# A Photoelectron Spectroscopic Study of the Adsorption and Reactivity of Oxygen on Platinum

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The technique of ultra high vacuum X ray photoelectron spectroscopy (XPS) has been applied to a study of the adsorption and reduction of oxygen on platinum. It was found that there are at least two adsorbed states of oxygen on platinum, desorbing below ~ 300 K and above 600 K, respectively.

The reduction of the strongly adsorbed state was studied in detail over a range of temperatures, and the transformation of adsorbed oxygen to adsorbed water has been directly observed. Water desorbs at $T \sim 160$ to 170 K, and is not dissociatively adsorbed.

The final product of reaction of adsorbed hydrogen and oxygen gas is adsorbed oxygen not adsorbed –OH.

The kinetics of reduction of oxygen ($d\theta_0/dt$) follow a simple rate law

$$d\theta_0/dt = K[H_2(gas)]\theta_0(1 - \theta_0),$$

where $\theta_0$ is the oxygen coverage normalized to one at saturation. This indicates that the kinetic species is weakly adsorbed hydrogen that requires only a single site for dissociative chemisorption. The sticking coefficient in this state is of the order 0.2.

## INTRODUCTION

There is very considerable interest in the adsorption and subsequent reduction of oxygen on platinum (*1–3*) as a means of measuring the platinum surface area of supported platinum catalysts. It is obvious that the stoichiometry of the adsorption and reduction reactions must be known so that the number of surface platinum atoms may be computed. Recently it has been reported (*4*) that hydroxyl groups are formed when oxygen reacts with a hydrogen covered surface, throwing doubt on the stoichiometries used in the earlier work. It is the purpose of the present investigation to examine the adsorption and reactivity of oxygen on platinum by X ray photoelectron spectroscopy (XPS), to elucidate the mechanism of the $H_2$–$O_2$ reaction, and to clarify the nature of the products of this reaction.

## EXPERIMENTAL SECTION

### a. *Spectrometer*

The experiments were carried out in a Vacuum Generators ESCA 3 photoelectron spectrometer. The spectrometer is a fully UHV device and pressures in the low $10^{-11}$ Torr range were readily attainable after 12-h bakes at 430 K.

The spectrometer is provided with a separate specimen preparation chamber in which the sample could be heated to >1400 K by electron bombardment, cooled to ~100 K, ion sputtered, and dosed with controlled amounts of gas whose composition could be monitored by a VGQ7B quadrupole mass spectrometer.

The sample could then be transferred into the spectrometer chamber where the pressure was routinely in the range 5 ×

$10^{-11}$–$1 \times 10^{-10}$ Torr, ensuring no further change in surface composition.

The preparation chamber was also provided with an ion gauge calibrated in the manner described earlier (5). The calibration for $O_2$, $H_2$ and CO is estimated to be good to ±5%, allowing the quadrupole mass spectrometer to be calibrated periodically to this degree of accuracy.

The temperature of the sample below ~700 K was measured to ±5 K by a chromel–alumel thermocouple embedded in the tip of the probe on which the sample was mounted. Temperatures above ~900–1000 K were measured using an optical pyrometer.

## b. Spectrometer Calibration

The spectrometer was calibrated against the N7 line of gold assuming a binding energy of 83.6 eV relative to the Fermi level of gold. On this basis the PtN7 line binding energy was 71.1 eV, in reasonable agreement with recent measurements (6).

Spectra could be excited with either Al$K\alpha$ or Mg$K\alpha$ X rays but the XPS spectra in this paper were all excited with Al$K\alpha$ X rays with the X ray source operating at 200–400 W. The overall resolution [convolution of Al$K\alpha$ line and spectrometer "window" (~0.4 eV)] was estimated experimentally to be ~1.2 eV. The peak positions were reproducible to ±0.1 eV.

Typical times for a 10 eV scan were 2–5 min.

## c. Samples and Surface Preparation

The platinum samples were taken from a 0.005 cm thick sheet of Johnson–Matthey 99.99% pure platinum and most of the results are reported for a sample of cross sectional area 0.75 cm². The samples were mounted on a ring of 0.025 cm diameter molybdenum wire that could be firmly attached to the end of the probe. In this way the sample could be heated by electron bombardment to >1400 K while

maintaining the probe below 700 K. Mechanical contact was however sufficient to ensure thermal equilibrium between the sample and probe when the probe temperature was controlled by the flow of liquid nitrogen or heated gas.

The initial XPS spectra of the platinum foil showed large carbon and oxygen peaks but no other elements within the detection limit of the technique, which is estimated to be ~1% monolayer equivalent in the surface region of the sample in which the photoelectrons lose no energy (7,8). The sample was first heated to ~1300 K for some hours and then subjected to Ar$^+$ ion bombardment (20 $\mu$A cm$^{-2}$, 2–4 kV) for 10 min. It was found that a dynamic equilibrium of removal and implantation of carbon (from CO impurity in the Ar$^+$ beam) was reached and so the sample was next oxidized in $10^{-6}$ Torr $O_2$ at 1000–1200 K for 10 min, followed by flashing at ~1400 K or reduction at 700 K in $10^{-6}$ Torr $H_2$. Both methods produced surfaces that showed only platinum photoelectron lines indicating that less than 1% of a monolayer of carbon or oxygen remained after cleaning. The sample was then annealed for periods of 10–30 min at ~1100 K at pressures < $10^{-10}$ Torr.

The surface composition could be monitored for several hours without appreciable build-up of adsorbed CO which was the main gas phase impurity. Independent measurements of the CO sticking coefficient ($S$) on the sample gave a value of $S$ of ~0.5 at low coverage. This together with the very slow build-up of adsorbed CO, confirms that the spectrometer pressure was in the low $10^{-11}$ Torr range.

