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).

Rate Measurements.—The cell containing ammonia vapor and amide was evacuated. A known volume of anhydrous ammonia was distilled into the cell. It was necessary to surround the side-arm area with a temporary aluminum foil jacket containing Dry Ice–ether mixture to condense ammonia which could then wash down traces of solid amide into the solution. Parahydrogen was introduced at 50 to 60 cm. pressure. The timer and stirrer were started simultaneously. The stirrer revolved at 1200 r.p.m., a speed which was fast enough to ensure that the hydrogen in solution was in equilibrium with that in the gas phase so that the rate of solution was not the rate-determining step of the process for amide concentrations below 0.005 *N*. Samples of hydrogen could be removed during the run by opening the reaction cell to a short section of capillary tubing which in turn could be opened to the 20-ml. sample tubes. The stopcock was always flushed before each sampling to ensure that the sample obtained was representative at the time of removal. At least four gas samples were removed over a period of time covering the half-life of the conversion whenever possible. After the run the ammonia was distilled off and water from which dissolved gases had been removed was distilled *in vacuo* onto the amide. When the amide was completely destroyed, the side-arm of the cell was opened. The hydroxide–ammonia solution was washed from the cell, boiled 10 minutes to remove the ammonia, and titrated with 0.01 *N* HCl to a phenolphthalein end-point. Precautions to hydrolyze the amide before letting air into the cell were not taken with the initial amide runs (no. 19, 21, 23, 25, 26), and there exists the possibility that a fraction of the amide was converted to nitrite.[6] However, the rate data on these points in comparison with the later ones indicate that no unusually large error occurred in these analyses.

The rate constants, k, k' and k° are defined in the previous paper.[4] k is evaluated directly from the measured resistance of the Pirani gage

$$k = -\frac{1}{t}\ln\frac{P_t - P_\infty}{P_0 - P_\infty} = -\frac{1}{t}\ln\frac{R_t - R_\infty}{R_0 - R_\infty}$$

where P_t, P_0 and P_∞ denote the concentration of percentage parahydrogen and R_t, R_0 and R_∞ denote the resistance values for hydrogen samples at time t, and 0, and ∞ respectively. k' is defined to correct for the presence of undissolved gas above the solution

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

and k^0, the specific reaction rate constant, permits one to correct for the conversion due to the solvent and to introduce the functional dependence of the rate upon the catalyzing ion or molecule.

With the use of these equations the rate data for the conversion of parahydrogen by potassium amide at −50° were calculated and are listed in Table I. A graph of molar rate constant k° *versus* potassium amide concentration is illustrated in Fig. 1.

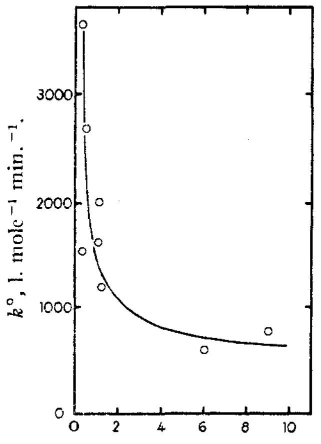

Fig. 1.—Molar rate constants for the conversion of parahydrogen by potassium amide in liquid ammonia at −50°.

TABLE I

RATES OF PARAHYDROGEN CONVERSION BY POTASSIUM AMIDE IN LIQUID AMMONIA SOLUTION AT −50°

Run No.	Concn., mole/l.	k, min.$^{-1}$	k', min.$^{-1}$	$k^\circ \times 10^{-3}$ l. mole^{-1} min.$^{-1}$
48	0.00035	0.0148	1.27	3.64
26	.00039	.0054	0.60	1.53
47	.00055	.0171	1.47	2.68
50	.00111	.021	1.79	1.61
25	.00116	.0084	2.3	2.01
23	.00122	.0076	1.46	1.19
45	.0061	.043	3.7	0.60
21	.0090	.039	7.0	.78
19	.026	.095	18.4	.70

The value used for hydrogen solubility in the amide solutions at −50° was that for pure ammonia extrapolated from the data of Larsen and Black[7]: 0.011 ml. H_2 (S.T.P.)/ml. ammonia. Since the volume of liquid ammonia was measured at Dry Ice–ether temperatures and the runs were made at −50°, a correction for volume increase was made using the density data of Cragoe and Harper.[8] The correction for parahydrogen conversion by the solvent was within the limit of error of the experiment and can be ignored.

