JOURNAL OF CATALYSIS **122**, 219–229 (1990)

Oxidation of Hydrogen over Supported Palladium

M. G. JONES[1] AND T. G. NEVELL[2]

Department of Chemistry, Portsmouth Polytechnic, Portsmouth PO1 2DT, United Kingdom

Received January 18, 1988; revised July 20, 1989

Oxidation of hydrogen (0.1–2.0% v/v) in air over supported palladium catalysts at 300–625 K and atmospheric pressure has been investigated using a microcalorimetric method. The kinetics are influenced by reactor design, with activated processes at low temperatures and diffusion-limited rates at high temperatures. The mechanism involves a surface layer of PdO and weakly adsorbed H_2. Water causes inhibition and reversible deactivation, particularly at low temperatures. The reaction is strongly inhibited by bromomethane (0.1–1.0% v/v) which competes with hydrogen for adsorption sites.

INTRODUCTION

The formation of water over noble metal catalysts is particularly sensitive to experimental conditions (*1–5*), reflecting the complex mechanisms involved. The reaction over platinum has been studied extensively, but that over palladium catalysts has attracted less interest despite their higher activity in some oxidations. The activity of platinum and palladium toward mixtures of hydrogen and oxygen depends on the state of oxidation of the surface (*2, 6*). Reproducible results are not readily obtained unless one or the other reactant is in large excess. Proposed mechanisms involve interactions between either weakly adsorbed hydrogen and an oxidized surface (*7*) or hydrogen and oxygen adspecies on a metal surface (*8, 9*), with the formation of adsorbed OH being rate determining in both cases.

Oxidized platinum surfaces are normally more reactive than reduced metal surfaces (*2*), but single-crystal studies on palladium (111) have shown that oxidized surfaces can be less active (*8*). Over unsupported (*1*) and alumina-supported (*10, 11*) platinum the reaction is inhibited by water. Similarly, water inhibits the oxidation of hydrocarbons over supported palladium (*12*), hydroxyl groups being strongly adsorbed on the oxidized metal surface (*9*).

In the present work kinetic measurements using the microcalorimetric pellistor technique (*13–16*) have been used to investigate the mechanism of the reaction of hydrogen with excess oxygen over supported palladium catalysts. The effects of some potential inhibitors have also been studied.

EXPERIMENTAL

Materials

Pellistors, each consisting of an 11-turn coil of 50-μm platinum wire encapsulated in a "bead" (ca. 1 mm) of α-alumina, were used to fabricate both catalytic and inert compensating elements. Catalysts were prepared either by coating pellistors with 20% w/w palladium/thoria or with 10% w/w palladium/zeolite [3A molecular sieve (*17*)]. The presence of metallic palladium and the supporting materials was established by XRD. No other phases were detected. Both types were activated by heating alternately in 12% v/v methane–air mixtures and in oxygen until stable behavior was obtained. Compensating elements were produced by treating pellistors with dilute aqueous potassium hydroxide (*15*).

---

[1] Present address: Department of Chemistry, The University, Southampton SO9 5NH, U.K.

[2] To whom correspondence should be addressed.

0021-9517/90 $3.00

Oxygen, hydrogen, and nitrogen (respectively 99.5, 99.99, and 99.9%, BOC Ltd.) were used without further purification in the flow system, but were redistilled (oxygen) or passed through cold traps (hydrogen and nitrogen) before use in the static system. Water vapor was generated from doubly distilled water. Bromomethane (99.5% BDH Ltd.) and freon 12 (9.55% v/v in air, BOC Ltd.) were used as supplied.

Apparatus and Procedure

Kinetic measurements were made using both standard gas flow and static systems (*18*). In the former, the compensating and catalytic pellistors were mounted centrally in vertical side-arms (3 × 1.5 cm) leading from a horizontal flow tube (1.5 cm diameter), with the compensator positioned upstream. In the static system, both pellistors were mounted within a sealed borosilicate glass reaction vessel (250 cm^3). The pellistors were connected into parallel low-resistance arms of a Wheatstone bridge network. With the catalytic pellistor maintained by electrical power W at temperature T (electrical resistance R), a surface reaction rate r (moles of hydrogen per second) caused an out-of-balance voltage V, given by (*15, 19, 20*)

$$V = Kf\Delta H(dR/dT)(dW/dT)^{-1}r \quad (1)$$

where f, the fraction of the heat of reaction (ΔH) detected by the bead, and dR/dT are independent of temperature (*15, 21*), and K is a constant determined by the components of the bridge circuit. Values of dW/dT, effectively constant during individual experiments, were deduced from measurements of W performed over a wide range of conditions.

Kinetic runs in the static system were started by switching on the power supply after admitting gases to the reactor. In the flow system, pellistors were preheated in flowing air, into which hydrogen was then introduced. The lowest measurable rates of oxidation of hydrogen in air at atmospheric pressure were ca. 1×10^{-9} mol s^{-1} in the flow system and 5×10^{-9} mol s^{-1} in the static system.

