

The Reaction between Hydrogen and Oxygen on Platinum

PROGRESS IN ESTABLISHING KINETICS AND MECHANISMS

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Nothing certain is understood concerning the mechanism of what is the oldest known, and the simplest, catalytic oxidation. Recent work in the Johnson Matthey Research Laboratories has partly explained some of the inconsistencies found in previous work, and has established the best conditions for studying the kinetics of this reaction. In this article new suggestions are put forward on possible reaction mechanisms.

The formation of water when platinum sponge or strip is exposed to a mixture of hydrogen and oxygen was one of the first catalytic reactions to be discovered and recognised as such (1), but in spite of numerous subsequent investigations there exists no accepted mechanism for this reaction. There are two related reasons for this gap in our catalytic knowledge: (i) in no instance are two sets of kinetic results identical (see table), and (ii) the activity of platinum catalysts has not been reproducible. Much more is known about the mechanism of catalytic exchange and hydrogenation reactions than about this, the simplest oxidation reaction.

Some Tentative Mechanisms

As with many other catalytic reactions, a classical kinetic approach has not yielded sufficient information for the development of a satisfactory reaction mechanism, and hence additional information has been sought. Isotopes have been used to determine the composition of the activated complex formed in the rate determining step (2, 3), and the phenomenon of catalyst activation by adsorbed oxygen has received considerable attention. From these and the kinetic results, four possible mechanisms have emerged:

- (a) Simultaneous adsorption of hydrogen and oxygen on the catalyst surface with subsequent reaction and desorption of water (5).

$$k \propto [\text{O}_2]^{0-1} [\text{H}_2]^{0-1}$$

- (b) Reaction between adsorbed oxygen and hydrogen molecules in a van der Waals layer (6).

$$k \propto [\text{O}_2]^{0-1} [\text{H}_2]^1$$

- (c) Reaction between adsorbed hydrogen and oxygen molecules in a van der Waals layer (3).

$$k \propto [\text{O}_2]^1 [\text{H}_2]^{0-1}$$

- (d) Complex two site and alternate reaction mechanisms (7, 8).

$$k \propto [\text{O}_2]^x [\text{H}_2]^y$$

where x and y can range from -1 to +1

Any one of these mechanisms will explain some but not all of the kinetic equations given in the table. None will apparently explain the observed phenomena of catalyst activation by adsorbed oxygen and deactivation by adsorbed hydrogen unless the formation of an active oxide layer on the surface of platinum is postulated. Roginsky indeed claims to have detected this oxide layer

Fig. 1 The apparatus used for studying the oxidation of hydrogen on platinum wires



(Pt₃O₄) on a platinum catalyst after it has been exposed to a hydrogen/oxygen mixture (4).

With so much information about this reaction already available, it should be possible to derive a mechanism without having to resort to any more practical work. However, although the special features of this reaction such as catalyst activation by adsorbed oxygen (4), deactivation by adsorbed hydrogen (9) and surface rearrangement of the catalyst are now well known, their effect on the kinetics of the reaction has not been established. Recent work in these laboratories enables us to account for some of the discrepancies between previous studies of the reaction and to throw some new light on possible reaction mechanisms.

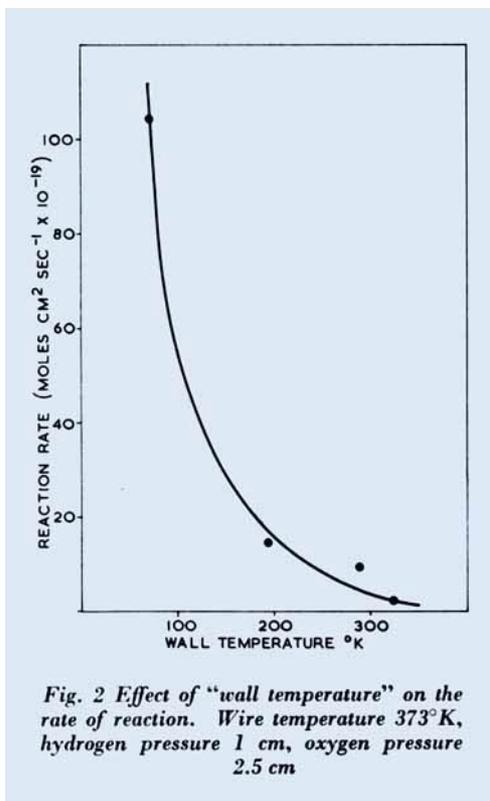
Experimental Procedure

The reaction was studied in an all-glass static system attached to a conventional vacuum line capable of lowering the pressure

in the system to less than 10⁻⁶ mm Hg. The catalyst was a platinum wire, 99.999 Pt, 0.203 mm in diameter and 15 cm long, rigidly fixed along the longitudinal axis of a cylindrical reaction vessel, and electrically thermostated. Adsorbed gases were removed from the wire by standard ion bombardment techniques (10). In a typical experiment, the reaction vessel was immersed in a bath of

