The vapor pressure data are shown graphically in Fig. 2 and Fig. 3 shows the isotherms plotted by taking values from Fig. 2. According to the results of Fig. 3, the concentration is a linear function of the sulfur dioxide content except at the lower temperatures of the low concentrations.

Summary

1. Partial vapor pressures for sulfur dioxide in the system sulfur dioxide in water have been determined over the temperature range 20–110° and total pressure range of 10 to 150 cm. of mercury for concentrations of 0.51, 1.09, 4.36 and 7.45 grams of sulfur dioxide in 100 grams of water.

2. These data extend the values of the International Critical Tables and show excellent agreement over the coincident ranges.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

The Energy and Entropy of Activation of the Hydrolysis of Ethyl Orthoformate in Deuterium Oxide

BY FRANK BRESCIA* AND VICTOR K. LAMER

Introduction

Current theory of chemical kinetics recognizes the energy of activation and the entropy of activation as the important factors governing the specific rate of a reaction in the presence or absence of a catalyst. LaMer[1] derived the equation

$$k = e^{-\Delta H^*/RT}\, e^{\Delta S_{\text{act}}/R}\, Z^\circ \qquad (1)$$

or

$$\log k = -(\Delta H^*/2{\cdot}3RT) + B \qquad (2)$$

where

$$\Delta H^* = RT^2 \frac{\mathrm{d} \ln k}{\mathrm{d}T} \qquad (3)$$

from Tolman's statistical treatment[2] and a collisional mechanism for formation of the intermediate complex. In Eyring's treatment[3]

$$k = \kappa e^{-\Delta H^*/RT}\, e^{\Delta S^*/R}\, RT/Nh \qquad (4)$$

Hence

$$B = \frac{\Delta S^*}{2{\cdot}3R} + \log \kappa \frac{T}{Nh} \qquad (5)$$

Classical theory ascribed the entropy contribution $\Delta S^*/2{\cdot}3R$, to a so-called "steric or probability factor" expressed by P in the equation

$$k = e^{-\Delta H^*/RT}\, PZ^\circ \qquad (6)$$

The symbols have been defined in the literature cited.

Many previous investigators[4] have shown that the deuterium ion is a more effective catalyst than the hydrogen ion in many reactions. A noteworthy exception is the mutarotation of glucose.[5]

This increase in reactivity has been ascribed[6] to an increase in the equilibrium constant for the process Substrate + H^+ = SH^+ on passing from H^+ to D^+. The ratio of the equilibrium constants would be equal to the measured ratio for the specific rates. This is apparent when the theoretical equations for the rate constant are expressed in the form

$$k = \nu K^* \qquad (7)$$

where ν is a frequency term. Several investigators[7] have expressed the view that the increase in the concentration of the deutero complex can be accounted for by the lower zero point energy of the *d*-complex or, hence, by an observable difference in the activation energies, $\delta\Delta H^*$, of the two systems. ($\delta\Delta H^* = \Delta H^*_{\text{H}} - \Delta H^*_{\text{D}}$.) This is equivalent to the assumption that the ΔH^* factor

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[1] LaMer, *J. Chem. Phys.*, **1**, 289 (1933); LaMer and Kamner, THIS JOURNAL, **57**, 2662, 2669 (1935); Liotta and LaMer, *ibid.*, **60**, 1972 (1938).

[2] Tolman, "Statistical Mechanics," Chemical Catalog Co., New York, 1927, Chaper 21.

[3] Eyring, *J. Chem. Phys.*, **3**, 107 (1935); Wynne-Jones and Eyring, *ibid.*, **3**, 492 (1935).

