261. *Isotopic Exchange between Gaseous Hydrogen and Liquid Ammonia. Part I.*

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The isotopic exchange of gaseous hydrogen with liquid ammonia has been studied by use of deuterium hydride, tritium hydride, and deuterium. It is catalyzed by alkali amides. The dependence of its rate on the concentration and the type of the catalyst, on the exchanging hydrogen, and on the temperature has been measured.

Catalysis was found to be due both to free amide ion and to undissociated alkali amide. The activation energy is 7·5 kcal./mole. The isotope effects found are analyzed and shown to be consistent with a two-step mechanism in which an intermediate complex, composed of a hydrogen, a catalyst, and a solvent molecule, participates.

CATALYTIC exchange between gaseous deuterium and hydrogen of liquid ammonia was investigated by Wilmarth and Dayton[1] and by Bigeleisen.[2] Wilmarth and Dayton, using dilute solution of potassium amide at —50°, determined the rates of exchange for deuterium and deuterium hydride and compared these with the rate of conversion of para- into ortho-hydrogen. They found the rate of conversion to be proportional to the concentration of amide ion in the solution and concluded that the para–ortho-conversion as well as the exchange proceeds through an intermediate hydride ion. But an alternative mechanism could not be excluded, whereby exchange occurs in a concerted attack of an amide ion and an ammonia molecule on the hydrogen molecule.

Bigeleisen and his co-workers studied isotopic exchange in solutions of high catalyst concentrations at —47° to —64°. They found equal exchange rates for deuterium and deuterium hydride and an energy of activation of 5·2 kcal./mole. They concluded that under these experimental conditions the rate of exchange was controlled by the rate of diffusion of gaseous hydrogen into the solution. More recently this exchange was studied by Bourke *et al.*,[3] who measured the chemical exchange at high catalyst concentrations

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[1] Wilmarth and Dayton, *J. Amer. Chem. Soc.*, 1953, **75**, 4553.

[2] Bigeleisen, Proc. Internat. Symposium on Isotope Separation, North-Holland Publ. Co., Amsterdam, 1958, p. 133.

[3] Bourke, Kenyon, Pepper, and Walker, Harwell report AERE–R3564, 1961; Bourke and Lee, *Trans. Inst. Chem. Engineers*, 1961, **39**, 280.

and concentrated their investigations more on the instrumental problems and on the mass transfer of hydrogen into the reacting solution.

No other reports on the exchange of gaseous hydrogen with liquid ammonia are known to us, although a considerable number of papers have been published [4] on the exchange of hydrogen of organic compounds with liquid ammonia.

Since the isotopic exchange of hydrogen with liquid ammonia is interesting from the mechanistic point of view as a reduction in a non-aqueous medium, we re-examined the sparse and sometimes contradictory experimental results of Wilmarth and Dayton and of Bigeleisen, and studied in greater detail the dependence of the rate of exchange on various parameters such as the nature of the catalyst, the concentration, the temperature, etc.

EXPERIMENTAL

Materials.—*Ammonia.* The material (from Fertilizer and Chemicals Ltd.) was 99·9% pure. It was transferred from the tank to a vessel cooled in liquid air, which contained small pieces of metallic sodium. When the liquid air was removed and the ammonia melted, a blue solution of the metal in ammonia was formed, from which the ammonia was distilled off in a vacuum into the reaction vessel. In this way, every trace of water and oxygen, which could attack the catalyst, was eliminated.

Heavy hydrogen. Gaseous deuterium and mixtures of deuterium, hydrogen, and tritium were prepared from corresponding mixtures of water and deuterium oxide acting on metallic sodium. After being dried by passage through a multiple trap cooled in liquid air, the gas was transferred to, and stored in, a 2-l. bulb.

Potassium amide solution. Potassium amide was prepared *in situ* as follows: Ferric oxide (a few mg.) was introduced into the reaction vessel C (Fig. 1); a small piece of metallic potassium freshly cut under light petroleum was introduced into tube A, which was closed by a stopper, and the apparatus was then evacuated. The metal was slowly heated and, when molten, fell through the constriction into B. Tube A was then sealed. Bulb B was heated cautiously and the metal distilled into the reaction vessel C. Bulb B was then sealed off and the vessel C was weighed. Ammonia was then distilled into vessel C, as described above, a blue solution being formed. Vessel C was then reweighed. This solution was shaken for ~0·5 hr.; owing to catalysis by the ferric oxide, the blue colour disappeared and the pale yellow colour of the amide in solution appeared.

