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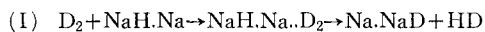
By

M. J. CHAPPELL, D. D. ELEY*¹⁾ and D. SHOOTER

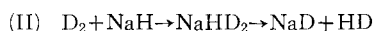
(Received August 6, 1980)

Abstract

The reactions $\text{H}_2 + \text{D}_2 \rightarrow 2\text{HD}$, $p\text{-H}_2 \rightarrow n\text{-H}_2$ and $o\text{-D}_2 \rightarrow n\text{-D}_2$ have been studied on sodium films, under conditions where there is a simultaneous formation of NaH, the stable phase under the reaction conditions. The Arrhenius graph has (I) a lower temperature line with activation energy $E \approx 0\text{--}13 \text{ kJ mole}^{-1}$, intersecting (II) a higher temperature line with $E \approx 40\text{--}60 \text{ kJ mole}^{-1}$. It is postulated that the dominant mechanism in (I) involves a metal plus metal hydride site



while the higher activation energy mechanism in II involves hydride sites only, and a triatomic single-site complex



Inactivation by heating in H_2 , activation by O_2 pretreatment, and anomalous pressure dependency effects are all explicable by the interplay of these two mechanisms.

Introduction

Sodium has been little studied as a heterogeneous catalyst. Apparently it shows no hydrogenation of ethylene below 300°C ,¹⁾ and Na/K alloy is equally inactive,²⁾ whereas Ca and CaH_2 are both catalysts for this reaction²⁾ and Cs shows a transient catalysis,¹⁾ at room temperature. Here we present our results for the spin isomerisation and isotope equilibration reactions of hydrogen and deuterium on evaporated films of sodium. The temperature range from 298 to 444 K necessarily passes through the melting point of sodium of 371 K. However, our working hydrogen pressure of *ca.* 1 torr is the dissociation pressure of the Na/NaH at 523 K,³⁾ and greatly exceeds it for the temperature range of these experiments. Accordingly, our catalytic film after its first initial exposure to hydrogen gas may be regarded as covered by a film of NaH, an ionic hydride with the rocksalt structure and a lattice constant of 0.488 nm.⁴⁾

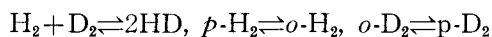
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Experimental

A earlier group of experiments were made with the high vacuum apparatus of Eley and Shooter.⁵⁾ The results obtained are very similar to the later results obtained in the ultrahigh vacuum apparatus⁶⁾ outlined in Fig. 1. The reaction space in the UHV equipment could be baked to 400°C; cooled, and with the trap at 77 K it gave 5×10^{-10} torr (1 torr = 133.3 Pa). Highly purified sodium was distilled several times, and finally to give a continuous film over the walls of the spherical reactor vessel, 9.0 cm diameter. $p\text{H}_2$ and $o\text{D}_2$ analyses were made with a micro-pirani gauge.⁷⁾ Samples for HD analysis were taken *via* a metrosil leak located near the centre of the reaction vessel to the head of an MS 10 mass spectrometer. This sampling technique gave good first order concentration-time curves. All hydrogens used were purified by passage through a Pd-Ag thimble.

The three reactions separately examined were



If x_0 , x_t and x_{eq} represent the fractions of HD (mass 3), $p\text{-H}_2$, or $o\text{-D}_2$, at times 0, t , and at equilibrium, all results obeyed the first-order time law with constants

$$k_e = \frac{1}{t} \ln \frac{x_0 - x_{\text{eq}}}{x_t - x_{\text{eq}}}, \quad \text{min}^{-1}$$

