reaction. Both Corey and Wechter[16] and Beringer and Schultz[17] have shown that these molecular substitution reactions take place predominantly with inversion of configuration. The termolecular mechanism of exchange of the benzoyl halides may involve a process very similar to the mechanisms proposed by these authors for the substitution reactions of saturated iodides.

Acknowledgment.—This work was supported in part by the U. S. Atomic Energy Commission under Contract AT(30-1)-1314.

NEW YORK 27, N. Y.

---

[16] E. J. Corey and W. J. Wechter, THIS JOURNAL, **76**, 6040 (1954).

[17] F. M. Beringer and H. S. Schultz, *ibid.*, **77**, 5533 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Deuterium Isotope Effect on the Rate of Reaction of Hydrogen and Iodine[1]

BY ELLINGTON M. MAGEE[2]

RECEIVED MAY 6, 1957

The ratio of rate constants has been determined for the reactions $H_2 + I_2$ and $HD + I_2$. An experimental method was used whereby errors in temperature, time and concentrations were negligible. The ratios of H_2:HD were determined in the reactants and in the first product formed. The value for k_{H_2}/k_{HD} was found to be 1.55. The significance of this result is discussed in relation to past experimental and theoretical work.

Introduction

The isotope effect on the rates of chemical reactions offers an excellent method for the accurate, experimental determination of the structural parameters of the activated complex. Recent calculations have been made by Polanyi,[3] using a "calibrated" activation energy barrier, for the reactions of various hydrogen isotopes with methyl radicals. Such calculations would be possible for simpler systems, such as the reaction of hydrogen and iodine if enough experimental data were available. This paper presents some of the necessary data.

The reaction of hydrogen with iodine to form hydrogen iodide and the reverse reaction are two of the best known, homogeneous, gaseous reactions. The rates were studied in the work of Bodenstein,[4] Kistiakowsky[5] and others and a review of much of the work is given by Kassel.[6] The reaction has been found to be first order with respect to each of the two reactants and homogeneous in the concentration range of 2×10^{-5} to 1×10^{-3} mole cc.$^{-1}$ when the reaction is carried out in quartz vessels.

Several workers have measured the rate constants for the reaction of deuterium with iodine and for the reverse reaction.[7,8] The average value for k_{H_2}/k_{D_2} from ref. 7a, 7b and 8a (the value obtained in ref. 8b is believed to be erroneous[7b]) is 1.97 ± 0.08 and the corresponding average ratio, k_{HI}/k_{DI} for the reverse reaction is 1.61 ± 0.06. The theoretical values calculated for the two ratios are 2.34 and 1.92, respectively.[9] The calculated values are seen to be in some disagreement with the values found experimentally. It was hoped that a measurement of the ratio of rate constants for the two reactions

$$H_2 + I_2 \xrightarrow{k_{H_2}} 2HI \qquad (1)$$

$$HD + I_2 \xrightarrow{k_{HD}} HI + DI \qquad (2)$$

would provide data that would point out corrections to be made in the *a priori* calculation of the potential surface for the hydrogen–iodine reaction.

Experimental

The ratio of rate constants for reactions 1 and 2 could be found by determining the rate constant for each reaction and taking the ratio of the two. This procedure would involve very precise measurements and control of temperature, time and concentration. Further, HD must be prepared free of H_2 and D_2. A simpler method was devised which removed the necessity of accurate measurement and control of the experimental conditions mentioned above.

By taking the ratio of rate expressions for reactions 1 and 2, eq. 3 is obtained.