After completion of the exchange experiment the ammonia was distilled off, and the vessel thoroughly evacuated. A little air-free water was introduced, the amide decomposing and ammonia and potassium hydroxide being formed in equivalent amounts. The ammonia was distilled off into standard acid, which was back-titrated. The potassium hydroxide was also titrated and the amount of amide determined.

Sodium amide solution. Sodium amide (from Fisher Chemicals) was ground under light petroleum and transferred to the reaction vessel. The petroleum was distilled off and the amide thoroughly dried in a high vacuum. The vessel was weighed, ammonia was distilled into it, as described above, and the whole weighed.

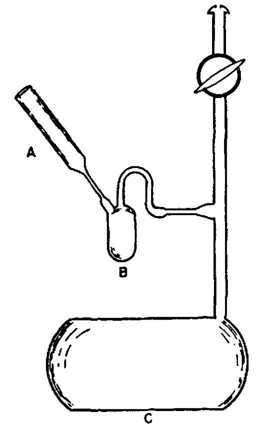

FIG. 1. Reaction vessel with attachment for the distillation of potassium.

For many experiments this catalyst is preferable to potassium amide, which decomposes easily in the presence of traces of air or water. Sodium amide, owing to its low solubility in liquid ammonia, gives saturated solutions with conveniently measurable rates of exchange. These solutions retain constant activity in the presence of an excess of solid sodium amide even if traces of air or water decompose a fraction of the dissolved catalyst.

Apparatus.—The reaction vessel was connected to a standard vacuum-line, which contained also hydrogen-storage bulbs, a Toepler pump, a mercury manometer, and a gas-sampling system. The temperature of the reaction vessel was kept constant within ±0·1° in the range of 0° to −80°.

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[4] See Heuberger and Botter, Commissariat à l'Energie Atomique, 1959, Bibliography No. 3.

Procedure.—Isotopic hydrogen (D_2, HD, or HT) was introduced into the reaction vessel after it had been charged with the catalyst and ammonia. The pressure of both ammonia and hydrogen was measured by means of the mercury manometer. The vessel C was then connected to a " Vibro-mixer " (A.G. für Chemie-Apparatebau, Männedorf-Zürich, model E-1) and shaken. This ensured perfect mixing of the gaseous and the liquid phase.[5] From time to time the shaking was interrupted and a sample of the gas phase taken for mass-spectrometric analysis.

In order to change the concentration of the solution from experiment to experiment, small amounts of ammonia were distilled into or out of the reaction vessel, which was then reweighed.

Calculations.—Rate constants were calculated from a semi-logarithmic plot of mole % isotopic hydrogen against time. These rates were corrected for the presence of undissolved gas in the gas phase by the equation:

$$k' = k\,\frac{\text{Total moles of gas}}{\text{Moles of gas in solution}} = k\,\frac{V_0 - m/\rho}{h\boldsymbol{R}Tm/\rho} + 1,$$

where k = measured rate constant, k' = corrected rate constant, V_0 = volume of reaction vessel, m = weight of ammonia, ρ = density of ammonia, h = gas absorption coefficient in ml. (S.T.P) ml.^{-1} atm.^{-1} (cf. ref. 5), $\boldsymbol{R}$ = gas constant, and T = absolute temperature.

RESULTS

Comparison of the Exchange Rates of the Isotopic Molecules D_2, HD, *and* HT.—In view of the large excess of liquid ammonia over hydrogen in the reaction system, only the following four unidirectional exchange reactions need be considered:

$$(1)\quad D_2 + NH_3 \longrightarrow HD + NH_2D$$

$$(2)\quad HD + NH_3 \longrightarrow H_2 + NH_2D$$

$$(3)\quad D_2 + NH_3 \longrightarrow H_2 + NHD_2$$

$$(4)\quad HT + NH_3 \longrightarrow H_2 + NH_2T$$

Denoting the mole fractions of the isotopic molecules $[H_2] = X$, $[HD] = Y$, and $[D_2] = Z$, one can derive for the rates of reactions (1—3) the differential equations:

