$$D(193/T) + 3E(321/T) + 4E(670/T) + E(1260/T)$$

which fits the measured heat capacity data between 51 and 298.16°K., with a maximum deviation of 0.9%. The entropy values appear in Table II.

TABLE II

ENTROPIES AT 298.16°K. (CAL./DEG. MOLE)

	Fe_2TiO_4	Fe_2TiO_5
0–51.00°K. (extrap.)	3.72	1.96
51.00–298.16°K. (meas.)	35.26	35.48
$S^\circ_{298.16}$	39.0 ± 0.6	37.4 ± 0.3

The results in Table II and the entropies of the elements listed by Kelley[11] give $\Delta S_{298.16} = -79.2 \pm 0.6$ and $\Delta S_{298.16} = -105.3 \pm 0.3$ cal./deg. mole as the entropies of formation of titanomagnetite and ferric titanate from the elements.

[11] K. K. Kelley, U. S. Bur. Mines Bull. 477 (1950).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Mechanism of Exchange of Hydrogen Gas and Aqueous Alkali[1a]

BY W. K. WILMARTH, JUNE C. DAYTON[1b] AND J. M. FLOURNOY

RECEIVED JANUARY 6, 1953

The conversion of parahydrogen in aqueous alkali has been shown to be a homogeneous non-photochemical process with a rate which is first order with respect to both hydrogen gas and hydroxide ion concentration. The rate constant in the temperature region 80–110° can be represented by the expression $k^\circ = 4.7 \times 10^{13} e^{-23,800/RT}$ l. mole^{-1} min.$^{-1}$. The exchange of deuterium gas to produce HD occurs at a slightly slower rate under comparable conditions. The mechanism has been discussed in terms of a solvated hydride ion as an intermediate.

Introduction

An account of exploratory studies in this laboratory has described the exchange of hydrogen gas with aqueous potassium hydroxide solutions.[1c] A similar exchange has been reported by two previous investigators. Wirtz and Bonhoeffer,[2] while investigating some phases of general acid–base catalysis, first discovered that potassium hydroxide catalyzed the homogeneous exchange between hydrogen gas and the deuterium in heavy water. Abe,[3] in a later paper, suggested that one would expect the change to be catalyzed as effectively by acid as by base, and since this was not the case, he postulated a catalysis by some trace impurity such as a colloidal iron compound. In support of this viewpoint he presented experimental evidence that the activity of the solution was destroyed by prolonged heating or by dialysis but was restored when the solution was brought in contact with an iron wire.

Neither of the above investigations was extensive enough to clarify the detailed mechanism of the exchange process. Since our preliminary data indicated a simple bimolecular reaction, Abe's experiments were repeated in greater detail, but in all cases our initial results were confirmed. A mass spectrometer was not available during the early phases of the work, and the bulk of the experiments were carried out using parahydrogen instead of an isotopic tracer. However, in the second part of this paper the essential identity of the exchange and the conversion processes has been established by observing the rate of exchange of both deuterium and hydrogen deuteride with aqueous alkali.

Experimental

The methods of preparation and analysis of parahydrogen have been previously described.[4] The reaction cell and the general techniques used in the kinetic studies were also essentially those of the previous paper. Except for the experiments described below, the potassium hydroxide solutions were obtained by dilution of a 0.707 N standard solution of Baker and Adamson C.P. potassium hydroxide and were used without further treatment. In run 106 the solution was dialyzed through a cellophane osmosis membrane supplied by Central Scientific Co. (70160-A, $1^1/_8''$). The membrane was checked for holes after the dialysis by replacing the potassium hydroxide solution with a sugar solution and noting the development of osmotic pressure. The 0.103 N solution used in run 104 was prepared by partially neutralizing the standard 0.707 N potassium hydroxide with concentrated hydrochloric acid. This effected a decrease in hydroxide concentration with only a small dilution of the stock solution. The potassium hydroxide for run 95 was prepared by carefully distilling water into an evacuated vessel containing previously distilled metallic potassium. Approximately a twofold increase in surface area was effected in run 90 by the introduction of 1.0 g. of 100–150 mesh ground glass. In runs 102 and 103 the solution was first heated in a sealed glass container for one week at 100°. The solution for run 136 was heated for one week at 100° in a tube with enhanced surface area.