$$d(H_2)/d(HD) = [k_{H_2}/k_{HD}][(H_2)/(HD)] \qquad (3)$$

The left side of (3) can be approximated closely by R_p, defined as the ratio of $(H_2)/(HD)$ in the first products of a reaction of iodine with a mixture of H_2 and HD. The ratio $(H_2)/(HD)$ at the right of eq. 3 is defined as R_0 and is the ratio of hydrogen to deuterium hydride in the initial reactants. Then

$$k_{H_2}/k_{HD} = R_p/R_0 \qquad (4)$$

Since the reaction must proceed far enough to give sufficient product for a determination of R_p, and since k_{H_2}/k_{HD} is larger than unity, this relation is not exact. A small correction may be made easily which gives a value of k_{H_2}/k_{HD} that is accurate to well within experimental error. Integration of eq. 3 gives

$$\ln(1 - f) = (k_{H_2}/k_{HD})\ln(1 - f^{\ddagger}) \qquad (5)$$

where the f and $f^{\ddagger}$ are the fractions of the H_2 and HD which have reacted. The value of f can be estimated from the initial concentrations of the reactants, the rate constant, and the time; and it needs to be only approximately correct. To a first approximation $f^{\ddagger}$ is equal to f divided by the approximate value of k_{H_2}/k_{HD} found by eq. 4. Solution of eq. 5 then gives a value of k_{H_2}/k_{HD} which is correct except for a third-order approximation.

---

[1] Presented in a thesis for the partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin, June, 1956.

[2] Humble Oil and Refining Co., Research and Development Division, Baytown, Texas.

[3] J. C. Polanyi, *J. Chem. Phys.*, **23**, 1505 (1955).

[4] M. Bodenstein, *Z. physik. Chem.*, **13**, 56 (1894).

[5] G. B. Kistiakowsky, THIS JOURNAL, **50**, 2315 (1928).

[6] L. S. Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., Inc., New York, N. Y., 1932, p. 154.

[7] (a) N. F. H. Bright and R. P. Hagerty, *Trans. Faraday Soc.*, 697 (1947); (b) A. H. Taylor, Jr., and R. H. Crist, THIS JOURNAL, **63**, 1377 (1941).

[8] (a) J. C. L. Blagg and G. M. Murphy, *J. Chem. Phys.*, **4**, 631 (1936); (b) K. H. Geib and A. Lendle, *Z. physik. Chem.*, **B32**, 463 (1936).

[9] A. Wheeler, B. Topley and H. Eyring, *J. Chem. Phys.*, **4**, 178 (1936).

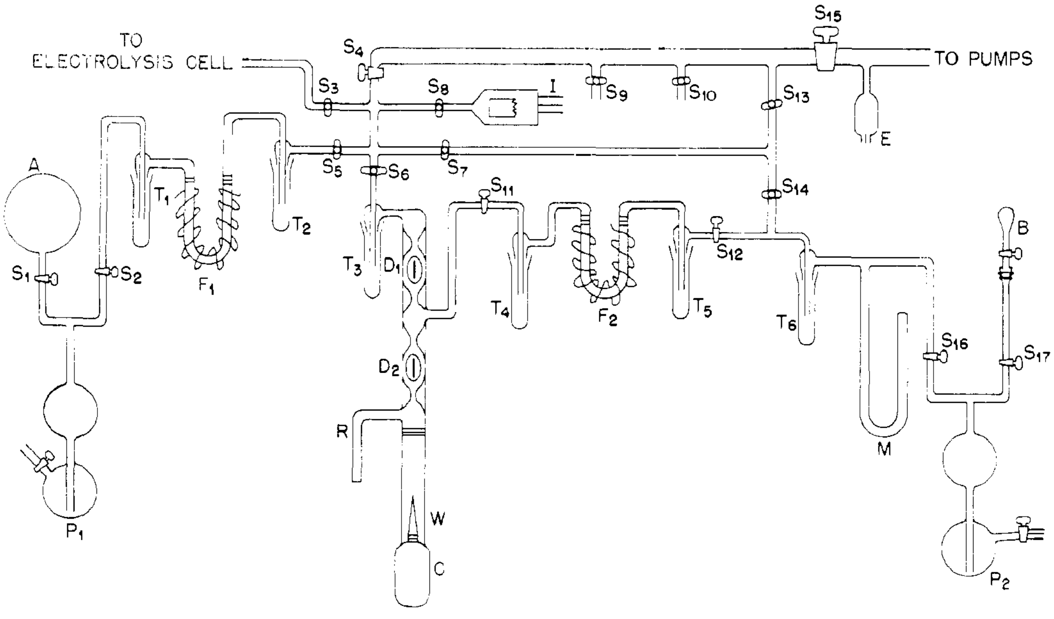

Fig. 1.—Reaction system.