RESULTS

Catalytic Activity

Fresh supported palladium catalysts showed measurable activity toward the oxidation of hydrogen in air (0.1–2.0%, atmospheric pressure) at temperatures above 300 K. Most catalysts showed constant activity over prolonged use, although early aging effects (30–50% loss of activity) preceded stable behavior in a few cases.

Reactivation of the catalyst was required after each experiment. In the flow system, catalysts were heated in dry air at 500–530 K for 2 min. Reactivation was incomplete at lower temperatures, whereas overheating caused a loss of activity which, however, was restored by leaving the catalyst at ambient temperature for several hours. In the static system, reactivation of catalysts involved degassing (ca. 10^{-3} Torr, ambient temperature) followed by heating in air (ca. 673 K). Employment of higher temperatures did not significantly deactivate the catalysts.

Activity was greatly reduced by leaving catalysts in moist air at ambient temperature, and was lost completely by heating catalysts in hydrogen/nitrogen mixtures (1%, atmospheric pressure). In both cases activity was restored by reactivation. No differences were observed between the XRD patterns of fresh, deactivated, and reactivated catalysts.

In each experiment a finite time elapsed before the reaction rate reached a maximum, referred to henceforth as the initial rate, r_0, with a corresponding out-of-balance voltage, V_0. This induction period was less reproducible than the initial rate but decreased with increasing temperature with an activation energy of 60 ± 5 kJ mol^{-1} (see Fig. 1).

Temperature Dependence

With all supported palladium catalysts used, linear Arrhenius plots were obtained

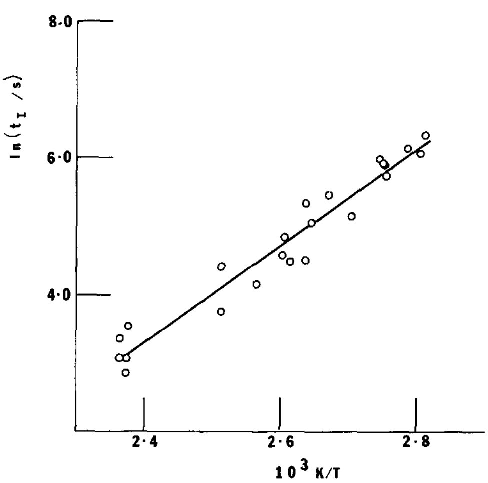

FIG. 1. Dependence of induction period t_I on temperature T in the oxidation of hydrogen (0.5%) in air at atmospheric pressure over palladium/thoria.

from measurements of initial rates of reaction of mixtures of constant composition (Figs. 2 and 3). However, in the flow system, limiting rates were reached at 370–430 K, according to catalytic activity (Fig. 2). These limiting rates were accurately proportional to the concentration of hydrogen, unaffected by aging of the catalyst, and differed only slightly between catalysts with a wide range of activities. Thus, these results show a transition between chemical control and bulk diffusion control, over a temperature range of ca. 40 K in a single series of experiments. In the static system, limiting rates were much higher so that chemical control was extended to higher temperatures. Self-consistent results were obtained when one catalyst was used in both systems (Fig. 3b).

Activation energies over the temperature range 340–400 K varied with catalytic activity and with the concentration of hydrogen. For example, a value of 23 kJ mol^{-1} was obtained for 0.1% H_2 over aged Pd/thoria, and for 0.5% H_2 the values were 43, 53, and 43 kJ mol^{-1}, respectively, over fresh Pd/thoria, aged Pd/thoria, and Pd/zeolite. Above 410 K, however, measurements with the static system gave an activation energy of 13 ± 1 kJ mol^{-1} for all mixtures used, over both fresh and aged catalysts.

Kinetics

Partial orders with respect to hydrogen and oxygen were determined from measurements of initial rate, using both static and flow systems. The linear double-logarithmic plots shown in Fig. 4a establish that the order in hydrogen (0.1–2.0% v/v in air)

