595. *The Isotopic Exchange of Gaseous Hydrogen with Liquid Aliphatic Amines. Part II.*[1]

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The isotopic exchange of hydrogen between gaseous deuterium and liquid aliphatic amines has been studied. Like the exchange between deuterium and ammonia, these reactions are catalyzed by aliphatic alkali amides.

The rates of exchange of deuterium, deuterium hydride, and tritium hydride with methyl-, dimethyl-, and ethyl-amine in presence of lithium, sodium, and potassium amide were measured. An energy of activation of 3·6 kcal./mole was found for these reactions, to be compared to 7·6 kcal./mole for the exchange with ammonia.

As in the exchange of deuterium with water, the exchange with methanol is catalyzed by methoxide ion; the energy of activation is 23·8 kcal./mole, the same as for the exchange with water.

The measured rates of exchange, energies of activation, and activities of the different catalysts confirmed the assumption that the catalyst molecule initiates the exchange by a rate-determining association with a deuterium molecule, and that transfer of a hydrogen atom from a solvent molecule to the complex concludes the exchange.

THE exchange of isotopic hydrogen gas with a liquid, $HD(g) + XH_n(l) \longrightarrow H_2(g) + XDH_{n-1}(l)$, has been studied only for XH_n = water [2] or ammonia.[1,3-6] In both cases the exchange occurs, in fact, between hydrogen and a catalyst of the type MXH_{n-1}, where M is an alkali metal, which is in isotopic equilibrium with the solvent XH_n. Another reaction of this type, the exchange of deuterium with phosphine has not yet been studied in detail.[5] It has been suggested [1] that the specific activity of the catalyst * depends on the availability of an electron pair or the basicity of the catalyst. Bourke *et al.*[5] come to a similar conclusion in regard to exchange with ammonia and added amines.

To test this hypothesis, we studied the exchange of deuterium with some homologous aliphatic amines and alcohols. Comparison of the specific rates of reaction, the activation energies, and kinetic isotope effects of these reactions was expected to yield further information on the mechanism of the electrophilic hydrogen exchange in non-aqueous solutions.

EXPERIMENTAL

Methylamine (Matheson and Co.) was distilled from a tank into a trap, cooled with liquid air and containing freshly cut metallic lithium [8] for drying. After removal of the coolant, the methylamine melted and a blue solution was formed, from which, after degassing, dry methylamine was distilled into the reaction vessel. The ammonia content, determined by Nessler reagent, was less than 0·5%.

Dimethylamine (Matheson and Co.) was purified by the same method as methylamine.

Ethylamine was obtained by adding its 70% aqueous solution to sodium hydroxide and

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* Heavy-metal complexes, activating hydrogen for the exchange with water, act probably by a more complicated mechanism than the alkali catalysts.[7]

[1] Part I, Bar-Eli and Klein, *J.*, 1962, 1378.

[2] (*a*) Wilmarth, Dayton, and Flournoy, *J. Amer. Chem. Soc.*, 1953, **75**, 4549; (*b*) Flournoy and Wilmarth, *ibid.*, 1960, **83**, 2257.

[3] (*a*) Claeys, Dayton, and Wilmarth, *J. Chem. Phys.*, 1950, **18**, 759; (*b*) Dayton and Wilmarth, *J. Amer. Chem. Soc.*, 1953, **75**, 4553.

[4] Bigeleisen, *Proc. Internat. Symposium on Isotope Separation*, North-Holland Publishing Co., Amsterdam, 1958, p. 133.

[5] Bourke, Kenyon, Pepper, and Walker, AERE-R 3464, 1961.

[6] Bourke and Lee, *Trans. Inst. Chem. Eng.*, 1961, **39**, 280.

[7] Mills, Weller, and Wheeler, *J. Phys. Chem.*, 1959, **63**, 403.