Deriving k_{H_2}/k_{HD} with respect to f in eq. 5, and using actual values of R_p and R_0 together with the approximate value of f, it is found that the error in R is about 0.6 times the error in f. Since the error in f is no more than 0.03, R has an error of no more than 0.018 due to the error in f.

Three ml. of better than 99.5% D_2O obtained from the Stuart Oxygen Company was diluted to 100 ml. with distilled H_2O. Using Na_2SO_4 as electrolyte, the solution was electrolyzed to give a gas containing approximately 1% HD. R_0 must have a value of 0.01 or less in order to avoid the presence of D_2 in the HD–H_2 mixture. Mass spectrometric analysis showed that the concentration of D_2 was negligible.

Figure 1 shows the final vacuum system used in these experiments. The system was evacuated by means of a mercury diffusion pump backed by a mechanical pump. High vacuum stopcocks, S_1 to S_{17}, were employed and greased with Apiezon N stopcock grease. A vacuum of 5×10^{-6} mm. could be reached in a short time after the system had been degassed. Pressures were determined by means of a mercury manometer M, by a thermocouple gage E, or by an ionization gage I, depending on the range of pressure. Mercury vapor was prevented from entering the system by means of Dry Ice traps.

The hydrogen from the electrolysis cell was purified during collection by drawing it through a quartz tube, F_1, filled with zinc and heated externally to about 400°. Any oxygen present either reacted with the zinc to form ZnO or reacted with hydrogen on the surface of the zinc to form water which was trapped in the liquid air trap at T_1. The hydrogen was stored in bulb A with the help of the Toepler pump, P_1.

The furnace used in this work consisted of an aluminum block, wound with two coils of nichrome wire and covered with magnesia pipe covering. The furnace was mounted on a jack so that it could be raised and lowered easily. Since the temperature dependency of the isotope effect is quite small,[7b] only a Variac was used to control the temperature. A variation in temperature of no more than ±1° was found during an experiment, and the variation in temperature over a sufficiently large region in the furnace did not exceed ±1°. Temperatures were measured with a calibrated chromel-alumel thermocouple. Quartz reaction cells with volumes of approximately 120 ml. were used in these experiments. In early experiments the reaction vessel had a break-seal and ground glass joint at one end. The other end was attached to the system in the position C in Fig. 1 by means of a graded seal.

In order to use eq. 3, it is necessary to allow the hydrogen-deuterium mixture to react with iodine to approximately 5 or 10% completion. The HI and DI which is formed must then be reconverted to hydrogen and deuterium for mass spectrometric analysis. The following paragraphs give the details of the procedure.

A short length of 10 mm. tubing, sealed at one end, was flamed with a Bunsen burner under vacuum and allowed to cool. Approximately 0.25 g. of Baker reagent grade iodine was weighed in the tube which was then sealed to the system at R. Trap T_3 was immersed in liquid air and the system was evacuated until iodine appeared in trap T_3. The iodine reservoir was then immersed in liquid air. Pumping was continued and the reaction cell was flamed to red heat. After the system had been at a pressure of 5×10^{-6} mm. for several hours, pumping was discontinued, and a small quantity of the hydrogen-deuterium mixture from A was passed through the hot zinc in F_1 into the reaction cell. The cell C was then heated to red heat several times and the mixture was allowed to remain in C overnight. The cell was flamed once more and the isotopic mixture was pumped off. This procedure of heating the reaction cell in the presence of hydrogen has been found necessary in order to remove all the oxygen adsorbed on the walls.[7b]

The plugs, D_1 and D_2, were small sealed tubes containing nails which could be raised and lowered with a magnet. The ends of the tubes had been ground to fit the sockets, forming a ball joint. After the reaction cell had been conditioned as outlined above, the plug D_2 was closed and the liquid air was removed from R and placed around C. The iodine in R sublimed into C and the very small amount of gas which had been adsorbed by the iodine was pumped off.