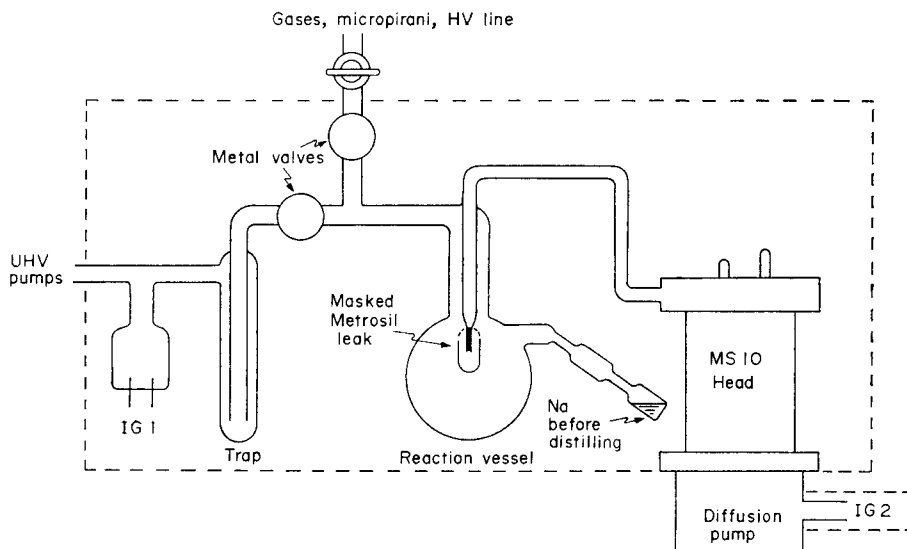


Fig. 1. The UHV reaction volume. I.G. denotes a Bayard-Alpert ion gauge. The dotted line denotes the furnace used for bakeout at 400°C.

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If n is number of molecules in the reaction volume V , and A the catalyst area, here taken as the geometric area, the absolute rate

$$k_m = k_e n/60A = k_e Vp/60AkT \text{ molecules m}^{-2}\text{s}^{-1}$$

Effects of temperature T and pressure p are described by

$$k_m = B_m \exp\left(-\frac{E}{RT}\right) \text{ and } k_m = k_m^\circ p^n$$

Results and Discussion

The Films

Two Na films were examined in the preliminary HV work, and five in the UHV studies presented here.* The average 298 K reaction volume was $469 \times 10^{-6} \text{ m}^3$, and film area 0.0216 m^2 . The pressure during film lay down was $\leq 10^{-7}$ torr, and the initial film was purple in colour but thickened to give an even film with a bright metallic lustre, with little tendency to globule formation. The surface area was taken on the geometric area, which should be a reasonable estimate for Na, with its low m. p. of 98°C .

Hydrogen Absorption

Contacting a fresh Na film with hydrogen resulted in an immediate absorption of gas to an apparent saturation value after about 15 minutes exposure. From Fig. 2. we see this saturation value tended to increase with temperature, runs 1, 2, & 3, but successive runs at a given temperature showed decreasing amounts of adsorbed hydrogen, unless the film was given a prolonged pumping between absorption runs. This behaviour can be reconciled with formation of a surface film of NaH of varying thickness. Run 6 appears to show a "breakaway phenomenon" such as might occur due to cracking a protective hydride film when it has reached a certain thickness and degree of strain.

The numbers of molecules of hydrogen taken up per m^2 after 15 minutes on each of the successive six runs of Fig. 2. are 1) 1.42×10^{20} 2) 4.55×10^{20} 3) 5.98×10^{20} 4) 3.53×10^{20} 5) 6.47×10^{19} and 6) 2.19×10^{20} . We can calculate that the 100 surface of an NaH crystal would have 8.4×10^{18} Na^+ sites per m^2 and 8.4×10^{18} H^- sites per m^2 . Therefore run 1) above would correspond to 33.8 monolayers of H atoms adsorbed on either Na^+ or H^- sites, which clearly points to formation of bulk hydride. Assuming that the film concerned, geometric area 0.022 m^2 , had a weight of 10 mg., then the

*) HV denotes high vacuum, UHV ultrahigh vacuum in what follows.

