbon monoxide preadsorbed contained isotope molecule ^{13}CO in the ratio $^{13}CO(a)/^{12}CO(a) = 2.0 \pm 0.1$.

[b] The initial compositions during transient experiments.

[c] Standard.

oxidized to carbon dioxide at room temperature via the E–R process, the contribution would increase accompanied by an increase in the carbon monoxide collision frequency. This possibility was examined by changing the pressure of the dosed gas of a fixed composition. Typical transient productions are shown in Fig. 5 and the results analyzed are summarized in Table 1. The initial rate of carbon dioxide production was a reaction of the first order in the pressure of the dosed gas. The ratio of $^{13}CO_2$ to $^{12}CO_2$ at $t = 0$ remained around two which was equal to that of $^{13}CO(a)$ to $^{12}CO(a)$ in carbon monoxide preadsorbed. Other kinetic data are summarized in

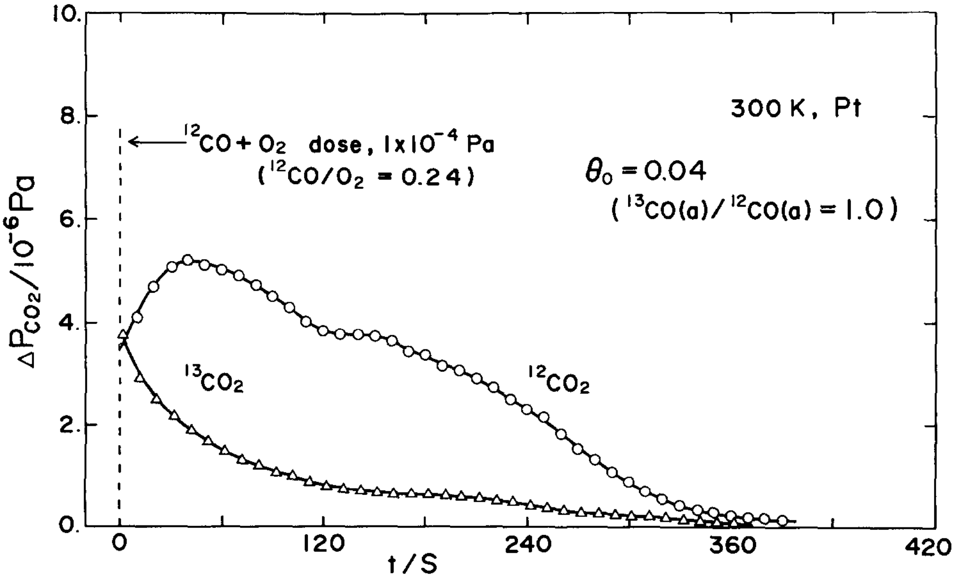

FIG. 4. Variation of the isotopic composition in carbon dioxide during a mixture gas ($^{12}CO + O_2$) dosed onto a surface covered by $^{13}CO(a)$ and $^{12}CO(a)$ at the ratio $^{13}CO(a)/^{12}CO(a) = 1.0$.

Table 1. The last two columns show the total amounts of carbon dioxide produced transiently and the isotope ratio. The former was almost independent of the mixture gas pressure. The isotope ratio was also constant. The relative contributions from carbon monoxide preadsorbed and from the gas phase did not vary with the pressure of the dosed gas.

The contribution from the E–R process was further tested by other experiments, i.e., by changing the composition of the gas mixture in order to increase the carbon monoxide collision frequency relative to the oxygen adsorption rate. The results are listed in Table 2. The ratio of carbon monoxide to oxygen was varied from 0.21 to 1.9, but the initial ratio of $^{13}CO_2$ to $^{12}CO_2$ was still equal to that of $^{13}CO(a)$ to $^{12}CO(a)$ in carbon monoxide preadsorbed within the margin of experimental errors. The total carbon dioxide produced decreased with the increase in ratio of carbon monoxide to oxygen, and the ratio of the amount of $^{13}CO_2$ to that of $^{12}CO_2$ decreased slightly with it.

Therefore it has been concluded that carbon monoxide consumed in the oxidation at room temperature is merely derived from the chemisorption state, in other words carbon dioxide is produced through the L–H process. No evidence of the E–R process was observed.