## d. Coverage Calibration

The XPS signal was converted to a coverage estimate in the following way. Carbon monoxide adsorbs readily on platinum to high coverage and can be removed by flashing with no cracking (as determined by XPS). The consequent pressure

change in a system of known volume, measured with the calibrated ion gauge, can be converted to a number of CO molecules. Assuming a roughness factor of 1 and a site density of $1.12 \times 10^{15}$ cm$^{-2}$ (5), we may define $\theta$ as the number of adsorbed CO molecules divided by the (calculated) number of surface platinum atoms. It was established experimentally that the line width of the oxygen 1s signal in adsorbed CO did not change with coverage and that the resulting XPS signal (both height and area) varied linearly with the coverage and went to zero at zero coverage. The cross section for oxygen (O1s) photoelectron production was assumed to be constant, irrespective of the chemical nature of the species in which the oxygen was bonded. This assumption is certainly valid to better than a few percent in the gas phase (9) and receives confirmation from the fact that the saturation coverages of adsorbed oxygen and adsorbed carbon monoxide were found by XPS to be equal, in agreement with previous work (10).

Where observed XPS peaks were asymmetric the peak area was used to calculate the coverage of the observed species.

## RESULTS

It has been established earlier (7) that XPS allows determination of the chemical state of the adsorbed atom or molecule. Table 1 shows the result of this study in which the O1s and carbon 1s (C1s) electron binding energies (relative to the Fermi level of platinum) of adsorbed O, CO and

TABLE 1

CARBON AND OXYGEN 1s BINDING ENERGIES[a]

| Adsorbed compound | C1s (eV) | O1s (eV) |
|---|---|---|
| Elemental C | 284.8 | — |
| CO | 286.6 | 532.7 |
| $CO_2$ | 291.1 | 534.5 |
| O | — | 530.2 |

[a] Referenced to PtN7 = 71.1 eV below platinum Fermi level.

$CO_2$ were measured on the present sample. The assignment was checked with pure gases and mixed adsorption. The "elemental" carbon (probably graphite) was produced by cracking adsorbed CO with an electron beam. The adsorbed $CO_2$ spectrum was run at $\sim 110$ K and $P_{CO_2}$ $\sim 5 \times 10^{-6}$ Torr.

Any accidental coincidences in the O1s binding energy of an adsorbed species and adsorbed CO (e.g., between weakly adsorbed oxygen and adsorbed CO) are resolved by the presence or absence of a C1s signal of the correct binding energy.

### a. Adsorption of Oxygen

i. 273 K. Exposure of a clean platinum surface at 273 K to $10^{-2}$ Torr $O_2$ for 10 min ($6 \times 10^6$ L, 1L = $10^{-6}$ Torr sec) leads to the formation of an O1s line centred at 530.2 eV. This is shown in Fig. 1a for $\theta \simeq 0.4$. The coverage changes very little for exposures between $6 \times 10^6$ and $6 \times 10^7$ L. Within experimental error, the position and shape of the line did not change with coverage. The signal to background ratio for $\theta = 0.4$ was approximately 0.1.

ii. 110 K. Figure 1c shows the result of adsorbing oxygen at $T = 110$ K for an exposure of $6 \times 10^6$ L. A shoulder appears at $\sim 533$ eV and the total oxygen coverage is $\sim 0.6$. Flash desorption experiments indicate that the shoulder is associated with a weakly adsorbed state of oxygen that desorbs below 300 K and has been observed before (11). A more detailed study of these adsorbed states by XPS and UPS will appear elsewhere (12), together with measurements of the adsorption kinetics. This state also appears if an adsorbed oxygen layer produced at 273 K is further exposed to $O_2$ at 110 K, (Fig. 1b) but the coverage in this state is much reduced. That it is not adsorbed CO is proven by the absence of a C1s line.

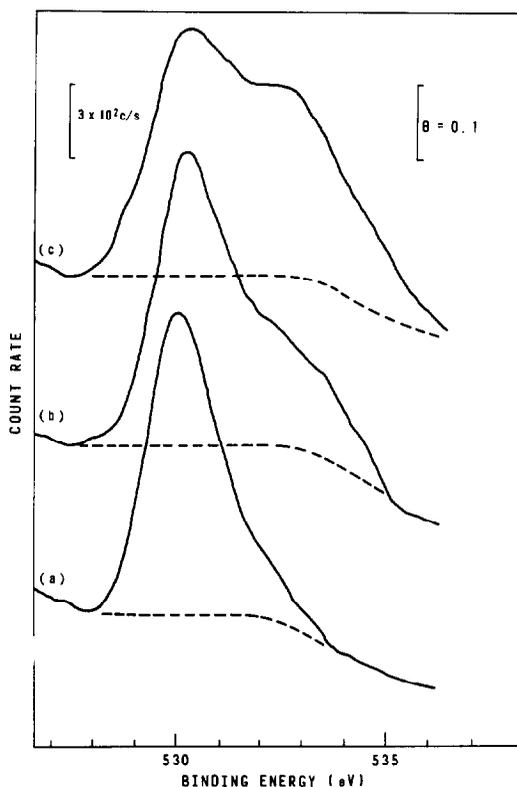It would appear that the distribution of adsorbed oxygen in the two states depends

FIG. 1. XPS Spectra of O1s region of platinum surface after: (a) $6 \times 10^6$ L $O_2$ exposure at 273 K; spectrum obtained at 273 K; Signal to background ratio $(S/B) \sim 0.1$. (b) $3 \times 10^6$ L $O_2$ exposure at 273 K, then $3 \times 10^6$ L $O_2$ exposure at 110 K; spectrum obtained at 110 K; (c) $6 \times 10^6$ L $O_2$ exposure at 110 K; spectrum obtained at 110 K.

upon the temperature of adsorption, low temperature adsorption partially blocking the strongly adsorbed state and vice versa. At 110 K the 533 eV state also seems to be fully populated before complete filling of the 530.2 eV one *(12)*.

iii. *200 K.* The adsorption of oxygen at 200 K is very similar to adsorption at 273 K and the final coverage at 200 K, after an oxygen exposure of $10^{-2}$ Torr for 10 min, is $\sim 0.4$.

iv. *Sticking coefficient measurements.* The initial sticking coefficient $(S_0)$ at both 273 K and 200 K is $\sim 0.01$ remaining constant up to $\theta \sim 0.1$, thereafter falling to $< 10^{-8}$ above $\theta \sim 0.4$.

