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).

constant boiling deuterochloric acid (DCl), purification of the water, and the details of the semimicro technique have been described.[8]

Calculations.—The maximum equivalent conductances, Λ_0, for the strong electrolytes in H_2O–D_2O were calculated from the measured equivalent conductance, Λ_c, using the equation

$$\left(\frac{\Lambda_c}{\Lambda_0}\right)_{H_2O} = \left(\frac{\Lambda_c}{\Lambda_0}\right)_{D_2O} \qquad (1)$$

derivable from the Onsager equation and shown to be of satisfactory accuracy.[9] The ratios $(\Lambda_c/\Lambda_0)_{H_2O}$ were taken from the "Int. Crit. Tables."[10] The measured Λ_c values and the calculated Λ_0 values are shown for sodium chloride, deuterochloric acid, and sodium acetate in Tables I, II, III, respectively. The Λ_0 values for deuteroacetic acid are given in Table IV. The measured Λ_C values for the deuteroacetic acid and the dissociation constants, K_M, calculated by the equation

$$K_M = \frac{C_i^2}{C - C_i} \qquad (2)$$

are shown in Table V. $C_i = \kappa\ (1000)/\Lambda_0$, κ is the specific conductance of the solution, and C is the stoichiometric concentration of the acid.

TABLE I

SUMMARY OF VALUES OF Λ_C AND Λ_0 FOR NaCl IN H_2O AND D_2O AT DIFFERENT TEMPERATURES

Solution concentrations: B-15, 0.01088 *M;* B-16, 0.01887*M*.

Temp., °C.	Solution	$\Lambda_0^{H_2O}$	$\Lambda_c^{H_2O}$	$\Lambda_c^{D_2O}$	$\Lambda_0^{D_2O}$	Av. $\Lambda_0^{D_2O}$	$\%_{\text{av. dev.}}$
44.86	B-15	174.54	168.83	144.8	149.7		
	B-16		165.21	141.4	149.4	149.6	0.1
35.00	B-15	150.26	143.79	121.1	126.5		
	B-16		140.86	118.1	126.0	126.3	.2
25.00	B-15	125.63	118.39	98.72	104.8		
	B-16		116.16	96.33	104.2	104.5	.3
14.36	B-15	99.44	92.75	76.29	81.79		
	B-16		91.05	74.36	81.21	81.50	.36

TABLE II

SUMMARY OF VALUES OF Λ_C AND Λ_0 FOR HCl AND DCl AT DIFFERENT TEMPERATURES

Solution concentration: B-17, 0.03707*M*; B-18, 0.01860 *M*.

Temp., °C.	Solution	Λ^{HCl}	Λ_c^{HCl}	Λ_c^{DCl}	Λ_0^{DCl}	Av. Λ_0^{DCl}	$\%_{\text{av. dev.}}$
44.86	B-17	551.5	518.95	385.5	409.7		
	B-18		526.13	391.7	410.6	410.2	0.1
35.00	B-17	488.7	464.3	343.0	361.0		
	B-18		470.8	348.2	361.4	361.2	.06
25.00	B-17	425.0	401.97	296.2	313.2		
	B-18		407.37	300.3	313.3	313.3	.02
14.36	B-17	357.2	339.30	243.3	256.1		
	B-18		343.74	246.3	256.0	256.1	.02

TABLE III

SUMMARY OF VALUES OF Λ_C AND Λ_0 FOR SODIUM ACETATE IN H_2O AND D_2O AT DIFFERENT TEMPERATURES, 0.02026 *M*

Temp., °C.	$\Lambda_0^{H_2O}$	$\Lambda_c^{H_2O}$	$\Lambda_c^{D_2O}$	$\Lambda_0^{D_2O}$
44.86	128.83	115.80	100.5	111.8
35.00	110.22	98.64	83.20	93.0
25.00	91.36	81.24	66.99	75.3
14.36	71.30	62.73	50.98	57.9

TABLE IV

SUMMARY OF VALUES OF Λ_0 FOR DAc AT DIFFERENT TEMPERATURES

Temp., °C.	Λ_0^{DAc}
44.86	372.4
35.00	327.9
25.00	284.1
14.36	232.5

TABLE V

SUMMARY OF K_M VALUES AT DIFFERENT TEMPERATURES, $F_D = 0.925$

Solution B-19, 0.03238 *M;* B-20, 0.12114 *M;* B-21, 0.04530 *M;* B-22, 0.07290 *M*.

