[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Relative Hydrogen Bonding of Deuterium. I. Ionization Constants of Maleic and Fumaric Acids and of Their Monoethyl Esters in H_2O and D_2O[1]

BY GEORGE DAHLGREN, JR., AND F. A. LONG

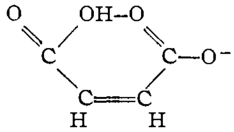
RECEIVED AUGUST 26, 1959

Ionization constants of the acids maleic, fumaric and their monoethyl esters have been determined for the solvents water and 99.5% deuterium oxide using a cell with silver–silver chloride and quinhydrone electrodes. The K^H/K^D ratios for ionization of the esters and for the first and second ionizations of fumaric acid are all close to the value 2.8, in reasonable accord with the Rule and LaMer data for other carboxylic acids. However, for maleic acid the ratios are $K_1^H/K_1^D = 4.2$ and $K_2^H/K_2^D = 2.4$, values which show qualitatively that there is less internal hydrogen bonding for the deuterio bimaleate ion in D_2O than for the hydrogen bimaleate ion in H_2O. Using the procedure of Westheimer and Benfey, the data for maleic acid and its ester permit a semi-quantitative calculation of K_H' and K_D', the ratios of concentrations of the hydrogen bonded and non hydrogen bonded forms of the bimaleate ion in the two solvents. The results are that $K_H' = 6.4$ and $K'_D = 4.0$, again indicating significantly less hydrogen bonding for the deuterio bimaleate ion.

The problem of the relative abilities of hydrogen and deuterium atoms to form hydrogen bonds is of interest from a variety of standpoints. One of these is mechanisms of chemical reactions where it is frequently postulated that H-bonding plays a significant role.[2] Since a major tool for mechanism studies is substitution of deuterium for hydrogen, it is clearly desirable to have knowledge on their relative H-bonding ability.

Even if one considers only the case of internal or intramolecular H-bonding, there are two different practical situations to consider. One is concerned with the change in the bonding for an isolated (*e.g.*, gaseous) molecule when a bonding hydrogen is replaced by deuterium. In the second situation the molecule of interest is dissolved in water (or similar H-bonding solvent) for the hydrogen experiment and is dissolved in deuterium oxide for the comparison. For this situation there will be a competition between internal H-bonding and H-bonding with the solvent so that the properties of the solvent will be of obvious importance. This paper deals with a study of the second type. Measurements have been made of the ionization constants of maleic and fumaric acids and also of their monoethyl esters in the solvents water and deuterium oxide.

Bimaleate ion is known to have the structure listed below and the OH—O distance of 2.44 Å. as measured in crystals is evidence of a strong hydrogen bond.[3,4] Hunter[5] noted some time ago that the existence of a strongly H-bonded bimaleate ion in solution offered a plausible explanation for the large difference in the first and second ionization constants of maleic acid. Specifically, K_1/K_2 for this acid is reported to be 20,000 whereas the same ratio for the *trans* isomer, fumaric acid, is only 27. McDaniel and Brown[6] expanded on this idea and discussed the role of H-bonding in the ionization of a variety of other dibasic acids. They also noted that comparison of the first ionization constant of a dibasic acid to the value K_E for the monoester of the acid could give additional evidence for H-bonding of the acid ion. As one example, for maleic acid and its monoethyl ester the reported value of K_1/K_E is 10.6, compared to the value of two which would be expected from simple statistics.



The last notion was developed further by Westheimer and Benfey[7] who give equations which permit numerical calculation of an upper limit for the hydrogen bonding of the acid ion in solution. Using $\overline{H_2A}$, $\overline{HA^-}$, etc., for the hydrogen bonded species and H_2A, etc., for that present in the non-hydrogen bonded form, they write for the concentration ratios, $(\overline{H_2A})/(H_2A) = K_H$, $(\overline{HA^-})/(HA^-) = K_H'$ and $(\overline{HE})/(HE) = K_H''$ where HE refers to the monoethyl ester. Then from a consideration of the expressions for the ionization constants of the various acids they arrive at the equation

$$K_H' = \frac{K_1}{K_E}\left[\frac{1 + 2K_H''}{2 + 2K_H''}\right] - 1 \qquad (1)$$

The factor in brackets should be close to $^1/_2$ leading to the approximate equation

$$K_H' = \frac{K_1}{2K_E} - 1 \qquad (2)$$

Thus a large value of the ratio K_1/K_E, relative to the statistical value of two, implies extensive hydrogen bonding of the acid ion.