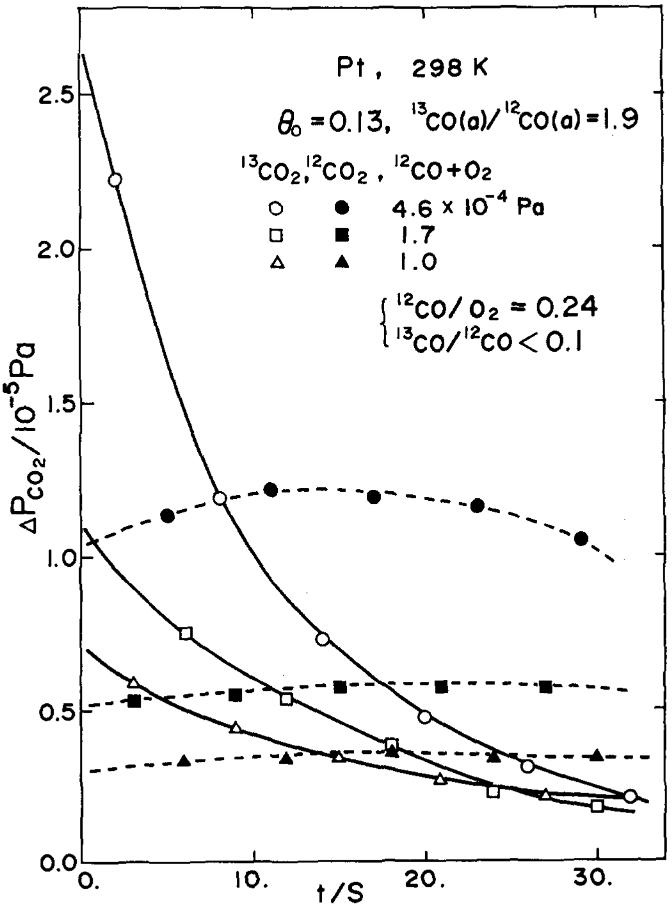

FIG. 5. Variation of isotopic carbon dioxide production with pressures of gas dosed.

TABLE 2

Typical Results of the Transient Isotopic Carbon Dioxide Production with Various Compositions of Mixture Gas[a]

No.	Isotope ratio in CO preads. $^{13}CO(a)/^{12}CO(a)$	Mixture gas dosed (Pa)[b]		Initial rate of CO_2 (Pa)	Initial isotope ratio in CO_2: $^{13}CO_2/^{12}CO_2$	Total amount of CO_2 (arb. units)[c]	Isotope ratio in whole CO_2: $^{13}CO_2/^{12}CO_2$
		^{12}CO	O_2				
1	1.9 ± 0.1	1.8×10^{-5}	8.8×10^{-5}	1.3×10^{-5}	1.7 ± 0.3	0.90	0.40
2	1.9 ± 0.1	3.8	9.3	1.4	1.8 ± 0.3	0.67	0.34
3	1.7 ± 0.1	2.4	5.1	0.75	2.2 ± 0.3	0.60	0.32
4	1.6 − 0.1	1.5	0.80	0.12	1.5 ± 0.5	0.42	0.27
5	1.7 − 0.1	2.6	1.6	0.23	1.5 ± 0.5	0.52	0.27
6	1.5 ± 0.2	5.8	4.2	0.67	1.6 ± 0.2	0.46	0.37
7	1.7 − 0.1	4.0	2.7	0.46	1.5 ± 0.3	0.47	0.29

[a] The initial coverage of carbon monoxide, θ_0, was 0.11–0.12.

[b] The initial compositions during transient experiments.

[c] The total CO_2 production at No. 2 in Table 1 was used as the standard.

DISCUSSION

The experimental results obtained by transient techniques (*3–8*) appeared to provide ample evidence that carbon dioxide is formed through both the E–R and L–H processes. The transient isotope tracer experiments, however, showed clearly that no contribution from the E–R process was observed at room temperature where the L–H process was thought to be much slower than the E–R process, as estimated below. Hence it becomes necessary to reexamine the experimental data reported so far.

