

Oxidation of Hydrogen on Polycrystalline Platinum Studied by Molecular Beam Reactive Scattering

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Received June 3, 1975

A reactive molecular beam is allowed to collide with a polycrystalline platinum ribbon immersed in a controlled gaseous atmosphere. This experimental technique permits the measurement of the reactive sticking probability, and thereby we have studied adsorption, molecular desorption, and atomization of hydrogen on platinum at high temperatures (1350–1700 °K) and low pressures ($<10^{-7}$ Torr). Then, the oxidation of hydrogen was studied from 300 to 1700 °K and low pressure ($<10^{-6}$ Torr), and it was found that reaction takes place between oxygen and hydrogen chemisorbed species (reaction of the type Langmuir–Hinshelwood). The activation energy for this process was determined to be 20 kcal mol⁻¹. The kinetic model proposed joins these results with those obtained at lower temperatures (<300 °K) and low pressures (10^{-7} Torr), and with those obtained at high temperatures (>300 °K) and high pressures of order 1 Torr).

INTRODUCTION

In general, the reaction rate of a surface catalyzed reaction is dependent on the surface coverages, θ_i , by the reactants, products, and/or reaction intermediates. Two important divisions, however, can be made with respect to the nature of this dependence: The reaction may take place via interaction between adsorbed species on the surface (Langmuir–Hinshelwood kinetics), or via kinetics describable as if there were interaction between an adsorbed species and an impinging gas phase molecule (Eley–Rideal kinetics). Indeed, the pressure dependence of the reaction rate, expressed as a turnover number \bar{N} (the average number of completed chemical transformations per

surface atom per second), may be quite different for these two cases. That is, for the former case, \bar{N} is dependent on the various θ_i , while for the latter, \bar{N} also depends directly on the collision density, g , of gas phase molecules with the surface; and, for a pressure change P_i , in component i from 1 to 10^{-6} Torr, g_i correspondingly changes by 6 orders of magnitude while θ_i may change by only one power of 10.

Typically, laboratory studies of kinetic processes at atmospheric pressure are conducted under conditions for which \bar{N} is of order 10^{-3} – 10^0 s⁻¹, since larger values may be accompanied by diffusional limitations, and small values may be difficult to measure. Of those Langmuir–Hinshelwood controlled reactions for which the θ_i are not greatly sensitive to the appropriate P_i , conditions corresponding to a value of $\bar{N} \sim 1$ s⁻¹ at near atmospheric pressure would then also correspond to a reactive

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sticking probability, b (the probability of reaction per unit collision with the surface), of order unity at 10^{-6} Torr ($\bar{N} \cong gb\sigma$, where σ is the effective area per surface atom). Thus, for such reactions a wide pressure range may be studied, and results obtained at low pressure (e.g., 10^{-6} Torr by molecular beam methods) and high pressure (ca. 10^2 Torr) may provide complementary information. Indeed, a successful comparison between results obtained in these two pressure regimes has been made for the carbon monoxide oxidation over platinum (1); however, in this case the presence of Eley-Rideal kinetics must also be considered. In this respect, the oxidation of hydrogen will be investigated in this paper at low pressure, and discussed with reference to studies at higher pressures.

The study of the reaction of oxygen with platinum has been the subject of a number of investigations, the results of which appear to be contradictory with respect to (i) the maximum quantity of oxygen adsorbed, (ii) the value of the sticking probability for chemisorption, and (iii) the binding energy of different chemisorbed states. These results have been summarized and discussed by Pentenero *et al.* (2). In general, one may draw the following conclusions. For monocrystals of platinum, the maximum quantity of oxygen adsorbed and the sticking probability for chemisorption are very small (3, 4), although recent results of Joebstl (5) are not in accord with these earlier findings and indicate a maximum oxygen coverage of monolayer order on the (111) plane; if the surface is not a low index plane, these two quantities increase to those values characteristic for polycrystalline samples (6, 7). In addition, all investigators are in agreement that the kinetic processes occurring at high temperatures (300–1700 °K) and low pressures are (i) dissociative oxygen adsorption, (ii) molecular oxygen desorption, and (iii) oxygen atomization for low coverage and high temperature (2, 7).

For hydrogen chemisorption on platinum, the following statements are suggested with reference to literature results. (i) Different adsorption states exist, (ii) the most strongly bound state is atomic hydrogen, with a heat of adsorption, E_{H_2} , of approximately 18 kcal mol⁻¹, and (iii) the zero coverage sticking coefficient, $b_{H_2}(0)$, is sensitive to the structure of the platinum surface, with $b_{H_2}(0)$ generally increasing with surface roughness on an atomic scale. The multiple adsorption states for hydrogen on platinum have been interpreted in terms of atomic hydrogen above and below the surface, respectively (8), and alternatively by the presence of both atomically and molecularly (or pseudo-atomically) adsorbed species (9). Experimentally, different adsorption states have been found using field emission (10), electrical resistivity (8), work function (8), thermal desorption (11), and H₂-D₂ exchange (12, 13) techniques. For the most strongly bound state (electronegative), Lewis and Gomer (10) estimated a heat of adsorption of ca. 16 kcal mol⁻¹ and the value E_{H_2} measured by Norton and Richards (14) was 24.7 kcal mol⁻¹. The zero coverage heat of adsorption on platinum black was found to be 17.5 kcal mol⁻¹ and on platinum foil a value of 16.3 kcal mol⁻¹ was measured by Tomezsko and Furukawa (15) and Procop and Völter (16), respectively; this compares favorably with the value of 17.5 kcal mol⁻¹ measured by Nisiyama and Wise (17) for a polycrystalline wire and with 17.5–20 kcal mol⁻¹ determined by Lu and Rye (11) for the (111) plane (for which a single adsorption state exists). With respect to the sticking coefficient of hydrogen on platinum, Somorjai *et al.* (18) found a value less than 10^{-2} at 300 °K for the (111) plane, and Lu and Rye (11) found a value of order 10^{-2} on this plane. In both investigations, increasing surface roughness (stepped-surfaces in the former case and different low index planes in the latter) had the effect of increasing $b_{H_2}(0)$, to a value of ca. 0.3 for the

(110) plane (11). For a platinum filament, Norton and Richards (12, 14) and Breakspere *et al.* (13) measured a value for $b_{\text{H}_2}(0)$ of order 0.1 at 300 °K, while on a platinum foil Procop and Völter (15) found $b_{\text{H}_2}(0)$ to be ca. 5×10^{-3} . However, unlike the case of oxygen chemisorption on platinum, with a variation in the sticking probability between monocrystalline and polycrystalline samples of order 10^4 , the variation of $b_{\text{H}_2}(0)$ with surface structure appears to be of order 10^2 for hydrogen adsorption.