At 110 K, $S_0$ was found to be $\approx 0.005$

for adsorption into the weakly adsorbed state and less than that into the strongly adsorbed state.

b. *Reduction of Adsorbed Oxygen,*
   *T = 273 K*

Oxygen was adsorbed up to $\theta \sim 0.4$ at 273 K in the manner described above and then exposed to $10^{-2}$ Torr $H_2$ at 273 K for 10 min. The O1s region was then scanned and no O1s peak was detectable. Flash desorption revealed only adsorbed $H_2$ at a coverage estimated to be $\theta \sim 0.3$.

c. *Reaction of Adsorbed Hydrogen with*
   *Oxygen, T = 273 K*

The surface was saturated with $H_2$ at 273 K and $10^{-6}$ Torr. The gas phase hydrogen was then evacuated leaving $3 \times 10^{14}$ H atoms/cm² on the surface as determined by flash desorption in separate experiments. This surface was then exposed to $10^{-2}$ Torr $O_2$ at 273 K for 10 min and the O1s region scanned. The spectrum was identical in all respects with that in Fig. 1a, i.e., that resulting from the adsorption of oxygen on clean platinum at 273 K.

d. *Reaction of Adsorbed Hydrogen with*
   *Oxygen, T = 200 K*

The reaction was studied at 200 K after saturation of the surface with $H_2$ at $10^{-6}$ Torr at 200 K and evacuation of the gas phase hydrogen. Under these conditions the coverage of adsorbed hydrogen was $\sim 0.4$.

Exposure of this surface to $10^{-2}$ Torr $O_2$ for 10 min produced an XPS spectrum identical to Fig. 1a. Figure 2 shows the results of a more detailed experiment. Figure 2a shows the increase of the O1s signal at 530.2 eV with time for adsorption on a clean surface at an oxygen pressure of $1 \times 10^{-7}$ Torr. The initial sticking coefficient is $\sim 0.01$. The inset shows the O1s region, indicating that the result is the same as that achieved before, i.e., the O1s line is centred at 530.2 eV.
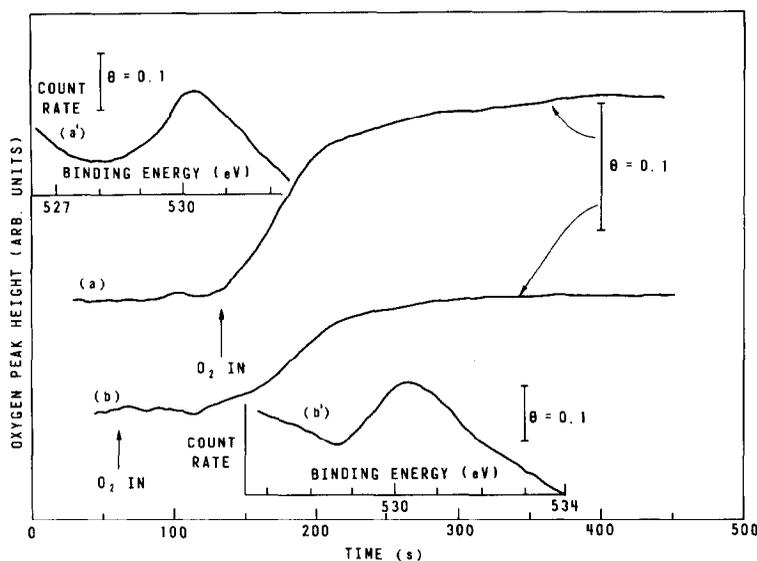
FIG. 2. Reaction of oxygen with adsorbed hydrogen. (a) kinetics of adsorption of O₂ on clean platinum, $T = 200$ K, $P_{O_2} = 1 \times 10^{-7}$ Torr. XPS signal at 530.2 eV. (a') O1s region, $T = 200$ K, $\theta = 0.15$. (b) kinetics of adsorption of oxygen on a platinum surface saturated with hydrogen at 200 K. $T = 200$ K, $P_{O_2} = 1 \times 10^{-7}$ Torr. XPS signal at 530.2 eV. (b') O1s region, $T = 200$ K, $\theta = 0.15$.

Figure 2b shows the variation of the O1s signal with time for reaction of a surface saturated with H₂ at 200 K with oxygen at a pressure of $1 \times 10^{-7}$ Torr. The inset shows the O1s region and again the O1s peak is centred at 530.2 eV. The initial sticking coefficient is lower ($<0.001$) than on the clean surface and there appears to be an induction period which is similar to one found in the reduction of adsorbed oxygen (see below). The coverage at which the sticking (or reaction) coefficient decreases again to very low values ($\ll 0.001$) is about half that for the clean surface ($\sim 0.05$–0.1 compared to $\theta > 0.15$).