$$(5)\quad \mathrm{d}Z/\mathrm{d}t = -\,(k_1 + k_3)\,Z;$$

$$(6)\quad \mathrm{d}Y/\mathrm{d}t = k_1Z - k_2Y;$$

$$(7)\quad \mathrm{d}X/\mathrm{d}t = k_3Z + k_2Y.$$

Integrating equations (5—7) one obtains:

$$(8)\quad Z = Z_0 \exp\,[-\,(k_1 + k_3)t];$$

$$(9)\quad Y = \left(\frac{k_1}{k_1 + k_3 - k_2}\,Z_0 + Y_0\right)\exp\,[-k_2t] - \frac{k_1}{k_1 + k_3 - k_2}\,Z_0 \exp\,[-\,(k_1 + k_3)t];$$

$$(10)\quad X = 1 - Y - Z.$$

Ratio of Rates k_3/k_1.—The mole fractions Y were plotted against X (Fig. 2), these fractions being from an experiment which started with a high concentration of deuterium gas (small Y_0 and X_0); the tangents $\mathrm{d}Y/\mathrm{d}X$ were then evaluated graphically and replotted as a function of Y (Fig. 3). Since the ratio k_1/k_2 (see p. 1381) is known, a straight-forward calculation allows one to estimate the ratio k_3/k_1 from equations (6) and (7). A value of $k_3/k_1 = 10^{-2}$ was found. For subsequent calculations k_3 will be neglected in comparison with k_1.

Ratio of Rates k_1/k_2.—A preliminary value for this ratio was found by comparing two sets of experiments: one performed with a high concentration of deuterium gas ($Z_0 \gg Y_0$; X_0), giving k_1 from the observed first-order rate of decrease of deuterium; and a second performed with a relatively low deuterium concentration ($Y_0 \gg Z_0$), giving approximately k_2. An upper value of $k_1/k_2 = 1{\cdot}77 \pm 0{\cdot}06$ was thus calculated.

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[5] Bar-Eli and Klein, *J. Chem. Phys.*, 1961, **35**, 1915.

To improve the accuracy experiments were performed starting with a high percentage of deuterium, the gases being analyzed simultaneously for D_2 and HD. Dividing equation (9) by (8) one obtains:

$$(11) \quad Y/Z = CZ^{(k_2-k_1)/k_1} + B,$$

where $$C = [Y_0 - Z_0k_1/(k_1 - k_2)]/Z_0^{k_1/k}$$

and $$B = k_1/(k_2 - k_1).$$

Evaluating equation (11) as a linear function for the experimental values of Y and Z, and assuming various ratios k_1/k_2, led by the least-mean-square method to a best value of 1·55 ± 0·02 at −40·7° for k_1/k_2. This result was used to recalculate, as a check, the slope C and intercept B of equation (11). These calculations were found to agree within ½% for C and 2% for B.

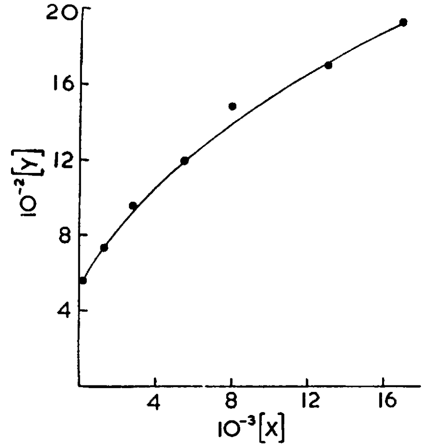

FIG. 2. Change of mole fractions of deuterium hydride (Y) and hydrogen (X) in the exchange of deuterium at −54·5°.

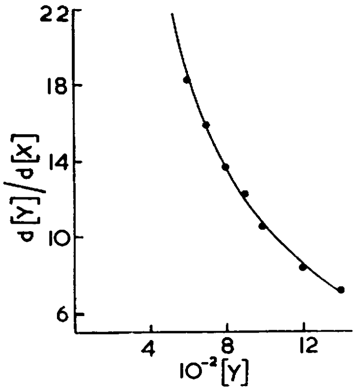

FIG. 3. Plot of differential change of deuterium hydride to hydrogen against mole fraction of deuterium hydride.

