Reaction of Hydrogen with Solutions of Metals in Liquid Sodium

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The reaction rate of hydrogen with solutions of lithium (0—8.6), barium (0—6.1), strontium (0—4.0), and mercury (0—50 atom %) in liquid sodium is directly proportional to hydrogen pressure (0—35 kN m^{-2}) in the temperature range 390—565 K under conditions that solution composition and liquid-metal surface area remain effectively constant throughout reaction. Hydrogen reacts more rapidly with solutions containing respectively Li, Sr, and Ba than with pure Na; the reaction with Na–Hg solutions, however, is less rapid. The observed changes in the absolute rate constants, k_a, with solute metal concentration cannot be accounted for solely on the basis of measured activation-energy changes; the pre-exponential factor varies with both the solute metal and its concentration. The results are discussed with reference to possible changes in the energy profiles of conduction-band electrons in the liquid-sodium solutions.

THIS paper is concerned with the reaction of hydrogen with various liquid alloys of sodium in the temperature range 390—565 K. Previous work[1] has shown that barium dissolved in sodium enhances the reactivity of the liquid metal towards hydrogen, and a more detailed study of this effect has been conducted. The effects of dissolved lithium, strontium, and mercury have also been investigated; these metals, like barium, have conveniently measurable solubilities at the temperatures involved. Hydrogen reaction rates have been measured as a function of alloy composition, temperature, and pressure (0—35 kN m^{-2}).

EXPERIMENTAL

The technique employed was to measure the rate of hydrogen uptake at constant volume (*ca.* 1.5×10^5 mm^3) by a large excess (*ca.* 4×10^4 mm^3) of vigorously stirred liquid metal. Apparatus similar to that previously described[2] was used and a detailed description is given elsewhere.[3,4] Stainless-steel reaction vessels were used for experiments involving lithium, while Pyrex glass was used to contain all other metal solutions.

Sodium (B.D.H., 99.8%) was filtered through a porosity 3 Pyrex sinter at 385 K under argon (itself purified by bubbling through liquid sodium) directly into the reaction vessels; this procedure typically gave liquid sodium containing <10 p.p.m. oxygen. The metals barium, lithium, and strontium (Koch-Light, 99.5%) were filed clean in a glove-box filled with argon (purified by passage through a column (2 m long × 50 mm diameter) of Linde molecular sieve (type 4A) before addition to the sodium. Sodium–mercury solutions were prepared by careful addition of distilled mercury to filtered sodium in the glove-box, followed

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[1] M. R. Hobdell and L. Newman, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1843.

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

[3] H. E. Evans and A. C. Whittingham, *J. Brit. Nuclear Energy Soc.*, 1971, **10**, 334.

[4] A. C. Whittingham and M. R. Hobdell, CEGB Report RD/B/N2548, 1973.

by filtration into the reaction vessels. Each metal solution was used for one experiment only, to avoid cumulative errors in estimating accurately metal solution composition.

The reaction vessels containing the metal solutions under purified argon were maintained at the desired temperature by means of a stirred silicone oil-bath. Prior to an experiment, the reaction vessel was evacuated and then hydrogen at a predetermined pressure introduced. Pressure (± 1 N m^{-2}) was measured as a function of time by means of mercury and capacitance manometers.[3] Two electromagnetic methods for stirring the liquid metal were employed; in one, specially wound coils, equivalent to the stator of a two-pole three-phase induction motor, were positioned around the oil-bath,[5] in the other method (used for experiments involving sodium-strontium alloys) the molten metal was circulated by a miniature electromagnetic pump, as described by Pulham.[6] The volumes of the reaction vessels were accurately determined by calibration with argon, although the surface area of the metal solutions (1.8×10^3—2.5×10^3 mm^2) could only be ' geometrically ' estimated in the stirred systems studied.

RESULTS

Effect of Pressure.—The reaction rate of hydrogen with pure sodium and the Na–Li, Na–Ba, Na–Sr, and Na–Hg solutions was found to be directly proportional to hydrogen pressure in the range 0—35 kN m^{-2}; the reaction rate was given by equation (1) where P is the pressure at time t and

$$-\mathrm{d}P/\mathrm{d}t = k_1P \qquad (1)$$

k_1 the first-order rate constant. Since reaction vessels of different internal volumes were used, reaction rates can only be compared by quoting results in terms of the absolute rate constant, k_a, defined in (2) where V (mm^3) is the gas volume and S (mm^2) the metal surface area. The units for k_a are mm^3 (at n.t.p.) mm^{-2} (alloy surface) (kN)$^{-1}$ m^2 s^{-1}.