### e. Controlled Reduction of Adsorbed Oxygen at Low Temperatures

Figure 3 shows the results of a more thorough study of the reduction at low temperatures. Oxygen was first adsorbed at 273 K and $5 \times 10^{-6}$ Torr for 10 min and then the system was evacuated. The sample was cooled to $< 120$ K in vacuum and the O1s spectrum shown in Fig. 3a
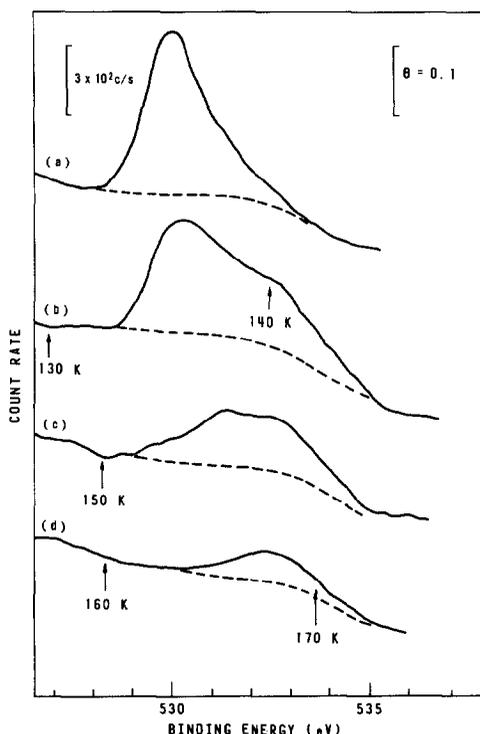


FIG. 3. Reduction of adsorbed oxygen. Temperature of oxygen adsorption = 273 K. (a) O1s region at 110 K. (b), (c), and (d) O1s scans as a function of temperature (and time). Time per scan ~ 5.0 min.

was obtained. The peak is centred at 530.2 eV and the coverage was ~0.25. Hydrogen was flowed over the sample at ~$10^{-7}$ Torr and the O1s region scanned repetitively as the temperature was raised slowly. The time (and temperature) sequence of events is shown in Figs. 3b, 3c, and 3d. It should be emphasized that the reaction was proceeding during scanning so that if there were any changes in line position during a scan it could appear that the total O1s signal (area of O1s peak(s)) had increased (viz, Fig. 3b). It is clear that as the temperature reaches ~140 K a reaction is proceeding with the build-up of a peak at ~533 eV. By 150 K (Fig. 3c) the peak at 530.2 eV has almost completely disappeared while that at ~533 eV remains. At 170 K this peak has also almost disappeared. Table 1 indicates that the O1s line in CO is centred near 533 eV but a C1s scan of the surface revealed no carbon. Independent experiments indicated that hydrogen would not displace adsorbed CO in this temperature range, nor would adsorbed CO desorb at 150 K. The purity of the hydrogen was also too high (CO background was <$10^{-10}$ Torr

during runs) to cause a CO build-up on the surface. Flash desorption experiments proved that the species was not the weakly adsorbed oxygen species detected at 110 K, and it therefore seems clear that a different oxygen containing species is formed on the surface which then desorbs at 160–170 K. The final product is undoubtedly water but whether the peak at 533 eV is due to -OH or $H_2O$ remains uncertain. The chemical transformation of adsorbed oxygen to adsorbed -OH or $H_2O$ has, however been observed directly on the surface for the first time.

### f. Adsorption of Water on Platinum

The platinum surface was cleaned in the usual way and then cooled to ~120 K. Water vapour was introduced into the spectrometer at about $10^{-6}$ Torr from a reservoir of deaerated distilled water. With the ion gauge filaments on, some $CO_2$ was observed, so the adsorption was carried out with all filaments off. The X-ray source had an aluminum window and was independently pumped so no spurious effects could arise from the source filament.
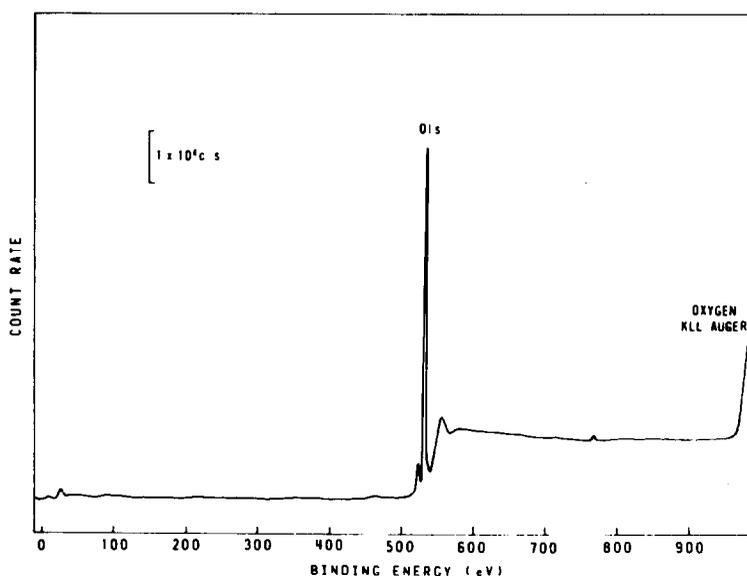
Figure 4 shows the spectrum of a layer



FIG. 4. XPS spectrum of ice film on platinum sample. $T = 120$ K.

TABLE 2
Oxygen 1s Binding Energies[a]

| Sample | O1s binding energy (eV) | Comments |
|---|---|---|
| Oxygen adsorbed on platinum (273 K) | 530.2 ± 0.2 | $\theta = 0$ to $\theta = 0.4$ |
| Oxygen adsorbed on platinum (110 K) | (a) 530.2 (b) 533 ± 0.5 | Weakly adsorbed oxygen species |
| Water adsorbed on platinum (120 K) | 535 ± 0.5 | At least 100 Å thick layer of ice |
| Reduction of adsorbed oxygen (T = 150 K) | 533 ± 0.5 | Coverage of species ≈ 0.2 |
| PtO₂ | 532 ± 1.5 | |
| K₂Pt(OH)₆ | 533 ± 1.5 | |

[a] Referenced to AuN7 = 83.6 eV, PtN7 = 71.1 eV.

of ice. The absence of platinum photoelectron lines indicates that it is probably > 100 Å thick. The O1s line is centred at ~ 535 eV.