The hydrogen-deuterium mixture was admitted to the cell to a pressure such that the cell contained approximately 3.5×10^{-3} mole of the mixture. The small tube connecting C to the system was then closed with a torch and melted through—thus detaching the cell. Part of the hydrogen-deuterium mixture remaining in the system was transferred with the Toepler pump P_2, into a sample bulb B, connected through a ground glass joint. This sample was labeled "standard."

The detached reaction cell was placed in the furnace and allowed to remain until approximately 5 to 10% of the hydrogen had reacted. The rate constant of Taylor and Crist[7b] was used to determine the approximate time. The reactants were then cooled quickly by first blowing a stream of air on the reaction cell for about 5 seconds and then immersing the cell in water.

In earlier experiments the tube to the left of S_{11} in Fig. 1 was not attached to the tube between D_1 and D_2, but ended in a ground glass joint. Another tube connected the vacuum main from S_9 to the tube at the left of S_{11}. The reaction cell was attached to the ground glass joint and immersed in liquid air. The joint was evacuated through S_9. A second furnace tube, F_2, containing zinc was heated to *ca.* 400° and evacuated. Stopcocks S_4, S_7, S_{11}, S_{12} and S_{15} were closed and the break-seal on the cell was broken with a nail sealed into glass tubing and operated with a magnet. The system was again evacuated and stopcocks S_9 and S_{14} were closed while S_{11} and S_{12} were opened. Trap T_5 was immersed in liquid air and Dry Ice–trichloroethylene mixture was substituted for the liquid air around the reaction cell. The hydrogen and deuterium iodides which were produced by the reaction vaporized and passed over the hot zinc where they were quickly reduced to hydrogen and deuterium hydride. This gas was collected in a second bulb by means of the Toepler pump, P_2, and labeled "product." That all the hydrogen iodide had been reduced to hydrogen was shown by the lack of condensate in trap T_5. The trap T_4 was included in the system so that the hydrogen iodide could be sublimed back and forth through F_2, but this was found to be unnecessary.

The two samples, standard and product, were then analyzed with a model 21-620 Consolidated Engineering Corporation mass spectrometer. The mass spectrometer was used through the courtesy of Professor I. Shain and operated by Mr. J. M. Ross. Peaks representing m/e of 2 and 3 were obtained on the automatically recorded charts. The ratio of peak 3 to peak 2 gives the ratio of HD to H_2 except for a small correction due to the formation in the mass spectrometer of H_3. At low ratios of HD to H_2, the graph of the ratio of the 3 peak to the 2 peak, $R_{3/2}$, *versus* pressure is a straight line. The intercept is the actual ratio of HD to H_2 because in the limit of zero pressure, H_3 is absent. Using HD to H_2 ratios in the range of 0.01, the graph was not straight and the extrapolation to zero pressure was difficult. Under these circumstances, since a ratio of the $R_{3/2}$'s for the "standard" and the "product" was the only quantity of interest, the best procedure was to compare the two values of $R_{3/2}$ at the same pressure. The errors in each should approximately cancel.[10]

Early results showed the $R_{3/2}$ of the standard to be about 0.0113 and the $R_{3/2}$ of the products to be 0.00208, both at a pressure of 10 mm. Using eq. 3, a value of about 5.5 was calculated for k_{H_2}/k_{HD}. After the third experiment, the value of k_{H_2}/k_{HD} dropped to 2.3. This indicated that the deuterium in the products had been exchanging with hydrogen in the zinc furnace F_2, inasmuch as a new reaction cell had been used for each experiment. This "memory effect" is quite well known in the reduction of water vapor by zinc.[11]

Fearing that such exchange might also be occurring on the walls of the reaction cell, the apparatus was modified as shown in Fig. 1. A cell equipped with a Willard seal[12] was used. This seal consists of a Pyrex capillary attached to the cell through a graded seal and surrounded by a quartz tube attached to the system. When the pressures in the cell and system are equal, the capillary can be closed by heating the surrounding quartz tube. When the pressure in the cell is greater than that in the system, the capillary can be opened by heating the quartz tube.

The cell was flamed and filled with the iodine as before. The hydrogen–deuterium mixture was run in and the tip of the capillary was sealed. The furnace at an average temperature of 405° was jacked up around the cell and allowed to remain until 5–10% of the reaction had taken place and was then lowered. The cell was cooled immediately, as before, and was then surrounded by liquid air.