Discussion

The plot of the specific rate constant against total potassium amide concentration in Fig. 1 shows that k^0 increases rapidly with dilution. The dissociation constant of potassium amide in liquid ammonia is not available at −50°, but an attempt to correlate the rate with the actual concentration of amide ion can be made by using the known dissociation constant at −33°, $K = 7.3 \times 10^{-5}$.[9] Amide ion concentrations calculated from this equilibrium constant are plotted against the rate constant k' in Fig. 2. Although the points scatter considerably, this plot is more satisfactory than that of Fig. 1. The slope of the least-mean-squares line represents a specific rate constant for amide ion, $k^0 = 7.7 \times 10^3$ l. mole^{-1} min.$^{-1}$.

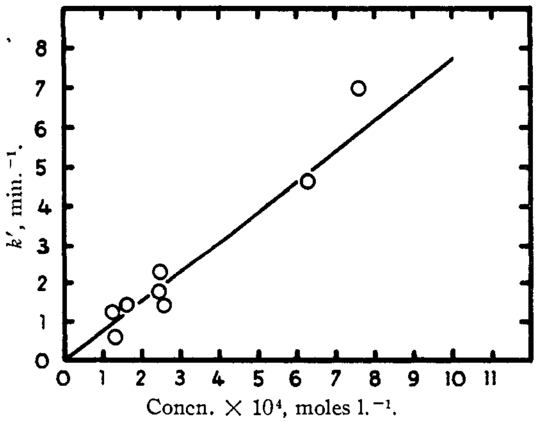

Fig. 2.—Rate of parahydrogen conversion in solution by amide ion in liquid ammonia at −50°.

In a general sense, the mechanism of the amide ion catalysis seems to be analogous to that for

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[6] F. W. Bergstrom and W. C. Fernelius, *Chem. Rev.*, **12**, 43 (1933).

[7] A. T. Larsen and C. A. Black, *Ind. Eng. Chem.*, **17**, 715 (1925).

[8] C. S. Cragoe and D. R. Harper, III, *Bur. Stand. Sci. Papers*, **420**, 313 (1921).

[9] W. W. Hawes, THIS JOURNAL, **55**, 4422 (1933).

hydroxide ion in water.[2] It can be formulated as

$$D_2 + NH_2^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} D^- + DNH_2$$

$$D^- + HNH_2 \xrightarrow{k_2} HD + NH_2^-$$

The appearance of HD as an intermediate rules out any appreciable one-step change of D_2 to H_2, a process which would occur if the two hydrogen atoms on the amide ion were displaced in a single step. The formulation of D^- may be an over-simplification in that D^- may react with a solvent proton before solvation equilibrium is established. Since the activation energy for the amide exchange is not known, attempts to distinguish between the two possibilities are even less fruitful than in the hydroxide system.

The exchange of deuterium gas was studied in only two experiments. The data are listed in Table II in terms of the mole percentages of D_2 and HD as a function of time. A plot of run 109, in which the exchange was followed almost to completion, is shown in Fig. 4.

TABLE II

DEUTERIUM EXCHANGE WITH POTASSIUM AMIDE IN LIQUID AMMONIA AT −52.6 ± 0.2°

Run no.	Concn. KNH_2, mole/l.	Time, min.	Mole % D_2	Mole % HD
107	0.000149	0	98.9	2.4
		15	87.9	14.3
		60	66.6	35.1
		135	43.3	54.4
		214	30.3	58.5
		314	18.3	54.0
		400	12.2	46.2
109	0.00268	0	100.0	0.9
		15	72.1	28.5
		31	49.8	43.3
		50	30.5	48.2
		101	10.5	37.2
		162	3.3	19.5
		210	0.9	10.1
		261	0.9	5.3
		310	0.7	2.1

The rate constants for the exchange of D_2 and HD are listed in Table III.