$$k_a = k_1(V/S)(273/T)(10.13)^{-1} \qquad (2)$$

From equation (1) we obtain (3). Plots of $\log_{10} P$ against

$$\log_{10} P = \text{constant} - (k_1t/2.303) \qquad (3)$$

time t for the reaction of hydrogen with a Na–Ba (5 atom %) solution are shown in Figure 1, and the linearity typifies the results obtained in all cases. Respective values of k_1 were obtained from the gradients of such plots corresponding to solutions with Li, Sr, and Ba concentrations within the range 0—10 atom % and Hg concentrations 0—50 atom %. Values of the absolute rate constant, k_a, were calculated using equation (2).

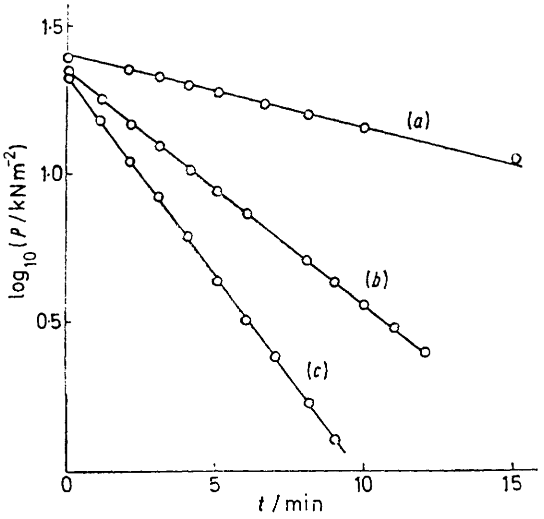

FIGURE 1 Variation of hydrogen pressure with time for reaction with Na–Ba (5 atom %) solution at 393 (*a*), 431 (*b*), and 453 K

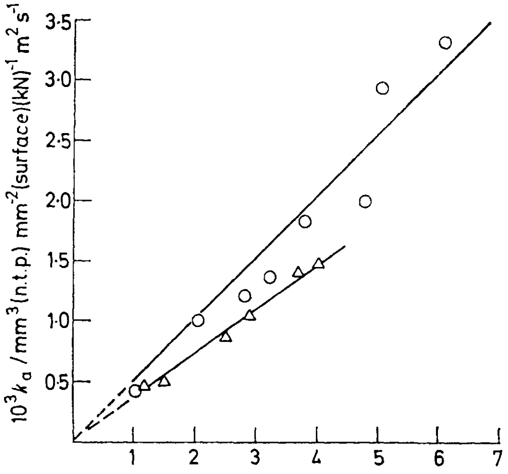

FIGURE 2 Rate constant, k_a, as a function of metal solution composition at 473 K for Na–Ba (○) and Na–Sr solutions (△)

Effect of Solute Metal Concentration.—In Figures 2 and 3, the variation of k_a with metal solution composition at 473 K is shown. Comparison of the k_a values shows that the rate increase per unit solute concentration relative to pure sodium is in the order Na < Na–Li < Na–Sr < Na–Ba. Sodium–mercury solutions, however, were less reactive than sodium

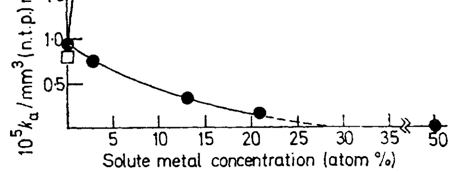

FIGURE 3 Rate constant, k_a, as a function of metal solution composition at 473 K for Na–Li (□) and Na–Hg solutions (●)

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[5] D. J. Hayes, M. R. Baum, and M. R. Hobdell, *J. Brit. Nuclear Energy Soc.*, 1971, **10**, 93.

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

alone, and no reaction could be detected (either by pressure change or by visual examination of the alloy surface) for a solution containing 50 atom % mercury at temperatures in the range 470—550 K. Interestingly, dilute solutions (0.7 and 1.0 atom %) of barium in *mercury* also showed no reactivity towards hydrogen at 473 K.