During an experiment the temperature was held to ±0.1° by pumping hot oil from a large thermostat through the outer jacket of the reaction cell. At appropriate time intervals a small fraction of the total hydrogen was removed and analyzed using the Pirani gage technique.

Results and Discussion

A rate constant k can be defined in terms of the measured resistance of the Pirani gage as

$$\frac{P_t - P_\infty}{P_0 - P_\infty} = \frac{R_t - R_\infty}{R_0 - R_\infty} = e^{-kt}$$

P_0, P_t and P_∞ denote the concentration of parahydrogen expressed in per cent. at time $t = 0$, t and ∞; R_0, R_t and R_∞ are the corresponding resistance values.

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[1] (a) A large portion of this investigation was carried out under Task Order IV, Contract No. N6onr-238, with the Office of Naval Research. (b) Based on a dissertation submitted by June C. Dayton, in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Southern California.

[1c] Y. M. Claeys, J. C. Dayton and W. K. Wilmarth, *J. Chem. Phys.*, **18**, 759 (1950).

[2] K. Wirtz and K. F. Bonhoeffer, *Z. physik. Chem.*, **177A**, 1 (1936).

[3] S. Abe, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **38**, 287 (1941).

[4] W. K. Wilmarth and C. F. Baes, Jr., *J. Chem. Phys.*, **20**, 116 (1952).

The rate constant k' for the solution reaction is related to k, by

$$k' = k\frac{\text{total moles of gas}}{\text{moles gas in solution}}$$

and to the constant, $k°$, by

$$k' = k°(\text{OH}^-) + k_{\text{H}_2\text{O}}(\text{H}_2\text{O})$$

The various rate constants for the conversion of parahydrogen by aqueous potassium hydroxide solutions at 80°, 100° and 110° are presented in Table I. Graphs of $k' - k_{\text{H}_2\text{O}}$ (H_2O) *versus* molar concentration of potassium hydroxide for these three temperatures are shown in Fig. 1, and a rate constant k^0 for each temperature calculated from the slope of the straight line appears in the last column of Table I. An activation energy of 23.8 kcal./mole was obtained from the slope of the plot of log k^0 against $1/T$, shown in Fig. 2.

TABLE I

RATES OF PARAHYDROGEN CONVERSION BY AQUEOUS POTASSIUM HYDROXIDE

Temp., °C.	Run	Concn. mole l.$^{-1}$	k', min.$^{-1}$	$k°$, l. mole^{-1} min.$^{-1}$
80.1 ± 0.1	96	0.1725	0.0156	
	98	.534	.042	0.086
	97	.882	.079	
100.4 ± 0.1	88	0.0451	0.020	
	104	.1203	.067	
	93	.1246	.070	
	86	.1246	.067	
	95	.1725	.103	
	106	.2411	.134	
	84	.2492	.140	0.56
	90	.3560	.190	
	82	.534	.28	
	87	.882	.53	
	102	.532	.042	Partially decomp. by pre-heating
	103	.532	.038	
	136	1.122	.160	
110.0 ± 0.1	100	0.225	0.026	
	99	0.1246	0.150	1.20

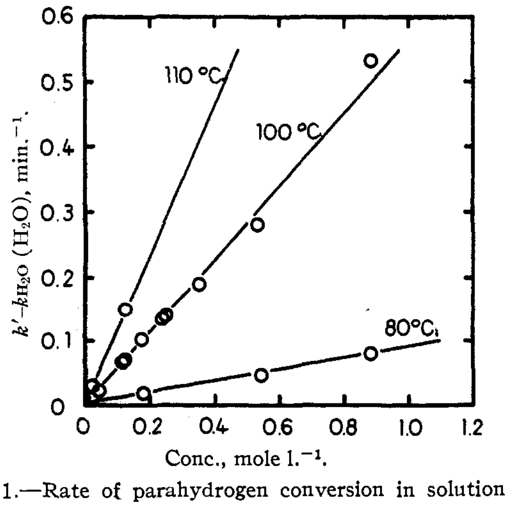

Fig. 1.—Rate of parahydrogen conversion in solution by aqueous potassium hydroxide.