In view of the wide disparity in the results for oxygen and hydrogen chemisorption on platinum, it seems necessary to begin the study of the hydrogen oxidation with investigations of the individual reactions of hydrogen and oxygen with platinum. In this respect, molecular beam reactive scattering will be used.

EXPERIMENTAL

Apparatus

The apparatus of this study has been described in detail elsewhere (19, 20), the essential features of which are shown in Fig. 1. A polycrystalline platinum ribbon, heated by the Joule effect, was placed in the reaction chamber, the residual pressure in which was 10^{-9} Torr (H_2 : 2×10^{-9} Torr, H_2O : 7×10^{-10} Torr, CO and N_2 : 6×10^{-10} Torr, CO_2 : 10^{-10} Torr, C_xH_y : 10^{-10} Torr). By means of an introduction valve, an isotropic pressure of gas with known composition could also be maintained in the chamber. To assure that the sample was always in its proper position in the molecular beam the ribbon was kept under a mechanically applied tensile stress. A supersonic molecular beam strikes the sample at an incident angle of 45° , and the particles emitted or reflected by the ribbon are analyzed by a mass spectrometer positioned with its axis coincident with the specular direction. Three metallic interrupters permit the interception of the incident or

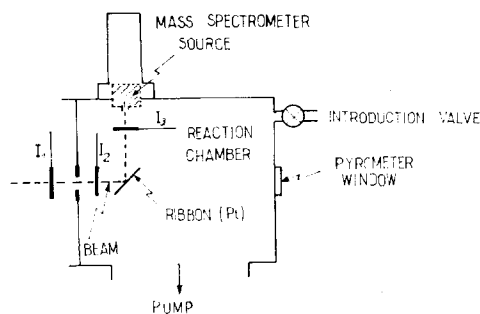


FIG. 1. Experimental apparatus.

reflected molecular beam. During the measurement of the reactive sticking probability, the reflected beam is intercepted by I_3 , which eliminates the possible influence of the reflection law for the beam and the accommodation coefficient. In this mode of operation, the atomic species emitted by the ribbon are not allowed to reach the mass spectrometer, but are instead trapped on the walls of the chamber. The signal measured with the incident beam intercepted by I_1 serves to define the "zero point"; the increase in the signal measured with I_1 open then gives the isotropic pressure, P , in the chamber resulting from the incident molecular beam when the latter is in turn intercepted by I_2 . When I_2 is then opened, the molecular beam is allowed to react with the sample. Indeed, the effective pressure (P_f) seen by the sample increases by a factor of 10^3 when I_2 is opened, for the experimental conditions of this study. As a result of reaction, the isotropic pressure decreases to $(1 - \beta)P$ in the chamber. These two signals then serve to define β (the maximum uncertainty in the value of β so measured is 5%).

Procedures

The sample of this study was a 40 mm long, 3 mm wide, and $30 \mu\text{m}$ thick platinum polycrystalline ribbon manufactured by Leico, and was of 99.95% purity; the gases used were prepared by Air Liquide of 99.995% purity. Temperature was mea-

sured using an infrared pyrometer (J. Izart, model 860), the latter calibrated with an optical pyrometer of known temperature characteristics (21). Prior to the experiments that will be described presently, the ribbon was heated in vacuum to 1700 °K in another apparatus with residual pressure of 10^{-7} Torr, at all times increasing the temperature sufficiently slowly to keep the pressure below 10^{-6} Torr; following this, the ribbon was kept at 1700 °K for $2\frac{1}{2}$ hr. The ribbon was then mounted in the previously described apparatus, and heated slowly in an isotropic pressure of oxygen (10^{-7} – 10^{-6} Torr) to 1700 °K, at which temperature continued heating took place for approximately 2–3 hr. That this procedure produces a clean platinum surface has been shown by Auger electron spectroscopy (22), and such a surface is characterized by a 1700 °K oxygen sticking probability, (β_{O_2}), of 0.12 (23); thus, β_{O_2} was measured before each experiment, and when departures from 0.12 were found the sample was further treated under oxygen at 1700 °K until these deviations disappeared.

When an oxygen (or hydrogen) molecular beam is intercepted by I_2 , the surface coverage by oxygen (or hydrogen) is determined by the isotropic oxygen (or hydrogen) pressure, typically 10^{-9} Torr; the

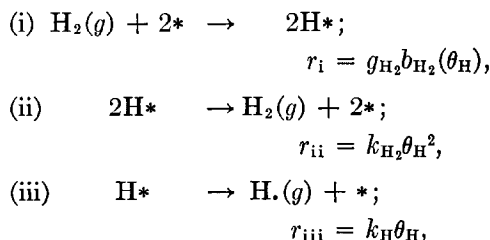
opening of I_2 , which generates a step function in the effective oxygen (hydrogen) pressure at the surface, then allows one to follow the transient behavior of β_{O_2} (β_{H_2}) with an initial value, $\beta_{O_2}^*$ ($\beta_{H_2}^*$) (see Fig. 2). Using this procedure, β_{O_2} was measured by Pacia *et al.* (24) and the results of β_{H_2} measurement will be reported in this paper.

For the oxidation of hydrogen, two types of experiments were performed. The first was the measurement of β_{H_2} with the ribbon under a known isotropic oxygen pressure; the second was the measurement of both β_{O_2} and β_{H_2} using a mixed molecular beam of oxygen and hydrogen.