Ratio of Rates k_3/k_4.—This ratio was determined in a kinetic experiment with hydrogen which contained both tritium hydride and deuterium hydride ($Y_0 \gg Z_0$). An equation analogous to (5) for the rate of decrease of HT gave k_3/k_4 = 1·64 ± 0·07 between −40° and −60°.

Effect of Temperature.—The rates of exchange of deuterium, deuterium hydride, and tritium hydride as a function of temperature were measured with potassium amide and sodium amide as catalysts. Fig. 4 shows the plots of k' against $1/T$. The following energies of activation (in kcal./mole) were calculated by the least-mean-square method:

	Catalysts	
Reactant gas	KNH_2	$NaNH_2$
D_2	7·4 ± 0·3	8·0 ± 0·3
HD	7·4 ± 0·3	7·7 ± 0·5
HT	7·6 ± 0·6	

A mean second-order entropy of activation of $\Delta S = -9{\cdot}2 \pm 1{\cdot}4$ e.u. was calculated by means of absolute-rate theory,[6] and the experimental rate of reaction k' (see p. 1382).

Hydrogen Pressure.—The rate of exchange is independent of the pressure of deuterium. Fig. 5 shows a semilogarithmic plot of deuterium concentration against time for an experiment during which the gas pressure was reduced, by withdrawing samples, to one-fifth of its initial value; the rate remained constant within the experimental error.

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[6] Glasstone, Laidler, and Eyring, "The Theory of the Rate Processes," McGraw-Hill Book Co., New York, 1941, p. 21.

Catalyst Concentration.—The dependence of the exchange rate k_1 of deuterium on the concentration (5—200 mmoles/l.) of potassium amide is shown in Fig. 6, which proves a linear dependence. The rate at unit concentration of the catalyst is found by the least-mean-square method to be (1·54 ± 0·01) × 10^5 ml. mole^{-1} min.$^{-1}$ at −61°. The intercept of the plot in Fig. 6 at zero catalyst concentration shows a value of 1·54 ± 0·13 min.$^{-1}$, which is larger than the experimental error. This is discussed below.

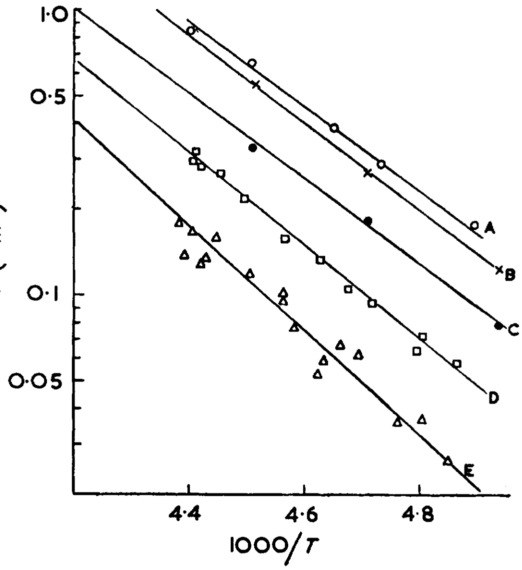

FIG. 4. Semilogarithmic plot of rates of exchange against inverse of absolute temperature, for (A, D) D_2, (B, E) HD, and (C) HT with (A, B, C) KNH_2 and (D, E) $NaNH_2$ as catalyst.

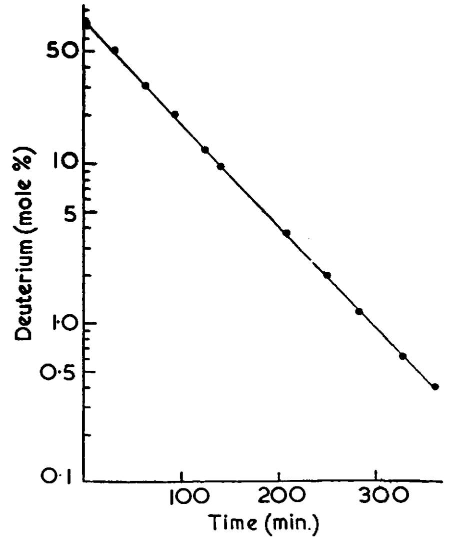

FIG. 5. Rate of change of mole fraction of deuterium with time as function of gas pressure.

