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Competitive Sorption Kinetics of Oxygen and Carbon Monoxide on Platinum*

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The sorption of oxygen on a polycrystalline platinum ribbon has been studied with the aid of a quadrupole mass analyzer in an ultrahigh vacuum system in the pressure range from 5 to 10×10^{-8} Torr. An evaluation of the reaction coefficient and the total mass of oxygen sorbed indicated that oxygen competes with carbon monoxide, present as a background contaminant ($P \simeq \times 10^{-9}$ Torr), for the sorption sites on the flash-cleaned platinum surface. Subsequent desorption of oxygen is not observed when the platinum is flash heated to temperatures up to 1100°K; carbon monoxide and carbon dioxide are predominant species leaving the platinum surface. The relative amount of each component depends on the length of exposure of the flash-cleaned platinum ribbon to the background gas and to oxygen. The experimental results suggest a high reaction coefficient of oxygen on a clean platinum surface at room temperature ($S \simeq 0.2$).

INTRODUCTION

In view of the importance of the interaction between oxygen and metals in such areas as upper atmosphere composition studies, heterogeneous catalysis and catalyst surface-area determination, we have examined the adsorption and desorption characteristics of molecular oxygen on a clean platinum surface in a pressure region where rates of sorption can be conveniently measured ($\sim 10^{-7}$). We have also evaluated the role of an ubiquitous contaminant gas, carbon monoxide, on the kinetics and path of the sorption/desorption process.

Recent investigators have studied the surface chemistry of oxygen on platinum in the form of evaporated films, (*1*) foils (*2*–*4*), single crystals (*5*), and supported catalysts (*6*–*8*). In all cases, a nonactivated process of chemisorption has been observed. The degree of surface coverage with oxygen has been a problem of major concern, with a limiting ratio of Pt/O = 2 generally assumed.

EXPERIMENTAL DETAILS

The apparatus used for the experimental measurements (Fig. 1) was a Pyrex vessel consisting of two main sections (A and B) separated by shutter 1 and evacuated by separate ion-getter pumps. Chamber A (5 liters in volume) contained a quadrupole mass analyzer[1] which served the purpose of monitoring the pressure and composition of the gas mixture brought into contact with the platinum specimen. Chamber B (0.8 liter in volume), which contained the specimen, could be isolated from its pump by shutter 2. Both shutters were composed of two ground-glass discs, each pierced off center by a 3.5-cm diameter circular hole. One disc was attached to a central shaft and could be rotated relative to the other. The shutters were opened or closed by bringing the holes in or out of coincidence. Shutters 1 and 2 were ganged on a common

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[1] Manufactured by EAI, Palo Alto, California.

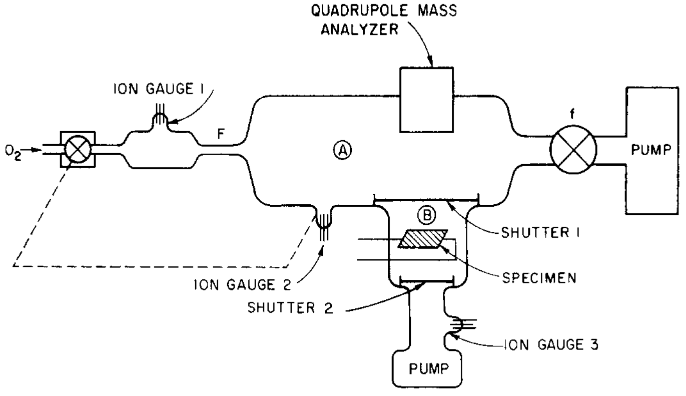

FIG. 1. Schematic diagram of experimental apparatus.

shaft and so oriented relative to one another that when shutter 1 was open, shutter 2 was closed, and vice versa. The shutters were operated under vacuum by means of a "rotary-motion-feed-through."[2] The specimen was a ribbon of 99.95% pure foil (<1 ppm Carbon) (0.005 in. thick) spotwelded at its ends to glass-shielded tungsten wire supports. The ribbon, which had a geometric surface area of 2.4 cm^2, could be heated by passage of an electric current. Oxygen was admitted into chamber A from a high-pressure reservoir (10 to 100 Torr) through a servo-operated valve[3] and a fixed conductance F (Fig. 1). The outflow of reactant from chamber A was controlled by a valve (conductance f, Fig. 1) leading to the 50 liter sec^{-1} ion-getter pump.