[8] Evers, Young, and Panson, *J. Amer. Chem. Soc.*, 1957, **79**, 5118.

drying the gas evolved by passage over solid sodium hydroxide. Further purification was accomplished as described above.

Deuterium was prepared from deuterium oxide and sodium.[1]

Monodeuteromethane was obtained by the hydrolysis of methylmagnesium iodide with deuterium oxide. The evolved gas was dried by passage through a trap cooled in solid carbon dioxide.

Catalysts.—Lithium methylamide and potassium ethylamide were prepared by a method similar to that described for potassium amide.[1] The lithium metal used was cut and its surface cleaned under light petroleum since its high b. p. prevented purification by vacuum-distillation in a glass vessel. The metal was then dissolved in the amine.

The concentration of each catalyst was estimated by titration of the amine evolved on hydrolysis.

The experimental procedure was identical with that described in Part 1.

RESULTS

Thermodynamic Results.—The effect of temperature on the rates of exchange of deuterium, deuterium hydride, and tritium hydride with various amines is shown in Fig. 1. The corresponding energies and entropies of activation calculated by the least-mean-square method are summarized in Table 1.

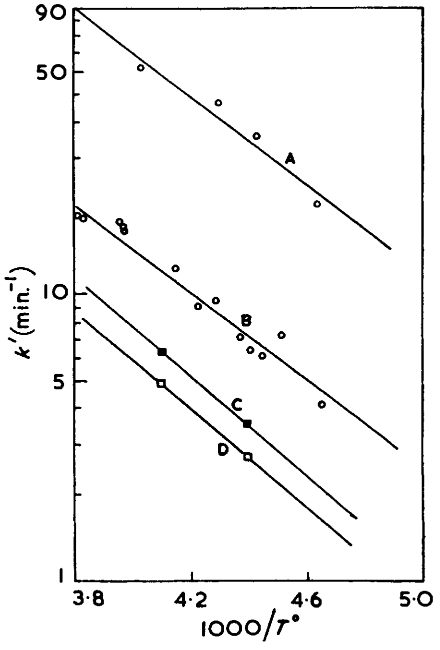

FIG. 1. Semilogarithmic plot of rates of exchange against the inverse of the absolute temperature for (A) D_2–$EtNH_2$ (KNHEt), (B) D_2–$MeNH_2$ (LiNHMe), (C) HD–$MeNH_2$ (LiNHMe), (D) HT–$MeNH_2$ (LiNHMe).

TABLE 1.

Solvent	Catalyst	Energy of activation (kcal. mole^{-1})	Entropy of activation (cal. deg.$^{-1}$ mole^{-1})
$MeNH_2$	LiNHMe	3·6 ± 0·2	−28
$MeNH_2$	$NaNH_2$	5·3 ± 0·2[a]	—
$EtNH_2$	KNHEt	3·5 ± 0·2	—
Me_2NH	$NaNH_2$	6·7 ± 0·2[a]	—
NH_3	KNH_2	7·6 ± 0·3	−9·2[b]
H_2O	KOH	23·8 ± 0·3	7·2[c]
MeOH	KOMe	23·8 ± 1·2	4·0

[a] The solution contained traces of ammonia (see p. 3087). [b] Ref. 1. [c] Ref. 2*a*.

Catalyst Concentration.—The rate of exchange of deuterium with methylamine shows (Fig. 2) a first-order dependence on the concentration of lithium methylamide up to a concentration of about 0·01M. Above this concentration the rate of exchange apparently becomes independent of concentration, because the solution is saturated with catalyst. A slight turbidity in the solution caused by traces of lithium hydroxide makes it difficult to observe the saturation of the solution directly. The linear concentration dependence of the exchange rate at −22° can be expressed by: $k' = (3{\cdot}44 \pm 0{\cdot}05) \times 10^2C + (0{\cdot}60 \pm 0{\cdot}66)$ min.$^{-1}$, where the concentration C is in mole/l. The positive intercept (Fig. 2) proves that, as for exchange with ammonia,[1] the free ion $MeNH^-$ also catalyzes the exchange. In this case no estimate of this rate is possible since the dissociation constant of lithium methylamide is not known.