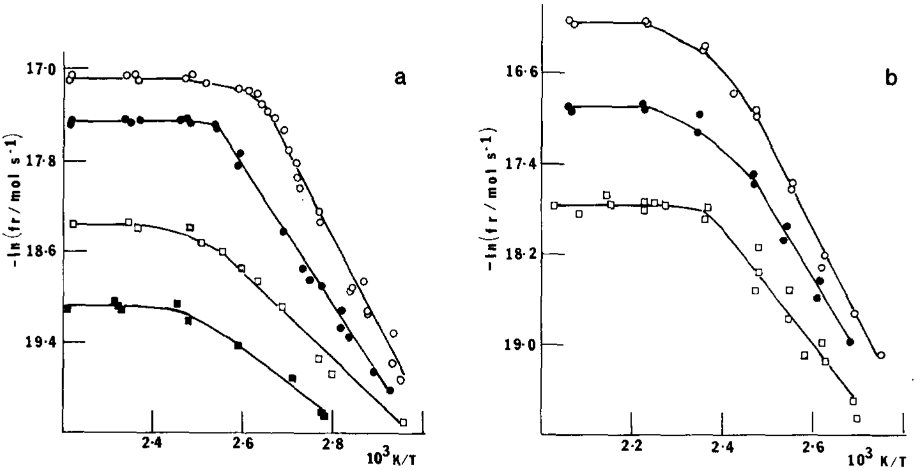

FIG. 2. Rates of catalytic oxidation of hydrogen in air at atmospheric pressure in the flow system. (a) Over palladium/thoria; [H_2] in % = (■) 0.1, (□) 0.2, (●) 0.5, (○) 0.7. (b) Over palladium/zeolite; [H_2] in % = (□) 0.5, (●) 1.0, (○) 2.0.

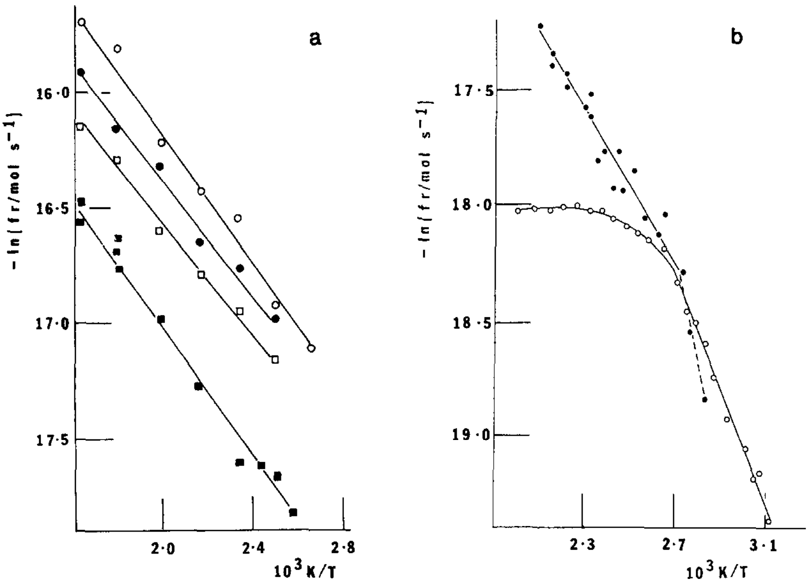

FIG. 3. Rates of catalytic oxidation of hydrogen in air at atmospheric pressure over palladium/thoria. (a) Static system, $[H_2]$ in % = (■) 0.4, (□) 0.6, (●) 0.8, (○) 1.0. (b) The same catalyst operated in the static (●) and flow (○) systems; $[H_2]$ = 0.2%.

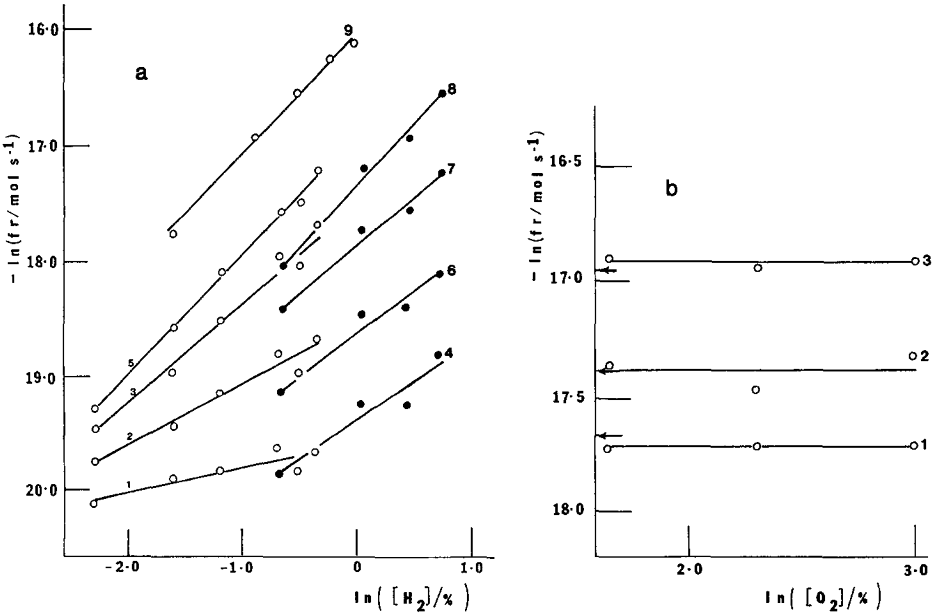

FIG. 4. Dependence of rate on concentrations of reactants. (a) Over palladium/thoria (○) and palladium/zeolite (●), in air at atmospheric pressure; temperatures in K = (flow system), (1) 345, (2) 357, (3, 4) 370, (5, 6) 385, (7) 400, (8) 417; (static system), (9) 455. (b) Over palladium/thoria, $[H_2]$ = 0.5% in oxygen and nitrogen at atmospheric pressure, ← denotes rate in the absence of oxygen; temperatures in K (static system) = (1) 435, (2) 500, (3) 625.