The sample was then warmed to ~ 160 K and the desorption (or sublimation) of the ice was detected by the mass spectrometer. After desorption was complete, the surface was rescanned. No oxygen photoelectron lines were detectable and no adsorbed hydrogen was detected by flash desorption. Water does not appear to adsorb dissociatively on platinum. Efforts to-date have failed to obtain a surface with approximately one monolayer of adsorbed water.

### g. XPS Studies on PtO₂ and K₂Pt(OH)₆

PtO₂ and K₂Pt(OH)₆ were studied in an attempt to measure O1s binding energies in known compounds. Both materials were obtained from Johnson–Matthey. Problems were experienced with sample charging and decomposition and thus the binding energies are given only to the nearest 1.5 eV. The PtO₂ was run as a powder on a thin film of silver dag and K₂Pt(OH)₆ was run as a film after evaporating a drop of solution on the gold plated probe tip. For convenience all the O1s binding energies of relevance in this work are collected in Table 2.

### h. Kinetics of the Reduction of Oxygen on Platinum

Figure 5a shows the time variation of the O1s signal (530.2 eV), when an adsorbed layer (10 min $10^{-2}$ Torr O₂; 273 K; $\theta \sim 0.4$) is exposed to a flow of hydrogen at $1.3 \times 10^{-7}$ Torr and 200 K. The arrow indicates the instant at which the hydrogen flow was started. There is evidently an induction period. Figure 5b also shows the same reaction under identical conditions except that $T = 273$ K. The induction period is shorter and the rate faster.

Figure 5c shows the effect of stopping and starting the hydrogen flow on the rate of reduction of adsorbed oxygen (initially $\theta = 0.4$) at 200 K. Hydrogen was introduced and the reaction was allowed to proceed slowly until about half the adsorbed oxygen had been reduced, at which point the hydrogen pressure was reduced to $< 10^{-9}$ Torr. It is evident that the reaction stopped almost immediately. On reintroduction of hydrogen at the same pressure as initially, the reaction started up again with a short induction period.

Figure 6a shows the reduction at 200 K. $P_{H_2} = 1.7 \times 10^{-7}$ Torr of oxygen adsorbed at 273 K for an initial oxygen coverage of 0.4. The S-shaped curve and induction period are again very evident. Figure 6b shows the reduction of oxygen adsorbed at
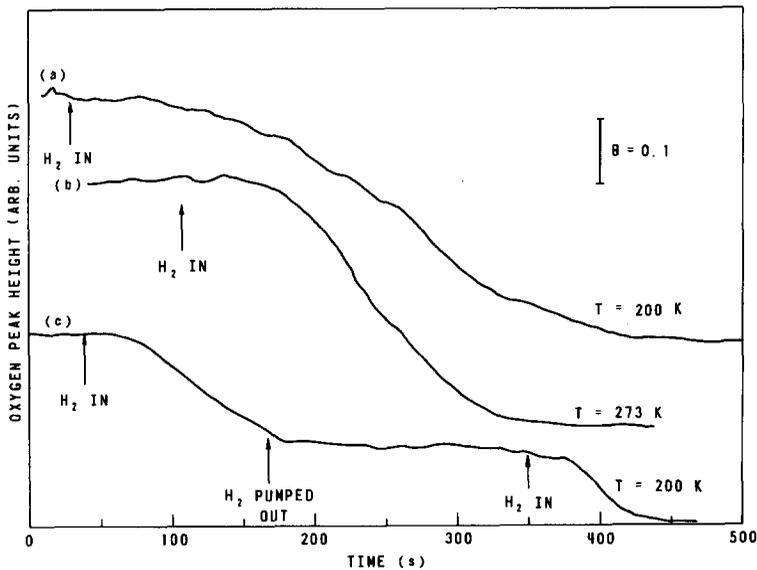
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FIG. 5. Reduction of adsorbed oxygen. XPS signal at 530.2 eV. Oxygen adsorbed at 273 K. (a) $T = 200$ K, $P_{H_2} = 1.3 \times 10^{-7}$ Torr, initial oxygen coverage $\simeq 0.4$. (b) $T = 273$ K, $P_{H_2} = 1.2 \times 10^{-7}$ Torr, initial oxygen coverage $\simeq 0.4$. (c) $T = 200$ K, $P_{H_2} = 1.3 \times 10^{-7}$ Torr, initial oxygen coverage $\simeq 0.3$. $H_2$ flow changed at arrows.

273 K at $1.8 \times 10^{-7}$ Torr $H_2$ and 200 K at an initial oxygen coverage of 0.25. The induction period is much shorter than in Fig. 6a but the slope of the curves at equivalent oxygen coverages is very similar. In the discussion it will become clear that the slope of the O1s signal versus time curve at half reduction ($\theta \simeq 0.2$) can be used as a measure of the kinetic rate.