Rate Equations for the Reaction between Hydrogen and Oxygen on Platinum

Rate Equation	Reference	Comments
$r \propto P_{O_2} P_{H_2}^{-1}$	Langmuir (15)	Catalyst irreproducible
$r \propto P_{O_2}^{1 \rightarrow 0} P_{H_2}^0$	Donnelly and Hinshelwood (5)	
$r \propto P_{O_2} P_{H_2}^0$	Boreskov, Slin'ko and Chesalova (16)	
$r \propto P_{O_2}^0 \text{ or } 1 P_{H_2}$	Tanner and Taylor (6)	Wire heated in air at white heat
$r \propto P_{O_2} P_{H_2}^{-\frac{1}{2}}$	Krylov and Roginsky (4)	Oxygen covered surface



sumably associated with changes in the heats of adsorption of oxygen and hydrogen on platinum after activation (11). Our results lend support to the hypothesis (4, 6) that a layer of adsorbed oxygen causes an enhanced activity, but this effect is only shown when gas mixtures containing an excess of hydrogen are used. It is probable that activation by adsorbed oxygen is an integral part of the reaction mechanism and should not be confused with activation caused by surface rearrangement.

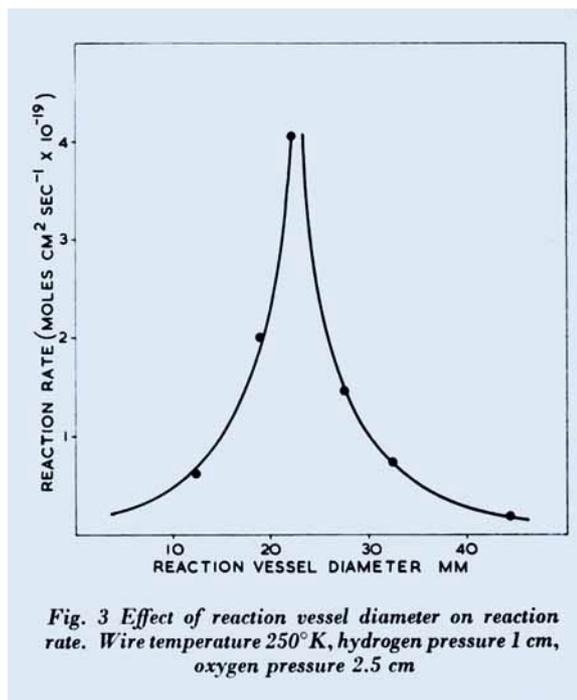
Effect of Water Vapour on the Reaction

The pressure of the water vapour produced during the reaction increases progressively unless it is either condensed or swept out of the system; we have found that the reaction is retarded by water vapour. The vapour pressure of water was controlled by varying the temperature of the walls of the vessel using suitable constant temperature baths. The effect of the "wall temperature" on the rate is shown in Fig. 2: this effect also occurs

liquid nitrogen and a hydrogen-oxygen mixture of known composition admitted; the rate was determined by following the change in pressure in the system. The apparatus is shown in Fig. 1.

Catalyst Activation

Activation of the catalyst by oxygen or the reacting gases is the probable cause of catalyst irreproducibility and is often accompanied by a change in surface structure (4). If an increase in surface area were solely responsible for the activity increase, no change in the activation energy of the reaction is expected: such a change has, however, been observed in our work and is pre-



with silver and gold catalysts (12, 13). We have also found that the diameter of the reaction vessel affects the rate as shown in Fig. 3; the magnitude of the effect varies with the pressure of gas in the reaction vessel.

Effect of Pressure on the Reaction

The effects of the pressures of hydrogen and of oxygen on the rate were investigated by varying one pressure while keeping the other constant at 1 cm: because of the activation effects mentioned above, a new wire was used for each gas mixture studied. The vessel diameter was 22 mm and the wall temperature -196°C . The total pressure and thermal conductivity of the gas mixture were kept constant by the addition of an inert gas, which was helium when hydrogen pressure was varied and nitrogen when oxygen pressure was varied. Under these conditions, pressure-time curves are linear and the zero order rate constant is directly proportional to oxygen pressure and to a negative power of the hydrogen pressure above 1 cm (Fig. 4). If, however, the catalyst is "activated" by the reacting gases or by pre-adsorbed oxygen, the reaction is not retarded by high hydrogen pressures (see also Fig. 4). The activation energy does not change with gas composition at constant total pressure.

The Reaction Mechanism

It is clear from our results that the reaction between hydrogen and oxygen is strongly poisoned by the water vapour which is produced: to obtain reasonable rates, it is essential to keep the pressure of the water vapour low and to encourage its transport away from the catalyst surface by keeping the walls of the reaction vessel at a low temperature. Meaningful orders of reaction are obtained when the water vapour pressure is less than 0.004 mm and when precautions are taken to keep the temperature gradient between the wire and the wall approximately constant. Even under these conditions, both the rate and the orders of reaction vary with the sequence of addition of the reactants.