Experimental

Materials.—Reagent grade inorganic chemicals were used throughout. All solutions were made up from distilled water and deuterium oxide (99.5%) both of which had been freed from carbon dioxide by flushing with carbon dioxide-free air for one hour or more.

Maleic acid was purified by recrystallization from water, giving a product of m.p. 132–133°. **Fumaric acid** was recrystallized from water, m.p. 276°. **Deuterioquinhydrone** was prepared by recrystallization of quinhydrone from deuterium oxide. A stock solution of **sodium deuteroxide** was prepared by passing carbon dioxide-free air through deuterium oxide and then over sodium. **Deuterium chloride**

---

[1] Work supported by a grant from the Atomic Energy Commission.

[2] See, for example, A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," John Wiley and Son, Inc., New York, N. Y., 1953, Chapter 9.

[3] S. W. Peterson and H. A. Levy, *J. Chem. Phys.*, **29**, 948 (1958).

[4] H. M. E. Cardwell, J. D. Dunitz and L. E. Orgel, *J. Chem. Soc.*, 3740 (1953).

[5] L. Hunter, *Chemistry & Industry (London)*, **17**, 155 (1953).

[6] D. H. McDaniel and H. C. Brown, *Science*, **118**, 370 (1953); see also H. C. Brown, D. H. McDaniel and O. Häfliger in E. A. Braude and F. C. Nachod, "Determination of Organic Structure by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, Chapter 14.

[7] F. H. Westheimer and O. T. Benfey, THIS JOURNAL, **78**, 5309 (1956 .

solutions were made up from reagent grade concentrated hydrochloric acid and deuterium oxide.

Ethyl potassium maleate was prepared by titrating maleic anhydride in methylene chloride to a phenolphthalein endpoint with a saturated solution of potassium hydroxide in absolute ethyl alcohol. The initial precipitate was removed by filtration and discarded since titration of the dried precipitate showed it to be very nearly an equimolar mixture of the dipotassium salt and the monoester. The solvent was then removed from the filtrate and the resulting residue was washed several times with ether. The dried material was a white, crystalline solid which decomposed at 180°. A titration curve showed that no dipotassium salt was present. The calculated titration curve using the value of Walker[8] for the dissociation constant of the monoester was essentially identical to the observed one. *Anal.* Calcd. for $C_6H_7O_4K$: C, 39.54; H, 3.88; K, 21.46. Found: C, 39.31; H, 3.97; K, 21.73. The salt did not add bromine at room temperature but readily decolorized permanganate solution. The same behavior was observed with maleic acid. Shields[9] found only a trace of dibromosuccinate when ethyl hydrogen maleate was brominated under conditions identical to the above.[10]

Ethyl hydrogen fumarate was prepared by refluxing a solution of maleic anhydride with a 10 mole % excess of ethyl alcohol for 15 hr. The hot liquid was decanted from the initial fumaric acid precipitate (Wasserman[12] also found fumaric acid in a similar procedure) and cooled to room temperature, which led to a white crystalline solid. Recrystallizations from ether and chloroform yielded a product which melted sharply at 69° (corr.). *Anal.* Calcd. for $C_6H_8O_4$: C, 50.00; H, 5.56. Found: C, 50.19; H, 5.55.

Apparatus.—A semi-micro cell similar to the one described by Rule and LaMer[13] was constructed from Pyrex glass. The silver–silver chloride electrodes were of the thermal electrolytic type described by Bates.[14] The silver–silver chloride electrodes and the quinhydrone electrodes, when intercompared, showed no deviations from the mean of greater than ±0.02 mv. even after two months use.

Buffer solutions of all compounds, with the exception of ethyl hydrogen maleate, were made up by weight from previously standardized stock solutions of acid, sodium hydroxide (or deuteroxide) and sodium chloride. Buffer solutions of ethyl hydrogen maleate were made up from stock solutions of ethyl potassium maleate and hydrochloric acid. The cell was immersed in an oil-bath maintained at 25.0 ± 0.01° and the potential differences between the duplicate silver–silver chloride and the duplicate quinhydrone electrodes were measured after 30 minutes. (Preliminary measurements had shown that thermal equilibrium was established within this time.) Potentials were measured with a Leeds and Northrup type K-1 potentiometer and a high sensitivity General Electric galvanometer. The stopcock between the half-cells was opened only at the time of measurement. Readings were taken at half-hour intervals for several hours and in most cases were found to be within ±0.03 mv. of the initial value. The potentials of the cells could be determined to ±0.02 mv. at high ionic strength and to ±0.05 mv. at low ionic strength. Table I gives concentrations, potentials and calculated *pK* values for all of the acids studied.