The rate of change of oxygen coverage ($\theta$) with time ($d\theta/dt$) at an oxygen coverage of 0.2 can be calculated from the experimental curves and hence the probability of reaction per collision ($R$) may be es-
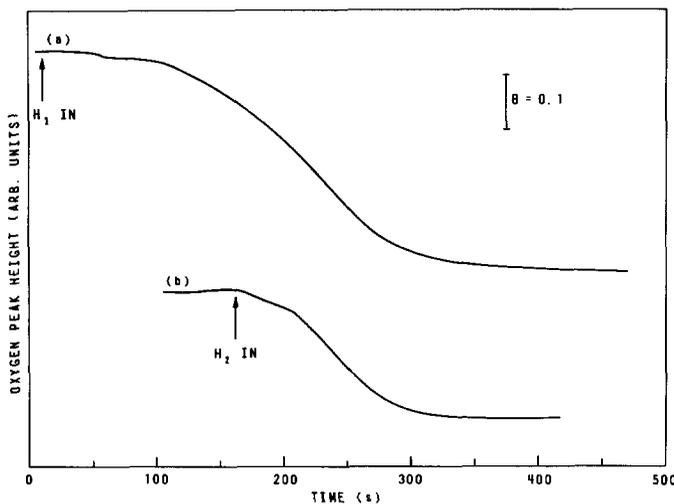


FIG. 6. Reduction of adsorbed oxygen. XPS signal at 530.2 eV. Oxygen adsorbed at 273 K. (a) $T = 200$ K, $P_{H_2} = 1.7 \times 10^{-7}$ Torr, initial oxygen coverage $=0.4$. (b) $T = 200$ K, $P_{H_2} = 1.8 \times 10^{-7}$ Torr, initial oxygen coverage $=0.25$.

TABLE 3

REDUCTION OF OXYGEN ADSORBED ON PLATINUM

| $T$ (K) | Initial oxygen coverage ($\theta$) | Pressure of $H_2$ (torr) | $(d\theta/dt) \times 10^3$ | $(d\theta/dt)_{H_2}$ | $R \times 10^2$ [a] |
|---|---|---|---|---|---|
| 273 | 0.4 | $1.6 \times 10^{-7}$ | 4.0 | 0.21 | 1.9 |
| 273 | 0.4 | $6.2 \times 10^{-8}$ | 1.4 | 0.08 | 1.8 |
| 273 | 0.4 | $1.7 \times 10^{-7}$ | 4.5 | 0.22 | 2.0 |
| 273 | 0.4 | $1.3 \times 10^{-7}$ | 3.0 | 0.17 | 1.8 |
| 273 | 0.3 | $1.6 \times 10^{-7}$ | 4.1 | 0.21 | 2.0 |
| 200 | 0.4 | $1.4 \times 10^{-7}$ | 1.9 | 0.18 | 1.1 |
| 200 | 0.4 | $1.7 \times 10^{-7}$ | 2.3 | 0.22 | 1.0 |
| 200 | 0.4 | $6.9 \times 10^{-7}$ | 10.0 | 0.89 | 1.1 |
| 200 | $0.2_5$ | $1.8 \times 10^{-7}$ | 2.3 | 0.23 | 1.0 |

[a] $R$ calculated at $\theta = 0.2$.

timated. The rate of collision of hydrogen with the surface may be calculated in units of monolayers per second through Eq. (1):

$$\left(\frac{d\theta}{dt}\right)_{H_2} = \frac{p(2\pi mkT)^{-1.2}}{1.12 \times 10^{15}} \quad \text{monolayers s}^{-1}.$$

$$(1)$$

This assumes that for $1.12 \times 10^{15}$ collisions cm$^{-2}$ s$^{-1}$

$$(d\theta/dt)_{H_2} = 1 \text{ monolayer s}^{-1}.$$

The reaction probability per collision is then just

$$R = \left(\frac{d\theta}{dt}\right) \Big/ \left(\frac{d\theta}{dt}\right)_{H_2}. \quad (2)$$

The data are collected in Table 3 and the rates calculated at an oxygen coverage of 0.2. The reaction probability $R$, is independent of pressure within the experimental error and the reaction rate increases by a factor of $\sim 1.8$ between 200 and 273 K.

## DISCUSSION

The purpose of this paper is to investigate the adsorption and reactivity of oxygen on platinum. The equally interesting problem of understanding the absolute magnitude of the electron binding energies is reserved for another publication (12).

### a. Products of Reaction

It is clear from Table 2 that the formation of adsorbed -OH groups or adsorbed $H_2O$ should be characterized by a photoelectron line in the range 533 to 535 eV.

The O1s line position in the reaction product is closer to that of -OH in the $K_2Pt(OH)_6$ complex than in ice, but it must be remembered that the water spectrum was obtained from a layer of ice, not adsorbed $H_2O$ and that in both cases the experimental uncertainty is large. No firm distinction between adsorbed -OH or adsorbed $H_2O$ is possible with the present experimental data. The temperature range in which the product of reduction desorbs is however consistent with it being $H_2O$.
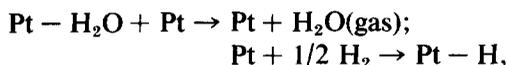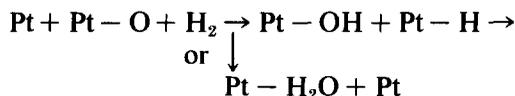
The result that the interaction of oxygen with preadsorbed hydrogen at 200 or 273 K produces an O1s peak at 530.2 eV that is identical with that produced by oxygen adsorption on a clean surface indicates that -OH groups, if formed, are not retained on the surface at 200 K, at least within the sensitivity of the method ($< 10\%$ monolayer). The sensitivity is smaller for such a mixed adsorption since the -OH (or $H_2O$) O1s signal would lie in the high binding energy wing of the adsorbed oxygen signal.

This is at variance with the conclusions of Morrow and Ramamurthy (4) for sup-

ported platinum catalysts on which they detected –OH groups at 298 K which were stable to high temperature (removed at 673 K) and constituted approximately one third of the adsorbed oxygen species formed by reaction of oxygen with adsorbed hydrogen.