RESULTS

Hydrogen Reaction on Platinum

As for oxygen, the following model can be proposed for the reaction of hydrogen on platinum.



where the first step is the dissociative chemisorption of hydrogen, the second is the molecular desorption of hydrogen from the surface, and the third step is the atomic desorption (or atomization); g_{H_2} is the collision density proportional to the hydrogen pressure, $b_{H_2}(\theta_H)$ is the chemisorption sticking probability dependent on the hydrogen coverage θ_H , and k_H and k_{H_2} are the rate constants for atomic and molecular hydrogen desorption, respectively. At stationary state, $2r_i = 2r_{ii} + r_{iii}$; and β_{H_2} , which measures the consummation of hydrogen per unit collision, is given by $(r_i - r_{ii})/g_{H_2}$. These two relations give

$$\beta_{H_2} = b_{H_2}(\theta_H) - \frac{k_{H_2} \theta_H^2}{g_{H_2}} = \frac{k_H \theta_H}{2g_{H_2}}. \quad (1)$$

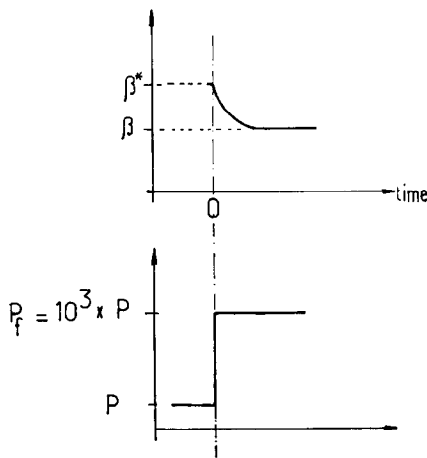


FIG. 2. Response of β_{H_2} to step-function change in hydrogen pressure (I_2 opened at $t = 0$).

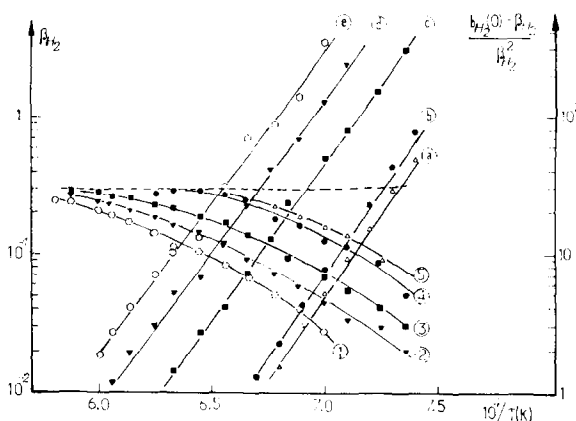


FIG. 3. Variation of β_{H_2} with $1/T$ (curves 1-5); variation of $(b_{\text{H}_2}(0) - \beta_{\text{H}_2})/\beta_{\text{H}_2}^2$ with $1/T$ (straight lines (a)-(e)). $P_f(\text{H}_2)/\text{Torr}$: \square , 9.3×10^{-7} ; \blacktriangledown , 4.5×10^{-7} ; \blacksquare , 1.6×10^{-7} ; \bullet , 2.4×10^{-8} ; \triangle , 1.8×10^{-8} .

For temperatures greater than 1300 °K, the oxygen coverage, θ_{O} , is less than ca. 10^{-3} for oxygen pressures of order 10^{-6} Torr (25); in addition, hydrogen desorbs at lower temperatures from platinum than does oxygen (11, 25). Thus, at this temperature, θ_{H} is also expected to be small ($<10^{-3}$). In this case, one can write,

$$b_{\text{H}_2}(\theta_{\text{H}}) = b_{\text{H}_2}(0) |1 - \theta_{\text{H}}|^2 \sim b_{\text{H}_2}(0),$$

and under these conditions Eq. (1) can be rewritten as

$$\frac{(b_{\text{H}_2}(0) - \beta_{\text{H}_2})}{\beta_{\text{H}_2}^2} = \frac{4k_{\text{H}_2}g_{\text{H}_2}}{k_{\text{H}}^2}. \quad (2)$$

In accord with the model proposed by Weber and Cassuto (26) for the interaction between oxygen and transition metal surfaces, the rate constants k_{H} and k_{H_2} above can then be expressed in Arrhenius form with activation energies given by $\chi_{\text{H}}(\theta_{\text{H}})$ and $2\chi_{\text{H}}(\theta_{\text{H}}) - D_{\text{H}_2}$, respectively, where $\chi_{\text{H}}(\theta_{\text{H}})$ is the coverage dependent binding energy of Pt-H, and D_{H_2} is the energy of the H-H bond. Equation (2) thus can be written as

$$(b_{\text{H}_2}(0) - \beta_{\text{H}_2})/\beta_{\text{H}_2}^2 = (4g_{\text{H}_2}\nu_{\text{H}_2}/\nu_{\text{H}}^2) \times \exp |D_{\text{H}_2}/RT|, \quad (3)$$

where ν_{H} and ν_{H_2} are the frequency fac-

tors for atomic and molecular desorption, respectively.

In Fig. 3, stationary state values of β_{H_2} are plotted for various hydrogen pressures at different temperatures (curves 1-5). At high temperatures and low hydrogen pressures, the value of β_{H_2} must approach that of $b_{\text{H}_2}(0)$, where molecular desorption is negligible. The value of $b_{\text{H}_2}(0)$ so found equals 0.30 and is independent of temperature. If as for oxygen (24), the value of $b_{\text{H}_2}(0)$ remains temperature independent down to ca. 1350 °K, the ratio in Eq. (3) can be calculated and is then reported in Fig. 3 [the straight lines (a)-(e)]. These straight lines, then, provide evidence for the validity of the chosen kinetic model and the value of $b_{\text{H}_2}(0)$ for the conditions of this study. Additional evidence is found in the excellent agreement between the value of D_{H_2} calculated from lines (a)-(e) (105 kcal/mol) and that found in the literature (104 kcal/mol) (27). Finally, at constant temperature, the ratio in Eq. (3) is predicted to vary linearly with hydrogen pressure, as shown in Fig. 4 at 1420 °K.