The system was checked by a determination of the *pK* values for acetic and phosphoric acids. The *pK* for acetic acid at an ionic strength of 0.045 was found to be 4.756 ± 0.006, which compares favorably with the value of 4.758 determined by Harned and Ehlers.[15] The first thermodynamic dissociation constant for phosphoric acid was measured as 2.153 ± 0.002, in good agreement with the value of 2.148 found by Bates.[16]

The solvent for the "deuterium oxide" experiments always contained at least 99.4 atom % deuterium. Since the results for this solvent will be within experimental error, the same as for pure deuterium oxide, no special extrapolation to the latter solvent has been attempted.

Calculation of *pK*

All of the cells may be represented by the following scheme Ag · AgCl | maleate or fumarate buffer, MCl, Q · QH_2 (or Q · QD_2) | Pt where MCl refers to either sodium or potassium chloride. For known values of the chloride ion concentration, the potentials of cells of this type provide a measure of ln ($m_{H^+}\gamma_{H^+}\gamma_{Cl^-}$), specifically

$$E = E^0 + \frac{2.303RT}{F} \log (m_{H^+}\gamma_{H^+}m_{Cl^-}\ \gamma_{Cl^-}) \qquad (3)$$

where m is the molal concentration and γ the molal activity coefficient. The other symbols have their usual significance. For comparison of data for solutions in water and in deuterium oxide, it is convenient to use a modified molal concentration, defined as moles of solute per 55.3 moles of solvent. However, for simplicity of presentation we shall continue to use the symbol m. Values of E^0 for concentration in these modified units are available from the data of LaMer and co-workers.[13,17] For water E^0 is 0.4774 v. and for 99.5% deuterium oxide the value from equation 11 of ref. 13 is 0.5137 v.[18]

Calculation of the *pK* values for the monoesters of maleic and fumaric acids and also of pK_1 of maleic itself were made by the method of Harned and co-workers.[15,19] For two of the acids, maleic and its ethyl ester, there was no significant variation of pK' with ionic strength over the range 0.02 to 0.10 (where K' is defined analogously to k_A' of ref. 19) for either of the solvents so that the thermodynamic *pK* could be obtained by a simple averaging of the calculated pK' values. The data for ethyl hydrogen fumarate showed a slight variation of pK' with ionic strength and the limiting value of *pK* was determined by extrapolation of plots of pK' *vs.* μ to $\mu = 0$.

The second dissociation constant of maleic acid could also be calculated by standard methods[20] and the limiting *pK* was again obtained by extrapolation to $\mu = 0$. Fig. 1 illustrates the linear character of this extrapolation and shows the magnitude of the ionic strength dependence.

The reported ratio of K_1/K_2 for fumaric acid is 27[21] which indicates that special methods of calculation must be used to obtain the separate *pK* values. Bates[22] has used approximation methods to separate similar constants for both dibasic and tribasic acids and reports several methods of calculation. The procedure given here was developed to

---

[8] J. Walker, *J. Chem. Soc.*, **61**, 696 (1892).

[9] J. Shields, *ibid.*, **60**, 736 (1891).

[10] Attempts to prepare ethyl hydrogen maleate according to the procedures of Shields[9] and of Sudborough and Roberts[11] yielded products which contained varying amounts of diester and diacid.

[11] J. J. Sudborough and D. J. Roberts, *ibid.*, **87**, 1844 (1905).

[12] A. Wasserman, *Ann.*, **488**, 211 (1931).

[13] K. C. Rule and V. K. LaMer, THIS JOURNAL, **60**, 1974 (1938).

[14] R. G. Bates, "Electrometric *p*H Determination," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 205.

[15] H. S. Harned and R. W. Ehlers, THIS JOURNAL, **55**, 652 (1933).

[16] R. G. Bates, *J. Research Natl. Bur. Standards*, **47**, 127 (1951).

[17] S. Korman and V. K. LaMer, THIS JOURNAL, **58**, 1396 (1936).

[18] In reporting some of these results at a recent meeting (Abstracts for 135th Meeting of the American Chemical Society, Boston, April 1959), we erroneously gave data from calculations with conventional molal concentration units but with use of the above E^0 values. As a consequence the numerical values for the ionization constants in D_2O solutions differed slightly from those given here.