The capillary was opened by flaming the quartz tube and the unreacted hydrogen–deuterium mixture was pumped off. Stopcocks S_6 and S_{14} and the plug D_1 were closed and stopcocks S_{11} and S_{12} were opened. Dry Ice was substituted for the liquid air around C and the HI and DI vaporized and flowed through the zinc furnace F_2. The resulting H_2 and HD were collected in B. The system was pumped for a short while and liquid air was again placed around C to prevent the removal of the iodine. The system was thoroughly evacuated and a new supply of the hydrogen–deuterium mixture was admitted. The procedure was repeated six times.

Results and Conclusions

Table I gives the result of six experiments carried out as just described.

TABLE I

APPARENT k_{H_2}/k_{HD}, R, AS A FUNCTION OF EXPERIMENT NUMBER

R	Expt. no.	R	Expt. no.
2.383	1	1.509	4
1.831	2	1.538	5
1.595	3	1.530	6

Figure 2 shows the apparent k_{H_2}/k_{HD}, R, plotted against the run number. The decrease in the apparent ratio of rate constants as the number of experiments with the same cell increases is quite apparent. As more experiments with the same cell are carried out, the ratio of deuterium to hydrogen in the cell wall increases and approaches the ratio of DI to HI in the cell. After four runs the wall-exchange effect disappeared. The ratio $R = R_p/R_0$ had a final value of 1.526 ± 0.01. This would be the value of k_{H_2}/k_{HD} if only an infinitesimal amount of the reactants had reacted, but a small correction was made with the help of eq. 5. The value of f was estimated in the present case to be 0.07. Using R = 1.526, a value of f^* of 0.0458 is found. Substitution of these values in eq. 5 gives a final value of k_{H_2}/k_{HD} of 1.548 at 405°.

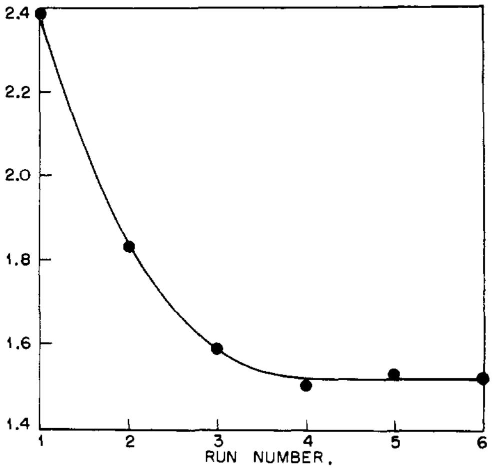

Fig. 2.—Wall exchange in the deuterium isotope effect.

Discussion

The method used in the present studies has inherent advantages over the measurement of the rate constants for each of the two isotopic reactions. The first advantage is the fact that precise temperature control is unnecessary. The temperature coefficient of the ratio of rate constants is very small. Taylor and Crist found no change in the H_2–D_2 isotope effect greater than experimental error over a 40° temperature interval.[7b] If a rate constant were measured for the reaction of H_2 with iodine and another for the reaction of HD with iodine, very precise temperature control would be necessary.

Furthermore, the concentrations of the initial reactants and the final products need be known only approximately. These concentrations only enter the results in the calculation of the correction term, and this term amounts to only 1.5% of the actual value of k_{H_2}/k_{HD}. For example, during the transfer of the iodine from R to C, a small, but un-

---

[10] Professor I. Shain, University of Wisconsin, private communication.

[11] R. F. Glascock, "Isotopic Gas Analysis for Biochemists," Academic Press, Inc., New York, N. Y., 1954, p. 147.

[12] J. E. Willard, THIS JOURNAL, **57**, 2328 (1935).

determined amount escaped through the plugs, D_1 and D_2. This caused no difficulty in the present work, but if a value of a rate constant were being measured, the initial concentration would be very important.

Finally, an exact measurement of the time is not necessary. The problem of determining the time at which the reactants reach the reaction temperature is thus avoided.