The rate constant for each solution, k', was calculated on the assumption that the hydrogen solubility was the same as that reported for pure water by Wiebe and Gaddy.[5] Their measurements, which cover the temperature range 0–100°, were extrapolated to yield a Bunsen coefficient of 0.0190 ml. gas (S.T.P.)/ml. at 110°. Although the hydrogen solubility undoubtedly decreases somewhat with increasing base concentration, the plot of k' *versus* hydroxide concentration shows no appreciable deviation from linearity. Experiments which are now in progress indicate that the specific rate constant begins to increase at concentrations around one molar and higher. This phenomenon may compensate for the salting-out effect in the region of 0.8 molar. Neither of the effects is important for solutions of less than 0.5 *M* KOH and will therefore have little influence upon most of the data presented here. Specific rate constants of 0.106 min.$^{-1}$ and 0.110 min.$^{-1}$ were obtained in two runs using Baker and Adamson C.P. sodium hydroxide in 0.194 and 0.187 *M* solutions, respectively. The average molar rate constant was 0.57 l. mole^{-1} min.$^{-1}$, in agreement with the potassium hydroxide figure. The result from one attempt using barium hydroxide was lower, but was discarded due to extensive decomposition of the solution during the run.

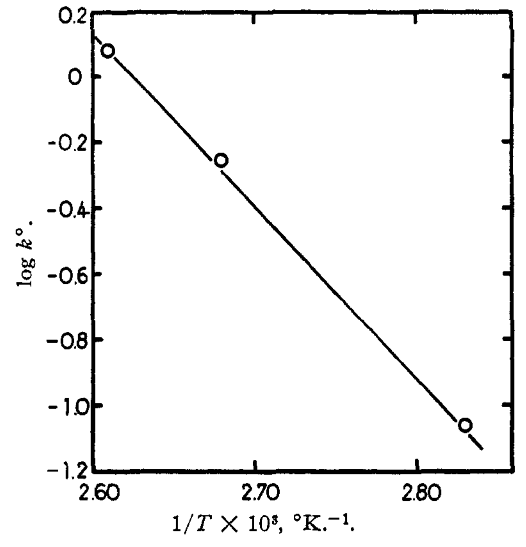

Fig. 2.—Temperature coefficient of parahydrogen conversion by aqueous potassium hydroxide.

The parahydrogen conversion by aqueous potassium hydroxide solutions appears to be a homogeneous, non-photochemical reaction since the rate is not influenced by increase in surface area or by light. The rate at 100° is about 40% faster than Wirtz and Bonhoeffer reported for the analogous base-catalyzed exchange of hydrogen with heavy water and over twice as fast as the rate Abe reported in attempting to duplicate their work. While our experiments reported below indicate that there is probably not a large isotope effect, a difference of this order of magnitude might be explained on this basis. The discrepancy between the Wirtz and Bonhoeffer studies and those of Abe is, however, more serious and of direct interest since the parahydrogen conversion seems to involve the same mechanism. Neither of the previous studies was very extensive or reported in great

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[5] R. Wiebe and V. L. Gaddy, THIS JOURNAL, **56**, 76 (1934).

detail, but it may be useful to consider some of their conclusions. Wirtz and Bonhoeffer report the reaction to be homogeneous, since glass packing in the reaction vessel produced only random effects which fall within the spread in individual rate constants calculated from the nine separate experiments. In each of their runs the rate constant was based on only a single analysis, and no details are given to indicate the limit of error which might arise from inadequate agitation or temperature control. There is no indication that the accuracy is less than might be expected for such exploratory work. In contrast to this, Abe reports that preheating of the alkali produces a marked decrease in catalytic efficiency. In addition, he states that the catalytic efficiency of the alkali depends upon its source and that no exchange was observed after dialysis of the solution.