Hydrogen Oxidation over Platinum

The reactions of hydrogen and oxygen with platinum having been individually

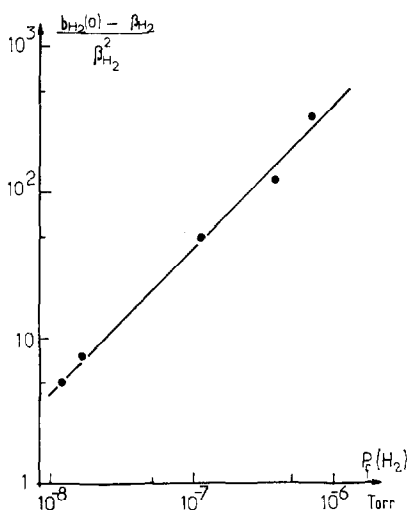


FIG. 4. Variation of $(b_{H_2}(0) - \beta_{H_2})/\beta_{H_2}^2$ with hydrogen pressure at 1420 °K.

studied, the additional effects of reaction between these two gases were first investigated with a $H_2:O_2$ mixed molecular beam (see Fig. 5). Unlike the results for hydrogen and oxygen alone, where β_{H_2} and β_{O_2} , respectively, were equal to zero at temperatures below 1300 °K in the stationary

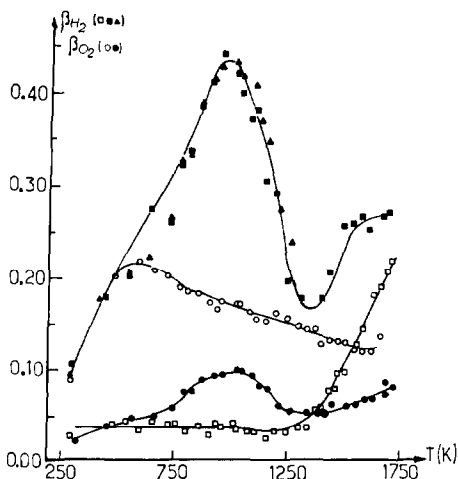


FIG. 5. Variation of β_{H_2} and β_{O_2} with T for two different g_{H_2}/g_{O_2} ratios of a mixed $H_2:O_2$ beam. $g_{H_2}/g_{O_2} = 0.43$ for the solid symbols; $g_{H_2}/g_{O_2} = 11.4$ for the open symbols. The triangular points are values of β_{H_2} calculated from the β_{O_2} curve.

regime, nonzero values of β_{H_2} and β_{O_2} are observed for all temperatures studied. This indication of additional hydrogen and oxygen consumption in the mixed beam case must be the result of chemical reaction. In search of the reaction products, I_2 was opened; except for water, no other products were detected. Indeed, the curve of water production versus temperature (300–1300 °K) followed that shape displayed in Fig. 5. Thus, for the reaction $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$, a material balance yields the result that $g_{H_2}\beta_{H_2} = 2g_{O_2}\beta_{O_2}$, and a measure of either β_{H_2} or β_{O_2} is sufficient to study this reaction. In accord with this statement, the curve for β_{O_2} is identical to that for β_{H_2} below 1300 °K (for which atomization can be neglected) differing by only a multiplicative constant, $g_{H_2}/2g_{O_2}$ (Fig. 5). As a consequence, and for experimental sensitivity, we have introduced an isotropic pressure of oxygen in the reaction chamber and a hydrogen molecular beam intensity for the measure of β_{H_2} . In Fig. 6, these results for the stationary state are reported.

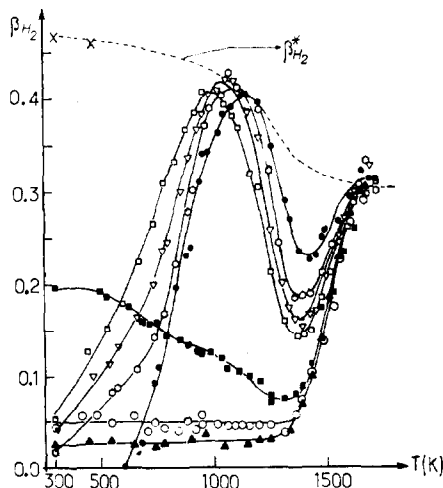


FIG. 6. Variation of β_{H_2} with T for a constant H_2 beam intensity and at different values of oxygen pressure. $\beta_{H_2}^*$ is identical to the zero coverage sticking probability $b_{H_2}(0)$. $P_f(H_2)/\text{Torr} = 8 \times 10^{-8}$; P_{O_2}/Torr : ●, 2.9×10^{-6} ; ○, 1.3×10^{-6} ; ▽, 6.7×10^{-7} ; □, 4.5×10^{-7} ; ■, 9.5×10^{-8} ; ○, 1.9×10^{-8} ; ▲, 5.7×10^{-9} .

At low oxygen isotropic pressures, the curve of β_{H_2} versus temperature follows that for hydrogen atomization alone for high temperatures (>1400 °K). As the oxygen pressure is increased at constant temperature in this region, β_{H_2} is seen to correspondingly increase. For low temperatures, where hydrogen atomization is negligible, the β_{H_2} curves are seen to pass through a maximum, the temperature at which increases with increasing oxygen pressure. From Eq. (1), β_{H_2} must be equal to or less than $b_{H_2}(0)$; thus, at low temperatures initial values (after opening I₂) of β_{H_2} were measured, $\beta_{H_2}^*$, serving to define a lower limit for $b_{H_2}(0)$. At high temperatures, the value of $b_{H_2}(0)$ is known from the previously presented hydrogen atomization results. Connecting these two regions with a curve similar to that found for $b_{O_2}(0)$ (β) passing above the maxima of the β_{H_2} curves, yields the $b_{H_2}(0)$ curve shown in Fig. 6. Taken as a hypothesis, the approximate validity of this curve will be seen later with respect to the results thereby obtained.

To further study the presence of maxima in the β_{H_2} curves, the oxygen isotropic pressure was varied at constant temperature (<1000 °K) and constant hydrogen beam intensity. Figure 7 shows the maximum β_{H_2} observed, $\beta_{H_2}^{max}$, and the corresponding oxygen pressure for various temperatures.