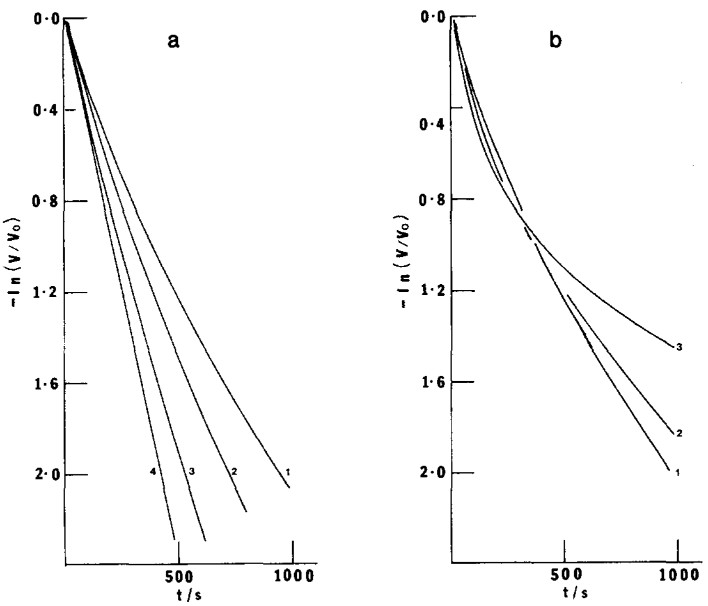

FIG. 5. Progress curves for catalytic oxidation of hydrogen in air (atmospheric pressure, static system) over palladium/thoria. (a) $[H_2]$ = 0.6%, temperatures in K = (1) 427, (2) 504, (3) 556, (4) 619. (b) At 461 K, $[H_2]$ in % = (1) 0.2, (2) 0.4, (3) 0.8.

increases from 0.2 at 345 K to 1.0 at 385 K, and remains at this value at higher temperatures. Values from individual plots show that these results are consistent between catalysts with different activities and between the two systems. From experiments in which the proportions of nitrogen and oxygen were varied (constant temperature, total pressure, and concentration of hydrogen), the initial rate was independent of the concentration of oxygen (0–20%, 400–625 K, Fig. 4b). However, in successive experiments using hydrogen (0.13%) in nitrogen, in the static system, between which the catalyst was degassed but not reheated in air, activity was reduced by ca. 75% per kinetic run.

Using the static system, progress curves at temperatures in the range 460–620 K were obtained as observations of V as a function of elapsed time (t). Derived plots of $\ln(V/V_0)$ against t were linear for reactions at higher temperatures and with lower concentration of hydrogen (Fig. 5). However, at lower temperatures and with higher initial concentrations of hydrogen curved plots were obtained [slope $d(\ln V)/dt$ decreasing with elapsed time]. The linear plots are consistent with first-order kinetics. If

$$r = kn_{H_2} \tag{2}$$

and Eq. (1) is written as

$$V = qr \tag{3}$$

then

$$\ln V = -kt + \ln(qkn^0_{H_2}) \tag{4}$$

$$= -kt + \ln V_0$$

where n_{H_2} (initial value $n^0_{H_2}$) is the number of moles of hydrogen in the reactor.

The curved plots correspond qualitatively with a higher order (x). If

$$r = kn^x_{H_2} \tag{5}$$

then for constant x,

$$d(\ln V)/dt = -kx/[(x-1)kt + n_{H_2}^{0(1-x)}]. \tag{6}$$

If the oxidation of hydrogen was inhibited by the water produced, the apparent order would be expected to increase with increasing conversion in a static experiment.

In experiments using the flow system, it was observed that rates decreased progressively after a maximum had been reached, at catalyst temperatures below 370 K for palladium/thoria and 410 K for palladium/zeolite. The effect was more marked at lower temperatures, but maximum rates were maintained indefinitely at higher temperatures.

The effects of ambient water vapor were examined in the flow system by saturating the reaction mixture (2.7% v/v). Over both palladium/thoria and palladium/zeolite, moisture produced considerable but fully reversible inhibition, with chemically controlled rates being decreased respectively by 70 and 92% (Fig. 6). However, the activation energy remained unchanged. Diffusion-limited rates were also reduced considerably. This effect was greater over palladium/thoria, but could be decreased by reactivating the catalyst with dry air between experiments (Fig. 6). The heat dissipation characteristic dW/dT was unaffected by the added water vapor.

Effects of Halocarbons

Concentrations of up to 1.0% v/v respectively of freon 12 and bromomethane were added to reaction mixtures in the flow and static systems. Freon 12 had no measurable effects on reaction rates (350–570 K), with initial rates being reproducible to within 0.2%.