With the single exception of the decrease in catalytic efficiency after prolonged heating of the alkaline solutions, none of the complications reported by Abe was observed. This decrease has been shown to be due to the formation of silicates and borates by reaction of the base with the Pyrex glass of the reaction vessel. In run 136, 125 ml. of 1.122 *N* KOH solution was heated for 90 hours at 100° in a tube having ten times the surface/volume ratio of the reaction vessel and suffered a 76% loss in catalytic activity. Quantitative analyses for boron and silicon indicated the presence of borates and silicates equivalent to 65% and 14% of the total base, respectively, and the *p*H of the solution after heating was correspondingly lower. There was no decrease in the total base titer of any of our solutions after heating. Apparently this was the case with Abe's work also, although his analytical method is not clear. To test further the "catalytic impurity" hypothesis, in addition to the repetition of Abe's dialysis experiment, a portion of the stock hydroxide solution was 83% neutralized with concentrated hydrochloric acid, and the resulting catalytic efficiency was just that predicted for the remaining hydroxide. This was less than 20% of the prediction from the impurity hypothesis.

Mechanism of the Base-catalyzed Deuterium Exchange

The original observation that deuterium gas exchanged with the solvent in aqueous alkali, at approximately the same rate as the parahydrogen conversion occurred, made it evident that the conversion occurred, at least in a large part, by an exchange mechanism.[1] The accuracy of these measurements was limited by the Pirani gage analysis of the ternary mixtures of the isotopic hydrogens, but by use of a mass spectrometer sufficient accuracy has been achieved, even in the exploratory experiments described below, to permit a semi-quantitative identification of the two processes. In addition it was possible to observe the exchange of the intermediate hydrogen deuteride.

Experimental

Deuterium gas of 99.9% purity was obtained from the Stuart Oxygen Company of San Francisco by arrangement with the Atomic Energy Commission. Analyses for deuterium and hydrogen deuteride were made with a Consolidated-Nier Model 21-201 mass spectrometer. The instrument was calibrated over the region of concentration of 0-1.0% for deuterium and hydrogen deuteride, and each sample was diluted with tank hydrogen to bring it into this range of concentration.

In three separate experiments at 100° pure deuterium was allowed to exchange with the hydrogen atoms in aqueous potassium hydroxide using the apparatus previously described. At appropriate time intervals small samples of the gas were removed, diluted with normal hydrogen, and analyzed for both deuterium and hydrogen deuteride. A typical graph of one such experiment is shown in Fig. 3. The ordinate measures the actual mole percentages of the two species in the reaction cell during the course of the run. A rate constant representing the first order disappearance of deuterium can be calculated directly from the observed decrease of deuterium concentration with time. A constant for the disappearance of the intermediate hydrogen deuteride can be calculated with somewhat less accuracy using the integrated equation for the two consecutive first order processes

$$N_{\mathrm{HD}} = \frac{k_{\mathrm{D_2}}}{k_{\mathrm{D_2}} - k_{\mathrm{HD}}} N^{0}_{\mathrm{D_2}}(e^{-k_{\mathrm{D_2}}t} - e^{-k_{\mathrm{HD}}t}) + N^{0}_{\mathrm{HD}}\, e^{-k_{\mathrm{HD}}t}$$

where N_{HD} = mole % HD at time t, N^{0}_{HD} = initial mole % HD, and $N^{0}_{\mathrm{D_2}}$ = initial mole % D_2, and $k_{\mathrm{D_2}}$ and k_{HD} are rate constants representing the disappearance of deuterium and hydrogen deuteride, respectively. These constants can be corrected for the concentration of hydroxide ion, but no accurate data are available for the solubility of either deuterium or hydrogen deuteride in aqueous alkali. Farkas and Sandler[6] report, as a preliminary value, that deuterium is 7% more soluble than hydrogen in water at 25°, and the solubility differences under our conditions are probably comparable. However, in order to compare the approximate rates of the isotopic exchange processes it seemed wiser to assume equal solubilities for all hydrogen species.