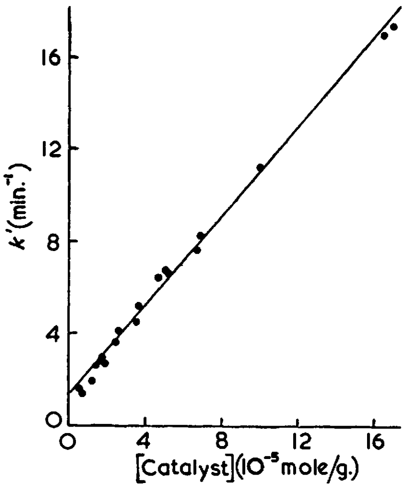

FIG. 6. Rate of exchange of deuterium as a function of the concentration of catalyst at −61°.

Influence of the Cation of the Catalyst.—When the rates of exchange at −61° for sodium amide and potassium amide were compared, a ratio $k_{KNH_2}/k_{NaNH_2} = 5·5$ was found. The value for the concentration of a saturated solution of sodium amide used ($17{\cdot}6 \times 10^{-3}$ mole/kg.) was obtained by extrapolation from data given by Levine and Fernelius.[7]

The catalytic activity of lithium amide was found to be even smaller than that of sodium amide. The ratio of rates of exchange for saturated solutions of sodium amide and lithium amide is $k_{\mathrm{NaNH_2}}/k_{\mathrm{LiNH_2}} = 23$ at $-43°$.

DISCUSSION

Though the experimental rate of exchange k is proportional to the concentration of the potassium amide (catalyst) over a wide range of concentrations, the positive intercept (see Fig. 6) (the apparent residual rate of exchange at zero concentration) seemed at first disturbing since no exchange was measurable in the absence of catalyst. In addition, Wilmarth and Dayton [1] had found that the rate of para–ortho-hydrogen conversion at low catalyst concentration was proportional to the amide-ion concentration though at higher concentrations their rates are greater than expected from this function alone. It is therefore suggested that the isotope exchange and the para–ortho-conversion are catalysed both by the free ion and by the undissociated potassium amide, as represented by the equation

$$(12) \quad k = k_{\mathrm{NH_2^-}}[\mathrm{NH_2^-}] + k_{\mathrm{KNH_2}}[\mathrm{KNH_2}],$$

where $k_{\mathrm{NH_2^-}}$ and $k_{\mathrm{KNH_2}}$ are the specific rate constants for reactions catalysed by amide ion and potassium amide respectively. By algebraic transformation one obtains

$$(13) \quad k/c = (k_{\mathrm{NH_2^-}} - k_{\mathrm{KNH_2}})\alpha + k_{\mathrm{KNH_2}},$$

where c is the total catalyst concentration in solution and α its degree of dissociation. Using the least-mean-square method one finds for the exchange of deuterium at $-61°$

$$k_{\mathrm{NH_2^-}} = (2{\cdot}18 \pm 0{\cdot}17) \times 10^6 \text{ ml. mole}^{-1} \text{ min.}^{-1}$$

and

$$k_{\mathrm{KNH_2}} = (1{\cdot}03 \pm 0{\cdot}10) \times 10^5 \text{ ml. mole}^{-1} \text{ min.}^{-1}$$

Hawes's value [8] of $7{\cdot}3 \times 10^{-5}$ mole l.$^{-1}$ was taken for the dissociation constant of potassium amide in calculating the degree of dissociation α.

The influence of the cation on the catalytic activity of the alkali amide is a function, not only of the specific activity of the undissociated catalyst molecule, but also of the dissociation constant of the alkali amide. No accurate value is available for the dissociation constant of sodium amide in liquid ammonia; Hawes [8] gives only an upper limit of $2{\cdot}65 \times 10^{-5}$ mole l.$^{-1}$ at $-33°$. From the rate constants given above and the experimental ratio of rates for potassium and sodium amide, one calculates a minimum value of 9·5 for the ratio of these dissociation constants. The sequence $\mathrm{K} > \mathrm{Na} > \mathrm{Li}$ for the experimental catalytic activities and the degree of dissociation is then reasonable.