The observation of –OH groups on supported platinum must therefore, be somehow connected with the support. Perhaps –OH groups are formed on Pt as unstable intermediates in the reaction and some migrate to the support where they are stably chemisorbed. If this is so it still has important implications for the stoichiometry of the reaction since one adsorbed oxygen atom has been effectively removed by *one* hydrogen atom. In summary it is possible that –OH groups could be formed on unsupported platinum, but they do not appear to be stable at temperatures $\gtrsim 150$ K. Based on the present data however, there is no reason to postulate the existence of adsorbed –OH groups and it is more probable that the species detected in this study is adsorbed $H_2O$.

It is clear from Fig. 3 that the reduction of adsorbed oxygen at low temperature can proceed even while the products of reaction are still present on the surface. The reaction and desorption are therefore separate processes and the whole process may presumably be broken into steps. One possible sequence is shown schematically below:

$$Pt + Pt - O + H_2 \rightarrow Pt - OH + Pt - H \rightarrow$$
$$\text{or} \downarrow$$
$$Pt - H_2O + Pt$$

$$Pt - H_2O + Pt \rightarrow Pt + H_2O(gas);$$
$$Pt + 1/2\ H_2 \rightarrow Pt - H,$$

where $Pt - O$, etc., represents adsorbed O, etc. Further evidence for this type of process is presented below.

As mentioned above, water does not appear to dissociatively adsorb on platinum.

It is possible however, that an equilibrium such as
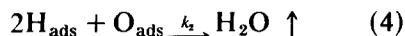
$$Pt + H_2O \rightleftharpoons Pt - H + Pt - OH$$
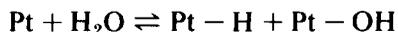
could exist in which the equilibrium lies almost completely to the left. Certainly the exchange of hydrogen between water and hydrogen gas is very rapid in the presence of a platinum catalyst (*13*) so water is presumably not simply physisorbed. The desorption temperatures of water and the products of reduction are both consistent with a heat of adsorption of $\sim 10$ kcal mole$^{-1}$ which is in approximate agreement with previous measurements (*14*). This is clearly larger than that expected from dispersion forces alone.

b. *Kinetics of Reduction*

There are several key experimental observations to explain. These are: 1) the S-shaped kinetic curves; 2) the first order pressure dependence (Table 3); 3) the decrease of the length of the induction period for lower initial oxygen coverages; 4) the fact that reaction stops almost immediately after removal of gas phase hydrogen.

All of these observations can be accounted for quite simply on the basis of a model which may be written in the following schematic form:

$$H_2(gas) + [Pt]_{site} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2H_{ads}, \quad (3)$$

$$2H_{ads} + O_{ads} \xrightarrow{k_2} H_2O \uparrow \quad (4)$$

where the vertical arrow indicates desorption of $H_2O$. If we now normalize the experimental oxygen coverages ($\theta$) to 1 at $\theta = 0.4$, (i.e., the layer appears saturated at $\theta = 0.4$) and define $\theta_0 = 1$ at $\theta = 0.4$ then

$$\frac{d\theta_H}{dt} = k_1[H_2(gas)](1 - \theta_0 - \theta_H)$$
$$- k_{-1}(\theta_H)^2 - k_2(\theta_H)^2(\theta_0), \quad (5)$$

where $\theta_H$ is the hydrogen coverage, $1 \geq \theta_0 \geq 0$ and the number of bare platinum sites $[Pt]_{site} = (1 - \theta_0 - \theta_H)$. The

rate of disappearance of adsorbed oxygen is given by

$$\frac{d\theta_O}{dt} = k_2(\theta_H)^2(\theta_O). \qquad (6)$$

We could of course write down similar equations for $\theta$ in which $0.4 \geqslant \theta \geqslant 0$ and $[Pt]_{site} = (0.4 - \theta - \theta_H)$. If we assume a very small steady state coverage for the adsorbed hydrogen, then $d\theta_H/dt = 0$ and $\theta_H \ll \theta_O$. Rearranging,

$$\frac{d\theta_O}{dt} = \frac{k_1 k_2 [H_2(gas)]\theta_O(1 - \theta_O)}{k_{-1} + k_2\theta_O}. \qquad (7)$$

If we also assume that adsorption equilibrium is established rapidly compared to reaction, then $k_{-1} \gg k_2\theta_O$, and Eq. (7) becomes

$$d\theta_O/dt = K[H_2(gas)]\theta_O(1 - \theta_O), \qquad (8)$$

where

$$K = k_1 k_2/k_{-1}. \qquad (9)$$

The first order pressure dependence is thus correctly predicted since $[H_2(gas)]\alpha P$. The integral of this equation has the form

$$\theta_O \propto 1/(e^{At} + 1). \qquad (10)$$

Figure 7 shows a fit of the data of Fig. 5a to an equation of this form. The data were normalized at one point and can be seen to fit the form of the equation very well. If a two site adsorption mechanism were used, i.e., the rate of hydrogen adsorption varied as $(1 - \theta_O)^2$, the final result would be a $\theta_O(1 - \theta_O)^2$ dependence which does not fit the data.

For rate equations written as functions of $\theta$ (*experimental* values of oxygen coverage) the maximum value of $\theta(0.4 - \theta)$ where $0.4 \geqslant \theta \geqslant 0$ occurs at $\theta = 0.2$ as was found experimentally, i.e., at half reduction. For the normalized equation in $\theta_O$ the maximum rate of course occurs at $\theta_O = 0.5$.