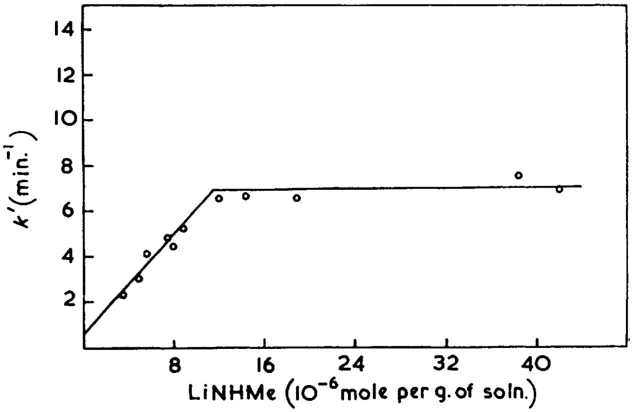

FIG. 2. Plot of rate of exchange of deuterium with methylamine against the concentration of lithium catalyst at −22°.

Comparison of the Rates of Exchange of Deuterium, Deuterium Hydride, and Tritium Hydride with Methylamine.—The following exchange reactions were considered: [1]

$$(1)\ MeNH_2 + D_2 \xrightarrow{k_1} MeNHD + HD$$

$$(2)\ MeNH_2 + HD \xrightarrow{k_2} MeNHD + H_2$$

$$(3)\ MeNH_2 + D_2 \xrightarrow{k_3} MeND_2 + H_2$$

$$(4)\ MeNH_2 + HT \xrightarrow{k_4} MeNHT + H_2$$

The ratio of rates k_1/k_2 was calculated from the rate of exchange of methylamine with highly enriched deuterium (k_1) and with deuterium hydride (k_2) of about 5 atom % deuterium content (corrected for the D_2 present).

A mean value of $k_1/k_2 = 1{\cdot}57 \pm 0{\cdot}13$ was found. This ratio is temperature-independent (within the experimental error) as shown in Fig. 1 by the equal slopes of the various curves.

The ratio k_2/k_4 was measured in an experiment where deuterium hydride and tritium hydride exchange competitively. A mean value of $k_2/k_4 = 1{\cdot}36 \pm 0{\cdot}05$ was found.

The ratio k_1/k_3 was obtained from the initial slope of a curve giving the mole fraction Y of deuterium hydride as a function of that of hydrogen X formed, in an experiment starting with highly enriched deuterium, where $\mathrm{d}Y/\mathrm{d}X = (k_1Z - k_2Y)/(k_3Z + k_2Y)$. This equation is obtained by dividing eqn. 6 by eqn. 7 of Part 1 (Z is the mole fraction of deuterium). For an initial slope $\mathrm{d}Y/\mathrm{d}X = 20$, at $Z = 0{\cdot}966$ and $Y = 0{\cdot}033$, by substitution of $k_1/k_2 = 1{\cdot}57$, the ratio $k_1/k_3 = 35 \pm 2$ was obtained for the exchange of deuterium in a solution of lithium methylamide in methylamine at −12·6°.

Comparison of Rates of Exchange in Liquid Ammonia and Aliphatic Amines.—Because of the experimental difficulty in dissolving alkali metals, other than lithium, in amines and the low solubility of lithium amide in ammonia, a direct comparison of the rates of exchange indifferent solvents is difficult. The following indirect methods of comparison were therefore used.