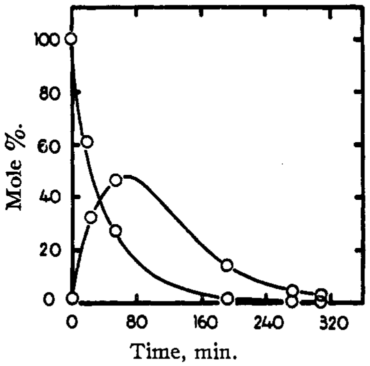

Fig. 3.—Variation in moles of D_2 and HD with time during exchange with aqueous potassium hydroxide at 100°, run 101.

Table II contains the actual mole percentages of deuterium and hydrogen deuteride in the gas phase in equilibrium with the solution at various times. These are the instrument readings obtained from the mass spectrograph, which have been appropriately corrected by calibration of the instrument with hydrogen samples containing both HD and D_2. In each study the appropriate first-order plot of log $(D_2)_t/(D_2)_0$ *versus* time gave a very good straight line, and the slopes permit the evaluation of k' as listed in Table II. Figure 4 shows the dependence of k' upon the concentration of hydroxide. The lines are drawn so that the two higher points for HD and for D_2 show the same relative deviations as for the parahydrogen curve, which is reproduced from Fig. 1, since these deviations appear to be due to real effects rather than experimental error.

Discussion

Preliminary studies with a number of systems show that other strong bases also catalyze the exchange of deuterium gas with protonic solvents.

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(6) L. Farkas and L. Sandler, *Trans. Faraday Soc.*, **35**, 337 (1939).

TABLE II

DEUTERIUM EXCHANGE WITH AQUEOUS POTASSIUM HYDROXIDE AT 100.4 ±0.1°

Run no.	Concn., mole/l.	Time, min.	Mole % D_2	Mole % HD
94	0.1246	40	90.5	13.6
		100	77.3	26.9
		160	67.8	37.7
		217	56.2	41.9
101	0.8819	0	95.9	2.1
		20	58.3	31.2
		55	26.2	44.6
		192	16.3	13.6
		273	7.9	4.5
		308	0.0	2.7
105	0.5340	25	67.9	27.4
		50	51.0	41.9
		75	36.8	50.7
		155	13.9	42.7
		302	2.4	16.2
		364	1.2	8.6

TABLE III

RATE OF EXCHANGE WITH AQUEOUS POTASSIUM HYDROXIDE AT 100°

Run no.	94	101	105
Concn., mole $l.^{-1}$	0.1246	0.8819	0.5340
k' D_2, $min.^{-1}$	.038	.32	.172
k' HD, $min.^{-1}$	.024	.205	.106
$k°$ D_2, l. $mole^{-1}$ $min.^{-1}$	.344 from Fig. 4		
$k°$ HD, l. $mole^{-1}$ $min.^{-1}$	.214 from Fig. 4		

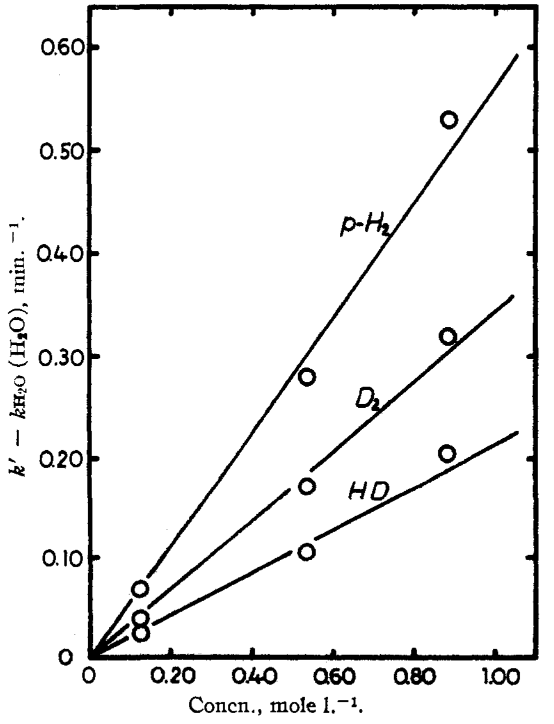

Fig. 4.—Rate of exchange in solution by aqueous potassium hydroxide at 100°.