Effect of Temperature.—The rate constant is empirically related to the temperature by the Arrhenius expression (4)

$$k_a = A \exp\,(-E^{\ddagger}/RT) \qquad (4)$$

where A is the pre-exponential factor, R the gas constant, and $E^{\ddagger}$ the activation energy. From (4), equation (5)

$$\log k_a = \log_{10} A - (E/19.2T) \qquad (5)$$

follows where $E^{\ddagger}$ is in kJ mol^{-1}. Values of the activation energy of the rate-determining step were obtained from gradients of linear plots of $\log_{10} k_a$ against $1/T$ by least-squares analysis. In Figure 4, activation-energy values obtained from such plots in the temperature range 390—565 K for the reaction of hydrogen with pure sodium and the Na—Li, Na—Sr, Na—Ba, and Na—Hg solutions are presented.

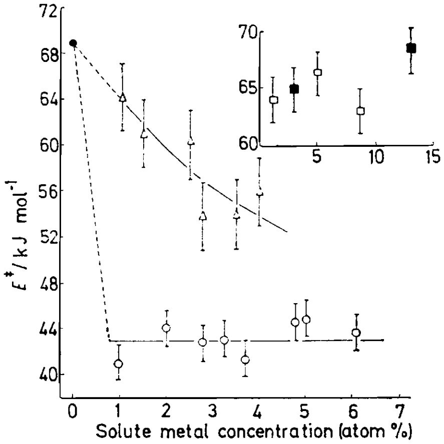

FIGURE 4 Measured activation energies, $E^{\ddagger}$, as a function of metal solution composition: (●), Na (see text); (□), Na–Li; (△), Na–Sr; (○), Na–Ba; (■), Na–Hg

Initial experiments were conducted to determine the activation energy for the reaction of hydrogen with pure sodium alone in order to resolve the discrepancies reported in the literature.[6] Values of 71.7 ± 3.0, 65.0 ± 4.0, and 70.1 ± 7.0 kJ mol^{-1} were obtained from experiments in Pyrex glass vessels and Pyrex glass vessels containing a stainless-steel (type 316) liner. These results give a mean value of 69 ± 8 kJ mol^{-1} for the activation energy of reaction; this is in close agreement with the value of 72.4 kJ mol^{-1} recently obtained.[6]

Strontium and barium were both found to reduce the activation energy for reaction, but this effect was more pronounced in the case of Ba; a sharp decrease in activation energy occurred between pure sodium and solutions containing 1 atom % Ba, but thereafter, for solutions containing 1—6 atom % Ba, the activation energy remained effectively constant at 43.1 ± 5 kJ mol^{-1}. The presence of lithium or mercury did not significantly (*i.e.* within experimental error) alter the activation energy of the reaction from that of pure sodium.

DISCUSSION

The Rate-determining Step.—Hydrogen interacts with the alkali and alkaline-earth metals to produce both metal–hydrogen solutions and metal hydrides. Dissolved hydrogen exists monatomically [7] in liquid sodium and the hydrides of the metals contain discrete H^- ions; dissociation of molecular hydrogen thus occurs during the reactions studied.

The observation of a first-order reaction with respect to hydrogen pressure implies that the hydrogen molecule is directly involved in the rate-determining step, and it is suggested that this is the 'weak' activated adsorption, with dissociation, of hydrogen at the liquid metal surface [equation (6)]. This rate-determining step precedes

$$H_2\,(g) \longrightarrow 2H \text{ (weakly adsorbed)} \qquad (6)$$

hydrogen solution and hydride formation, and the observed kinetics are independent of the final chemical state of hydrogen ('strong' adsorption would lead to zero- rather than first-order kinetics). A reaction with a rate-determining step involving the reaction of adsorbed or dissolved *monatomic* hydrogen (in equilibrium with molecular hydrogen) would exhibit half-order kinetics. The measured kinetic parameters are thus considered to correspond to the process of adsorption with dissociation.

The persistence of first-order behaviour within a particular experiment demonstrates that both the reactive surface area and the solution composition remained effectively constant. The final reaction product with each alloy depends on the relative stabilities of the hydride of sodium and the solute metal; thus *X*-ray diffraction analysis [8] showed that BaH_2 was produced in the case of Na–Ba solutions, whereas NaH was the sole product with Na–Hg solutions.

Effect of Solute Metals.—Inspection of the respective absolute rate constants with reference to equation (5) shows that in the case of the sodium–lithium and –strontium solutions studied the observed variations in reactivity can be accounted for on the basis of measured activation energies within experimental error. This is not the case for sodium–mercury and –barium solutions, and significant changes in the pre-exponential factor, A, are involved. (There is evidence from surface-tension measurements that Na–Ba solutions exhibit a surface excess of barium for concentrations up to 4.8 atom %;[9] surface Ba concentrations, however, would be expected to vary non-linearly with bulk concentration and thus the observed values of k_a and $E^{\ddagger}$ are not readily rationalised on this basis.)