Bromomethane strongly inhibited hydrogen oxidation over both supported catalysts (Figs. 7a and b). Recovery was extremely slow in the flow system and activity was not fully restored by heating the catalyst in air. However, prolonged degassing (static system) did restore activity. Linear Arrhenius plots were obtained (Fig. 7c), with the transition to diffusion control displaced to higher temperatures but with diffusion-limited rates unchanged. The effect of bromomethane on initial rates corresponded with orders of −0.7 at 340 K and −0.4 at 370 K (Fig. 8a). The overall order was increased by increasing the bromomethane concentration (Fig. 8b).

Infrared spectra of the reaction mixtures

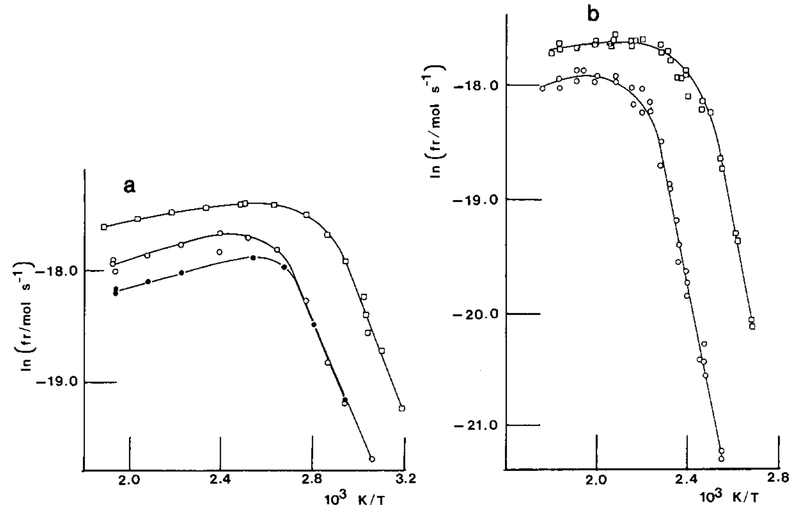

FIG. 6. Effect of water vapor (2.7%) on catalytic oxidation of hydrogen (0.5%) in air (atmospheric pressure, flow system). (□) Rate without added water. (a) Over palladium/thoria: dry reactivation (○), wet reactivation (●). (b) Over palladium/zeolite: dry and wet reactivation (○).