If both are added simultaneously to a clean surface, moderate rates are found, pressure-time curves are linear and the reaction is first order in oxygen and of negative order in hydrogen above about 1 cm pressure. When pre-adsorbed oxygen is present before the mixture is added, rates are faster, but pressure-time curves are still linear although the reaction is now zero order in hydrogen. Very slow rates are found when pre-adsorbed hydrogen is present. The importance of pre-adsorbed gases has not been clearly appreciated before.

An unusual feature of this system is that the surface seems reluctant to change from the conditions obtaining at the start of an experiment. Despite the well-established fact that oxygen is more strongly chemisorbed than hydrogen (14) pre-adsorbed hydrogen is not rapidly displaced by oxygen nor does an extensive oxygen layer seem to accumulate in the presence of hydrogen. This point also has not been clearly stated before.

Many years ago Donnelly and Hinshelwood (5) obtained orders similar to those we find when no pre-adsorbed gas is present. The interpretation must be that the reactive oxygen is adsorbed only weakly or not at all, and that vacant sites (progressively filled at higher hydrogen pressures) are required for reaction. The linear pressure-time curve could result from the opposite signs of the reaction orders, but this cannot be so at hydrogen pressures below about 1 cm and some additional form of explanation may be required.

Different conditions exist when pre-adsorbed oxygen is present. Work on the adsorption of oxygen on platinum films has shown that only 63 per cent of the surface can be covered, at which time the heat has fallen from 70 kcal/mole⁻¹ at zero coverage to 30 kcal/mole⁻¹ (14). The limit is apparently set by geometric rather than energetic factors. The remaining surface is presumably covered by adsorbed hydrogen and the reaction is then zero order in hydrogen. It is difficult to see why rates under these

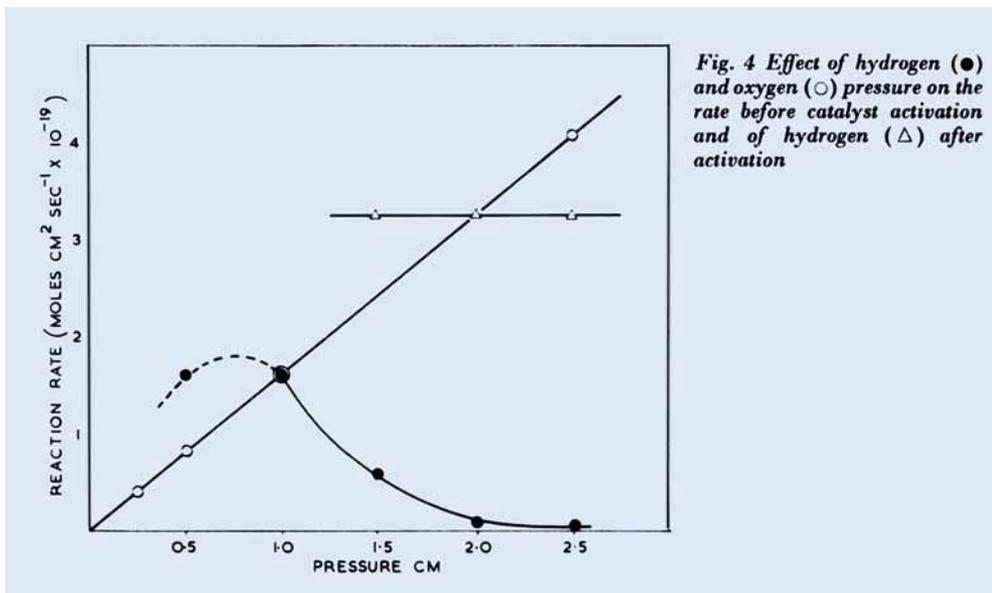
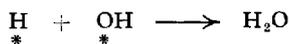


Fig. 4 Effect of hydrogen (●) and oxygen (○) pressure on the rate before catalyst activation and of hydrogen (Δ) after activation

conditions are faster than those found when no pre-adsorbed oxygen is present. A possible explanation is that between the pre-adsorbed oxygen atoms there are sites prohibited to oxygen atoms but available to weakly adsorbed oxygen molecules and hydrogen atoms.

The effect of vessel diameter on rate (Fig. 3) is complex and its form varies with the composition of the gas mixture. This effect is connected with the retarding effect of water vapour which is interpreted as follows. The reaction of hydrogen atoms with oxygen molecules or weakly adsorbed oxygen atoms leads to adsorbed hydroxyl radicals: the slow step is the reaction



(asterisks indicate bonding to the surface), and hence if the water formed is not efficiently removed the reverse reaction will occur with consequent retardation of the reaction (see Fig. 2).

Conclusion

The present work has by no means resolved all the outstanding problems of the mechanism of the reaction of hydrogen with oxygen on platinum, but it has served to define more

closely the variables that need to be controlled if worth-while kinetic measurements are to be obtained.

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