The induction period is also satisfactorily explained. The decrease in the induction period for lower initial oxygen coverages is also explicable in terms of this model since the term $(1 - \theta_O)$, [or $(0.4 - \theta)$ in experimental coverage units] is larger at the start of the reduction, al-


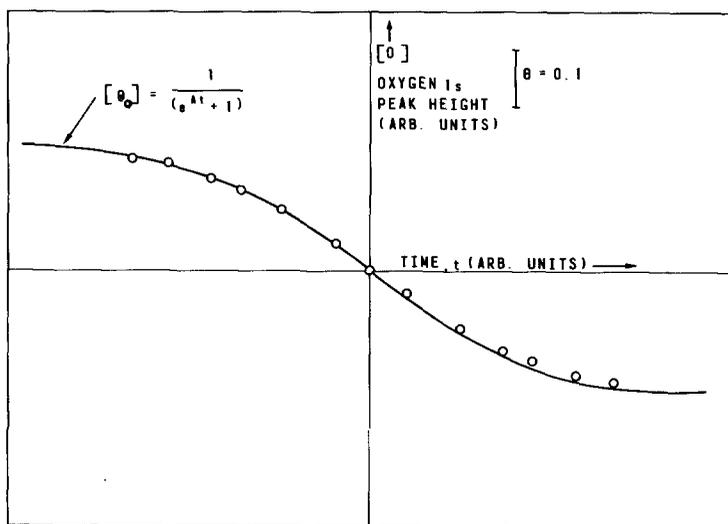
FIG. 7. Fit of data of Fig. 3b (reduction of adsorbed oxygen) to $\theta_0 = 1/(e^{At} + 1)$, where $\theta_0 = 1$ at $\theta = 0.4$ and $1 > \theta_0 > 0$.

lowing the more rapid adsorption of hydrogen on the bare platinum sites until dynamic equilibrium is again established. At this point the rates of reduction at equivalent oxygen coverages should be equal as indeed they are found to be (Figs. 6a and 6b, Table 3).

The remaining experimental observation that the reaction at 200 K stops very soon after the removal of the gas phase indicates that the kinetic species of hydrogen must be weakly adsorbed, with a heat of adsorption of $\leqslant 15$ kcal mole$^{-1}$ in agreement with the necessary assumption that $\theta_H$ is small. It was not established whether any hydrogen remained on the surface after the half reduction point was reached, but certainly hydrogen adsorbed irreversibly to a coverage of $\sim 0.4$ on the clean sample at 200 K. If the presence of 0.2 monolayers of oxygen does not affect the heat of adsorption of hydrogen on the bare platinum, then the termination of the reaction must indicate that the strongly bound hydrogen is not involved in the reduction but that a weakly adsorbed state is the kinetic species. Such a state has been suggested (5) to explain the kinetics of adsorption and equilibration of hydrogen isotopes on platinum. An alternative explanation would be that the heat of adsorption of the strongly bound hydrogen is reduced by the presence of adsorbed oxygen and thus is reversibly adsorbed at 200 K. The former explanation is supported by data on the reaction of adsorbed hydrogen with gas phase oxygen (see below).

Table 3 shows that the reaction probability per collision is $\sim 0.02$ at 273 K. The sticking coefficient of hydrogen must be at least that large. The assumption that adsorption equilibrium is established rapidly compared to reaction implies that the sticking coefficient of the kinetic species must be of the order of ten times the reaction probability, i.e., $\sim 0.2$. The present results would then suggest that this state requires only a single site for adsorption.

### c. Kinetics of Oxidation of Adsorbed Hydrogen

Figure 2a and b shows that the presence of adsorbed hydrogen reduces the rate of adsorption (reaction) of oxygen. This is in agreement with Langmuir (15) who found that hydrogen could poison the hydrogen–oxygen reaction, apparently by blocking oxygen adsorption. The reaction shows an induction period followed by a period in which the reaction probability per collision (R) increases to 0.005, a factor of two lower than that found for the reduction of adsorbed oxygen at half reduction. The induction period presumably indicates that reaction between oxygen and hydrogen is occurring on the surface. In a similar way to the model for the reduction process, the rate increases as $\theta$ $(0.4 - \theta)$ (experimental coverage units).

The reaction appears to stop, or slow down by a factor of at least 10 at a coverage of 0.05–0.1 on our scale. Since $R$ is as high as 0.005 at an oxygen coverage of $\approx 0.05$, (compared to an oxygen sticking coefficient of 0.01 up to $\theta = 0.1$) the difference in the kinetics of oxygen adsorption on clean and hydrogen saturated surfaces above this coverage must imply that hydrogen is still present on the surface and that the reaction between it and the adsorbed oxygen is very slow. This lends further support to the hypothesis that a weakly held hydrogen species is the important one in the reduction reaction. It is difficult then to explain why only a fraction of the hydrogen adsorbed at 200 K can be readily oxidized, unless weakly and strongly adsorbed hydrogen coexist at a hydrogen coverage of $\sim 0.4$ at 200 K.

### d. Heat of Adsorption of Water

Recent calorimetric measurements (16) of the oxygen titration reaction have yielded a heat of adsorption of water on Pt–$\gamma$Al$_2$O$_3$ of 18 kcal mole$^{-1}$. This value is too large to permit desorption at $\sim 160$ K

and it seems probable that it represents, at least in part, the heat of adsorption of water on the support. The heat of adsorption of water at low coverage on an alumina surface, outgassed at $\sim 430$ K has been measured (17) and found to be $\sim 20$ kcal mole$^{-1}$. The interpretation of calorimetric data for the heat of adsorption of water on supported platinum should thus be viewed with caution.

## CONCLUSIONS

The reduction of adsorbed oxygen and the subsequent desorption of water have been directly observed as has the reaction of adsorbed hydrogen with gas phase oxygen. It was not possible to unequivocally identify the product of reduction that was detected by XPS but because no evidence was found for the production of stable –OH groups on platinum, it is more probable that the species detected was adsorbed water.

The kinetics of oxygen reduction fit a simple rate law and are explicable in terms of a mechanism which is not inconsistent with the known behaviour of oxygen and hydrogen on platinum and involves a weakly bound state of adsorbed hydrogen.

## ACKNOWLEDGMENTS

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