(1) The exchange of deuterium with a solution of potassium amide in ammonia was measured, the solution was then evaporated, and the dry potassium amide redissolved in methylamine or ethylamine. The rate of exchange was again measured. Table 2 summarizes the results. These values were not corrected for differences in solubility of deuterium (see below). The results are lower limits, since by dissolving potassium amide in methylamine only part of the catalyst is converted into potassium methylamide and in addition small amounts of ammonia are released into the amide solvent. Either or both these facts reduce the rate of exchange in the amide solvent (see below). The observed dependence of the solvent effect on temperature is to be expected from the difference in activation energies for amines and ammonia solutions (see Table 1).

TABLE 2.

The ratio of rates of exchange of deuterium with different solvents.

Temp.	k_{MeNH_2}/k_{NH_3}	k_{EtNH_2}/k_{NH_3}
−48°	10·6 ± 2	5·1 ± 1
−61	28·6	—
−66	35	—

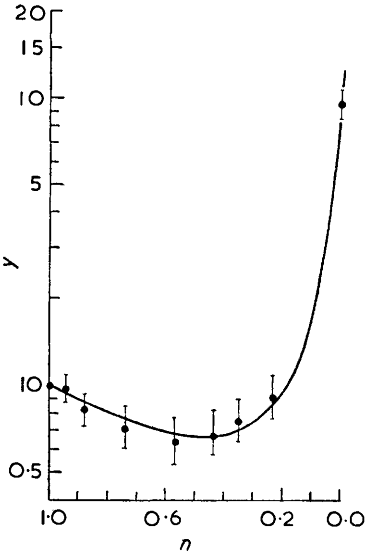

FIG. 3. Plot of rate of exchange of deuterium against mole fraction of ammonia in a mixed solvent of ammonia and methylamine at −66°. (Rate of exchange in pure ammonia taken as unit.) Points are experimental results. The curve was calculated to fit these results.

A similar experiment, comparing the activities of lithium catalyst in methylamine and ammonia, showed much higher ratios of activity, which were caused partly by the limited solubility of lithium amide in ammonia.

(2) A more accurate method for comparing rates of exchange in methylamine and ammonia is the following: To a solution of potassium amide in ammonia increasing amounts of methylamine are added. The rate of hydrogen exchange is then measured as a function of the mole fraction n of ammonia in the solvent. Four separate contributions to the total rate of exchange v have to be considered: $v = k_a(KNH_2)(NH_3) + k_b(KNH_2)(MeNH_2) + k_c(KNHMe)(NH_3) + k_d(KNHMe)(MeNH_2)$. Since both catalytic species are completely soluble, their total concentration is constant: $a = (KNH_2) + (KNHMe)$. Assuming immediate establishment of the equilibrium, $MeNH_2 + KNH_2 = KNHMe + NH_3$, with the constant $K = (KNHMe)(NH_3)/(KNH_2)(MeNH_2)$, gives the following expression for the ratio y of rates measured in a solution of mole fraction n to the rate in pure ammonia ($n = 1$):

$$y = [n^2 + (k_b/k_a + Kk_c/k_a)n(1 - n) + Kk_d/k_a(1 - n)^2]/[n(1 - K) + K].$$

A plot of y (corrected for changes in solubility of deuterium [9] in the solvent) as a function of n

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[9] Bar-Eli and Klein, unpublished work.

is given in Fig. 3. The mole fraction of ammonia in the most concentrated solution of methylamine was estimated to be less than 0·01 (ammonia content of pure solvent $<0{\cdot}5\%$, amount of potassium amide $<0{\cdot}5\%$).

Fitting the above equation to the experimental results, we find the following constants: $K = 2 \times 10^{-2}$; $k_b/k_a \ll 1$; $k_c/k_a = 5$; $k_d/k_a = 12{\cdot}5$, all at $-66°$. These values are only approximate but they demonstrate the relative activities of the catalytic species in both solvents.

" Conjugate Acid–Base " Test.—No measurable exchange of deuterium was found in a 10M-solution of methylamine hydrochloride in liquid methylamine at $-30°$. A similar experiment with a solution of ammonium chloride in liquid ammonia gave the same negative result.