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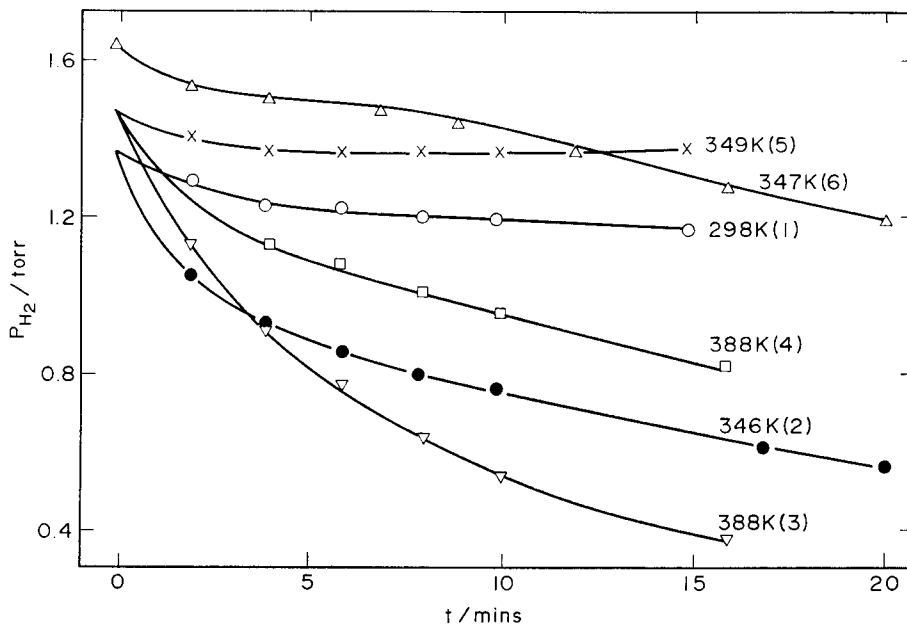


Fig. 2. Hydrogen uptake by Na film (B). The experiments were in the order of the numbers in brackets.

gas uptake of expt. 1) would correspond to 2.38% of NaH, presumably concentrated on the surface of the film.

Parahydrogen Conversion at 77 K

This was examined on Na Film C ($A=0.0212 \text{ m}^2$, V at 298 K $=493 \times 10^{-6} \text{ m}^3$). It was found that at 1.05 torr and 299 K, $k_o=1.73 \times 10^{-4} \text{ min}^{-1}$, hence $k_m=2.28 \times 10^{15} \text{ molecules m}^{-2} \text{ s}^{-1}$, and at 1.11 torr and 77 K $k_o=2.36 \times 10^{-4} \text{ min}^{-1}$, from which we can estimate (not having an exact figure for the number of molecules in the reaction space) $k_m=2.90 \times 10^{16} \text{ molecules m}^{-2} \text{ s}^{-1}$, which is a little faster than the corresponding value for Zn at 90 K⁵⁾ of $8.2 \times 10^{15} \text{ molecules m}^{-2} \text{ s}^{-1}$. The "activation energy" estimated as $-524 \text{ cal mole}^{-1}$ corresponds to what might reasonably be expected for the heat of van der Waals adsorption. The absolute rate found here is 20 times less than the value calculated from Wigner theory for localised vibration over sites each with one unpaired electron.⁶⁾ This corresponds with the idea that the surface is largely diamagnetic NaH.

