by first-order kinetics. The temperature is taken to be 21.5 ± 1.5°K. If equation 1 is applicable and if $\Delta S^{\circ\ddagger} = 0$, then the disappearance of the band at 865 cm.$^{-1}$ is governed by a process with a heat of activation of 1500 ± 130 cal.

The two features which vary with time, 868 and 818 cm.$^{-1}$, are assigned, respectively, to the *cis* and *trans* forms of nitrous acid, HNO_2. This species is presumed to form in the reactions 2, 3 and 4, followed by 5.

$$HN_3 + h\nu = NH + N_2 \qquad (2)$$

$$NH + O_2 = HONO\ (\textit{trans}) \qquad (3)$$

$$NH + O_2 = HONO\ (\textit{cis}) \qquad (4)$$

$$HONO\ (\textit{cis}) = HONO\ (\textit{trans}) \qquad (5)$$

The identification is supported by the vibrational assignment proposed by earlier workers.[6,7] They assign the intense absorptions at 856 and 794 cm.$^{-1}$ to the O–N stretching modes of the gaseous *cis* and *trans* isomers, respectively.

The energy of the *cis* form is 506 ± 250 cal./mole above the *trans* form.[7] Jones, *et al.*, estimate the barrier to internal rotation to be about 12 kcal./mole,[7] More recently but without new data Palm[8] has expressed agreement with this estimate. It is not possible to rationalize a 12 kcal. barrier with the measured rate either by adjustment of $\Delta S^{\circ\ddagger}$ or of the (kT/h) factor. It is possible but unlikely that the reaction under study is not the *cis–trans* isomerization of HNO_2. More detailed studies of this system are in progress, both to corroborate the assignment and to measure $\Delta S^{\circ\ddagger}$.

Conclusion

It is clear that the matrix isolation technique offers unique possibilities in the study of reaction kinetics. There are limitations and difficulties of interpretation whose importance cannot be evaluated without more experience. The most serious of these is probably that the matrix may influence the activation thermodynamics of the reactions studied. Nevertheless it seems likely that the method will prove to be a valuable tool for the study of extremely fast reactions, including the reactions of free radicals.

Acknowledgment.[9]—The author wishes to thank Professor Robert E. Connick for many helpful and critical discussions.

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[9] The research described was supported in part by the American Petroleum Institute, Research Project 50, and by the United States Air Force through the AFOSR of the Air Research and Development Command, under Contract No. 49(638)-1. Reproduction in whole or in part is permitted for any purpose of the U. S. Government.

BERKELEY, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, COLLEGE OF PHYSICIANS AND SURGEONS, COLUMBIA UNIVERSITY]

The Catalysis of the H_2–D_2O Exchange by Aqueous Buffer Solutions[1]

BY S. L. MILLER AND D. RITTENBERG

RECEIVED AUGUST 9, 1957

The exchange between molecular hydrogen and D_2O is known to be catalyzed by hydroxide ion and follows the rate law[3] $d(P_{HD})/dt = k(P_{H_2})(OH^-)$. The exchange has been investigated at lower *p*H values in the temperature range 110–190° using borate, phosphate, glycine, succinate and acetate buffers. The same rate law is obeyed provided the OH^- concentration measured at 25° is corrected for the change in the *pK* of the acid and the *pK* of the water at the higher temperatures. The heat of activation is 28 ± 3 kcal. Neither dilute nor concentrated acids catalyze the exchange.

During an investigation of the catalysis by various compounds of the H_2–D_2O exchange reaction, it was necessary to correct for the exchange reaction which occurs in the absence of added catalysts. It is known that hydroxide ion will catalyze the exchange.[2] More recently[3] an investigation of the mechanism has shown that the rate of exchange is proportional to the pressure of hydrogen gas and the OH^- concentration in the range 0.1 to 1 *M*. An extension of the exchange experiments to lower values of *p*H is reported in this paper.