[4] Moelwyn-Hughes and Bonhoeffer, *Naturwissenschaften*, **22**, 174 (1934); Gross, Suess and Steiner, *ibid.*, **22**, 662 (1934); Schwartz, *Akad. Anzeiger*, 26 April, 1934, Wien; Gross, Steiner and Suess, *Trans. Faraday Soc.*, **32**, 883 (1936); Hornel and Butler, *J. Chem. Soc.* (London), 1361 (1936); Gross, Steiner and Krauss, *Trans. Faraday Soc.*, **32**, 877 (1936); Reitz, *Naturwissenschaften*, **24** 814 (1936); *Z. physik. Chem.*, **179A**, 119 (1937); Brescia and LaMer, THIS JOURNAL, **60**, 1962 (1938); Nelson and Butler, *J. Chem. Soc.*, 957 (1938); Reitz, *Z. physik. Chem.*, **A183**, 371 (1939).

[5] Hammill and LaMer, *J. Chem. Phys.*, **2**, 891 (1934); **4**, 395 (1936).

[6] Moelwyn-Hughes, *Z. physik. Chem.*, **B26**, 272 (1934). LaMer, *Chem. Revs.*, **19**, 363 (1936); Bonhoeffer and Reitz, *Z. physik. Chem.*, **A179**, 135 (1937); Bonhoeffer, *Trans. Faraday Soc.*, **34**, 252 (1938); Wynne-Jones, *ibid.*, **34**, 245 (1938); *J. Chem. Phys.*, **2**, 381 (1934); Brescia and LaMer, THIS JOURNAL, **60**, 1962 (1938).

[7] Wynne-Jones, *J. Chem. Phys.*, **2**, 381 (1394); *Chem. Revs.*, **17**, 115 (1935); Halpern, *J. Chem. Phys.*, **3**, 456 (1935).

is solely responsible for the change in K^* and that the entropy of formation for the two complexes is identical. A test of this hypothesis by Gross, Steiner and Krauss,[8] who investigated the decomposition of diazoacetic ester catalyzed by protons and deutons, shows that the difference in the energies of activation ($\delta\Delta H^*$) is indeed largely responsible for the three-fold increase in the decomposition by deuterium ions. The marked decrease in the rate of reactions involving deuterium in the gas phase may also be explained satisfactorily in many cases on the basis of the lower zero point energy of the deuterium molecule, E^0_{D}.

However, $\delta E^0 = E^0_{\mathrm{H}} - E^0_{\mathrm{D}}$, does not account for the reaction rate ratios observed in other gas phase reactions.[9] The resultant $\delta\Delta H^*$ based on δE^0 of the hydrogen and deuterium molecules may be augmented or partially compensated by a δE^0 for the light and heavy complexes or by a difference in the entropy of activation ($\delta\Delta S^* = \Delta S^*_{\mathrm{H}} - \Delta S^*_{\mathrm{D}}$) in forming the two complexes. Similarly, the difference in the ΔH^* factor ($\delta\Delta H^*$) in a liquid phase reaction involving a light and heavy complex may be augmented or compensated by a difference in the ΔS^* factor ($\delta\Delta S^*$).

The hypothesis that the entropy factor may often be of primary importance in determining the rate ratio on passing to D_2O is subjected to test with a study of the rate of hydrolysis of ethyl orthoformate at different temperatures.

Experiment and Calculations.—The rate constants, k, at constant buffer strength, 0.001 M Ac_2O/0.1 M NaAc, measured, in ordinary water and in a deuterium oxide mixture at 14.977 and 35.008°, by the dilatometric method previously used[10] to study the rate at 25°, are converted to specific rate constants by dividing k by the total hydrogen ion concentration. Hydrogen ion concentrations in ordinary water are obtained from the dissociation constants of protoacetic acid[11] at an ionic strength of 0.1; 2.85×10^{-5} at 35° and 2.81×10^{-5} at 15°.