Equilibration and Conversion, 298~450 K

All the $p\text{-H}_2$ results, together with the $o\text{-D}_2$ results, show an increase

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in activation energy at a temperature T_e , which moved to lower temperatures, as indicated by the dotted line in Fig. 3, on temperature cycling in hydrogen. This general behaviour is shown in Fig. 3 and the results summarised in Table 1. Such an increase in activation energy was also apparent

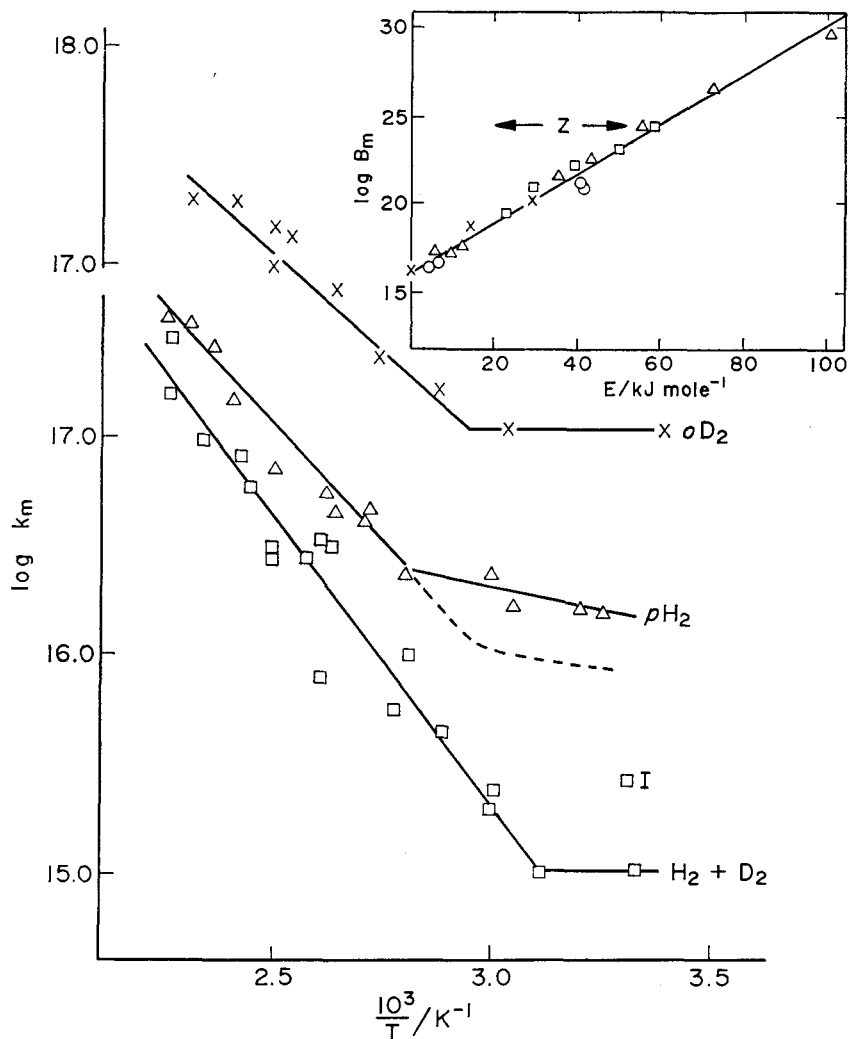


Fig. 3. Arrhenius plots for $H_2 + D_2 \rightarrow 2HD$ (\square Film E, 1.2 torr) $p\text{-}H_2 \rightarrow n\text{-}H_2$ (\triangle Film E, 2.7 torr) and $o\text{-}D_2 \rightarrow n\text{-}D_2$ (X Film F, 1.4 torr). The dotted line indicates the behaviour after heating in hydrogen. The inset compensation plot includes all the data in Table 1 (the B_m 's refer to 1 to 3 torr) \odot HV, $p\text{-}H_2$ \triangle UHV, $p\text{-}H_2$ \square UHV, $H_2 + D_2$ and X UHV $o\text{-}D_2$. I denotes first run, $H_2 + D_2$, Film E.