Since the experimental rate of exchange is the sum of two separte terms, functions of the rates $k_{\mathrm{NH_2^-}}$ and $k_{\mathrm{KNH_2}}$, the value of the experimental energy of activation will, in principle, be some intermediate value of the two energies of activation $E_{\mathrm{NH_2^-}}$ and $E_{\mathrm{KNH_2}}$. The heat of dissociation of potassium amide, according to Higginson and Wooding,[9] is negligible; the dissociation constant can therefore be taken as constant in the range of temperature measured. It can then be shown from our experimental results that the maximum error introduced by equating [9] $E_{\mathrm{NH_2^-}}$ and $E_{\mathrm{exp.}}$ is 0·1 kcal. mole^{-1}, which is smaller than the experimental error.

In the same way the respective entropies of activation may differ by at most 6 e.u., that for the free ion being the greater.

Since the rate constant k_3 of a simultaneous transfer of two deuterium atoms is

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[7] Levine and Fernelius, *Chem. Rev.*, 1954, **54**, 449.

[8] Hawes, *J. Amer. Chem. Soc.*, 1933, **55**, 4422.

[9] Higginson and Wooding, *J.*, 1952, 766.

negligible, the isotopic exchange is believed to proceed mainly by a transfer of one hydrogen atom per reaction step.

The experimental energy of activation was shown to be independent, within the experimental error, of the kind of isotopic hydrogen exchanging and of the cation of the catalyst.

On the basis of our experimental evidence it is possible now to discuss a reaction mechanism. The isotope effects determined experimentally will be used to describe a transition state for the rate-determining step and an intermediate complex.

From the exchange rates of the isotopic hydrogen molecules (D_2; HD; and HT) and the para–ortho-conversion of hydrogen, measured by Wilmarth and Dayton,[1] three independent experimental isotope effects were calculated, namely: $2k_{HD}/k_{D_2} = 1{\cdot}28 \pm 0{\cdot}03$; $k_{HD}/k_{HT} = 1{\cdot}64$ $(\pm 0{\cdot}07)$; $2k_{H_2}/k_{D_2} = 2{\cdot}36 \pm 0{\cdot}30$ (calc. from the ortho–para conversion; [1] 1·24 and 3·26 are the isotope effects for the OH^--catalyzed exchange, in water,[10] in the first and the third case).

The characteristics of these effects are that (*a*) they belong to the category of small hydrogen-isotope effects, and (*b*) they are practically independent of temperature (see above). The first property shows that the rate-determining step does not inolve a simple H–H bond fission, and the second that the transition state of this step, at least for hydrogen exchanging with ammonia, must be of more complex structure than a simple solvated hydride ion.[1, 10]

We shall assume, therefore, that isotopic exchange of hydrogen and ammonia proceeds by an associative mechanism, which consists of a rate-determining step yielding an intermediate complex, followed by a second and faster step in which this complex either re-forms the initial reactants or decomposes into the exchanged products:

$$\text{HD} + \text{Catalyst} \underset{k_{-b}}{\overset{k_a}{\rightleftharpoons}} \text{Intermediate complex} \xrightarrow{k_b} \text{H}_2 + \text{Catalyst}$$

The experimental rate constant is then given by

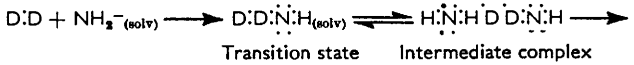
$$(14) \quad k = k_a k_b/(k_b + k_{-b}) = k_a/(1 + k_{-b}/k_b),$$

and an overall kinetic effect between the isotopically substituted hydrogen molecules i and j, by

$$(15) \quad k_i/k_j = (k_{ai}/k_{aj})(1 + k_{-b}/k_{bj})/(1 + k_{-b}/k_{bi})$$

The experimental isotope effects given above are then seen to be the result of two effects, namely, an intermolecular k_{ai}/k_{aj} and an intramolecular isotope effect k_{-b}/k_b.*

In order to evaluate the various isotope effects, the following will be assumed: The catalyst, in the form of a solvated amide ion or an ion pair, forms in the transition state a partial bond with the deuterium molecule through its lone pair of electrons and thereby weakens the D–D bond. The amounts of forming and weakening of the bonds are such that the difference of zero-point energies of the isotopically substituted molecules in the reactant state equals approximately the difference of zero-point energies of the transition state; the intermolecular isotope effect k_{ai}/k_{aj} becomes then practically independent of temperature (see above). The rate of the first step will be a function of the availability of the lone electron pair, *i.e.*, the basicity, in the Lewis sense, of the catalyst. The transition state is then stabilized by further bond formation between the second deuterium atom and a hydrogen atom of a solvent molecule, forming the symmetrical intermediate complex:



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* This is similar to the case of hydrogen transfer in electrophilic aromatic substitution.[11]

[10] Flournoy and Wilmarth, *J. Amer. Chem. Soc.*, 1961, **83**, 2257; Wilmarth, Dayton, and Flournoy, *J. Amer. Chem. Soc.*, 1953, **75**, 4549.