Pressure measurements were made with inverted Bayard-Alpert type ionization gauges[4] operated with low temperature thoria-on-iridium filaments. The mass spectrometer was calibrated with oxygen against ion gauge 2 in the range 5×10^{-9} to 1×10^{-6} Torr. The readings were found to be linearly related at pressures greater than about 5×10^{-8} Torr for emission currents of 0.1 and 1.0 mA.

The experimental ratios of the pressures indicated by gauges 1 and 2 (Fig. 1) corresponded to those calculated from mass flow considerations. These results demonstrated that the pumping characteristics of the two gauges were similar in the range employed.

The gas-handling system could be operated in two modes: (1) the constant-flow condition, by fixing the rate of flow of reactant into chamber A, and (2) the constant-pressure condition, by controlling the leak rate through the servo-operated valve with signals received either from the total pressure gauge (ion gauge 2, Fig. 1) or from the quadrupole mass spectrometer (Fig. 1). Both modes of operation were employed in our experimental measurements.

In a typical constant-pressure experiment, a steady state pressure of oxygen at 1×10^{-7} Torr was established in chamber A, while at the same time, the platinum ribbon in chamber B was cleaned by flash heating at 1100°K for 30 sec. Attempts to heat to higher flashing temperatures caused the ribbons to pull apart. Similar failures occurred when thinner ribbons were employed in hope of reducing the thermal inertia of the specimen. With the mechanically satisfactory 0.005″ ribbons, a time interval of 120 sec was required for cooling of the ribbon to room temperature in a background pressure of 5×10^{-9} Torr. Subsequently, chambers A and B were connected by closing shutter 2 and opening shutter 1, while the pressures monitored by ion gauges 1 and 2 were continuously recorded. The rate of sorption of oxygen on the platinum specimen (and the walls of chamber B) was reflected in the observed change in gas flow into the system through

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[2] Ultek Corp., Palo Alto, California.

[3] Granville-Phillips Automatic Pressure Controller.

[4] General Electric Co., Schenectady, New York.

TABLE 1

EXPERIMENTAL PROCEDURE

Operation	Inlet valve	P_2* (Torr)	P_B* (Torr)	Shutter 1	Shutter 2	Specimen temp (°K)
(1) Starting condition	Closed	$<5 \times 10^{-9}$	$<5 \times 10^{-9}$	Closed	Open	298
(2) Inlet valve control set to admit O_2 and stabilize P_2	Open	1×10^{-7}	$<5 \times 10^{-9}$	Closed	Open	298
(3) Specimen heated (cleaned)	Open	1×10^{-7}	Peaks	Closed	Open	1113
(4) Specimen cooled	Open	1×10^{-7}	$<5 \times 10^{-9}$	Closed	Open	298
(5) Sorption commenced. Rate of sorption and quantity sorbed measured by recording P_1	Open	1×10^{-7}	1×10^{-7}	Open	Closed	298
(6) Sorption completed	Open	1×10^{-7}	1×10^{-7}	Open	Closed	298
(7) System evacuated	Closed	1×10^{-8}	1×10^{-8}	Open	Closed	298
(8) Specimen heated (desorbed); total quantity of all gas desorbed evaluated from ΔP_2; identity of gas established with quadrupole analyzer	Closed	Peaks	Peaks	Open	Closed	1113
(9) Specimen cooled	Closed	1×10^{-8}	1×10^{-8}	Open	Closed	298
(10) Starting condition restored	Closed	$<5 \times 10^{-9}$	$<5 \times 10^{-9}$	Closed	Open	298

* Subscripts refer to ion gauges and chambers identified in Fig. 1.

the inlet conductance F. The sorption rate, R, is given by

$$R = F(P_1 - P'_1), \tag{1}$$

where P'_1 denotes the oxygen pressure in gauge 1 prior to exposure of the specimen, and P_1 that at time t. In addition, the total mass, M, of gas adsorbed at any time was evaluated by integration of the area of the curve of P_1 versus time

$$M = \int_0^t F(P_1 - P'_1)\,dt. \tag{2}$$

The sequence of operations for the sorption experiments under isobaric conditions is presented in Table 1.