Temp., °C.	Solution	$K_M \times 10^5$	Average $K_M \times 10^5$	% a.d.
44.86	B-19	0.610		
	B-20	.609		
	B-21	.605		
	B-22	.611	0.609	0.3
35.00	B-19	.622		
	B-20	.622		
	B-21	.617		
	B-22	.623	.621	.3
25.00	B-19	.613		
	B-20	.613		
	B-21	.609		
	B-22	.615	.613	.2
14.36	B-19	.605		
	B-20	.605		
	B-21	.603		
	B-22	.607	.605	.2

The accuracy of these measurements is indicated by the agreement of our Λ_0 values for sodium chloride, Λ_0 value for HOAc–DOAc, and our dissociation constant value at 25° with the corresponding values of previous work at the same temperature:

Λ_0^{NaCl}	Chittum and LaMer[8] conductance	Korman and LaMer[2] e. m. f.	This paper conductance
Λ_0^{NaCl}	104.8 at $F_D = 0.937$	....	104.5 at $F_D = 0.925$
Λ_0^{DOAc}	285.9 at $F_D = .93$	....	284.1 at $F_D = .925$
$K_M \times 10^5$	0.608 at $F_D = .93$	0.612 at $F_D = 0.917$	0.613 at $F_D = .925$

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(8) LaMer and Chittum, THIS JOURNAL, **58**, 1642 (1936); Chittum and LaMer, *ibid.*, **59**, 2425 (1937); references 1 and 6.

(9) LaMer and Chittum, *ibid.*, **58**, 1642 (1936).

(10) "Int. Crit. Tables," Vol. VI, pp. 230–248.

The excellent agreement between the conductance and e. m. f. data at 25° is not obtained at other temperatures. In the preliminary work on acetic acid,[2] the various precautions necessary to establish that the quinhydrone electrode had not deteriorated over the period of time that was required to obtain electrode equilibrium at a second (later) temperature were not realized as fully as in the later work on HCl.[5]

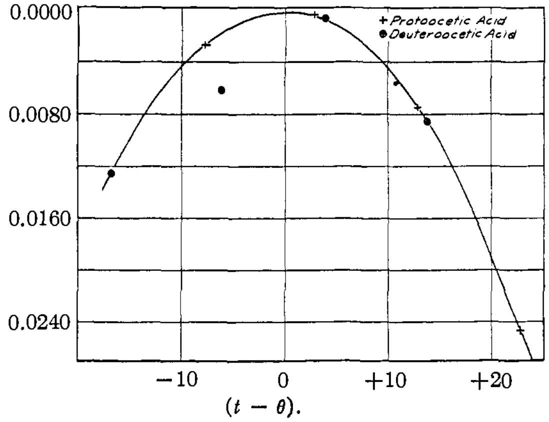

Fig. 1.—Protoacetic acid, +; deuteroacetic acid, ⊕.

K_D was determined by extrapolating the dissociation constant K_M observed in the mixed waters (H_2O–D_2O) to $F_D = 1$ with the equation[11]

$$K_M = K_D\left[1 + 3.76\,\frac{C_{H_2O}}{C_{HDO}}\Big/1 + 3.76\left(\frac{K_D}{K_M}\right)\frac{C_{H_2O}}{C_{HDO}}\right] \qquad (3)$$

In equation (3), K_D is the dissociation constant of the deuteroacid; K_H, the dissociation constant of the protoacid. K_H values (converted to the classical dissociation constant) at the different centigrade temperatures t were calculated from the equation.

$$\log K_{H,t} - \log K_{H,m} = -\,p(t - \theta)^2 \qquad (4)$$

$K_{H,m}$ is the maximum value of K_H which occurs at the characteristic temperature θ; p is a constant.