Experimental

The exchange reactions were carried out in Pyrex tubes of about 3-ml. capacity with a break seal at one end. 0.5 ml. of buffer and 0.5 ml. of D_2O were placed in the tube, and the gas phase replaced by hydrogen. The reaction tubes were kept at a constant temperature (±1°) in an oven which was rocked about 10 times per minute. After various time intervals the deuterium concentration of the gas phase was determined by mass spectrometric analysis. The average of the initial and final *p*H values was taken as the *p*H of the system. The data were reproducible within ±5%.

Consider a system in which the gas phase initially contains H_2, and the aqueous phase contains D_2O of mole fraction N_D. If the exchange is catalyzed only by hydroxide ion, the rate law is

$$d(HD)_l/dt = kN_D(OH^-)(H_2)_l \qquad (1)$$

where k is expressed in liters mole^{-1} hr.$^{-1}$, $(HD)_l$ and $(H_2)_l$ are the molar concentrations of these gas species in solution. This equation ignores the isotope effect between H_2O and D_2O, but it can be included in the constant N_D. Let V_l be the volume of solution, V_g the volume of gas, K_s the constant of Henry's law, P_{H_2} the partial pressure of H_2. We will consider the case where the reaction proceeds only to a small extent. The number of moles of HD, n_{HD}, produced after t hours in V_l liters of solution is obtained by integrating eq. 1 to give

$$n_{HD} = kN_D\,(OH^-)K_sP_{H_2}V_lt$$

The HD produced in solution is mixed with the $P_{H_2}V_g/RT$ moles of H_2 in the gas phase, therefore, the ratio of HD to H_2 in the gas phase after t hours is

$$(HD/H_2)_g = kN_DK_s(OH^-)\ RT(V_l/V_g)t$$

or

$$(HD/H_2)_g = k'(OH^-)(V_l/V_g)t \qquad (2)$$

where $k' = kN_DK_sRT$. This equation requires that the rate of increase of HD/H_2 be independent of the pressure of the hydrogen, proportional to the ratio of the liquid to gas volumes, and proportional to the concentration of hydroxide ion if the exchange is catalyzed only by hydroxide ion.

Since the experiments were carried out at temperatures above 100° it was necessary to calculate the hydroxide ion

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[1] This research was supported by Atomic Energy Commission Contract #AT(30-1)1803 to Columbia University.

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concentration from data obtained at 25°. The concentration of hydrogen ion in a solution of an acid (HA) and its anion (A^-) is (H^+) = $K_A^T(HA)/A^-$), where K_A^T is the ionization constant of HD at temperature T. Since (OH^-) $= K_W^T(H^+)$, where K_W^T is the ion product constant for water at temperature T, we have $(OH^-) = K_W^T(A^-)/K_A^T$ (HA). In the buffer region $(A^-)/(HA)$ will not change appreciably with temperature, therefore

$$\frac{(OH^-)^T}{(OH^-)^{25}} = \frac{K_W^T/K_A^T}{K_W^{25}/K_A^{25}}$$

With sodium hydroxide solutions the concentration of OH^- does not change appreciably with temperature.

The ionization constants at elevated temperatures were calculated by extrapolation of the empirical equations obtained for water[4] and the acids[5] in the 0–60° region. The range of the extrapolations is much greater than the data warrant, but the error is probably not more than 0.2 *p*H unit. These extrapolations yield the *pK* values in Table I.

TABLE I

CALCULATED VALUES OF *pK* AT ELEVATED TEMPERATURES

	25°	130°	150°	170°	190°
Water	14.00	11.88	11.70	11.56	11.47
Borate	9.23	9.05	9.13		
Glycine (pK_2)	9.78	7.88	7.65	7.45	7.28
Phosphate (pK_2)	7.20	7.55	7.72	7.90	8.10
Succinate (pK_2)	5.64		6.37	6.57	6.79
Acetate	4.76		5.27	5.41	5.57

Results

The dependence of the exchange on hydrogen pressure and gas volume is shown in Table II. It is seen that the exchange is independent of the hydrogen pressure and proportional to V_l/V_g. It also was found in other experiments that the exchange is directly proportional to the reaction time as predicted by eq. 2.