[19] H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolyte Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, page 498.

[20] See, for example, ref. 19, Chapter 15, and also ref. 13.

[21] B. Adell, *Z. physik. Chem.*, **A185**, 161 (1939).

[22] (a) R. G. Bates and G. D. Pinching, THIS JOURNAL, **71**, 1274 (1949); (b) R. G. Bates, *ibid.*, **70**, 1579 (1948); (c) M. Eden and R. G. Bates, paper presented at the National Meeting of the American Chemical Society, Chicago, 1958.

TABLE I

POTENTIALS AND pK VALUES FOR BUFFERS, 25°. CONCENTRATIONS IN MOLES SOLUTE PER 55.3 MOLES SOLVENT

(a) First dissociation, maleic acid

m, H_2A	m, NaHA	m, NaCl	E, v.	pK_1
Water				
0.02263	0.01450	0.03122	0.2569	1.909
.03765	.00782	.02550	.2650	1.915
.04942	.01140	.03265	.2743	1.905
				1.910 ± 0.004
Deuterium oxide				
0.03886	0.02645	0.04987	0.2871	2.540
.04156	.02825	.05648	.2909	2.531
.05325	.03368	.02478	.2730	2.534
				2.535 ± 0.003

(c) First dissociation, fumaric acid

m, H_2A	m, NaHA	m, NaCl	E, v.	pK_1
Water				
0.01081	0.005133	0.01494	0.1964	3.086
.01713	.009584	.03268	.2172	3.068
.01083	.005168	.06441	.2327	3.070
.02125	.01165	.06717	.2360	3.080
.02353	.01268	.07510	.2399	3.072
.02070	.00989	.1011	.2490	3.050
.02220	.01053	.1713	.2625	3.036
.01302	.006399	.2378	.2662	3.001
Intercept, pK_1^H = 3.095 ± 0.007				
Deuterium oxide				
0.006190	0.003178	0.02732	0.2226	3.550
.006025	.003026	.06217	.2437	3.537
.006384	.003227	.1004	.2552	3.548
.006380	.003358	.1276	.2612	3.528
.006305	.003127	.1561	.2664	3.531
.006124	.003103	.2131	.2740	3.510
Intercept, pK_1^D = 3.557 ± 0.005				

(e) Dissociation of ethyl hydrogen maleate

m, HA	m, KA	m, KCl	E, v.	pK_E
Water				
0.03651	0.03184	0.03651	0.2113	3.078
.01111	.00995	.01111	.1770	3.083
.02447	.02245	.02447	.1997	3.069
				3.077 ± 0.005
Deuterium oxide				
0.02164	0.01791	0.02164	0.2095	3.536
.01469	.01347	.01469	.1970	3.531
.02753	.03001	.02753	.2095	3.531
.03707	.03847	.03707	.2185	3.531
				3.532 ± 0.002

(b) Second dissociation, maleic acid

m, NaHA	m, Na_2A	m, NaCl	E, v.	pK'_2
Water				
0.003364	0.002144	0.008873	0.0007	6.341
.01878	.01239	.01009	.0074	6.373
.01433	.01206	.02190	.0228	6.374
.01427	.01210	.1046	.0674	6.423
.01709	.01022	.1768	.0919	6.470
Intercept, pK_2^H = 6.332 ± 0.002				
Deuterium oxide				
0.005286	0.005961	0.02500	0.0305	6.740
.01432	.01615	.02880	.0369	6.775
.01914	.02158	.02537	.0347	6.786
.01458	.01643	.1013	.0733	6.823
.01250	.01410	.2065	.0946	6.849
.02060	.01944	.2799	.1078	6.934
Intercept, pK_2^D = 6.711 ± 0.005				

(d) Second dissociation, fumaric acid

m, NaHA	m, Na_2A	m, NaCl	E, v.	pK'_2
Water				
0.004687	0.008316	0.01315	0.0878	4.635
.006941	.01540	.02126	.0969	4.667
.006682	.01402	.02803	.1062	4.654
.007367	.01482	.06925	.1325	4.690
.004409	.1013	.1212	.1436	4.736
.008541	.01452	.1323	.1545	4.747
Intercept, pK_2^H = 4.602 ± 0.007				
Deuterium oxide				
0.002972	0.005991	0.009234	0.0848	5.062
.003531	.006544	.04502	.1305	5.107
.003227	.006537	.07219	.1410	5.137
.003164	.006037	.1040	.1535	5.153
.003505	.006585	.1448	.1619	5.220
Intercept, pK_2^D = 5.025 ± 0.004				