Exchange of Deuterium with Methanol.—The rates of exchange of deuterium with a 2·72M-solution of potassium methoxide in methanol have been determined between 47° and 65°. The energy of activation was $E_A = 23{\cdot}8 \pm 1{\cdot}2$ kcal./mole.

The ratio of rate constants, comparing the exchange of deuterium with methanol and with water was calculated, $k_{MeOH}/k_{H_2O} = 0{\cdot}2$, by using the rate data for exchange with water from Wilmarth *et al.*[3] and the solubility data of hydrogen in methanol from Just.[10] An entropy of activation $\Delta S = 4{\cdot}0$ e.u. was obtained.

Isotopic Hydrogen Exchange between Methane and Ammonia.—Monodeuteromethane was added to a solution of potassium amide in ammonia. The isotope exchange was followed by observing the disappearance of mass 17 of monodeuteromethane in the gas mixture in a mass spectrometer. The rate of isotopic exchange was found to be at least 10^5 times slower than the exchange with gaseous deuterium under similar conditions.

A test to detect methane in the gas from the deuterium exchange with a solution of sodamide in methylamine at $-49°$ gave a negative result. The ratio of the rate of methane formation to the rate of deuterium exchange is much smaller than 10^{-5}.

Activity of Lithium Hydride as an Exchange Catalyst.—Lithium hydride is relatively stable in liquid ammonia and methylamine in contrast to its behaviour in water. The catalytic activity of lithium hydride could therefore be tested directly by preparing saturated solutions of this compound in ammonia or methylamine. No exchange of deuterium could be detected in these solutions except for a very slow exchange caused by traces of lithium metal (about 10^{-3} %) in the lithium hydride.

Activity of Sodium Amide as an Exchange Catalyst in Various Aliphatic Amines.—The rate of exchange of deuterium in solutions of sodium amide in methyl-, ethyl-, and dimethyl-amide was found to be of the same order of magnitude. Accurate results were difficult to obtain, since sodium amide and aliphatic amines form other catalytic species by the reaction: $NaNH_2 + RNH_2 \longrightarrow NaNHR + NH_3$. It could be shown qualitatively that the rates of isotope exchange increased considerably with decreasing ammonia concentration in these solutions (achieved by distilling off part of the solution). A similar effect has been observed for the analogous potassium compounds (p. 3086).

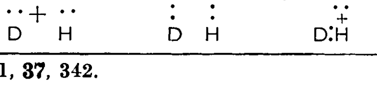
DISCUSSION

When relative rates of exchange, isotope effects on the reaction rate constants, energies of activation, and rate ratios are compared for the two systems, ammonia and aliphatic amines, the similarity in chemical behaviour is obvious. It may be assumed, therefore, that the same reaction mechanism is active in these systems.

Several possible reaction mechanisms should be considered:

(1) Hydride-ion mechanism. If hydride ions were formed in liquid ammonia or amine solution as a reaction intermediate, as suggested by Wilmarth *et al.*[3] it could be expected that a metal hydride, such as LiH, supplies enough hydride ions to catalyze the exchange to some extent. The fact that lithium hydride does not act as a catalyst shows that in this case hydride ions cannot be active.

(2) A four-centre exchange between the dissolved deuterium gas and the amide catalyst, such as:



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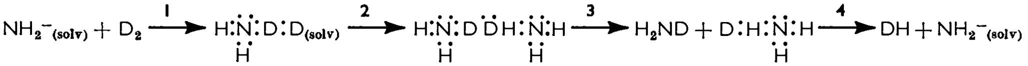
[10] Just, *Z. phys. Chem.*, 1901, **37**, 342.

was disproved by measuring the isotopic exchange with dimethylamine and showing that the rate of exchange is of the same magnitude as that of the monosubstituted amine. Evidently at least one solvent molecule, containing an exchangeable hydrogen atom, participates in the act of exchange. The same is true for the exchange with methanol.