The only source of error in the results presented here is believed to be the mass spectrometric readings. The error in k_{H_2}/k_{HD} from this source should be no greater than 1 or 2%.

Bigeleisen[13] has derived an equation expressing the ratio of two isotopic reactions only in terms of the vibrational frequencies of the reacting molecule and the activated complex

$$k_1/k_2 = S(\nu_1{}^*/\nu_2{}^*) \prod_{i}^{3n-6} (u_{i2}/u_{i1}) \frac{e^{-u_{i2}/2}/(1 - e^{-u_{i2}})}{e^{-u_{i1}/2}/(1 - e^{-u_{i1}})}$$

$$\prod_{i}^{3n^*-7} (u^*{}_{i1}/u^*{}_{i2}) \frac{e^{-u^*{}_{i1}/2}/(1 - e^{-u^*{}_{i1}})}{e^{-u^*{}_{i2}/2}/(1 - e^{-u^*{}_{i2}})} \quad (6)$$

The terms in eq. 5 were defined by Bigeleisen.

According to eq. 5, all that is necessary to check k_{H_2}/k_{HD} from theoretical considerations are the vibrational frequencies of the reacting molecules and the activated complex. A potential surface for the activated complex has been calculated for this reaction and the vibrational frequencies for the H_2I_2 and D_2I_2 complexes were determined.[9] The same surface can be used to calculate the vibrational frequencies for the HDI_2 complex. A method has been presented[14] for carrying out the calculations, but the procedure is quite long because the determinantal equation cannot be factored due to lack of symmetry in the activated complex.

The iodine atoms are much heavier than the hydrogen atoms and hence will move very little during a vibration. Since this is true the following relation was assumed to hold for the vibrational frequencies of the activated complexes H_2I_2 and HDI_2

$$\nu_{i,HDI_2} = \nu_{i,H_2I_2}\sqrt{\mu_{H_2}/\mu_{HD}} \quad (7)$$

where the μ's are the reduced masses of H_2 and HD, respectively. This equation is assumed to hold for all the vibrational frequencies of the activated complex with one exception; the normal mode of vibration in which only the iodine atoms move in the H_2I_2 complex was assumed to be the same for the two activated complexes. It is believed that the values of ν_{i,HDI_2} calculated in this way are very close to the values which would be calculated by a more rigorous treatment. Actually, Eyring and co-workers[9] found that the frequencies for the H_2I_2 and D_2I_2 complexes fit such a relationship exactly.

Ignoring the value of the vibrations involving only I_2, the frequencies calculated[9] for the H_2I_2 activated complex are, 994, 1280, 965i, 1400 and 1730—all in cm.$^{-1}$. Herzberg[15] gives the vibrational frequency of the H_2 molecule as 4395.2 cm.$^{-1}$. Using eq. 7, the corresponding frequencies of the HDI_2 activated complex are found to be 861, 1109, 836i, 1212 and 1498 cm.$^{-1}$ while the frequency of HD, using the same equation, is 3806 cm.$^{-1}$. Substitution of these values of ν into eq. 6 gives a value for k_{H_2}/k_{HD} of 1.366, without correcting for the tunnel effect. This correction for leakage through the energy barrier is given by $1 - (h\nu^*/kt)^2/24$, where ν^* is the imaginary frequency along the reaction coördinate.[16] Substituting the imaginary frequencies given above into this equation, a correction factor of 1.039 is found. The product of 1.366 and 1.039 gives a value of 1.42 for the ratio k_{H_2}/k_{HD}. It is interesting to note that this value is approximately 10% too low, whereas the value calculated[9] for k_{H_2}/k_{D_2} was too high by about 10%. It seems that corrections are necessary in the calculated potential energy surface.

Daniels[17] has given a simple method for estimating the isotope effect. This method is summarized in eq. 8

$$k_1/k_2 = \exp[-{}^1/{}_2 h\nu_1(\sqrt{\mu_1/\mu_2} - 1)/kT] \quad (8)$$

where k_1 and k_2 are the rate constants for the isotopic reactions, ν_1 is the vibrational frequency of the lighter isotope, the μ's are the reduced masses of the atoms forming the bonds being broken, and h, k and T have their usual significance. Using eq. (8) and assuming that the relative rates of breaking the hydrogen–hydrogen bond and the hydrogen–deuterium bond determine the isotope effect, a value of 1.87 is found for k_{H_2}/k_{HD}. This value is too high by 21%.