The general correlation between catalytic efficiency and base strength suggests that in the first step of the exchange the deuterium molecule is acting as an acid. The results of the kinetic studies require that this step be rate-determining and that the transition state contain D_2, OH^- and an unknown number of water molecules. For the aqueous hydroxide system this can be most simply represented by the equations

$$D_2 + OH^- \longrightarrow D^- + DOH \qquad (1)$$

$$HOH + D^- \longrightarrow OH^- + HD \qquad (2)$$

The over-all enthalpy change for equation 1, written for H_2 instead of D_2, can be calculated as 20 kcal., using Latimer's data[7] for the estimation of the heat of formation of aqueous hydride ion. This value should set a lower limit upon the activation energy for the process. The observed activation energy of 24 kcal. is in reasonable agreement with this, considering the possible errors in the calculation. The solvation energy of H^- is based upon a crystal radius of 1.50 Å., and the discrepancy of 4 kcal. would correspond to an error of about 0.05 Å. This is within the variation in values obtained experimentally with various alkali hydrides.[8] The rather large limit of error indicates that the agreement may be fortuitous, but it may be said at least that the calculation does not serve to rule out the D^- mechanism.

The most questionable feature of the above mechanism lies in the assumption that the D^- ion reaches momentary solvation equilibrium with all of the water molecules in its solvation sphere before it is "neutralized" by a single water molecule, as indicated in equation 2. Alternatively, the approach to the transition state could involve a concerted attack upon the hydrogen molecule, the heterolytic fission proceeding through simultaneous proton attachment by the base OH^- and hydride neutralization by the acid H_2O. If this were a better representation of the process, one would predict that the acidic properties of the solvent would be of considerable importance and that an acid catalysis of the exchange might be observed in strongly acid solutions. In the postulated acid catalysis the hydroxide ion would be replaced by the weaker base H_2O while the much stronger acid H_3O^+ would replace the water molecule in its attack upon the latent hydride ion. Experimentally we have observed that no appreciable exchange occurs after five hours in 10 *M* sulfuric acid at 120°. Very little can be said at present about the effect of variation in the acidity of the solvent; it has been established only that in the presence of a base as strong as NH_2^- the exchange proceeds very rapidly, even at −50° in as weakly acidic a solvent as liquid ammonia. Qualitatively we feel that these observations tend to favor the solvated hydride mechanism over the alternative of a concerted attack, although either point of view may be too extreme with regard to the nature of the transition state.

The relative rates of exchange of the various isotopic hydrogen molecules should also yield information about the transition state. The rate constants for HD and D_2 are directly comparable,

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[7] W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952.

[8] E. Zintl and A. Harder, *Z. physik. Chem.*, **B14**, 265 (1931).

but the rate of parahydrogen conversion only sets an upper limit for the rate of exchange of H_2 under the same conditions. This arises from the fact that conversion may occur in some collisions of insufficient energy to cause exchange. Preliminary calculations, using the data of Libby,[9] require that D^- must have a solvation energy approximately 800 cal. greater than that of H^- if the observed differences in rate constants for D_2 and HD are interpreted in terms of equation 1. A difference in solvation energy is not impossible, since the two ions are known to differ somewhat in size in their alkali metal salts and in addition would have different vibrational frequencies in their solvent cages. Both factors would tend to stabilize the D^- ion, but the magnitude of the effect is difficult to estimate. If a concerted attack occurred, the formation of HD would produce a similar effect, thus making the two mechanisms indistinguishable from these data. Exchange studies in heavy water should help to clarify the question of the participation of the solvent.

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[9] W. F. Libby, *J. Chem. Phys.*, **11**, 101 (1943); **15**, 339 (1947).

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Mechanism of the Exchange of Hydrogen Gas with Solutions of Potassium Amide in Liquid Ammonia[1a]

BY W. K. WILMARTH AND JUNE C. DAYTON[1b]

RECEIVED JANUARY 6, 1953

It has been shown that the rate of conversion of parahydrogen by liquid ammonia solutions of potassium amide is proportional to the concentrations of amide ion and parahydrogen. The specific rate constant at $-50°$ was found to be 7.7×10^3 l. mole^{-1} min.$^{-1}$. Deuterium gas exchanges with these solutions at approximately the same rate, and HD has been established as the initial product. The possibility of a solvated hydride or deuteride ion in the transition state is discussed.