TABLE II

DEPENDENCE OF EXCHANGE ON HYDROGEN PRESSURE AND GAS VOLUME

Expts. 1–5; T = 140°, 3 hours, 0.055 M NaOH. Expts. 6–10; T = 140°, 0.75 hour, borate buffer, *p*H 10.2.

	$(HD/H_2) \times 10^2$	pH_2 (cm.)	V_g/V_l	(HD/H_2)-$10^2V_g/V_l$
1	6.12	4.9	3.69	22.6
2	7.07	16.2	3.15	22.2
3	6.97	35.0	3.23	22.5
4	7.16	54.7	3.22	23.0
5	6.50	66.4	3.46	22.5
6	2.62	63.5	0.70	1.83
7	1.61	63.5	1.12	1.80
8	1.00	63.5	1.85	1.86
9	0.655	63.5	3.00	1.96

Changing the concentration of buffer does not alter the rates of exchange indicating that the exchange does not involve the anion of the acid. The addition of Versene, tris-(hydroxymethyl)-aminoethane or citrate does not alter the rate of exchange. Some metal ions catalyze the exchange but not sufficiently that trace amounts of these metal ions could account for the exchanges found with these buffers.

The values of $(HD/H_2)_g t V_g/V_l$ for various buffers are plotted against the calculated (OH^-) for several temperatures in Fig. 1. The rate of exchange is directly proportional to the concentration of hydroxide ion in the range of 10^{-1} to 10^{-5} M as predicted by eq. 2. At lower values of (OH^-) the rate of exchange does not decrease as the (OH^-) decreases but remains roughly constant. The exchanges at low (OH^-) were somewhat erratic.

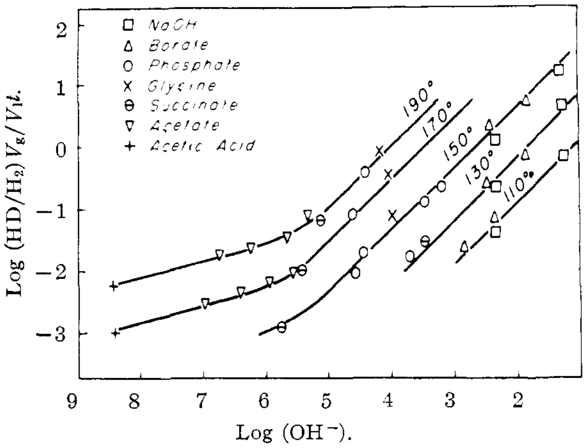

Fig. 1.—Rate of exchange as a function of OH^- concentration at various temperatures.

In the range of (OH^-) concentrations of 10^{-1} to 10^{-5} M, the heat of activation calculated from these data is 28 ± 3 kcal. Wilmarth, *et al.*,[3] reported 24 kcal. for the heat of activation of the conversion of ortho- to parahydrogen and about 25 kcal. for the exchange reaction in potassium hydroxide solutions in the region 80–110°. These values are in essential agreement with the 28 kcal. obtained in these experiments.

The failure of the rate of exchange to fall off as rapidly as the hydroxide ion concentration below 10^{-5} M may be due to an exchange reaction catalyzed by water instead of hydroxide ion.

No exchange was observed with dilute or concentrated phosphoric, hydrochloric, nitric or sulfuric acids at 150°. Dilute perchloric acid did not catalyze the exchange, but concentrated perchloric acid (70%) oxidized most of the hydrogen and also catalyzed the exchange. Fuming sulfuric acid (15% SO_3) oxidized the hydrogen.

The rate-determining step of the hydroxide ion catalyzed exchange seems to involve the formation of a hydride ion[2,3] according to the reaction

$$H{:}H + OD^- \longrightarrow H^- + HOD \qquad (3)$$

$$H^- + D_2O \longrightarrow HD + OD^- \qquad (4)$$

A similar reaction can be written for the exchange catalyzed by the weak base water giving

$$H{:}H + D_2O \longrightarrow H^- + HD_2O^+ \qquad (5)$$

Whether the reactions 3 and 4 act together in a concerted reaction cannot be told by simple kinetic data.[3] A study of the isotope effects in the OH^- catalyzed exchange may give some information on the nature of activated complex, and these experiments are in progress.

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