The K_H and K_D values and their ratios are given in Table VI.

TABLE VI

SUMMARY OF K_H, K_D, AND K_H/K_D AT DIFFERENT TEMPERATURES

Temp., °C.	$K_H \times 10^5$	$K_D \times 10^5$	K_H/K_D
44.86	1.74	0.545	3.19
35	1.81	.555	3.26
25	1.84	.548	3.36
14.36	1.83	.540	3.39

Discussion

As was expected, the temperature dependences of K_H and K_D follow the same general type of parabolic curve as shown in Fig. 1. K_D however, passes through the maximum at a higher temperature than K_H. Thus, the characteristic temperature θ is about 22° for protoacetic acid and about 31° for deuteroacetic acid. The ratio of K_H/K_D, Table VI, decreases with increasing temperature so that the two values probably approach each other at higher temperatures.

The data for K_D for the range of temperatures investigated may be represented by

$$\log K_{D,t} + 5.2550 = -4.5 \times 10^{-5}(t - 31.06)^2 \qquad (5)$$

with an accuracy of 1%. The corresponding equation for protoacetic acid, over the same temperature range, is

$$\log K_{H,t} + 4.7348 = -4.5 \times 10^{-5}(t - 22.09)^2 \qquad (5a)$$

A plot of equations (5) and (5a) is given in Fig. 1 in which it is seen that the resulting curves for each acid are superimposable. This behavior is quite general for weak protoacids,[3] and shows that p is the same for deutero- and protoacetic acids.

The differences of the heats, free energies and entropies of dissociation of the deutero- and protoacetic acids, corresponding to the exchange process

$$\begin{aligned} HOAc(H_2O) + D^+(D_2O) + OAc^-(D_2O) &= \\ DOAc(D_2O) + H^+(H_2O) + OAc^-(H_2O) & \qquad (6) \end{aligned}$$

where the solvent involved[12] is inclosed in parentheses, have been calculated (Table VII). The chemical equation (6) is obtained by subtracting equation (6b) from equation (6a)

$$HOAc(H_2O) = H^+(H_2O) + OAc^-(H_2O) \qquad (6a)$$
$$DOAc(D_2O) = D^+(D_2O) + OAc^-(D_2O) \qquad (6b)$$

The ΔH for deuteroacetic acid decreases more slowly with increasing temperature than the corresponding function for protoacetic acid. Also,

TABLE VII

DIFFERENCES OF HEATS, FREE ENERGIES, AND ENTROPIES OF DISSOCIATION, CORRESPONDING TO THE THERMODYNAMIC PROPERTIES OF THE EXCHANGE PROCESS (6)

Subscript D refers to deuteroacetic acid; subscript H to protoacetic acid.

Temp., °C.	$\Delta H_D - \Delta H_H$, cal.	$\Delta F_D - \Delta F_H$, cal.	$\Delta S_D - \Delta S_H$, cal./deg.	K_6
14.36	308.6	697.6	−1.3	0.530
25.00	329.2	717.7	−1.3	.526
35.00	349.2	724.0	−1.3	.513
44.86	368.9	733.6	−1.1	.504

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[11] Brescia, THIS JOURNAL, 60, 2811 (1938).

[12] See reference 13 for the importance of including the solvent.