A blank experiment was carried out to determine the extent of oxygen sorption by surfaces other than the platinum specimen, such as the walls of chamber B. After completion of step 7 (Table 1) of the sorption measurement, chamber B was isolated and evacuated to the background pressure (5×10^{-9} Torr) without flash cleaning of the platinum specimen. Subsequently, chambers A and B were connected (steps 5 and 6, Table 1). The mass of gas sorbed under these conditions was attributed to wall pumping since the platinum ribbon was covered with oxygen from the preceding experiment.

In the constant-flow experiments, the sorption process was followed by monitoring the decrease in total pressure and partial pressure of O_2 as a function of time by means of ion gauge 2 and the mass analyzer set at amu 32. The downstream conductance f was evaluated in the conventional manner by calculating the mass flux from the steady state pressure readings at ion gauges 1 and 2. The wall pumping correction was made in a manner similar to that used in the isobaric experiments.

Desorption data were obtained both in the presence and absence of oxygen under constant-flow conditions. Desorption was accomplished by flashing the sample ribbon at the same temperature and at the same rate as in the initial cleaning procedure with shutter 1 open and with conductance F fixed (steps 6–10, Table 1).

RESULTS

The kinetic results obtained in a typical experiment for the sorption of oxygen on "clean" platinum are shown in Fig. 2. These measurements refer to the constant-pressure mode of operation at two platinum temperatures and various lengths of heating time during flash cleaning. The sorption kinetics are expressed in terms of a reaction coefficient, S, which represents that fraction of the incident molecules which adsorb (or react) on the surface (*4*, *9*)

$$S = R/ZA, \tag{3}$$

where Z is the collision frequency and A the geometric area of the platinum specimen.

Since Z may be expressed in terms of the product of the impingement rate ν and the oxygen pressure (Torr-liter sec^{-1}), one obtains by substitution from Eq. (1)

$$S = [F(P_1 - P'_1)]/(A\nu P_2). \tag{4}$$

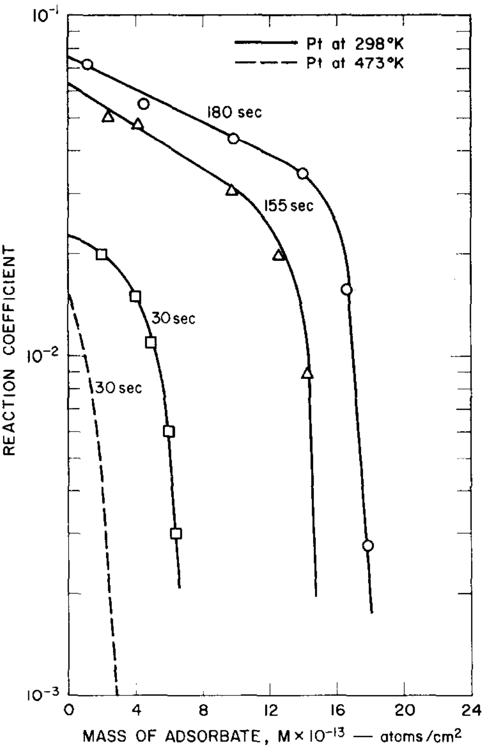

FIG. 2. Reaction coefficient of oxygen on platinum as a function of surface coverage and temperature. Time values indicate duration of heating during presorption cleaning.

In the experiments just described, ion gauge 2, which reflects the total pressure in the system, controlled the mass flux into the system at any time during the constant-pressure sorption measurement. In other experiments, the signal of the mass analyzer set at amu 32 was employed to govern the influx of oxygen into the system as demanded by the sorption process for constant-pressure operation. All other conditions including the cleaning procedure were maintained. At a steady state pressure of oxygen of 1×10^{-7} Torr, the platinum surface at 298°K sorbed 1.7×10^{-6} Torr-liter of O_2 which compares favorably with a value of 2.3×10^{-6} Torr-liter observed with the ion gauge. The difference is undoubtedly due to the different response of the two instruments to CO present as a background contaminant.