The most striking feature of the amide catalysis is the remarkable rapidity with which exchange occurs. At −50° the rate constant is approximately 10^4 times that for hydroxide at 100° and, assuming a constant activation energy and pre-exponential factor in the latter case, 10^{14} larger than the hypothetical constant for hydroxide in water at −50°. If one now assumes the same pre-exponential factor for the amide and hydroxide processes and ignores the difference in solvent, one can calculate an activation energy of 10 kcal./mole for the parahydrogen conversion. The decrease from the 23.8 kcal./mole observed for hydroxide should be related to the difference in base strengths of the two ions, presumably through the appropriate use of the Brönsted relation. However, even the base strengths are not available at comparable temperatures or in a single solvent, but an approximation can be obtained from the heats of the two processes

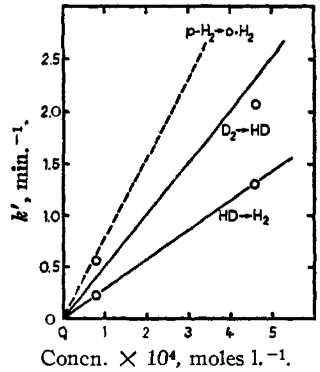

Fig. 3.—Rate of exchange in solution by amide ion in liquid ammonia at −53°.

TABLE III

RATES OF EXCHANGE WITH POTASSIUM AMIDE IN LIQUID AMMONIA AT −53°

Run no.	107	109
Concn. KNH_2, mole $l.^{-1} \times 10^4$	1.49	26.8
Concn. NH_2, mole $l.^{-1} \times 10^4$	0.80	4.6
k', D_2, min.$^{-1}$	.56	2.1
k', HD, min.$^{-1}$	.23	1.31
$k°$ D_2, l. mole^{-1} min.$^{-1}$	4.9×10^3	from Fig. 3
$k°$ HD, l. mole^{-1} min.$^{-1}$	2.8×10^3	from Fig. 3

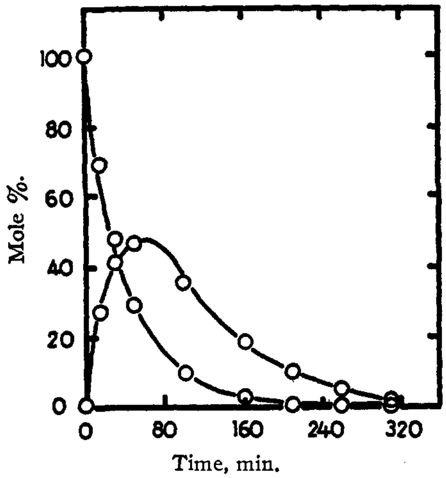

Fig. 4.—Variation in moles of D_2 and HD with time during exchange with potassium amide in liquid ammonia at −53°, run 109.

$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$; $\Delta H = -0.9$ kcal./mole (in H_2O at 25°)

$NH_4^+ + NH_2^- \longrightarrow 2NH_3$; $\Delta H = -26.1$ kcal./mole (in liq. NH_3 at −33°)

Since both equilibria involve the formation of uncharged molecules from charged ions, the medium effects are undoubtedly large, but even an error of 50% would not invalidate the mechanism. It is interesting to note that metal salts of the isoelectronic base methide ion, when exposed to hydrogen, form metal hydrides and methane as the stable products.[10] The similarity between this reaction and the mechanism we have proposed is obvious, but formation of a stable hydride in a solvent of low dielectric constant would support only the gross features of a hydride mechanism for the exchange.

A comparison between the rates of reaction for the various isotopic hydrogen species is shown in Fig. 3. Isotope effects are undoubtedly partly responsible for the different slopes, but other factors are also present. The exchange of HD may produce either H_2 or HD by reaction with a solvent proton, so the disappearance of HD represents only about half the rate at which it reacts. The higher rate for parahydrogen as compared with deuterium may be due to some conversion by perturbations too low in energy to produce exchange. Thus the positive identification of the isotope effect will be complicated, and we are able to say at present only that it is probably not very large.

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[10] H. Gilman, A. L. Jacoby and H. Ludman, THIS JOURNAL, **60**, 2336 (1938).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OKLAHOMA A. AND M. COLLEGE]

Aquo and Chloro Complexes of Cobalt(II) and Nickel(II) in 2-Octanol[1]

BY W. D. BEAVER, L. E. TREVORROW, W. E. ESTILL, P. C. YATES AND T. E. MOORE

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A study has been made of the extent of chloro and aquo complexing of cobalt(II) and nickel(II) in 2-octanol solutions. Spectrophotometry was employed to identify the complexes and to estimate their stability. Evidence for the existence of $CoCl^+$, $CoCl_2$, $CoCl_3^-$ and $CoCl_4^-$ was obtained. Results of varying the water concentration in solutions of constant cobalt and chloride concentration showed stoichiometric reaction of two water molecules with $CoCl_2$ leading to the formation of a monochloro complex and further reaction of approximately eleven water molecules with $CoCl^+$ leading to an aquated cobalt species, presumably Co^{++}_{aq}. Evidence is presented for the formation of a single unstable colored chloro complex of nickel. Both cobalt and nickel chlorides may be polymerized in 2-octanol. These results may be significant in regard to the separation of cobalt and nickel chlorides through the extraction of cobalt chloride by 2-octanol.