From kinetic theory, the rate constant for adsorption

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[7] R. J. Pulham and P. A. Simm, 'Liquid Alkali Metals,' *Proc. BNES Conf.*, Nottingham, April 1973.

[8] A. J. Hooper, personal communication.

[9] C. C. Addison, J. M. Coldrey, and W. D. Halstead, *J. Chem. Soc.*, 1962, 3868.

can be written as in (7) where θ is the degree of surface

$$k_a = K(1 - \theta)\alpha \exp(-E^{\ddagger}/RT) \qquad (7)$$

coverage ($\ll 1$ for first-order kinetics), K is a constant, and α the 'sticking probability' or 'adsorption coefficient.' Thus, changes in the pre-exponential factor can be qualitatively discussed in terms of changes in α; these will be related to changes in the electronic energy profile of the metal.

Electronic Effects.—The chemisorption of hydrogen at the surface of the electropositive metal solutions studied will presumably involve formation of liquid-metal surface–hydrogen bonds with a net electron transfer to hydrogen [equation (8)]. The observed changes in

$$H_2\text{ (g)} + 2e^- \text{ (from liquid-metal conduction band)} \longrightarrow 2H^- \text{ (adsorbed)} \qquad (8)$$

reaction rate with solute metal and its concentration could thus reflect changes in the electron-energy profile of the metal conduction band, which could affect the nature of surface bonds and hence adsorption coefficients. A similar approach has been adopted by other workers to explain the enhanced reactivity of liquid-sodium solutions containing dissolved Li,[10] Ba,[11,12] and K [13] towards other gases, N_2,[10,11] C_2H_2,[12,13] and C_2H_4.[12,13]

It is possible to relate the hydrogen reaction rate more closely to the electron-energy profile of the metal. The pre-exponential factor, A, given by equation (9) is

$$A = K(1 - \theta)\alpha \qquad (9)$$

associated with an entropy of activation, $\Delta S^{\ddagger}$, according to the transition-state theory [14] of reaction kinetics by relation (10). Wise [15] suggested that, for processes at

$$\Delta S^{\ddagger} = R \ln A \qquad (10)$$

solid metal surfaces involving electron transfer, the entropy of activation is related to the gradient of the density of states curve at the Fermi level by equation (11), where $\boldsymbol{k}$ is Boltzmann's constant and $n(E)$ the

$$\Delta S^{\ddagger} = \frac{1}{3}\pi^2 \boldsymbol{k}^2 T \left(\frac{\mathrm{d}\ln n(E)}{\mathrm{d}E}\right)_{E=E_F} \qquad (11)$$

density of electronic states at the Fermi level, E_F. The implication is thus that modifications in the function $[\mathrm{d}\ln n(E)/\mathrm{d}E]_{E=E_F}$ could alter A and hence reaction rates, even for the relatively dilute solutions studied here.

The inference is that, at the concentrations studied, there is little change in this function for lithium and strontium where changes in k_a can be accounted for by small changes in E (within experimental error) and a gradual decrease with increasing mercury concentration. For the sodium–barium solutions there is a sharp decrease in this function (0—1.0 atom % Ba) followed by a gradual increase as the reaction rate constant increases at constant activation energy.

Interestingly, there is no comprehensive correlation between liquid-metal reactivity (as measured by k_a) and the work functions of the metals involved. Sodium (220) and barium (230 kJ) have comparable work functions, whereas strontium (267), lithium (300), and mercury (437 kJ) have higher values than sodium. Nonetheless, a low value of the work function, which would facilitate electron transfer to hydrogen, is expected to be a necessary, if not sufficient, condition for enhanced reactivity.

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[10] C. C. Addison and B. M. Davies, *J. Chem. Soc.* (*A*), 1969, 1827.

[11] C. C. Addison, B. M. Davies, R. J. Pulham, and D. P. Wallace, 'The Alkali Metals,' *Chem. Soc. Special Publ.*, no. 22, 1967, p. 290.

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

[13] C. C. Addison, M. R. Hobdell, G. Parry, and R. J. Pulham, 'Liquid Alkali Metals,' *Proc. BNES Conf.*, Nottingham, April 1973, p. 13.

[14] S. Glasstone, K. J. Laidler, and H. Eyring, 'The Theory of Rate Processes,' McGraw-Hill, New York, 1941.

[15] H. Wise, *J. Catalysis*, 1968, **10**, 69.