DISCUSSION

Kinetic Model for H₂:O₂ Reactions on Pt

As mentioned in the Introduction, one may expect two types of reactions between hydrogen and oxygen over platinum, namely, a Langmuir-Hinshelwood reaction or an Eley-Rideal reaction, and the results of this study indicate that the former is applicable to our system. Specifically, the observation of a maximum in the rate of reaction with varying oxygen pressure at constant temperature is incompatible with a rate expression of the form $r_{ER1} = kP_{H_2}\theta_O$

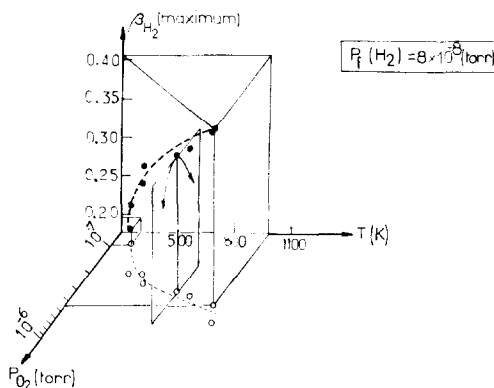


FIG. 7. Variation with temperature of the maximum β_{H_2} and the corresponding oxygen pressure.

(kinetics describable as if there were reaction between molecular hydrogen and adsorbed oxygen atoms); rate expressions of the form $r_{ER2} = kP_{O_2}\theta_H^x$ (kinetics describable as if there were reaction between molecular oxygen and adsorbed hydrogen atoms) or $r_{LH} = k\theta_O\theta_H^x$ (kinetics describable by reaction between adsorbed oxygen and hydrogen atoms) are thus needed to explain the maxima in β_{H_2} with oxygen pressure. The transient behavior of β_{H_2} (upon opening I₂ at constant temperature and oxygen isotropic pressure), however, distinguishes between these latter two alternatives, as shown in Fig. 8. It is therein seen that the initial value of β_{H_2} is zero, and thereafter passes through a maximum value in time. For the rate expression r_{ER1} , the zero initial value of β_{H_2} is not possible to explain. In the rate expression r_{ER2} , the only time-dependent term is θ_H , which would unrealistically be required to pass through a maximum in time to explain

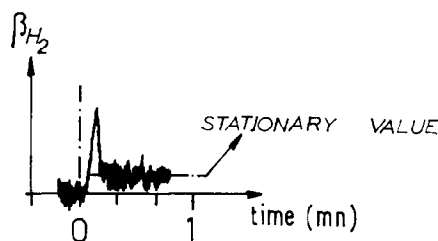
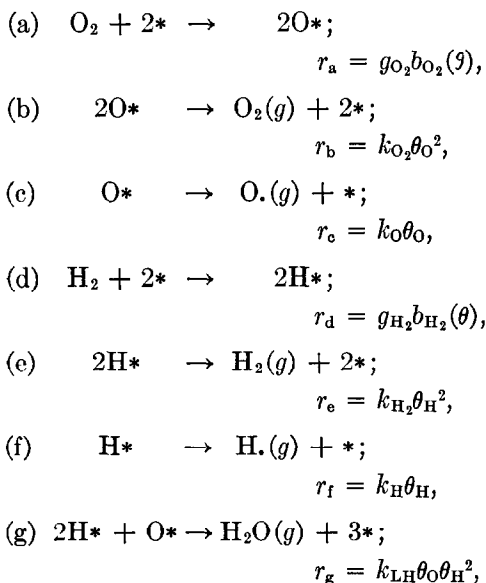


FIG. 8. Transient behavior of β_{H_2} at 300 °K (I₂ opened at $t = 0$).

the data; however, the transient behavior of β_{H_2} is quite simply explained by r_{LH} , in which θ_{O} and θ_{H} , respectively, decrease and increase smoothly with time while the product passes through a maximum value. Thus, adding r_{LH} to the kinetic processes deduced by the individual investigations of the hydrogen and oxygen reactions with platinum, gives the following kinetic model.



where $\theta = \theta_{\text{O}} + \theta_{\text{H}}$, and the other parameters have been defined previously.

At stationary state for the chemisorbed species, two similar relations result:

$$2r_{\text{a}} = 2r_{\text{b}} + r_{\text{c}} + r_{\text{g}}, \quad (4)$$

$$2r_{\text{d}} = 2r_{\text{e}} + r_{\text{f}} + 2r_{\text{g}}. \quad (5)$$

These equations, combined with the definitions of β_{H_2} and β_{O_2} [see Eq. (1)], give

$$\beta_{\text{H}_2} = b_{\text{H}_2}(\theta) - \frac{k_{\text{H}_2} \theta_{\text{H}}^2}{g_{\text{H}_2}} = \frac{1}{2g_{\text{H}_2}} \times [2k_{\text{LH}} \theta_{\text{O}} \theta_{\text{H}}^2 + k_{\text{H}} \theta_{\text{H}}], \quad (6)$$

$$\beta_{\text{O}_2} = b_{\text{O}_2}(\theta) - \frac{k_{\text{O}_2} \theta_{\text{O}}^2}{g_{\text{O}_2}} = \frac{1}{2g_{\text{O}_2}} \times [k_{\text{LH}} \theta_{\text{O}} \theta_{\text{H}}^2 + k_{\text{O}} \theta_{\text{O}}]. \quad (7)$$

It is these equations that will be used to analyze different regions of the β_{H_2} versus

temperature curves for different oxygen pressures where various physical approximations can be made. The effects of hydrogen atomization at temperatures greater than 1350 °K were pointed out earlier; in the equations above, however, the quantitative description of both atomization and chemical reaction is difficult. The analysis of the β_{H_2} curves at temperatures lower than 1350 °K, where r_{c} and $r_{\text{f}} \ll r_{\text{g}}$, provides a much more tractable approach, one that will be used in the present study.

