Reaction of Hydrogen with Liquid Potassium

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A jet of clean potassium is continuously injected into hydrogen. A miniature electromagnetic pump is used to recirculate the molten metal. Rates of reaction of the gas with the metal surface over the pressure range 22·2—0·3 kN m^{-2} have been measured at temperatures between 210 and 333 °C. The reaction obeys first-order kinetics with an apparent activation energy of 66·5 kJ mol^{-1} which is slightly lower than that (72·4) for sodium. At the higher temperatures the process is complicated by the gradually increasing dissociation pressure of potassium hydride.

In the self-hydrogenation of alkynes and alkenes at liquid sodium surfaces, molecular hydrogen is also produced, the proportion of which increases with increasing temperature.[1,2] The rate at which this is subsequently converted into metal hydride is influenced by the nature of the hydrocarbon present. As a precursor to analogous reactions with potassium, the rate of absorption of hydrogen at a liquid potassium surface in the absence of hydrocarbon has been determined. The reaction is less well characterized than for sodium largely due to the difficulty in handling the metal, and to the less commercial exploitation of liquid potassium.

EXPERIMENTAL

Apparatus and Procedure.—The apparatus (Figure 1) was considerably modified from that previously used to study the reaction of hydrogen with liquid sodium.[3] In place of glass, steel (AlSl type 321) was used to construct a vessel capable of withstanding higher temperatures and the gas volume was increased to compensate for the faster reaction. An improved design of electromagnetic pump comprising a single duct but a more powerful magnet was employed, and the more bulky assembly was entirely enclosed in a capacious heated cabinet.

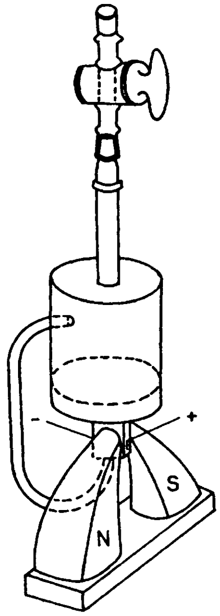

Figure 1 Apparatus

The majority of the liquid metal was contained in a cylindrical reservoir (100 mm long, 70 mm diam.). This was equipped with a steel neck and was connected through a glass-to-metal seal to a glass tap. A pump duct of rectangular cross section was welded to the base of the reservoir and connected by a C-shaped tube (7 mm diam.) to the upper half of the reservoir to make a loop. Silver electrical leads were silver soldered to the narrow faces of the pump duct.

The interior of the apparatus was cleaned and dried as before [4] and filled with potassium. The metal (Koch–Light 99·4%) was washed free of protecting oil with petrol which was subsequently distilled off. The surface impurity was cut off under argon in a glove box and ingots (30 × 2 g) melted and filtered at 65—68 °C through a sintered glass pad (porosity 3) into the reservoir. The apparatus was closed and mounted in a heated cabinet which could be controlled to $\pm\frac{1}{2}$ °C at 300 °C, with the neck protruding through a vent in the oven roof for attachment to a vacuum frame. A large permanent magnet (0·5 T) was positioned across the pump duct. In a typical experiment the reservoir was evacuated and heated. The metal melted (64 °C) and ran into the pump duct. On passage of a direct current (up to 50 A) through the duct at right angles to the magnetic field, the liquid metal conductor was drawn from the base of the reservoir and returned through the orifice at the top of the loop. This procedure produces a horizontal jet of clean liquid metal continuously which impinges on the opposite wall. The flowing liquid sweeps any solids to a small area at the side of the reservoir thus maintaining a clean surface of constant area. Hydrogen (Air products, 99·98%), purified as before,[3] was admitted to the required pressure. The absorption of gas by the potassium was then followed by the fall in pressure with time. Pressures inside the apparatus were measured by means of a capillary manometer. At the end of an experiment the reservoir was evacuated at 300 °C. The hydrogen removed in this way included unchanged gas and that which had accumulated as potassium hydride. At this temperature the dissociation pressure of potassium hydride is appreciable (1·0937 kN m^{-2}) [5] and pumping at 0·01 N m^{-2} rapidly removes hydrogen without excessive distillation of metal. The reaction was then repeated at different temperatures.

RESULTS AND DISCUSSION

The change in hydrogen pressure, expressed as ln$p$/N m^{-2}, with time, t/s, is shown in Figure 2 for seven

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[1] C. C. Addison, M. R. Hobdell, and R. J. Pulham, *J. Chem. Soc.* (*A*), 1971, 1704.

[2] C. C. Addison, M. R. Hobdell, and R. J. Pulham, *J. Chem. Soc.* (*A*), 1971, 1708.

[3] R. J. Pulham, *J. Chem. Soc.* (*A*), 1971, 1389.

[4] C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, *J. Chem. Soc.* (*A*), 1969, 1482.