(f) Dissociation of ethyl hydrogen fumarate

m, HA	m, NaA	m, NaCl	E, v.	pK'_E
Water				
0.01009	0.01169	0.02582	0.1767	3.390
.02950	.03312	.01851	.1703	3.391
.03421	.03045	.05386	.2039	3.381
.03299	.03026	.08201	.2156	3.377
.01112	.01132	.1574	.2264	3.368
Intercept, pK_E^H = 3.396 ± 0.002				
Deuterium oxide				
0.01209	0.01101	0.01960	0.1864	3.848
.03419	.03341	.02294	.1898	3.840
.04520	.03719	.04328	.2102	3.844
.01159	.01247	.1078	.2262	3.840
.01121	.01247	.1625	.2358	3.838
Intercept, pK_E^D = 3.847 ± 0.004				

reduce the number of successive approximations necessary in the Bates methods. The procedure utilizes experimental data for two stages of neutralization of the fumaric acid.

Case I.—Buffer solutions of fumaric acid H_2A and its first anion HA^- in the ratio $m_{H_2A}{}^{i}/m_{HA^-}{}^{i}$ 2, where the superscript i is used to indicate "initial" or stoichiometric concentrations. With the usual definitions of K_1 and K_2 and the usual conservation equations, one can derive the relation between K_1 and K_2

$$K_1 = \frac{m_{H^+}{}^2\, \gamma_{H^+}{}^2\, \gamma_{A^-}\, \gamma_{HA^-}\,(m_t + m_{H^+} + m_{H_2A}{}^{i})}{K_2\gamma_{HA} - \gamma_{H_2A}(m_{H_2A}{}^{i} + m_t - m_{H^+}) + m_{H^+}\gamma_{H^+}\gamma_{A^-}\gamma_{H_2A}(m_{H_2A}{}^{i} - m_{H^+})} \qquad (4)$$

where m_t refers to total fumarate concentration. The hydrogen ion concentrations can be calculated by the method of Harned and Owen[19] and the activity coefficients can be estimated by use of the Debye–Hückel limiting law. The ionic strength is given by

$$\mu = m_{Cl^-} + m_{HA^-}{}^{i} + m_{H^+} + m_{A^=} \qquad (5)$$

For buffer solutions in which $m_{H_2A}{}^{i} = 2\, m_{HA^-}{}^{i}$ it

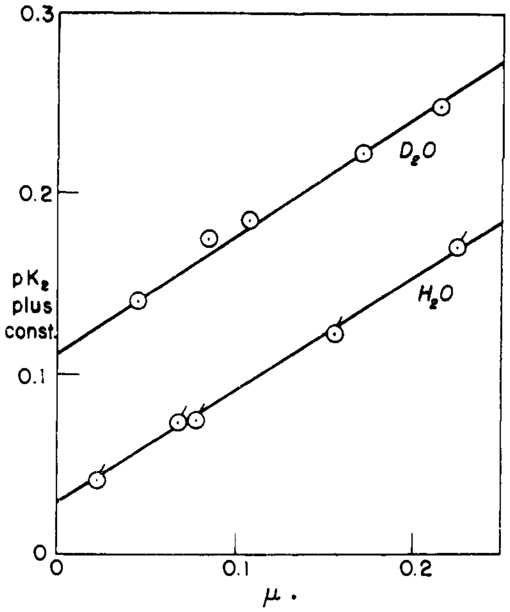


Fig. 1.—Plot of pK_2 *versus* μ for second dissociation of maleic acid, ⊙, $(pK_2^D - 6.6)$; ⊙, $(pK_2^H - 6.3)$.

was found that the term m_{A^-} of equation 5 was negligible and could be neglected in the calculation of μ.

Case II.—Buffer solutions of fumarate ion A^- and of the acid anion HA^- in the ratio $m_{A^{-i}}/m_{HA^{-i}} = 2$. Proceeding as before one can express K_2 as a function of K_1 and the various concentrations

$$K_2 = \frac{K_1 m_{H^+}\gamma_{H^+}\gamma_{A^-}\gamma_{H_2A}(m_{A^{-i}} + m_{H^+}) + m_{H^+}^{\ 2}\gamma_{H^+}^{\ 2}\gamma_{A^-}\gamma_{HA^-}(m_{A^{-i}} + m_{H^+} + m_t)}{K_1\gamma_{HA^-}\gamma_{H_2A}(m_t - m_{H^+} - m_{A^{-i}})} \quad (6)$$

The ionic strength is given by

$$\mu = m_{Cl^-} + m_{HA^{-i}} + 3m_{A^{-i}} + 2m_{H^+} + m_{H_2A} \quad (7)$$

but for this case the term m_{H_2A} can be neglected.