Bigeleisen has pointed out[18] that for isotopes of elements other than hydrogen, $[(k_m/k_{m + 2\Delta m}) - 1]/[(k_m/k_{m + \Delta m}) - 1] = 2$. This is inherent in the fact that the isotope effect is due only to a mass difference. A ratio close to the one above is seen to exist for the present work. The ratio $(k_{H_2}/k_{D_2} - 1)/(k_{H_2}/k_{HD} - 1)$ is 1.76. For this reaction at least, substituting a second deuterium atom has somewhat the same effect as increasing the isotopic weight by another mass unit.

Another point of interest is the fact that the isotope effects observed for the hydrogen–iodine reaction are proportional to the total mass of the hydrogen atoms in the isotopic activated complex. That is, $k_{H_2}/k_{D_2} = M_{H_2}/2 = 1$ and $k_{H_2}/k_{HD} = 1.55$, whereas $M_{HD}/2 = 1.5$. Again, $k_{H_2}/k_{D_2} = 1.97$, whereas $M_{D_2}/2 = 2$. No theoretical reason is known for this relationship.

The present work includes the determination of the independent deuterium isotope effects in the reaction of hydrogen with iodine. The ratio, k_{D_2}/k_{HD} can be obtained by dividing the ratio k_{H_2}/k_{HD}, by k_{H_2}/k_{D_2}. The result is 0.786. The equilibrium constant for the reaction of the hydrogen isotopes may be measured or calculated from spectral data. These equilibrium constants

---

(13) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

(14) W. Altar and H. Eyring, *ibid.*, **4**, 661 (1936).

(15) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1950.

(16) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw–Hill Book Co., Inc., New York, N. Y., 1941, p. 191.

(17) F. Daniels, "Chemical Kinetics," Cornell University Press, Ithaca, N. Y., 1938, p. 248.

(18) J. Bigeleisen, *J. Phys. Chem.*, **56**, 823 (1952).

together with the isotope effects for the forward reactions determine the isotope effects for the reverse reactions.

Tritium offers the possibility of determining three more independent isotope effects for the hydrogen–iodine reaction. These may be k_{H_2}/k_{T_2}, k_{H_2}/k_{HT} and k_{H_2}/k_{DT}. When these isotope effects are available, an excellent picture of the configuration of the activated complex may be obtained. Eventually, it may be possible to measure the effect of substituting the isotopes of iodine. This will indeed complete the picture.

The author desires to acknowledge the help of Professor Farrington Daniels under whose direction this research was done, and to express appreciation to the National Science Foundation for a pre-doctoral fellowship.

MADISON, WIS.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions of Complex Ions. XIII. Reactions of Some *trans*-$Co(AA)_2Cl_2^+$ in Methanol[1,2]

BY RALPH G. PEARSON, PATRICK M. HENRY AND FRED BASOLO

RECEIVED MAY 25, 1957

Rates of substitution reactions in methanol are reported for a series of *trans*-$Co(AA)_2Cl_2^+$ complex ions with several anionic reagents. Within experimental error the same rates of reaction are obtained for both basic and non-basic anions with a given complex ion except in one case. Abnormally large rates with basic anions are usually completely repressed by strong buffering, showing that methoxide ion alone produces an increased rate. The rates with methoxide ion in methanol are correlated with the rates of base hydrolysis in water and the rates of reaction with other anions in methanol are correlated with the rates of acid hydrolysis in water. Dissociation mechanisms are indicated in all cases.

