Rate of Reaction of Hydrogen with Liquid Lithium: Comparison with Sodium and Potassium

By **Graham Parry** and **Richard J. Pulham,*** Chemistry Department, University of Nottingham, Nottingham NG7 2RD

Rates of reaction of hydrogen with a clean liquid-lithium surface have been determined at 217, 244, 257, 270, and 295 °C at pressures up to 23.7 kN m^{-2}. The rates range from 4.683×10^6 to 27.919×10^6 mm s^{-1} (kN $m^{-2})^{-1}$ at 217 and 295 °C respectively. The reaction is first order with an activation energy of 52.8 kJ mol^{-1} which is lower than that for potassium (66.5 kJ mol^{-1}) and sodium (72.4 kJ mol^{-1}). Liquid lithium reacts more rapidly than do these metals; the rates at 250 °C for Li, K, and Na are in the nearest whole number ratio of 43 : 4 : 1. The results are consistent with a report that small additions of lithium to sodium enhance the rate of hydrogen absorption.

THE liquid alkali metals, M(l), are known to react with hydrogen to form the simple hydrides, MH(s), at the surface according to equation (1). The rate of reaction is

$$M(l) + \tfrac{1}{2}H_2(g) \longrightarrow MH(s) \qquad (1)$$

sufficiently slow at temperatures immediately above the m.p. of the metal that the decrease in hydrogen pressure can be followed manometrically. The solubility of the metal hydride is probably no more than 0.05 mol % at 200 °C, however, so that solid hydride collects at the surface and an efficient method of exposing fresh metal surface is necessary to allow continuous reaction. With increasing temperature the dissociation pressure of the hydride becomes appreciable and restricts low-pressure kinetic measurements.[1] In some respects, lithium presents fewer practical problems than the other alkali metals. Although the liquid metal cannot be handled in glass it is less susceptible to atmospheric contamination. Also lithium hydride exerts a lower vapour pressure of hydrogen [2] than the other alkali-metal hydrides so that interference with the kinetics of hydride formation is least with lithium. The relatively low vapour pressure [3] of the metal is also an advantage since co-condensation of metal vapour with hydrogen to form hydride on cool parts of the apparatus is minimized.

---

[1] G. Parry and R. J. Pulham, *J.C.S. Dalton*, 1975, 446.

[2] W. M. Mueller, J. P. Blackledge, and G. G. Libowitz, *Metal Hydrides*, Academic Press, London, p. 165, 1968.

[3] 'Liquid Metals Handbook,' 2nd edn., NAVEXOS-P733, U.S. Government Printing Office, Washington, 1952, p. 40.

This article describes the rate of absorption of hydrogen by liquid lithium under conditions previously employed for liquid sodium [4] and potassium.[1] The reaction with lithium, like Na and K, is first order but proceeds more rapidly and with the lowest activation energy.

EXPERIMENTAL

The steel apparatus and method of injecting a jet of liquid metal into hydrogen by means of a miniature electromagnetic pump were as described previously.[1] The reaction vessel was charged with solid pieces (20 × 0.5 g) of lithium (Koch-Light, 99.98%) under pure argon and mounted in an air oven. Connection to a vacuum frame was made through an aperture in the oven roof. The temperature was raised to 400 °C to melt the lithium (m.p. 180.50 °C) and wet the internal surfaces of the steel. This enabled the electromagnetic pump to efficiently draw liquid from the bulk and return it through a nozzle into the gas above. The argon was removed and replaced with a known pressure of hydrogen (Air Products, 99.98%) which had been purified as before.[4] The decrease in pressure was followed manometrically as a function of time at selected constant temperatures. Starting pressures were all near 23.7 kN m^{-2} at temperatures of 217, 244, 257, 270, and 295 °C.

RESULTS AND DISCUSSION

Effect of Pressure.—The pressure of hydrogen fell smoothly with time at all temperatures. This feature is shown in Figure 1 where ln (P/kN m^{-2}) is plotted as a function of t/s. A linear relation was obtained at all pressures and temperatures which is expected for first-order kinetics according to equation (2) where k_p is the

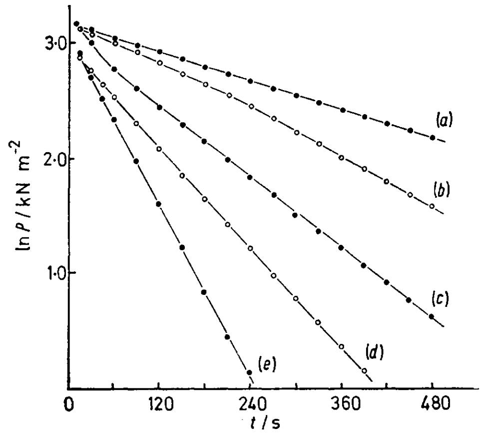

FIGURE 1 Effect of temperature on the absorption of hydrogen by liquid lithium at 217 (*a*), 244 (*b*), 257 (*c*), 270 (*d*), and 295 °C (*e*)

$$-\mathrm{d}P/\mathrm{d}t = k_pP \quad \text{or} \quad \ln P = -k_pt + \ln P_0 \quad (2)$$

rate constant. There was no levelling of pressure at the higher temperatures as seen with potassium where the higher dissociation pressure of the hydride interfered with the kinetics.[1]

Effect of Temperature: the Activation Energy.—As expected the rate of reaction increased with increasing temperature. A linear relation was observed between ln k_p and reciprocal absolute temperature and under these circumstances the activation energy, $E^‡$, for the process is provided by the gradient since $\ln k_p = -(E^‡/RT) + \ln A$. The activation energy so derived is 52.8 kJ mol^{-1}. There is no other value reported.