[5] A. Herold, *Ann. Chim.*, 1951, **7**, 536.

temperatures. Some absorption isotherms have been transposed along the time axis for clarity. Starting pressures were all near 20 kN m^{-2}. The hydrogen reacts with the metal surface to produce solid potassium hydride. The solubility of the salt in the metal is so small that the liquid is instantly saturated on exposure to the gas at all temperatures. The amount of hydride produced in each experiment is also small. The rate of reaction increased with both increasing pressure and temperature. With this clean liquid-metal surface there was a linear relationship over all pressures between ln$p$ and t at 210, 240, 260, and 272 °C. This is typical of first-order kinetics. For the equilibrium (1) the

$$K + \tfrac{1}{2}H_2 \rightleftharpoons KH \qquad (1)$$

equilibrium hydrogen pressure does not rise above 0·305 kN m^{-2} at 272 °C. At this pressure the forward and backward rates are equal but at higher pressures the rate of hydride formation is much greater than its rate of dissociation. The straight lines at 210 to 272 °C in Figure 2, therefore, which were obtained between 22·144 and 0·573 kN m^{-2}, can be regarded as a true reflection of the rate of formation of potassium hydride.

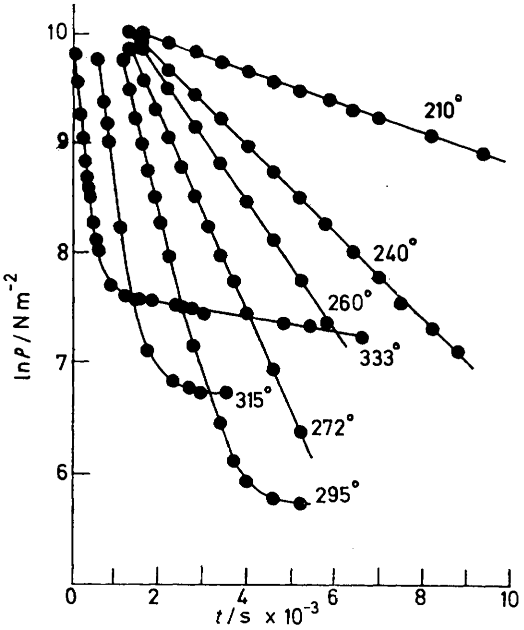

FIGURE 2 Absorption of hydrogen with time

At 295, 315, and 333 °C, the linear relationship was lost with increasing temperature at progressively shorter times. The pressure did not continue to fall but levelled off at 0·307, 0·840, and 1·360 kN m^{-2} respectively. These constant pressures were *lower*, however, than the equilibrium values which rise to 0·879, 2·056, and 4·216 kN m^{-2} at 295, 315, and 333 °C respectively.[5] At first sight this does not appear feasible but unless the system is completely isothermal, the pressure can drop to a pseudo-equilibrium value which, though constant, is lower than the isothermal value. This is attributed to co-condensation of hydrogen with metal vapour to form hydride on cool parts of the apparatus. This occurs at high temperatures where the vapour pressure of the metal becomes appreciable. In our experiments the cooler neck of the reservoir provided a region where a small loss of hydrogen could occur. For this reason, only the initial linear portions of the 295, 315, and 333° isotherms were used to determine rates. The approximate surface area (5740 mm^2) of metal exposed to the gas at any instant was calculated from the diameter and length of the liquid jet, from dimensions of the cascade and the diameter of the liquid pool below. Variations in pumping speed above a minimum value produce only a marginal increase in rates. The small amount of metal hydride produced is swept to the wall leaving fresh metal exposed to the gas.[3]

The slopes of the straight lines in Figure 2 provide a measure of the absolute rate constant, k [equation (2)],

$$k = \frac{dv}{dt} \cdot \frac{1}{s} \cdot \frac{1}{p} \qquad (2)$$

when pressures are converted into volumes; where dv/dt is the volume/mm^3 at s.t.p. of hydrogen absorbed per second under pressure p/kN m^{-2} at the metal surface of area s/mm^2. The rates, when expressed in this way, can be directly compared with those from other sources despite variations in experimental conditions. Values of the rate constant are given in the Table.

Reaction rates

t/°C	p/kN m^{-2}	$\frac{10^4k}{mm^3\,s^{-1}\,N^{-1}}$
210	22·145—7·199	2·511
240	20·132—1·200	6·846
260	22·224—1·560	10·15
272	19·052—0·573	15·64
295	17·158—0·307	28·36
315	17·438—0·840	49·95
333	18·065—1·360	71·81

Activation Energy.—The activation energy, E, for the reaction is derived from the temperature dependence of the rate according to equation (3) where C is assumed

$$\ln k = -\frac{E}{RT} + C \qquad (3)$$

to be constant. In Figure 3, ln$k$ is plotted against reciprocal absolute temperature to give a straight line with slope E/R. The value of the activation energy so obtained is 66·9 kJ mol^{-1}. This is slightly less than that, 72·4 kJ mol^{-1}, for sodium.[3] Rates of reaction of hydrogen with static potassium have been determined previously by Herold[5] at lower temperatures (69·6—127·0 °C) and at higher pressures (44 kN m^{-2}). We have calculated a value of 52·3 kJ mol^{-1} for the activation energy from these rates. This is substantially lower than our value. Although the conditions were dissimilar in most respects, the static metal surface, however, was not completely covered with hydride film and allowance was made for the diminishing area (known to within ±25%) of free metal surface as the reaction progressed.