Of considerable interest are the results obtained from a series of desorption measurements (Table 2). During these studies the total gas pressures (measured by ion gauge 2) and the partial pressures of several components (measured by the mass analyzer) were monitored as the platinum ribbon temperature was rapidly raised to 1110°K after completion of the sorption process at 298°K. No oxygen was desorbed from the surface when the ribbon heating was carried out in the presence of molecular oxygen ($P_{O_2} = 10^{-7}$ Torr) at a steady state flow. As a matter of fact, the quadrupole mass analyzer showed that the partial pressure of oxygen diminished and the partial pressures of CO and CO_2 increased. In another experiment in which the ribbon was heated in a system evacuated to $<10^{-8}$ Torr, similar results were obtained, i.e., no liberation of O_2 but desorption of CO and CO_2.

The relative distribution of CO and CO_2 appeared to depend on the time interval between flash cleaning of the platinum ribbon at a base pressure of 5×10^{-9} Torr and exposure to a given gas pressure of O_2. It can be seen from the data presented in Table 2 that (1) the mass of O_2 sorbed decreases with dwell time of the platinum specimen in the background gas (at 5×10^{-9} Torr), (2) the mass of CO_2 desorbed attains a maximum value, and (3) the mass of CO desorbed increases. The origin of the CO in the system is not known precisely, but the mass analyzer indicated that at the base pressure of 5×10^{-9} Torr about 80% (by volume) of the residual gas is carbon monoxide. Based on this concentration, and on the mass of CO and CO_2 recovered from the platinum surface after various sorption time intervals (Table 2), we estimate that CO sorbs with an initial sticking efficiency approaching unity.

Discussion

Since the oxygen sorbed on the platinum specimen is not recovered as O_2, we conclude that chemical reaction occurs on the surface between the oxygen and the platinum and other sorbed species. Based on the observed residual partial pressure of CO in the vacuum system and on the identification of the desorbed gas as CO_2, we conclude that a primary chemical process occurring on the surface is the catalytic oxidation of CO to CO_2.

The disparity in the mass balance between sorbed and recovered gas (Table 2) can be accounted for by proposing a second chemical reaction at the surface to form a platinum oxide (*10*) (such as PtO or PtO_2). Platinum oxides are known to be volatile (*11*) under the conditions of temperature

TABLE 2

Effect of Background Gas on Oxygen Sorption by Platinum at 298°K
(Base pressure = 5×10^{-9} Torr, oxygen pressure = 1×10^{-7} Torr)

Dwell time after flash cleaning (sec)	Mass of O_2 sorbed (Torr-liter) $\times 10^6$	Mass desorbed[a] (Torr-liter) $\times 10^6$ amu 28	amu 32	amu 44
120	2.3	0.2	0	1.5
240	1.9	—	0	4.5
600	1.6	—	0	2.9
3,000	0.6	16	0	—
300,000	0	20	0	—

[a] Quadrupole mass analyzer calibrated using O_2 with ion gauge.

and oxygen pressure employed in our experiments. Hence, it seems likely that, upon heating, the fraction of the surface-sorbed oxygen which does not react with sorbed CO volatilizes as PtO or PtO_2. These species would be present at concentrations below the limits of detection of our apparatus and could condense on adjacent cool surfaces.

The diminution in mass of oxygen sorbed with increasing dwell time of the cleaned specimen in the evacuated system suggests that CO sorption preempts sites that would otherwise be available for oxygen. For reaction to occur, both O_2 and CO need to be chemisorbed. The data suggest that CO_2 is not chemisorbed at room temperature.

On the basis of these observations a mechanism may be postulated to describe the interaction of oxygen and CO with a platinum surface:

$$\begin{array}{lll}
\text{CO sorption} & CO(g) & \rightarrow CO(s); \\
\text{Flash desorption} & CO(s) & \rightarrow CO(g); \\
\quad\text{preceding } O_2 \text{ sorption} & & \\
O_2 \text{ sorption and} & \left\{\begin{array}{l} O_2(g) \\ O(s) + CO(s) \end{array}\right. & \begin{array}{l} \rightarrow 2O(s) \\ \rightarrow CO_2(s); \end{array} \\
\quad\text{reaction with CO} & & \\
\text{Flash desorption} & \left\{\begin{array}{l} O(s) + Pt \\ CO_2(s) \end{array}\right. & \begin{array}{l} \rightarrow PtO(g) \\ \rightarrow CO_2(g). \end{array} \\
\quad\text{following } O_2 \text{ sorption} & &
\end{array}$$

To obtain some measure of the energy of adsorption of CO on Pt, we carried out a series of experiments in which the maximum temperature attained by the platinum ribbon during flash cleaning was limited to 815°K rather than 1100°K. Under these conditions, no subsequent uptake of oxygen by the ribbon could be detected. Using the "rule of thumb" that desorption occurs at a significant rate (*12*) when the specimen temperature is greater than $20(Q_d)$, where Q_d is the heat of adsorption, one obtains a value of $41 < Q_d < 55$ kcal/mol.