Low Coverage; 1100 °K < T < 1350 °K

From the results of Weber *et al.* (22) one may extrapolate that the oxygen coverage on a polycrystalline platinum ribbon at oxygen pressures of 10^{-6} Torr should be small at 1000 °K ($\theta_{\text{O}} = 0.1$; $P_{\text{O}_2} = 5 \times 10^{-7}$ Torr; $T = 835$ °K). In this case and for higher temperatures, the approximation that $b_{\text{O}_2}(\theta) = b_{\text{O}_2}(0)$ can be made. Additional evidence that this approximation may be valid for each β_{H_2} curve past its maximum is found in analysis of the low temperature maxima (Fig. 7). Deviations of β_{O_2} from $b_{\text{O}_2}(0)$ arise from two effects: the θ term in $b_{\text{O}_2}(\theta)$, and the term representing molecular desorption of oxygen [see Eq. (1)]. At low temperatures the first term predominates while at higher temperatures the latter is more important. Analysis of Fig. 7 reveals that at the maximum β_{H_2} , the value of β_{O_2} equals $b_{\text{O}_2}(0)$ for maxima at temperatures less than ca. 800 °K. This indicates that in the $b_{\text{O}_2}(\theta)$ term, the surface coverage is small, and can be neglected. For β_{H_2} maxima above this temperature, one may then expect the same situation for the surface coverage. Thus, for the region of the β_{H_2} curve past (in temperature) the maximum but before the onset of atomization the two above approximations are valid, i.e., for r_{c} and $r_{\text{f}} \ll r_{\text{g}}$,

$$b_{\text{O}_2}(\theta) = b_{\text{O}_2}(0),$$

$$b_{\text{H}_2}(\theta) = b_{\text{H}_2}(0).$$

For Eqs. (6) and (7) the oxygen and hydrogen coverages can now be calculated.

$$\theta_{O_2} = (b_{O_2}(0) - \beta_{O_2})g_{O_2}/k_{O_2}, \quad (8)$$

$$\theta_{H_2} = (b_{H_2}(0) - \beta_{H_2})g_{H_2}/k_{H_2}, \quad (9)$$

and the expression for β_{H_2} becomes

$$\beta_{H_2} = k_{LH}\theta_{O_2}^2/g_{H_2}. \quad (10)$$

Eliminating θ_O and θ_H from the above three equations and using the material balance gives the final result shown below.

$$\frac{\beta_{H_2}}{g_{O_2}^{\frac{1}{2}}(b_{H_2}(0) - \beta_{H_2})(b_{O_2}(0) - (g_{H_2}/2g_{O_2})\beta_{H_2})^{\frac{1}{2}}} = \frac{k_{LH}}{k_{H_2}k_{O_2}^{\frac{1}{2}}} = R_1. \quad (11)$$

Figure 9 shows the ratio R_1 versus $1/T$, allowing the determination of $E_{LH} - E_{H_2} - \frac{1}{2}E_{O_2}$, where the various E_i are the respective activation energies. Specifically, the value of R_1 is found to be

$$R_1 = 4.31 \times 10^{-12} \times \exp[+30,000/RT] \text{ cm s}^{\frac{1}{2}}.$$

With a value for E_{O_2} of 58 kcal mol⁻¹ (25), the activation energy difference shown below is

$$E_{LH} - E_{H_2} = -1 \text{ kcal mol}^{-1}.$$

Maximum Rate Analysis

In the previous section, it was noted that $b_{O_2}(\theta) \cong b_{O_2}(0)$ at the maximum rate. As one deviates from this maximum, but remains at low coverage, the form of $b_{O_2}(\theta)$ is expected to be $b_{O_2}(0)(1 - \theta)^2$. For the β_{H_2} curves measured with small oxygen isotropic pressures (see Fig. 6), the value of β_{O_2} was calculated and found to be equal to $b_{O_2}(0)$. Under these conditions, θ_H has its maximum value compared to the other β_{H_2} curves at higher oxygen pressures, and still the hydrogen coverage does not reduce the reactive sticking probability. Thus, in all cases $b_{O_2}(\theta)$ can be written as $b_{O_2}(\theta_0)$. One may also expect then, that $b_{H_2}(\theta)$ can

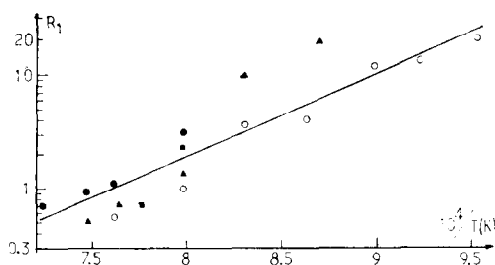


FIG. 9. Variation of R_1 [see Eq. (11)] with $1/T$ for different oxygen pressures: \circ , 4.5×10^{-7} Torr; \blacktriangle , 6.7×10^{-7} Torr; \blacksquare , 1.3×10^{-6} Torr; \bullet , 3.0×10^{-6} Torr. The unity of R_1 corresponds to 3.8×10^{-7} cm s^{1/2}.

be written as $b_{H_2}(\theta_0)$. Indeed, the fact that hydrogen desorbs at lower temperatures than does oxygen from platinum is consistent with the statement that only θ_O need be considered in the sticking probability terms, $b_{H_2}(\theta)$ and $b_{O_2}(\theta)$ for the temperatures of this study.

Thus, near the maximum rate one can write β_{H_2} as

$$\beta_{H_2} = b_{H_2}(0)(1 - \theta_0)^2 - (k_{H_2}\theta_{H_2}^2/g_{H_2}). \quad (12)$$

At the maximum rate, $(\partial\beta_{H_2}/\partial P_{O_2})_{T, \theta_{H_2}} = 0$, and differentiation of Eqs. (10) and (12) gives

$$\begin{aligned} \left(\frac{\partial\theta_O}{\partial P_{O_2}}\right)_{T, P_{H_2}} &= -\frac{k_{H_2}\theta_H}{g_{H_2}b_{H_2}(0)(1 - \theta_O)} \left(\frac{\partial\theta_H}{\partial P_{O_2}}\right)_{T, P_{H_2}} \\ &= -\frac{2\theta_O}{\theta_H} \left(\frac{\partial\theta_H}{\partial P_{O_2}}\right)_{T, P_{H_2}}. \end{aligned} \quad (13)$$

For nonzero $(\partial\theta_H/\partial P_{O_2})_{T, P_{H_2}}$, the combination of Eqs. (12) and (13) allows the calculation of $\theta_0\theta_{H_2}^2$ at the maximum rate, and this result taken with Eq. (10) yields the relation

$$\frac{k_{LH}}{k_{H_2}} = \frac{13.5\eta}{1 - 9\eta + (1 + 3\eta)|4 - 3(1 - \eta)|^{\frac{1}{2}}} = R_2, \quad (14)$$

where $\eta = \beta_{H_2}^{\text{max}}/b_{H_2}(0)$.