Potassium reacts with hydrogen nearly four times more rapidly than does sodium. At 250 °C for example, the values of k are $8{\cdot}749 \times 10^{-4}$ and $2{\cdot}383$ $\text{mm}^3\ \text{s}^{-1}\ \text{N}^{-1}$ for potassium and sodium[3] respectively. This is a significant difference. Data for these metals are strictly comparable since these were obtained under very similar conditions. The order of rates is consistent with a general trend reported by Herold,[5] which, under his experimental conditions, decreased in the order Cs > Rb > K > Na.

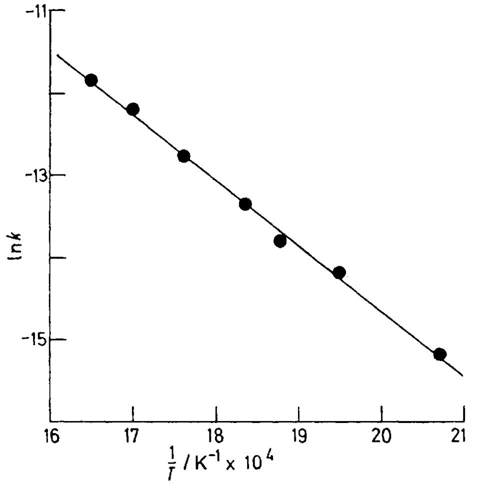

FIGURE 3 The effect of temperature on the rate of reaction

In view of the chemical similarity between potassium and sodium, and that there is not a large disparity between the activation energies, it is reasonable to assume that the rate-determining step in the reaction with hydrogen is the same for both metals. This may be the electron transfer from the metal to adsorbed hydrogen atoms. The free energy of formation[6] of the metal hydride and hence the driving force of the reaction is not widely different for KH (−104·9) and NaH (−101·4 kJ mol^{-1}) and is not expected to greatly influence the kinetics. Similarly the dissociative adsorption of hydrogen is usually fast and non-activated on most clean metal surfaces.[7] A slower process, however, may be electron transfer from metal to adsorbed hydrogen atom. The conversion of the gaseous hydrogen molecule into crystalline potassium hydride [equation (1)] must involve at some stage dissociation into atoms and the formation of hydride anions. Dissociation and ionization may occur stepwise [equations (4) and (5)]. Adsorbed hydride ions

$$H_{2(g)} \longrightarrow H_{(ads)} + H_{(ads)} \qquad (4)$$

$$H_{(ads)} + e \longrightarrow H^-_{(ads)} \qquad (5)$$

then either dissolve in the metal or, if the potassium is saturated as in the present case, potassium hydride crystals nucleate and grow at the potassium surface. On a homogeneous transition-metal surface, a dissociative reaction, where atoms are produced and subsequently released, often leads to half-order kinetics.[8] With the alkali metals, however, atomization is only part way toward the formation of the anion and half-order kinetics need not be expected.

Both the absorption by, and the desorption of hydrogen from, liquid potassium–sodium eutectic are reported as kinetically first-order processes.[9] Molecular desorption by recombination of two adatoms might be expected to be second-order in adsorbed hydrogen[8] [*i.e.* the reverse of equation (4)]. It seems possible, therefore, that the rate-controlling step for desorption also might be electron transfer, the reverse of equation (5).

It appears probable that the relative strength of the hydrogen adsorption is largely responsible for the different rates. The more strongly the atom is adsorbed the easier becomes the ultimate electron transfer. This demands that hydrogen is more strongly adsorbed on potassium than on sodium and probably even more strongly adsorbed on rubidium and caesium. In the absence of appropriate adsorption data for hydrogen on these metals this is not readily verified. The reaction with hydrogen is not an isolated example of potassium reacting more rapidly than sodium but fits in with the general trend of increasing chemical reactivity with atomic number within the group.

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[6] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, 'Selected Values of Chemical Thermodynamic Properties,' Natl. Bur. Std. Circ. 500, 1952.

[7] D. O. Hayward and B. M. W. Trapnell, 'Chemisorption,' p. 75, Butterworths, London, 1964.

[8] D. Brennan, *Adv. Catalysis*, 1964, **15**, 1.

[9] M. N. Arnol'dov, M. N. Ivanovski, V. A. Morozov, S. S. Pletenets, and V. I. Subbotin, *Atomnaya Energiya*, 1970, **28**, 18.