Bonzel and Burton (*3*) analyzed the kinetics of the L–H process on Pt(110) plane using a transient technique. Their results showed that the reaction was fast with a second order rate constant, $k = 1.84 \times 10^{-11} \exp(-33 \text{ kJ molecule}^{-1}/RT)$ cm^2 molecule^{-1} sec^{-1}. The general similarities of the kinetics on polycrystalline, (111) and (110) Pt suggest that the rate constant on Pt(110) is not so different from that on Pt(111). Assuming that the substrate used here consists predominantly of (111) oriented crystallites (*17*) and that the saturation concentration of carbon monoxide and oxygen are 7.5×10^{14} molecules/cm^2 (*18–20*) and 6.8×10^{14} atoms/cm^2 (*21*), respectively, the maximum rate of the L–H process at room temperature is estimated to be 4×10^{12} molecules/cm^2 sec for $\theta_{CO(a)} = \theta_{O(a)} = 0.5$. The E–R process has been reported to be very rapid with unity reaction probability of incident CO on the oxygen-covered surface (*3–8*). Assuming that the reaction probability is 0.5 on the surface half covered by oxygen, and introducing carbon monoxide at a pressure of 1×10^{-5} Pa, the rate of the E–R process is estimated to be 1.4×10^{13} molecules/cm^2 sec. If the transient is started at $\theta_0 = 0.1$, the rate ratio of the E–R process to the L–H process would be roughly 40, i.e., the E–R process should be much more rapid than the L–H process. Experimental results described in the former section, however, show clearly that the reverse is true. Many assumptions were introduced in the above calculations. But the fact that no evidence of the E–R process was observed suggests that the kinetics of the above two processes reported so far contains some unexpected ambiguous points.

The kinetics of the E–R process has been studied through analysis of transient carbon dioxide production from an interaction of gaseous carbon monoxide with the surface fully covered by oxygen. The observed rate was extremely high, showing that the reaction probability of incident carbon monoxide was close to unity. It indicates that it is very difficult to isolate only the surface process from the overall carbon dioxide production involving the mass transfer step of carbon monoxide. Even if the incident carbon monoxide must stay but for a short duration in the chemisorption state before being oxidized, the observed kinetics will behave as if the reaction took place via the E–R process, under the conditions that the surface process is as rapid as all incident carbon monoxide is oxidized to carbon dioxide.

Similar difficulties should also be considered on the observation of the L–H process. The process has been studied kinetically (*3*) from the transient production of carbon dioxide in an interaction of gaseous oxygen with the surface almost fully covered by carbon monoxide. As Fig. 2 shows, oxygen adsorption is inhibited strongly by the carbon monoxide adsorbed. Above the coverage of 0.5 it is hardly adsorbed (*16*). The rate of the carbon dioxide production in Table 1 increased with the increase in the supply rate of surface oxygen at a fixed carbon monoxide coverage. Therefore the oxygen adsorption is in general rate-determining in the interaction between oxygen gas and carbon monoxide-covered surfaces. The surface L–H process itself is inferred to be extremely rapid even at room temperature. The observed kinetics is hardly controlled by the surface L–H process. In most of the papers published (*3, 9, 11, 12*) the rate of the L–H process has been assumed to be proportional to the product of the coverages of oxygen and carbon monoxide. On palladium, however, adsorbed oxygen and carbon monoxide make their islands on the surface (*22*) and do not behave homogeneously. Inhomogeneity in the kinetics of the reaction of adsorbed oxygen with carbon monoxide adsorbed has been observed on palladium (*13*) and platinum (*16*).

Finally the conditions for the transient isotope tracer experiments will be compared with those for the other transients (*3, 7*) and also the kinetic experiments in a steady state (*1, 2, 15*). In the experiments described in this paper, the surface was always precovered by carbon monoxide, but not oxygen. The oxygen-covered surface interacts with carbon monoxide at such a rapid rate (*3, 7*) that it is quite difficult to control the amount and the isotopic compositions of carbon monoxide adsorbed. The transient isotope tracer method has not been successfully applied on those surfaces. Kinetic studies on the CO oxidation in a steady state have shown that the inhibition region by carbon monoxide appears for $P_{CO} > P_{O_2}$ and is narrowed with an increase in the temperature. Even outside the inhibition region the amount of CO(a) is significant (*15*). These phenomena have been ascribed to a contribution from the L–H process, i.e., the inhibition is observed when the rate of the L–H process, which plays a main role in eliminating CO(a) from the surface, is less than that of the CO adsorption. The noninhibition region is very narrow at room temperature (*15, 23*). Therefore the experimental conditions used here correspond to the inhibition region in the kinetics in a steady state.

ACKNOWLEDGMENT

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