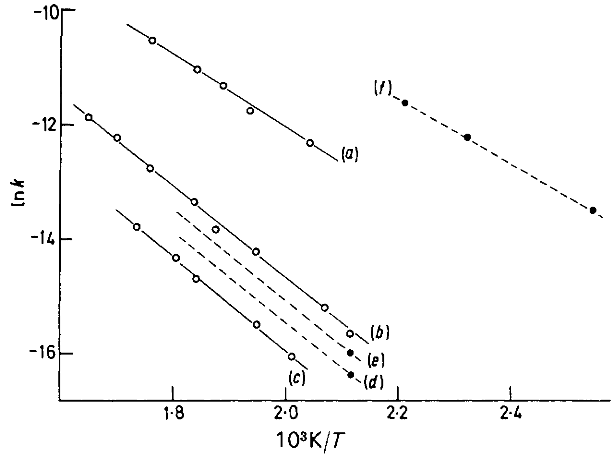

FIGURE 2 Comparison of the rate of hydrogen absorption by liquid alkali metals and their solutions over the respective temperature ranges: (*a*), Li, this work; (*b*), K;[1] (*c*), Na;[4] (*d*) and (*e*), Na (1.1 and 5.0 mol % Li respectively);[5] (*f*), Na (5.0 mol % Ba)[5]

Absolute Rate Constant.—The rates cannot be adequately compared with others which may subsequently be obtained for lithium or for other metals unless normalized to unit surface area of liquid metal. The area in the present experiments included the jet, cascade, and pool below and was estimated from the geometry of the apparatus to be 1 150 mm^2. Using this value and by converting pressures to volumes, the absolute rate constant, k, was determined from equation (3) where dv/dt

$$k = (\mathrm{d}v/\mathrm{d}t)(S^{-1})(P^{-1}) \qquad (3)$$

is the volume/mm^3 at standard temperature and pressure (s.t.p.) of hydrogen absorbed per second under pressure P/kN m^{-2} at the metal surface of area S/mm^2. Values of k are given in Table 1 with the appropriate pressure range and temperature.

TABLE 1

Rate constants, k

θ_c/°C	Pressure range/ kN m^{-2}	10^6k/mm s^{-1} (kN m^{-2})$^{-1}$
217	23.7–8.9	4.683
244	23.5–4.9	8.030
257	23.1–1.9	12.488
270	17.8–1.2	16.400
295	18.5–1.2	27.919

Comparison with Sodium and Potassium.—The variation in k (as ln k) over the respective temperature (as reciprocal absolute temperature) ranges is shown for all three metals in Figure 2 as full lines. Lithium reacts much faster than Na and K; the rate constant diminishes in the order Li $\gg$ K $>$ Na. Included in the Figure are values [5] for a solution of barium (5.0 mol %) and for two

---

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

[5] M. R. Hobdell and A. C. Whittingham, 'Liquid Alkali Metals,' *Proc. Internat. Conf. BNES*, Nottingham, April 4—6, 1973, p. 5

solutions of lithium (1.1 and 5.0 mol %) in sodium. These are shown as broken lines; for lithium solutions the lines were derived from single values at 200 °C and the quoted mean activation energy for concentrations up to 8.6 mol % Li. As is expected from the present lithium work, addition of lithium progressively increases the rate; the effect is appreciable for an addition of only 1.1 mol %. Solutions of barium have not been studied over the same temperature range but if the data are extrapolated then clearly addition of Ba to Na would also increase the rate and to a much greater extent than does lithium. These features are shown quantitatively in Table 2 at 250 °C, a temperature near the midpoint (except for Ba) of the ranges covered, together with corresponding activation energies since these are not readily derived from the gradients in Figure 2. Of the pure metals, lithium reacts with hydrogen at this temperature more than 10 and 40 times faster than K and Na respectively. The activation energy of the rate-determining step decreases for the pure metals, and also for the sodium solutions, as the rate increases. The slowest step has been assigned to electron transfer from metal to adsorbed hydrogen atoms.[1] The present work does not alter this view. The trend in activation energy, however, suggests that this is becoming easier progressing from Na to K to Li. This is not the order of ionization energies of the metals and, therefore, as suggested previously,[1] the relative strength of the hydrogen adsorption may be significant. Strong adsorption would be necessary on lithium since the more strongly the hydrogen atom is adsorbed the easier becomes the ultimate electron transfer with consequent decrease in activation energy.

TABLE 2

Activation energies, $E^{\ddagger}$

Metal	$E^{\ddagger}$/kJ mol^{-1}	k (at 250 °C)/mm s^{-1} (kN m^{-2})$^{-1}$
Na	72.4	2.505×10^{-7}
Na–Li (5.0%)	(64.1)	5.860×10^{-7}
K	66.5	9.010×10^{-7}
Li	52.8	1.065×10^{-5}
Na–Ba (5.0%)	45.0	4.821×10^{-5}

We thank the S.R.C. for the award of a maintenance grant (to G. P.).

[4/2525 *Received, 5th December*, 1974]