Introduction

The exchange of deuterium gas with solutions containing the strong bases amide and hydroxide ion has been reported in a previous note.[2] Much more detailed experiments involving the exchange and parahydrogen conversion in solutions of aqueous alkali have elucidated the principal details of the exchange process in this medium.[3] The following is an account of similar experiments performed with solutions of potassium amide in liquid ammonia. The difficulties involved in preparing and handling the air-sensitive potassium amide and the extreme rapidity of this exchange process limit the accuracy of the present data. However, in view of the rather extensive effort that will be required for a detailed analysis of the amide exchange mechanism, it seems desirable to present the preliminary work at this time. Most of these experiments, as in the hydroxide-catalyzed exchange, involve the study of the parahydrogen conversion, since a mass spectrometer was not available in the early stages of the research. However, two experiments reported below again indicate that the parahydrogen conversion is effected principally through an exchange mechanism.

Experimental

The experimental procedures reported previously[4] were used with the following modifications and additions.

Reaction Cell.—The rate measurements of the parahydrogen conversions by solutions of potassium amide in liquid ammonia were made in a magnetically stirred reaction vessel surrounded by a jacket through which a thermostated liquid was pumped. A stopcock above the vessel permitted the removal of gas samples during a run, and a side-arm immediately below this stopcock facilitated the introduction of potassium amide solution from the preparation vessel.

Preparation of Potassium Amide.—An apparatus was designed for the preparation and transfer of the potassium amide to the reaction cell *in vacuo* because the amide is oxidized to nitrite in contact with air.

The amide was prepared by the decomposition of a potassium–ammonia solution using Raney nickel as a catalyst. (Spongy platinum[5] was also tried, but its use was discontinued because of the longer time required for the decomposition.) The Raney nickel was prepared in the usual manner, by the action of sodium hydroxide upon a powdered nickel–aluminum alloy, and was stored under alcohol.

In a given experiment a small quantity of the alcohol-nickel slurry was put into a small, thin-walled bulb from which the alcohol was removed *in vacuo*. The bulb was sealed and introduced into the amide preparation vessel, which was then evacuated. Metallic potassium was introduced into the vessel by allowing the molten metal to pass through several very small constrictions in a temporary side-arm after the apparatus had been evacuated. The bulb containing the catalyst was broken by means of a glass-covered, magnetically operated hammer, allowing the nickel to fall upon the potassium. Anhydrous ammonia was then distilled onto the catalyst and the potassium, and the reaction to form amide was usually complete within 20 minutes at $-45°$, as evidenced by the disappearance of the blue color of the metal–ammonia solution. (With one preparation of Raney nickel it was noticed that the amide solutions were a light green color. Solutions prepared using this Raney nickel were discarded, since divalent nickel was apparently present.) More ammonia was distilled into the amide solution, and stirring was accomplished by allowing the solution to boil. An estimated quantity was then forced by means of its own vapor pressure through a sintered glass filter into the reaction cell which was cooled by filling the jacket with liquid nitrogen. The ammonia was then distilled back, leaving pure potassium amide and ammonia vapor in the reaction cell, and the connection to the preparation vessel was sealed.

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[1] (a) A large portion of this investigation was carried out under Task Order IV, Contract No. N6onr-238, with the Office of Naval Research. (b) Based on a dissertation submitted by June C. Dayton, in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Southern California.

[2] Y. M. Claeys, J. C. Dayton and W. K. Wilmarth, *J. Chem. Phys.*, **18**, 759 (1950).

[3] W. K. Wilmarth, June C. Dayton and J. M. Flournoy, THIS JOURNAL, **75**, 4549 (1953).

[4] W. K. Wilmarth and C. F. Baes, Jr., *J. Chem. Phys.*, **20**, 116 (1952).

[5] R. Feulgen, *Ber.*, **54B**, 360 (1921).