The specific rate constant in the H_2O–D_2O mixture, k_{m}, is obtained from the concentrations of protons and deuterons calculated from the equations

$$K = \frac{1}{C_{\mathrm{D^+}}}\left[\frac{2C_{\mathrm{Ac_2O}}}{C_{\mathrm{Ac^-}}}(K_{\mathrm{H}} - K_{\mathrm{M}}) + C_{\mathrm{D^+}}\right] \quad (8)$$

and

$$K_{\mathrm{M}} = \frac{(C_{\mathrm{H^+}} + C_{\mathrm{D^+}})C_{\mathrm{Ac^-}}}{2C_{\mathrm{Ac_2O}}} \quad (9)$$

Equation (8) is derivable from equations 2, 3, 4 of our previous work[10] and equation (9), this paper. $K = K_{\mathrm{H}}/K_{\mathrm{D}}$, where K_{H} is the dissociation constant of protoacetic acid and K_{D} is the dissociation constant of the deuteroacetic acid. K_{M} is the dissociation constant in the mixed waters. K is 3.39 at 15°, 3.26 at 35°; K_{M} is obtained from the ratios $K_{\mathrm{H}}/K_{\mathrm{M}} = 3.02$ at 15° and $= 2.91$ at 35°.[12]

The specific rate constant in pure deuterium oxide, $k_{\mathrm{D^+}}$, is then obtainable from the equation

$$k = k_{\mathrm{H^+}}\,C_{\mathrm{H^+}} + k_{\mathrm{D^+}}\,C_{\mathrm{D^+}} \quad (10)$$

where $k_{\mathrm{H^+}}$ is the specific rate constant in ordinary water.

The energy of activation is obtained from equation (3), B from (2), and ΔS^* from (5) assuming, as usual, $\kappa = 1$. All results are summarized in Tables I and II. The value for the energy of activation in ordinary water is in substantial agreement with that of Harned and Samaras.[13]

TABLE I

Temp., °C.	$F_{\mathrm{D}} = \Delta S/0.1079$	k	Specific rate constant	$k_{\mathrm{D^+}}/k_{\mathrm{H^+}}$
14.977	0.0	0.0129	2.30×10^4	
	0.925	.0107	5.75×10^4	
	1.00		6.22×10^4	2.70
35.008	0.0	.0782	1.37×10^5	
	0.917	.0564	2.88×10^5	
	1.00		3.16×10^5	2.31

TABLE II

	ΔH, kcal.	B	ΔS^*
H_2O	15.7 ± 0.2	16.3	7.83
D_2O	14.3 ± 0.2	15.7	4.90

Discussion

The observed difference in the energy of activation predicts a nine-fold increase in the rate in passing from ordinary water to deuterium oxide, whereas the observed increase is about three-fold. The large decrease in ΔH^*_{D} is partially compensated by a decrease in the ΔS^* on deuterium substitution. Both factors are, therefore, important in explaining the observed increase in the rate of the hydrolysis of ethyl orthoformate in D_2O. The importance of an entropy of activation has already been emphasized for several ionic reactions,[14] and for the base catalyzed[15] decomposi-

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(8) Gross, Steiner and Krauss, *Trans. Faraday Soc.*, **34**, 351 (1938).

(9) Urey and Teal, *Rev. Modern Phys.*, **7**, 34 (1935).

(10) Brescia and LaMer, THIS JOURNAL, **60**, 1962 (1938).

(11) Harned and Embree, *ibid.*, **56**, 1050 (1934); Harned and Hickey, *ibid.*, **59**, 1284 (1937).

(12) Brescia, LaMer and Nachod, *ibid.*, **62**, 614 (1940).

(13) Harned and Samaras, *ibid.*, **54**, 1 (1932).

(14) LaMer and Kamner, *ibid.*, **57**, 2662, 2669 (1935); LaMer and Miller, *ibid.*, **57**, 2674 (1935); Percival and LaMer, *ibid.*, **58**, 2413 (1936).

(15) Liotta and LaMer, *ibid.*, **60** 1967 (1938).

tion of nitramide in D_2O. The observed difference for the rate of mutarotation of glucose[16] in H_2O and D_2O is accounted for mainly by the change in the entropy term since $\delta \Delta H^*$ is zero within the experimental error.