Moreover, the absence of isotopic exchange in deuteromethane and the absence of methane formation in these reaction systems give further evidence, that a four-centre exchange does not occur.

(3) A concerted mechanism,[2] where a base and its conjugated acid attack the deuterium molecule simultaneously, cannot account for the absence of isotope exchange in the experiment, where the solvent serves as a base and methylamine hydrochloride as conjugate acid. In this system the available proton is apparently unable to initiate the exchange and the unshared electrons of the base cannot form a bond with the hydrogen.

The free electron pair in the catalyst ion or ion-pair seems to be necessary to initiate the exchange by stretching the D–D bond and partly by forming a N–D bond. The solvent molecule then supplies a hydrogen atom and the exchange is completed by the transfer of the charge. As was shown,[1] the following mechanism:



$$\mathrm{NH_2{}^-{}_{(solv)}} + \mathrm{D_2} \xrightarrow{1} \mathrm{H\!:\!\underset{\underset{H}{\cdot\cdot}}{\ddot{N}}\!:\!D\!:\!D_{(solv)}} \xrightarrow{2} \mathrm{H\!:\!\underset{\underset{H}{\cdot\cdot}}{\ddot{N}}\!:\!D\,\ddot{D}H\!:\!\underset{\underset{H}{\cdot\cdot}}{\ddot{N}}\!:\!H} \xrightarrow{3} \mathrm{H_2ND} + \mathrm{D\!:\!H\!:\!\underset{\underset{H}{\cdot\cdot}}{\ddot{N}}\!:\!H} \xrightarrow{4} \mathrm{DH} + \mathrm{NH_2{}^-{}_{(solv)}}$$

appears the most probable, since it is in accord with the kinetic data of reaction rates, the kinetic isotope effects on step 1 and 3, and with energetic considerations to be given below.*

Comparing the energies of activation for the exchange of deuterium with water, methanol, ammonia, and methylamine (Table 1) shows the following considerations concerning the rate-determining step (1) to hold.

The energy of activation E_A is the sum of the energy necessary to stretch partly the bond D–D and the energy gained by formation of a partial bond between O and D or N and D. If the amount of stretching of the D–D bond is assumed to be about the same for all four systems, the difference of the energy of activation will be determined mainly by the second part, the O–D or N–D bond formation. A comparative measure for this energy is found in the proton affinity of the solvated catalyst ion, *i.e.*, the energy calculated from the autoprolotytic constant of the solvent: $\mathrm{XH^-{}_{\mathit{n}-1(solv)}} + \mathrm{H^+{}_{(solv)}} = \mathrm{XH}_n$. Table 3 compares the calculated and the experimental values.

TABLE 3.

	H_2O (25°)	MeOH (25°)	NH_3 (−50°)	$Me{\cdot}NH_2$ (−50°)
pK autoprotolysis	14	16	35 [a]	>38 [b]
$\boldsymbol{R}T \ln K_{\mathrm{H_2O}} - \boldsymbol{R}T \ln K_{\mathrm{XH}_n}$ (kcal.-mole)	—	3	15	>17
$E_{\mathrm{H_2O}} - E_{\mathrm{XH}_n}$ (kcal./mole)	—	0	16	20

[a] R. P. Bell, "The Proton in Chemistry," Cornell Univ. Press, 1959, p. 88. Estimate from effect of substitution on acid strength.

It can be concluded, therefore, that the proposed mechanism is in agreement also with the energetic data.

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* A direct proof that the above mechanism is a concerted one, by showing the rate of exchange to be proportional to the concentrations of the catalyst and of methylamine, in an inert solvent, has not yet been done, because no suitable solvent (one that dissolves both amine and catalyst in sufficient quantity to perform an exchange experiment) is available. Trimethylamine, hydrocarbons, and carbon tetrachloride are not suitable for this experiment.