Figure 10 shows the maximum β_{H_2} values plotted as R_2 versus $1/T$, and from this plot it follows that

$$R_2 = 6.25 \times 10^2 \exp[-2600/RT].$$

The exponential in this result must then be interpreted as

$$E_{\text{LH}} - E_{\text{H}_2} = 2.6 \text{ kcal mol}^{-1},$$

in agreement with that determination of this quantity presented in the previous section.

A more demanding test of the consistency between the analysis of the low coverage-high temperature region of the β_{H_2} curves (the previous section) and the $\beta_{\text{H}_2}^{\text{max}}$ curve is found by calculating the ratio R_2^2/R_1^2 , which should equal k_{O_2} . The result of this calculation is

$$R_2^2/R_1^2 = k_{\text{O}_2} = 2.1 \times 10^{23} \\ \times \exp[-65,000/RT] \text{ cm}^{-2} \text{ s}^{-1}.$$

This value is in good agreement with that determined by Weber *et al.* (25) for this rate parameter, i.e., $3.8 \times 10^{30} \times \exp[-58,000/RT]$. Finally, choosing a value for E_{H_2} of 18 kcal mol⁻¹ for the most strongly bound hydrogen state (the state expected to be dominant at the high temperatures used in this study, i.e., > 400 °K), the value of E_{LH} is found to be

$$E_{\text{LH}} = 20 \text{ kcal mol}^{-1}$$

for $E_{\text{LH}} - E_{\text{H}_2} = 2 \text{ kcal mol}^{-1}$.

Summary and Comparison with Other Investigations

The results shown in Figs. 6 and 7 can now be interpreted in the following manner.

(i) For temperatures greater than 1350 °K, hydrogen atomization is the major contribution to β_{H_2} at low oxygen pressures, and as the latter is increased the contribution to β_{H_2} from chemical reaction increases accordingly.

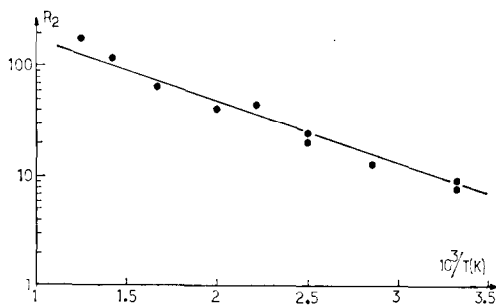


FIG. 10. Variation of R_2 [see Eq. (14)] with $1/T$.

(ii) From 1100 to 1350 °K hydrogen (and oxygen) atomization can be neglected, and the reaction takes place on a surface with low coverage. In this case, the mathematical treatment of the problem is possible, and kinetic information is obtainable.

(iii) From 300 to 1350 °K at low oxygen pressures ($< 10^{-6}$ Torr), the value of β_{O_2} nearly equals $b_{\text{O}_2}(0)$, also indicating a surface with low coverage in both θ_{O} and θ_{H} . Alternatively, the β_{H_2} curve under these conditions can be calculated from the known $b_{\text{O}_2}(0)$ curve and Eq. (11). However, the large uncertainty in calculating $b_{\text{O}_2}(0) - \beta_{\text{O}_2}$ does not allow the calculation of rate parameters under these conditions.

(iv) From 300 to 1100 °K for large oxygen pressures the value of β_{H_2} decreases with increasing oxygen pressure, and taken with the result above (iii) indicates significant oxygen adsorption. Indeed, at low coverages ($\theta_{\text{O}} < 0.1$) where $b_{\text{O}_2}(\theta)$ may be expected to equal $b_{\text{O}_2}(0)(1 - \theta_{\text{O}})^2$, the β_{H_2} curves in this region can be approximately reproduced with a value of k_{O_2} equal to that determined by Weber *et al.* (25). However, in general the complex (and not well understood) dependence of $b_{\text{O}_2}(\theta)$ on θ makes the analysis of β_{H_2} curves in this region uncertain.

(v) At $\beta_{\text{H}_2}^{\text{max}}$ (Fig. 7) the surface coverage is again small, allowing the approximation $b_{\text{O}_2}(\theta) = b_{\text{O}_2}(1 - \theta)^2$ to be made. The mathematical treatment of the problem is possible and kinetic parameters can be obtained.

In conclusion, the kinetic model presented is consistent with all results obtained in this study. The comparison of this model with results obtained by other investigators must now be made, in hopes of understanding the latter in a common framework. A fairly direct comparison is possible with the results of Norton (28); he also studied the hydrogen oxidation over platinum (using XPS) at pressures of order 10^{-7} Torr, although at lower temperatures (< 273 °K) than those of the present investigation. The kinetic model that was found to fit the data best is essentially identical to that found in our study; the single exception is the dependence on θ of $b_{\text{H}_2}(\theta)$, which Norton found to be $b_{\text{H}_2}(0)(1 - \theta)^1$. From his data, it is possible to calculate $E_{\text{LH}} - E_{\text{H}_2}$, and a value of 1 kcal mol^{-1} was so found, in good agreement with our result. To understand the dependence of $b_{\text{H}_2}(\theta)$ on θ , it must be remembered that there are essentially two states of adsorbed hydrogen on platinum; an atomic state (strongly bound), and a pseudo-atomic state (more weakly bound). The latter desorbs at a temperature of approximately 250 °K, leaving the atomic state on the surface at temperatures greater than 300 °K. In addition, at the low temperatures that Norton studied, the more strongly bound species reacts much more slowly than the weakly bound pseudo-atomic species (by a factor of 10^{-4} for an activation energy difference of 3 kcal mol^{-1} at 200 °K). Thus, it is the pseudo-atomic state ($b_{\text{O}_2}(\theta) = b_{\text{O}_2}(0)(1 - \theta)$) that Norton studied, while in the present investigation the atomic state ($b_{\text{O}_2}(\theta) = b_{\text{O}_2}(0)(1 - \theta)^2$) is responsible for the reaction. In Fig. 11, the results of Norton and those of this study are summarized. At temperatures below ca. 300 °K the reaction follows the dashed curve, while at higher temperatures the reaction path is the solid curve. It is interesting to note that the energy level of the activated complex at both high and low temperatures is the same, perhaps

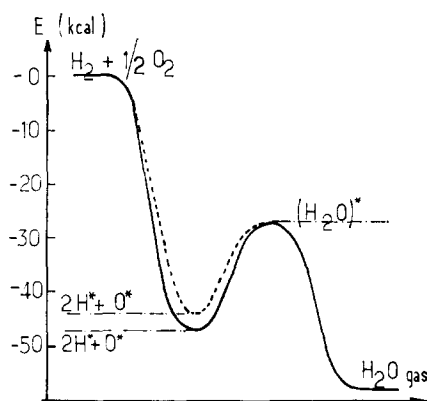


Fig. 11. Comparison of the present results (solid curve) with those of Norton (28) (dashed curve).

indicating the same complex in both cases (the rate of formation proportional to $\theta_{\text{O}}\theta_{\text{H}}^2$).