Recently, Stern, Johnston and Clark[17] picture two general cases covering the effect of a catalyst on the reactant and the activated complex which may lead to positive or negative catalysis. A decrease in the energy of activation in passing from one solvent to another is taken to indicate that the catalyst has a greater tendency to combine with the activated complex than with the reactant and this effect is partly compensated by a decrease in ΔS^*. This mechanism corresponds to the explanation given previously that the increased rate in passing to D_2O is due to an equilibrium shift favoring the formation of the D-complex.

Summary

1. The rate of hydrolysis of ethyl orthoformate has been measured at 14.977 and 35.008° in ordinary water and in deuterium water.

2. The observed difference in the energy of activation predicts a nine-fold increase in the rate; experimentally the increase is about three-fold. The entropy of activation is, therefore, an important factor in determining the ratio of the two rates.

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[16] Hammill and LaMer, *J. Chem. Phys.*, **4**, 395 (1936).

[17] Stern, Johnston and Clark, *J. Chem. Phys.*, **7**, 970 (1939).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

The Temperature Dependence of the Dissociation Constant of Deuteroacetic Acid

BY FRANK BRESCIA,* VICTOR K. LAMER AND FREDERICK C. NACHOD*

Introduction

Current investigations of the activation energies for reactions involving deuteroacetic acid, for example, the hydrolysis of ethyl orthoformate[1] in ordinary water and deuterium oxide, require data for the dissociation constants of deuteroacetic acid which are comparable in precision with those available for the protoacetic acid. Some preliminary data for the dissociation constant of deuteroacetic acid obtained on severely limited quantities of solvent at 12.5°, 25° and 37.5° using the quinhydrone electrode[2] indicated a possible minimum, while the corresponding and well-established constants for protoacetic acid[3] exhibit a maximum. In general,[4] differences between the properties of the deutero and proto compounds tend to become less important at higher temperatures, since the differences in zero point energies ΔE^0 of the two hydrogens determine the properties as an exponential factor, exp. $[\Delta E^0/RT]$. Also, Rule and LaMer[5] have demonstrated that the temperature coefficient of the electromotive force of the cell Pt/QQH_2-QQD HCl-DCl (H_2O-D_2O)/AgCl-Ag involving the strong acid HCl–DCl is identical in pure H_2O and in pure D_2O. It is questionable, therefore, whether the temperature dependence of the two weak acids should be opposite in sign.

The determination of the dissociation constant of deuteroacetic acid at different temperatures has, therefore, been undertaken, using the conductance method.

Experimental

The equivalent conductances of sodium acetate, sodium chloride, hydrochloric acid and acetic acid solutions have been determined at 14.36, 25, 35 and 44.86°, for a solvent whose deuterium content, $F_D = S_g/0.1079$, where S_g is the difference in specific gravity of the solvent and of ordinary water, was approximately 0.925. A vacuum tube oscillator of the heat frequency type[6] and a Jones bridge[7] were employed. The constants, 0.4481 and 0.7017, of the two conductance cells, designed to be free from the Parker effect, were determined at 25° by the method of Kohlrausch. The temperatures were standardized with a Pt resistance thermometer, B. S. calibration.

The preparation of the salts, acetic anhydride,

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[1] Brescia and LaMer, THIS JOURNAL, **60**, 1962 (1938); *ibid.*, **62**, 612 (1940).

[2] Korman and LaMer, *ibid.*, **58**, 1396 (1936).

[3] Harned and Embree, *ibid.*, **56** 1050 (1934); Harned and Hickey, *ibid.*, **59**, 1284 (1937).

[4] Urey and Teal, *Rev. Modern Phys.*, **7**, 34 (1935).

[5] Rule and LaMer, THIS JOURNAL, **60**, 1974 (1938).

[6] Baker and LaMer, *J. Chem. Phys.*, **3**, 406 (1935).

[7] Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).