In water the direct reaction between an octahedral complex of cobalt(III) and a nucleophilic reagent cannot be studied since an intermediate hydrolysis step invariably occurs. In a weakly complexing solvent such as methanol this complication apparently is absent and a number of direct reactions seem to occur. Thus Brown and Ingold[3] studied the rates of reaction of *cis*-$Co(en)_2Cl_2^+$ in methanol with several anionic reagents. Their results were very interesting inasmuch as several weakly basic anions such as NO_3^-, Br^-, CNS^- and $^*Cl^-$ reacted at the same rate which was independent of the concentration of the reacting anion and equal to the rate of racemization if optically active *cis*-$Co(en)_2Cl_2^+$ was used. This was interpreted as evidence for a common S_N1 or dissociation mechanism in these cases. Certain basic anions, CH_3O^-, N_3^- and NO_2^- reacted more rapidly and at a rate roughly proportional to the concentration of the anion. This was assumed to show an S_N2 or displacement mechanism for these reactions.

However, it may be pointed out that the methoxide ion reaction in methanol is very likely the analog of the hydroxide ion reaction in water. This latter reaction seems to go by a special dissociation mechanism of the conjugate base of the original complex ion.[4] Thus complexes which do not have acidic protons react at the same rate in acid and in alkali because the conjugate base cannot be formed. Furthermore in cases such as *cis* and *trans*-$Co(en)_2Cl_2^+$ the reaction with hydroxide ion is so much greater than with water in acid solution that even at *p*H 7 the reaction can involve primarily the hydroxide ion path. Since the previous work in methanol using basic reagents was done in unbuffered systems, it is obvious that the increases in rate observed may be almost entirely due to methanolysis producing methoxide ion, *e.g.*

$$N_3^- + CH_3OH \longrightarrow NH_3 + OCH_3^- \qquad (1)$$

Accordingly a study of the reactions of a number of complex ions of cobalt(III) in methanol with several anions has been carried out using buffered systems of variable composition. The results on a series of *trans*-$Co(AA)_2Cl_2^+$ where AA is a substituted ethylenediamine are presented here

$$trans\text{-}Co(AA)_2Cl_2^+ + X^- \longrightarrow Co(AA)_2ClX^+ + Cl^- \qquad (2)$$

Experimental

Preparation of Compounds.—The synthesis of the complex salts $[Co(AA)_2Cl_2]Cl$ has been described elsewhere.[5] These were purified by converting them to their perchlorate salts with $NaClO_4$ to eliminate cobalt(II) salts and HCl impurities. The purity of the salts was then determined by total chloride analyses which agreed well with theory.

Sodium acetate and glacial acetic acid were used without purification. Sodium azide was recrystallized from acidified aqueous solution. Reagent grade absolute methanol was used without further treatment after it was ascertained that up to 0.5% added water had no effect on the measured rates. Radioactive HCl in aqueous solution was obtained on allocation from the Oak Ridge National Laboratory with a specific activity of 0.367 mc./g. It was converted to LiCl with lithium hydroxide and recovered by evaporation.

Acetate buffers were made by mixing stock solutions of acetic acid and sodium acetate. The acetic acid solution was standardized by titration and remade frequently because of the slow methanolysis. Azide buffers were made by adding a methanol solution of *p*-toluenesulfonic acid monohydrate to a methanol solution of sodium azide. Generally a small amount of this acid or methanolic HCl was added to the thiocyanate and chloride solutions to ensure that they were on the acid side.

Kinetic Measurements.—The reactions studied occur in two steps, reaction 2 being followed by

$$Co(AA)_2ClX^+ + X^- \longrightarrow Co(AA)_2X_2^+ + Cl^- \qquad (3)$$

---

[1] For previous papers in this series see THIS JOURNAL, **79**, 4055 (1957). AA is a substituted ethylenediamine.

[2] Presented in part at the Dallas Meeting of the A.C.S., April, 1956. This investigation supported by a grant from the U. S. Atomic Energy Commission under Contract AT(11-1)-89-Project No. 2.

[3] D. D. Brown and C. K. Ingold, *J. Chem. Soc.*, 2680 (1953).

[4] R. G. Pearson, R. E. Meeker and F. Basolo, *J. Inorg. Nuc. Chem.*, **1**, 342 (1955); THIS JOURNAL, **78**, 709 (1956); R. G. Pearson and F. Basolo, *ibid.*, **78**, 4878 (1956).

[5] F. Basolo, *ibid.*, **75**, 227 (1953).