To extrapolate these results to higher hydrogen and oxygen pressures, essentially three phenomena must be considered. First, at constant temperature, the ratio of the hydrogen coverage with the weakly bound species to that with the more strongly bound species increases with increasing hydrogen pressure. Second, the form of $b_{\text{H}_2}(\theta)$ may change with increasing coverage and thus with increasing pressure. Finally, for sufficiently high oxygen pressures (but small enough hydrogen pressures) oxide formation may take place, thereby changing the nature of the catalyst surface. These concepts are illustrated nicely in the work of Gentry *et al.* (29). These authors studied the hydrogen oxidation over platinum at pressures of order 10^{-1} Torr and at temperatures from 300 to 470 °K. For hydrogen to oxygen pressure ratios greater than 5, no oxide formation was observed, and a rate expression of the form

$$r = k_{\text{R}}P_{\text{O}_2}/P_{\text{H}_2}^{\frac{1}{2}}$$

was found. If the form of $b_{\text{H}_2}(\theta)$ is $b_{\text{H}_2}(0) \times (1 - \theta)^1$, as found by Norton, or $b_{\text{H}_2}(0) \times (1 - \theta)^2$, as found at the low coverages in the present study, the following rate ex-

pression is obtained from our kinetic model,

$$r = k_R P_{O_2} / P_{H_2}^x$$

with

$$k_R = b_{O_2}(0)k_{H_2}^x / b_{H_2}^x(0).$$

Since $b_{O_2}(0)$ and $b_{H_2}(0)$ are only weakly temperature dependent, the activation energy for k_R ($x = \frac{1}{2}$) is predicted to be $E_{H_2}/2$ or 9 kcal mol⁻¹ for the case of Gentry *et al.*; a value of 12 kcal mol⁻¹ was measured by these authors, in good agreement with the prediction. For oxygen to hydrogen pressure ratios greater than 20, oxide formation was observed, and the chemical reaction that takes place is the hydrogen chemisorption on and reaction with the oxide surface. In rate expression r_g of our kinetic model, θ_O is a constant equal to unity, and θ_H is determined by dynamic equilibrium on the oxide. These two assumptions give a rate expression of the form,

$$r_g = k_{LH}\theta_H^2 = k_{LH}K P_{H_2} / [1 + K^{\frac{1}{2}} P_{H_2}^{\frac{1}{2}}]^2,$$

where $K = b_{H_2}(0)/k_{H_2}$. Alternatively, for nondissociative hydrogen chemisorption on the oxide, the following expression is obtained.

$$r_g' = k_{LH}\theta_H = k_{LH}K P_{H_2} / (1 + K P_{H_2}).$$

Both of the above expressions are compatible with the results of Gentry *et al.* over their oxide surface. From the experimental results of Gentry *et al.*, however, the activation energy for k_{LH} can be calculated to be 20 kcal mol⁻¹, in surprisingly good agreement with our result of 20 kcal mol⁻¹ for this parameter.

Three other investigations of the hydrogen oxidation over platinum must now be noted. Gidaspow and Ellington (30) studied this reaction at atmospheric pressure and found that the reaction rate divided by the hydrogen pressure (proportional to β_{H_2} of this study) passed through a maximum value at 600 °K. Using molecular beam

methods, Smith and Palmer (31) also observed a maximum at 600 °K for the rate of the deuterium oxidation over platinum. Further comparisons with this investigation are not possible due to the high deuterium beam temperatures (ca. 1275 °K) used by Smith and Palmer. The results of a recent study of the hydrogen oxidation over supported platinum have been graciously communicated to us by Hanson and Boudart (32). For oxygen to hydrogen pressure ratios greater than 7 ($P_{O_2} = 230$ Torr; $P_{H_2} < 32$ Torr), the reaction was found to be first order in hydrogen (the oxygen order was not determined) with an activation energy of 1.8 kcal mol⁻¹. From our kinetic model (the second case discussed with reference to the work of Gentry *et al.*), the rate constant for this case is predicted to be $k_{LH}b_{H_2}(0)/k_{H_2}$, and an activation energy of 2 kcal mol⁻¹ is expected. The agreement between these two values is surprisingly good. For hydrogen to oxygen pressure ratios greater than ca. 12 ($P_{O_2} < 39$ Torr; 210 Torr $< P_{H_2} < 700$ Torr), Hanson and Boudart found the reaction to be first order in oxygen and zero order in hydrogen with an activation energy of 3.4 kcal mol⁻¹. While these reaction orders can be obtained with the present kinetic model ($x = 0$ for the first case discussed with reference to the work of Gentry *et al.*), an excessively large preexponential factor is predicted for this case. Thus, for the case of large hydrogen to oxygen pressures, the present model explains the results of Gentry *et al.* for pressures of order 10⁻¹ Torr, but the results of Hanson and Boudart for pressures of order 10² Torr seem to indicate the presence of additional effects at these higher pressures.

Thus, it appears that the hydrogen oxidation results obtained at temperatures from 200 to 1700 °K and at pressures from 10⁻⁷ to approximately 10 Torr can be understood in terms of a simple kinetic model.

ACKNOWLEDGMENTS

One of us (J. A. D.) gratefully acknowledges the support of a NATO Postdoctoral Fellowship during the course of this work. We also acknowledge frequent and fruitful discussions with Drs. B. Weber, A. Cassuto, and A. Pentenero. In addition, we express our gratitude to all members of the Centre de Cinétique Physique et Chimique.

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