The value for the reaction coefficient of oxygen on platinum at 298°K is of the same magnitude as that reported by Vanselow and Schmidt (*3*) on a platinum ribbon. However, S appears to be strongly affected by the length of time the platinum filament was heated to 1100°K during the flash desorption step (Fig. 2). Similarly, the total mass of gas sorbed is a function of the duration of flash cleaning of the platinum ribbon at a background pressure of 5×10^{-9} Torr (Table 3). As a matter of fact, there appears to be a proportionality between the mass of oxygen sorbed, M, and the reaction coefficient, S, as evidenced by the constant value obtained for the ratio M/S (Table 3). On the basis of these results, we conclude that the duration of flash cleaning at 1100°K was insufficient to completely remove the gases sorbed on the surface of our platinum ribbon. Undoubtedly the strong binding of chemisorbed oxygen by platinum, for which process an energy of adsorption of 67 kcal/mol has been reported (*1*), is reflected in this result. Furthermore, the temperature gradients in the platinum ribbon during flash heating add to the problem of completely removing the sorbed layer.

TABLE 3

EFFECT OF FLASH-CLEANING TIME ON OXYGEN SORPTION BY PLATINUM RIBBON AT 298°K[a]

Flash-cleaning time at 1100°K (sec)	Mass O_2 sorbed at saturation, M (atoms/cm^2 $\times 10^{-13}$)	Pt/O[b]	Reaction coefficient S	M/S $\times 10^{-15}$
30	6.5	18	0.023	2.8
155	15.0	8	0.063	2.4
180	18.4	6	0.075	2.5

[a] The platinum ribbon was allowed to cool for 120 sec before exposure to oxygen at $P = 5 \times 10^{-8}$ Torr.

[b] Based on 1.2×10^{15} surface atoms of Pt per square centimeter of area.

Several investigators (*3, 5*) have reported that the upper limit of sorbed oxygen coverage corresponds to a ratio Pt/O $=2$.[5] This degree of surface coverage would correspond to 6×10^{14} atoms/cm^2, assuming 1.2×10^{15} Pt atoms/cm^2 on the basis of a surface area of 8.1 Å^2/Pt atom, averaged over the various crystal orientations (*13*). The highest surface density of adsorbed

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[5] In a recent paper [Surface Sci. **12**, 405 (1968)], Morgan and Somorjai report that oxygen does not sorb at all on the (100) surface of a platinum single crystal. These authors suggest that prior contamination or a different crystal face may be prerequisite to oxygen chemisorption.

atoms attained in our experiments was 2×10^{14} atoms/cm^2. If the relationship between total mass sorbed and reaction coefficient were to be maintained up to a surface coverage of 6×10^{14} oxygen atoms/cm^2, one would expect an initial value of $S = 0.2$. Such reaction coefficients are comparable to those obtained for hydrogen on platinum (*14*). Our experimental results confirm the nonactivated chemisorption of oxygen on platinum as is found to be the case with hydrogen.

As for the competitive and preemptive adsorption of carbon monoxide, the data obtained emphasize the problems associated with oxygen sorption on platinum as a method for surface-area determinations. Obviously the product of reaction coefficient and partial pressure of gas need to be considered in an evaluation of the relative importance of the sorption kinetics of the individual gaseous components. In a conventional vacuum system operating at moderate background pressures of 10^{-6} to 10^{-5} Torr, of which a large proportion may be made up of carbon monoxide with a reaction coefficient approaching unity, one can expect up to 10^{15} sites occupied each second. Thus for a supported catalyst with platinum surface area of 1 m^2 complete coverage might be expected within approximately 100 min of exposure to the background. It must be concluded, therefore, that prolonged exposure of a platinum catalyst of moderate surface area to the background gas of a vacuum system operating at 10^{-6} Torr may lead to high carbon monoxide coverage that will falsify the surface area determination on subsequent sorption of oxygen.

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