Increasing attention is being given to the chemistry of inorganic salts in non-aqueous solvents largely as a result of interest in liquid–liquid extraction procedures.[2] However, of the numerous salt solvent-pair combinations investigated, only a few have been studied intensively in an effort to interpret the nature of the interactions occurring in the non-aqueous phase.

Garwin and Hixson[3] have reported the separation of $CoCl_2$ from $NiCl_2$ by the selective extraction of $CoCl_2$ into 2-octanol. Good separation factors coupled with high extractibility of the cobalt salt were found only if the aqueous phase contained a high concentration of HCl or $CaCl_2$ as an extraction-promoting agent. This extraction system has been studied in these laboratories, and since the octanol-rich phases at equilibrium have been shown to contain considerable amounts of the promoting agent and water as well as $CoCl_2$, it seemed desirable to investigate the nature and extent of complexing which occurs in octanol between these components of the system.

Experimental

Materials.—Anhydrous $NiCl_2$ and $CoCl_2$ were prepared by repeated grinding and heating the corresponding recrystallized C.P.-grade hydrated salts at 120° in air. Care was taken to use only those materials in each case which contained a negligible amount of the other metal. C.P. anhydrous LiCl was further dried for 24 hours at 120° before use.

Anhydrous octanol solutions of $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ were obtained by metathesis of anhydrous octanol solutions of $AgClO_4$ and $CoCl_2$ or $NiCl_2$. Preliminary experiment showed that metathesis at room temperature of equivalent quantities of these salts resulted in a quantitative precipitation of AgCl. Anhydrous nickel and cobalt perchlorates could not be prepared by vacuum dehydration of the perchlorate hydrates.

"Anhydrous" octanol (Matheson Company's best grade) was found by Karl Fischer analysis to have no more than 0.002% water and was used without further drying.

Analytical Methods.—Water determinations were made by the Karl Fischer[4] method employing a dead-stop end-point.

Chloride analysis was done by a modified Volhard titration using alcoholic silver nitrate and aqueous potassium thiocyanate in the back titration. The operations were carried out directly in the octanol solutions without prior back extraction into water.

Nickel was estimated colorimetrically by a modification of a procedure described by Snell[5] employing the color of bis-(dimethylglyoximo)-nickel in methanol-pyridine mixtures. The octanol solutions were treated directly with alcoholic dimethylglyoxime and then diluted with pyridine. Standards were prepared over the expected concentration range of $NiCl_2$ and the optical densities compared at 360 mμ.

Procedures.—Spectrophotometric measurements were made employing a Beckman DU spectrophotometer at 30° with 1-cm. Corex cells. Solutions of optical densities greater than 1.5 were studied by decreasing the light path to 0.1 cm. by means of quartz spacers inserted in the cells.

Solubility determinations of $NiCl_2$ in LiCl–octanol mixtures were performed on a series of 30 solutions in which the LiCl concentration varied from 0.04 to 1.5 molal. The solutions were shaken first at 50° for several hours and then at 30° for over two weeks. Excess $NiCl_2$ was separated, the solutions were analyzed for nickel and chloride, and the absorption spectrum was obtained.

Treatment of Data.—Interaction between $Co(ClO_4)_2$ and LiCl was studied by the method of continuous variations developed by Job[6] and others.[7] Interactions between $CoCl_2$

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[1] Presented in part at the 8th Southwest Regional Meeting of the American Chemical Society, Little Rock, Ark., 1952. Supported under Contract AT(11-1)-71 No. 1 with the U. S. Atomic Energy Commission.

[2] H. M. Irving, *Quarterly Rev.*, **5**, 200 (1951).

[3] L. Garwin and A. N. Hixson, *Ind. Eng. Chem.*, **41**, 2303 (1949).

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[5] F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," 3rd Ed., Vol. II, D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 345.

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[7] L. I. Katzin and E. Gebert, THIS JOURNAL, **72**, 5464 (1950).