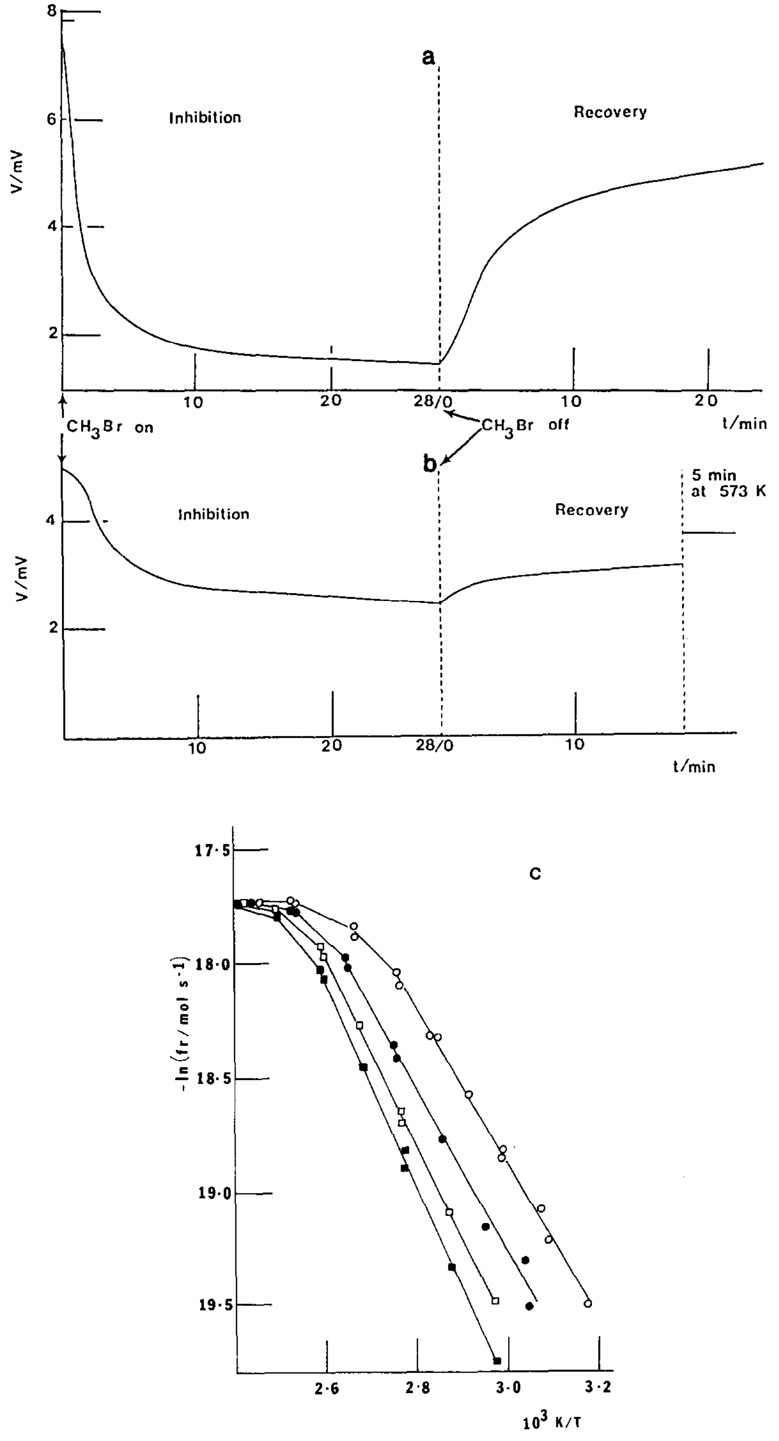

FIG. 7. Inhibition by bromomethane of catalytic oxidation of hydrogen in air (atmospheric pressure, flow system). (a) Over palladium/thoria, $[H_2] = 0.7\%$, $[CH_3Br] = 1.0\%$, temperature = 389 K. (b) Over palladium/zeolite, $[H_2] = 0.5\%$, $[CH_3Br] = 1.0\%$, temperature = 483 K. (c) Over palladium/zeolite, $[H_2] = 0.5\%$, $[CH_3Br]$ in % = (○) 0.25, (●), 0.50, (□) 0.75, (■) 1.00.

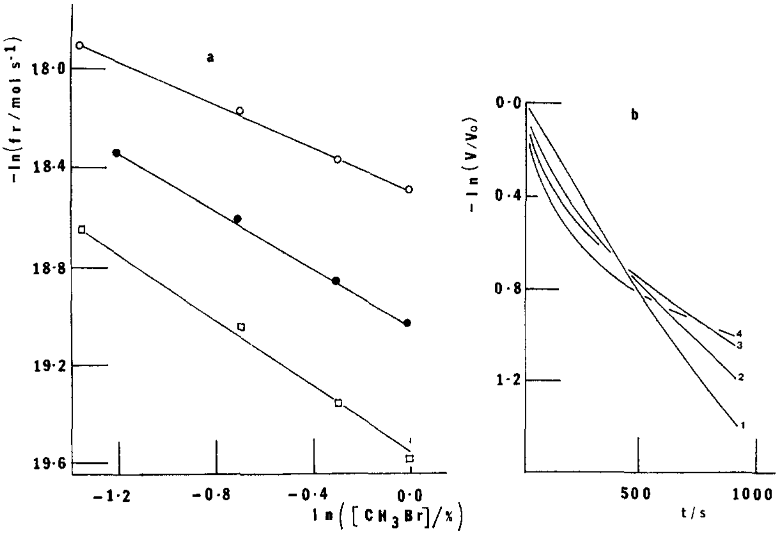

FIG. 8. Kinetics of inhibition by bromomethane, hydrogen in air (atmospheric pressure) over palladium/thoria. (a) Effect on reaction rates in the flow system, $[H_2] = 0.5\%$, temperatures in K = (□) 340, (●) 352, (○) 370. (b) Effect on progress curves in static system, temperature = 625 K, $[CH_3Br]$ in % = (1) nil, (2) 0.025, (3) 0.050, (4) 0.100.

showed that the concentration of bromomethane remained unchanged throughout static experiments and that no detectable amount of any other product was formed. Mixtures of bromomethane and air or oxygen gave no kinetic response.

DISCUSSION

Chemical and Diffusion Control of Reaction Rates

Characteristics of the surface reaction may be distinguished from physical factors by comparing observations made with static and flow systems. Bulk diffusion control in the latter at higher temperatures is established by the very low apparent activation energy and the precise first-order dependence of rate on hydrogen concentration. Similar transitions between chemical and diffusion regimes have been observed in previous studies of catalytic combustion (*2, 12, 22, 23*). The transition temperature is determined by the kinetics of the surface reaction, the diffusivity of the reactants, and the design of the reactor. The spherical reactor used in the static system minimizes diffusion limitations, enabling kinetic characteristics of the surface reaction to be measured at higher temperatures.

No kinetic features were observed which would have indicated the influence of pore diffusion at temperatures between the regions of bulk diffusion control and chemical control (*24*).

Kinetics and Mechanisms

The order with respect to hydrogen, determined from measurements of V_0, increases from 0.2 to 1.0 over the temperature range 345–385 K. Hence after the induction period, the rate-determining step involves chemisorbed molecular hydrogen, the adsorption of which is moderately strong at lower temperatures. The induction period in individual experiments corresponds with the surface concentration of adsorbed hydrogen increasing to a maximum.