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TABLE 1. Pressure given in torr, k_m and B_m in molecules $m^{-2} s^{-1}$ and E in $kJ\ mole^{-1}$

Film, Pressure of gas	$\log k_m$ 298 K	$\log B_m, E$ $T < T_c$	T_c°	$\log B_m, E$ $T > T_c$
HVA, 1.2 <i>p</i> -H ₂	16.4	16.4, 4.2	400	21.0, 40.6
HVB, 1.2 <i>p</i> -H ₂	16.5	17.0, 6.3	400	21.0, 41.4
UHVB, 1.4 <i>p</i> -H ₂	16.2	18.1, 12.6	350	26.9, 72.4
"	15.4		330	24.4, 55.6
UHVC, 1.0 <i>p</i> -H ₃	15.4	17.0, 10.0	370	29.7, 100.4
UHVE, 2.7 <i>p</i> -H ₂	16.2	17.4, 6.7	360	22.7, 43.1*
UHVF, 1.1 <i>p</i> -H ₂	16.1	17.1, 6.3	330	21.7, 35.1
UHVA, 3.5 H ₂ D ₂	15.4	16.1, 0	330	20.0, 23.8
1.9 H ₂ D ₂			330	19.4, 23.4
UHVE, 3.0 H ₂ D ₂	15.4		330	22.1, 39.7
1.2 H ₂ D ₂			330	23.1, 50.2*
UHVF, 1.5 H ₂ D ₂	14.2 before baking 15.6 after baking out		—	24.5, 59.0 20.9, 30.1
UHVF, 1.4 <i>o</i> -D ₂	16.2	16.4, 0	350	21.8, 36.4*

* denotes "plotted in Fig. 3".

for H₂+D₂, although the evidence here is less conclusive. The initial run on a clean film was always faster, by as much as a factor 3 or more at room temperature, although the effect was less marked above T_c . A possibly related matter is that oxygen pretreatment could effect a transient increase in activity, *e.g.* by a factor 6 at 320 K but, as Fig. 4 indicates by a relatively smaller amount at 414 K. Taken together, this evidence suggests that above T_c the catalysis occurs on the hydride surface, but that below T_c bare sodium metal sites are in some way involved.

The data of Table 1 show that below T_c we have $E \approx 0-13\ kJ\ mole^{-1}$ and $\log B_m$ (at *ca.* 1.0 torr) ≈ 17 , while above T_c E ranges from 23 to 100 $kJ\ mole^{-1}$, with a corresponding range of $\log B_m$ values, but with most values around or below the collision number Z (mass 3, 298 K, 1 torr) of 25.07. The inset in Fig. 3 shows a rather good compensation law holds for all the values, above and below T_c , for all 3 reactions.

The pressure dependency data were expressed as Freundlich plots, $\log k_m$ vs $\log p$, an example for H₂+D₂ being shown in Fig. 4. Here there are two anomalous features a) an initial low pressure zero order reaction, not however found for *p*-H₂ and *o*-D₂ reactions, which could not be followed

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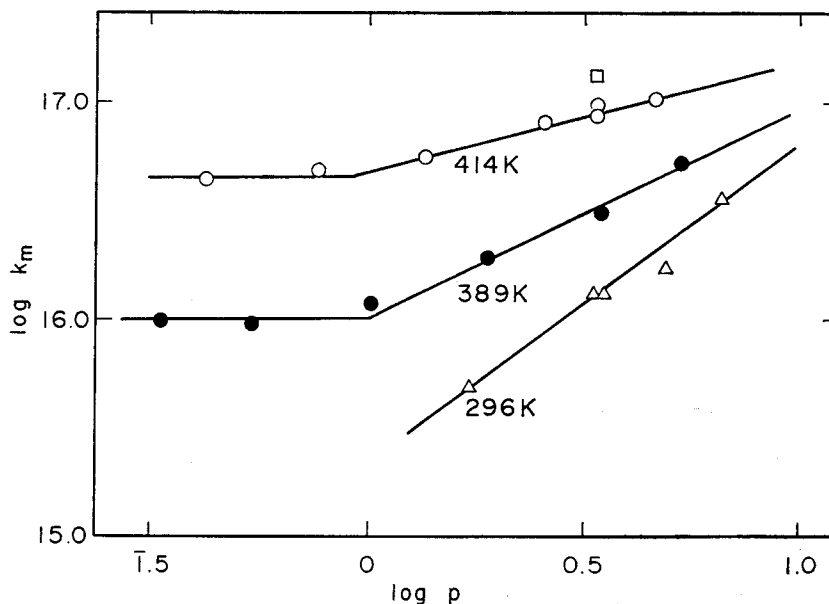