ΔF for the dissociation of DOAc increases more rapidly with the temperature than does ΔF for the dissociation of HOAc. On the other hand, the entropy differences are constant. Thus, the greater increase in K_D with increasing temperature is due to the greater increase in ΔH_D over ΔH_H. Since $\Delta F_D - \Delta F_H$ equals $-\Delta F$ for the exchange process (6), the reverse reaction, as expected, is favored on increasing temperature. The values for K_6, the equilibrium constant for the exchange process (6), calculated from $\Delta F_D - \Delta F_H$, are given in Table VII. Also

$$\left(\frac{\partial \Delta H_D}{\partial T}\right)_p - \left(\frac{\partial \Delta H_H}{\partial T}\right)_p = \Delta C_p$$

for process (6) is sensibly independent of temperature and equal to 2.0 cal. deg.$^{-1}$ mole^{-1}. Noonan and LaMer,[13] who made a careful study of the e. m. f. of the cell without transport

$$\begin{array}{c|cc|c} D_2 & DCl & D_2O & \\ & & & AgCl\text{-}Ag \\ H_2 & HCl & H_2O & \end{array}$$

over a wide range of deuterium solvents, found that ΔC_p for the process

$${}^1/{}_2H_2 + DCl(D_2O) = {}^1/{}_2D_2 + HCl(H_2O) \quad (7)$$

is also very small if not zero.

The almost zero value of ΔC_p in these exchange processes results from the fact that ions of the same valence type and almost identical chemical properties are involved in these equilibria. The partial molal heat capacity of an ionic species is determined primarily by its net charge and only secondarily by its internal constitution.[14]

Summary

1. The equivalent conductances of sodium chloride, sodium acetate, hydrochloric acid, and acetic acid have been measured at 14.36, 25, 35 and 44.86° in a solvent whose deuterium fraction is 0.925. From these data, the dissociation constant of deuteroacetic acid at $F_D = 1$ is calculated at corresponding temperatures.

2. The dissociation constant of deuteroacetic acid follows the Harned–Embree equation and passes through a maximum at 31°; protoacetic acid at 22°.

3. The ratio K_H/K_D decreases with increasing temperature.

4. The differences in the heats, free energies and entropies of ionization of the deutero and proto acids have been calculated. ΔC_p for the exchange process $HOAc(H_2O) + D^+(D_2O) + OAc^-(D_2O) = DOAc(D_2O) + H^+(H_2O) + OAc^-(H_2O)$ is sensibly zero; ΔS is sensibly constant and equal to -1.3 cal. deg.$^{-1}$ mole^{-1}.

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[13] Noonan and LaMer, *J. Phys. Chem.*, **43**, 247 (1939); LaMer and Noonan, THIS JOURNAL, **61**, 1487 (1939).

[14] Rossini, *Bur. Standards J. Research*, **4**, 313 (1930); **7**, 47 (1931); LaMer and Cowperthwaite, THIS JOURNAL, **55**, 1004 (1933).

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Electrostatic Effects on Ionization Constants

BY VICTOR K. LAMER AND FRANK BRESCIA*

In a recent paper, E. C. Baughan[1] derived on the basis of theoretical suggestions of Gurney,[2] the equation

$$\Delta H_T = \Delta H_x + c\,1/D_T\left[1 + T\frac{\partial \ln D}{\partial T}\right]_T \quad (1)$$

for the heat of ionization ΔH_T of a weak acid of the electric charge type $HA + H_2O \rightleftarrows H_3O^+ + A^-$, as a function of the temperature T, on the assumption that the electrical work involved in creating the electric field is adequately expressed by the well known formula of Born

$$c = \frac{\epsilon^2}{2}\left(\frac{1}{r_+} + \frac{1}{r_-}\right)$$

where ϵ is the elementary electric charge, r_+ and r_- are the radii of the cation and anion, and D is the dielectric constant of the solvent.

ΔH_x may be regarded either as the heat of ionization in a medium of infinite dielectric constant where no electrical work would be involved, or as the heat effect if there were no separation of electric charges in the dissociation process.

Since ΔH is zero at the characteristic temperature for which the dissociation constant is a maximum, equation (1) may also be expressed as

$$\Delta H_T = c\left[1/D_T\left(1 + T\frac{\partial \ln D}{\partial T}\right) - 1/D_\Theta\left(1 + \Theta\frac{\partial \ln \Theta}{\partial T}\right)\right] \quad (1a)$$

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[1] E. C. Baughan, *J. Chem. Phys.*, **7**, 951 (1939).

[2] Gurney, *ibid.*, **6**, 499 (1938).