The reaction is zero order in oxygen over the whole temperature range (425–625 K) for $O_2 : H_2$ ratios of up to 80 : 1. Over reactivated catalysts, initial rates are unchanged even in the absence of gaseous oxygen. However, catalysts reduced by heating under hydrogen are deactivated. These observations are consistent with the involvement of palladium oxide. Since negative orders, which reflect competition between adspecies for sites, were not observed, oxygen adsorbed on metallic palladium cannot be involved. However, only metallic palladium was detected by XRD, even in aged or deactivated catalysts. Therefore the oxide must be formed as a surface layer. Previous studies of the adsorption of oxygen on unsupported palladium (*25*) have shown that mobile atomic adspecies are formed at temperatures up to 500 K, whereas a layer of oxide predominates above 800 K. Much higher concentrations of gaseous oxygen have been used in the present work, so that oxidation of the surface at somewhat lower temperatures would be expected.

It is unlikely that absorbed hydrogen (*26–29*) plays any part in the reactions over oxidized surfaces. Although in previous work (*8*), enhanced reaction rates have been attributed to a "reservoir" of dissolved hydrogen, the conditions were probably such that adsorbed oxygen rather than a surface layer of oxide was involved.

The presence of water vapor inhibits the reaction considerably at low temperatures, but the effect decreases with increasing temperature. Added water vapor (2.7%) reduces the rate of oxidation of 0.5% hydrogen in air by ca. 25% at 455 K (Fig. 6a) but the effect of self-generated water in the static experiments is negligible above 550 K. Since chemically controlled initial rates are similar over a catalyst reactivated alternatively in dry and moist air, water is competing for adsorption sites on the layer rather than inhibiting reoxidation of the surface because of slow desorption. This is supported by the relative ease with which catalysts are reactivated, since H_2O adsorbed on PdO would be displaced much more easily than OH adsorbed on Pd.

The gradual loss in activity which was observed in individual experiments at very low temperatures will have been due mainly to progressive reduction of the oxide layer. Even with a considerable excess of gaseous oxygen, reoxidation of the surface is slow at these temperatures. Inhibition by self-generated water will have contributed to a reduction in the rate, but would not have caused complete deactivation.

Effects of Halocarbons

The absence of any effect of freon 12 (a possible atmospheric contaminant in some applications) contrasts with its inhibition of hydrocarbon oxidation, also observed using Pd/thoria-on-alumina pellistors but at higher temperatures (*30*). Since this reaction involves a partially oxidized surface (*12*), freon 12 must be adsorbed by metallic palladium but not by the oxide layer.

The observed effects of bromomethane were considerable, both in reducing initial rates and in increasing inhibition by water. The difficulty encountered in restoring full activity to catalysts exposed to bromomethane indicates relatively strong attachment to the sites most active for the adsorption of hydrogen. This would leave hydrogen more susceptible to competition with water for the less active sites. No evidence of the dissociative adsorption of bromomethane was obtained. This contrasts with previous studies of the effects of halocarbons on oxidations over palladium at high temperatures, which established dissociative adsorption leading to poisoning by deposited carbon and inhibition by strongly adsorbed halogen atoms (*31–33*).

Catalyst Supports, Interactions with Water Vapor, and Reactivation Procedures

Palladium/zeolite catalysts were less active than palladium/thoria, but the kinetic results were consistent between both. However, the reduced inhibition by bromomethane of hydrogen oxidation over palladium/zeolite is modest in comparison with previous reports concerning other catalytic oxidations (*34–36*). Any potential advantage in practical applications is negated by the greater difficulty in restoring activity to palladium/zeolite catalysts after exposure to the inhibitor.

The presence of water vapor has physical effects on the supported catalyst as well as the chemical effects discussed above. Thus, the apparent reduction in diffusion-controlled rates (Fig. 6) was not shown in the corresponding experiments involving bromomethane (Fig. 7c). Therefore reversible uptake of water by the pellistor must have caused the factor f [Eq. (1)] to decrease. This factor represents the proportion of heat of the catalytic reaction retained by the pellistor, and would be affected by its heat capacity. A decrease of ca. 25% in f (Pd/ThO_2) points to the uptake of relatively large amounts of water, involving the alumina base from which the pellistor is formed.

This is supported by the differences between the reactivation procedures required by the static and flow systems. In the former, degassing by evacuation at room temperature removed small amounts of water, most of which was weakly adsorbed on PdO. As standard practice, pellistors were then heated in air to re-form (if necessary) the layer of PdO. Heating the pellistor while evacuating was counterproductive, because it led to migration of some of the adsorbed water to the alumina base. In experiments using the flow system, catalysts were heated in constant concentrations of hydrogen for considerable periods, leading to some uptake of water by the supporting materials. Evacuation between experiments was not practicable, and heating in a stream of dry air was much less effective for removing the larger amounts of adsorbed water. If the temperature of the pellistor was too high during reactivation, the adsorbed water was dispersed through the alumina base more rapidly than it was desorbed. Then the base acted as a reservoir for water competing with hydrogen for adsorption sites on PdO, so that activity was greatly reduced. "Drying out" was then extremely slow, with activity being restored only after several hours. The practical consequences of adsorption of water by Pd/Al_2O_3 catalysts used for eliminating hydrogen from confined atmospheres have been reported elsewhere (*18*).