[11] Zollinger, *Experientia*, 1956, **12**, 165; Olsson, *Arkiv Kemi*, 1961, **16**, 489.

In the second step the intermediate complex either returns to the former transition state by reopening the D–H bond or it progresses into a new, but equivalent transition state by opening the stretched D–D bond. The difference in zero-point energy between these two transition states constitutes the main component of the intramolecular isotope effect k_{-b}/k_b.

This detailed mechanism is in agreement with the experimental results discussed above, and it will be shown by the following calculations that the experimental isotope effects agree qualitatively with these assumptions.

Using equation (15) for the three experimental isotope effects and giving consideration to symmetry numbers, we obtain:

$$(16)\quad \frac{k_{\mathrm{HD}}}{k_{\mathrm{D_2}}} = \frac{k_{a(\mathrm{HD})}}{k_{a(\mathrm{DD})}} \cdot \frac{1 + k_{-b(\mathrm{HD})}/k_{b(\mathrm{DD})}}{1 + k_{-b(\mathrm{HH})}/k_{b(\mathrm{HD})}};$$

$$(17)\quad \frac{k_{\mathrm{HD}}}{k_{\mathrm{HT}}} = \frac{k_{a(\mathrm{DD})}}{k_{a(\mathrm{HT})}} \cdot \frac{1 + k_{-b(\mathrm{HH})}/k_{b(\mathrm{HT})}}{1 + k_{-b(\mathrm{HH})}/k_{b(\mathrm{HD})}};$$

and

$$(18)\quad \frac{k_{\mathrm{H_2}}}{k_{\mathrm{D_2}}} = \frac{k_{a(\mathrm{HH})}}{k_{a(\mathrm{DD})}} \cdot \frac{1 + k_{-b(\mathrm{HD})}/k_{b(\mathrm{DD})}}{1}.$$

Since the transition state is assumed to be linear and the isotope effect essentially temperature-independent, equation (32) of Bigeleisen *et al.*[12] can be used to calculate the intermolecular isotope effect:

$$(19)\quad k_{ai}/k_{aj} = A = [(\mathrm{m_j}/\mathrm{m_i}) \,.\, (\mathrm{M_i}/\mathrm{M_j})]^{\frac{1}{2}},$$

where m and M are the masses of the reactant hydrogen and of the transition state, respectively. Since the values for k_{ai}/k_{aj} are known, the intramolecular isotope effects k_{-b}/k_b can be evaluated from equations (16—18). The results are summarized in the Table.

Intermolecular and intramolecular isotope effects.

k_{ai}/k_{aj}	HD/D_2	1·125	k_{-b}/k_b	HD/D_2	2·52
	HD/HT	1·125		H_2/HT	2·10
	H_2/D_2	1·340		H_2/HT	3·51

The logarithmic correlation factor, log $k_{b(\mathrm{HT})}$/log $k_{b(\mathrm{HD})} = 1{\cdot}69$. This rather high value is caused by a relatively large uncertainty in the rate constant of the para–ortho-conversion.[1] *

The magnitude of the intramolecular effect shows, again qualitatively, that the activation of the intermediate complex does not require the cleavage of a normal H–H bond, which would have resulted in an isotope effect of the order of at least 6, but that the bonds in the intermediate complex are partially stretched from the first step in the reaction.

More accurate calculations on the relative force constants active in the transition state are in progress.

This research was supported in part by a grant from Louis J. Glickman, New York.

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[*Received, October* 17*th*, 1961.]

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* A value of 1·44, more in line with the above mechanism, is found when using the isotope effect for the hydrogen exchange catalysed by hydroxyl ions (see above).

[12] Bigeleisen, Klein, Weston, and Wolfsberg, *J. Chem. Phys.*, 1959, **30**, 1340.