Fig. 4. Pressure dependency Freundlich plots for $\text{H}_2 + \text{D}_2 \rightarrow 2\text{HD}$ on Na Film (A). \square 414 K, after oxygen pretreatment. p is given in torr.

below 1 torr, b) at high pressure an exponent which may be as high as 1.5 at low temperatures but which decreases towards zero with increase in temperature, reaching 0.3 to 0.5 at 410 K. These two effects cannot be reconciled with any simple adsorption mechanism, but probably stem from the complexities of catalysis occurring on a more or less growing hydride film, while the catalytic activity depends on the structure of the hydride film.

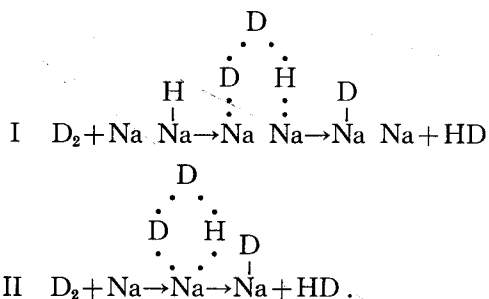
A proposed mechanism

Since NaH, with a rocksalt structure and lattice constant of 0.488 nm is growing on Na with a B. C. C. structure and lattice constant of only 0.424 nm, a true protective film growth is not possible. However, the curves for hydrogen absorption in Fig. 2 do show some evidence for a temporary protective effect. Pumping out the film between experiments will lead to some dissociation of the hydride, although the activation energy for this dissociation is 104.2 kJ mole⁻¹.³⁾ This would mean a half-life of dissociation of 27.8 hours at 298 K, given a frequency factor 10¹⁸ sec⁻¹. We must expect therefore a rather complex catalytic surface with both NaH and some Na sites present.

In earlier studies of the exchange of LiH single crystals with D₂ gas there is rather definite evidence for the surface species involving the triatomic

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species HD_2^- , postulated in Eley-Rideal mechanisms for the spin isomerisation and HD equilibration reactions.^{9,10,11} It seems therefore very likely that in the present case both of these mechanisms are active, viz.



If we postulate the reaction I in which a bare metal site is available to adsorb a D_2 molecule has the lower activation energy, viz. $E=0\sim 13$ kJ mole⁻¹, this would be responsible for the reactions observed at low temperatures below T_c . The resultant B_m will be less than the collision number Z because of the small number of free Na sites available in the NaH film. Any hydridisation of these bare sites, *i.e.* formation of NaH, will further reduce the reaction rate. This effect appears irreversibly in the temperature cycling effect on the rate below T_c , and also appears reversibly in the two anomalous pressure dependency effects. The activating effect of oxygen is presumably due to removal of hydrogen to give bare sites plus water, or perhaps by the formation of active OH sites. Because of the close relationship of these two mechanisms it is reasonable that all the results should lie on one compensation law line. The activation energy for mechanism II is presumably about $40\sim 60$ kJ mole⁻¹ and the $B_m \leq$ collision number as expected. Where $B_m < Z$, we need to invoke a negative entropy of activation, and possibly a reduction in the surface concentration of suitable surface hydride sites. The two very high experimental E values of 72.4 and 100.4 kJ mole⁻¹ might point to the involvement of bulk hydride ion H^- diffusing to the surface, as in the $\text{LiH}\cdots\text{D}_2$ exchange where an activation energy of this value was observed. Mechanism (I) can also yield pressure dependency exponents as high as 1.5, as observed.

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