ACKNOWLEDGMENTS

The authors are indebted to Dr. S. J. Gentry of the Health and Safety Executive, Sheffield, and Mr. E. Jones of the English Electric Valve Company, Chelmsford, for supplying the palladium/thoria pellistors. This work was carried out with the support of the Procurement Executive, U.K. Ministry of Defence.

REFERENCES

1. Acres, G. J., *Plat. Met. Rev.* **10,** 60 (1966).

2. Gentry, S. J., Firth, J. G., and Jones, A., *J. Chem. Soc. Faraday Trans. 1* **70,** 600 (1974).

3. Dannetun, H. M., Soderberg, D., Lundstrom, I., and Petersson, L. G., *Surf. Sci.* **152/153,** 559 (1985).

4. Gorodetskii, V. V., Sobyanin, V. A., Cholach, A. R., and Smirnov, M. Yu., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. III, p. 323. Verlag Chemie, Weinheim, 1984.

5. Petersson, L. G., Dannetun, H. M., and Lundstrom, I., *Surf. Sci.* **163,** 273 (1985).

6. Hanson, F. V., and Boudart, M., *J. Catal.* **53,** 56 (1978).

7. Lam, Y. L., Criado, J., and Boudart, M., *Nouv. J. Chim.* **1,** 461 (1977).

8. Engel, T., and Kuipers, H., *Surf. Sci.* **90,** 181 (1979).

9. Nyberg, C., and Tengstaal, C. G., *Chem. Phys.* **80,** 3463 (1984).

10. Leder, F., and Butt, J. B., *AIChE J.* **12,** 718 (1966).

11. Maymo, J. A., and Smith, J. M., *AIChE J.* **12,** 845 (1966).

12. Cullis, C. F., and Nevell, T. G., *Proc. R. Soc. London A* **349,** 523 (1976).

13. Baker, A. R., U.K. Patent 892,530 (1962).

14. Baker, A. R., and Firth, J. G., *Min. Eng.* **128,** 237 (1969).

15. Firth, J. G., *Trans. Faraday Soc.* **62,** 2556 (1966).

16. Firth, J. G., *Trans. Faraday Soc.* **67,** 212 (1971).

17. Firth, J. G., Gentry, S. J., and Jones, A., U.S. Patent 4,111,658 (1978).

18. Jones, M. G., and Nevell, T. G., *Sens. Actuators* **16,** 215 (1989).

19. Jones, A., Firth, J. G., and Jones, T. A., *J. Phys. E* **8,** 37 (1975).

20. Cullis, C. F., Nevell, T. G., and Trimm., D. L., *J. Phys. E* **6,** 384 (1973).
21. Baker, H. D., Ryder, E. A., and Baker, N. H., "Temperature Measurements in Engineering," Vol. 2. Wiley, New York, 1961.
22. Dabill, D. W., Gentry, S. J., Holland, H. B., and Jones, A., *J. Catal.* **53,** 164 (1978).
23. Firth, J. G., Gentry, S. J., and Jones, A., *J. Catal.* **34,** 159 (1974).
24. Satterfield, C. N., "Heterogeneous Catalysis in Practice," p. 318. McGraw–Hill, New York, 1980.
25. Engel, T., and Ertl, G., *Adv. Catal.* **28,** 2 (1979).
26. Aldag, A. W., and Schmidt, L. D., *J. Catal.* **22,** 260 (1971).
27. Lynch, J. F., and Flanagen, T. B., *J. Chem. Soc. Faraday Trans. 1* **70,** 814 (1974).
28. Benson, J. E., Hwang, H. S., and Boudart, M., *J. Catal.* **30,** 146 (1973).
29. Wicke, E., and Nernst, G. H., *Ber. Bunsenges. Phys. Chem.* **68,** 224 (1964).
30. Gentry, S. J., and Walsh, P. T., *Sens. Actuators* **5,** 239 (1984).
31. Anderson, J. R., and McConkey, B. H., *J. Catal.* **11,** 54 (1968).
32. Cullis, C. F., and Willatt, B. M., *J. Catal.* **86,** 187 (1984).
33. Hucknall, D. J., Willatt, B. M., and Hockham, R. J., *in* "Catalyst Deactivation" (B. Delmon and G. F. Froment, Eds.), p. 213. Elsevier, Amsterdam, 1980.
34. Firth, J. G., Jones, A., and Jones, T. A., *Ann. Occup. Hyg.* **15,** 321 (1972).
35. Firth, J. G., and Holland, H. B., *Nature (London)* **212,** 1036 (1966).
36. Firth, J. G., Gentry, S. J., and Jones, A., U.K. Patent 1,596,623 (1981).