The procedure for using equations 4 and 6 is to calculate successive approximate values for K_1 and then for K_2 until a pair of values is obtained which does not change on further application of the equations. Initial calculations were always with equation 4. The first approximate values for pK_2 were taken as 4.45 for the solvent water[21] and as 4.95 for deuterium oxide. The first calculated values for pK_1 were extrapolated to zero ionic strength and the resulting approximate thermodynamic value for pK_1 then was used in equation 6 to get a next approximation for pK_2, etc. Two and sometimes three such approximations for pK_2 were needed to get a self-consistent pair of thermodynamic pK_1 and pK_2 values. In a few cases the calculations were repeated using the methods developed by Bates. The agreement between the two was invariably excellent.

Results and Discussion

Table II summarizes the final values of the twelve ionization constants that have been measured and Table III summarizes ratios. Table II includes for comparison the best of the previous data for the hydrogen acids. Remembering that the earlier studies utilized more approximate experimental methods and, at least for the maleate ester, a compound of uncertain purity, the agreement with the present data is all that can be expected. The new data leave virtually unchanged the significant aspects of the comparison between maleic and fumaric acids. For the hydrogen acids the values for the K_1/K_2 ratios are 26,000 and 32, respectively, and the ratio K_1/K_E is 14.7 for the maleate system compared to 2.0 for the fumarate system. Thus the evidence for pronounced H-bonding of the bimaleate ion remains unchanged. If one makes the plausible assumption that there is virtually no internal H-bonding for the monoethyl ester of maleic acid, then equation 2 is applicable and this leads to a value for K_H' of 6.4 implying that 86% of the bimaleate ion is present in water in the hydrogen bonded form.

TABLE II

SUMMARY OF pK VALUES; CONCENTRATIONS IN MOLES PER 55.3 MOLES OF SOLVENT

Acid	Solvent H_2O	D_2O	H_2O (lit).
Maleic acid			
pK_1	1.910	2.535	1.905,[a] 1.921[b]
pK_2	6.332	6.711	6.269,[a] 6.225[b]
Fumaric acid			
pK_1	3.095	3.557	3.019,[a] 3.019[b]
pK_2	4.602	5.025	4.455,[a] 4.384[b]
Ethyl hydrogen maleate	3.077	3.532	2.959[c]
Ethyl hydrogen fumarate	3.396	3.847	3.325[c]

[a] B. Adell, ref. 21, potentiometric method, cell with liquid junction, 18°. [b] W. L. German, A. I. Vogel and G. H. Jeffrey, *Phil. Mag.*, 22, 790 (1936), titration method, 25°. [c] J. Walker, ref. 8.

TABLE III

RELATIVE IONIZATION IN H_2O AND D_2O, 25°

Acid	K^H/K^D	ΔpK
Maleic	4.2	0.625
Bimaleate ion	2.4	.379
Fumaric	2.9	.462
Bifumarate ion	2.7	.423
Ethyl hydrogen maleate	2.8	.455
Ethyl hydrogen fumarate	2.8	.451

The available ionization data permit two approaches to the question of the relative H-bonding of deuterium. One approach is that of Westheimer and Benfey.[7] For the deuteriomaleic acids in D_2O the ratio K_1/K_E is 9.9 (compared to 1.95 for fumaric) and application of equation 2 leads to

$$\frac{(\overline{DA^-})}{(DA^-)} \equiv K_D' = 4.0$$

where $\overline{DA^-}$ and DA^- refer to the bonded and unbonded forms of the deuterio acid ion. The conclusion is that deuterio bimaleate ion in deuterium oxide exhibits significantly less internal H-bonding than does the hydrogen bimaleate ion in water. In fact it is quite reasonable to assume that the approximations which lead to equation 2 will be very similar for the hydrogen and deuterium cases and thus to expect that the ratio of 1.6 for K_H'/K_D' is an accurate measure of the relative hydrogen bonding for this particular system.[23]

---

(23) If one *assumes* that the variation in H-bonding in the two solvents is a reflection only of an energy change, the observed K_H'/K_D'

A second, somewhat less precise approach to the relative H-bonding can be made through comparisons of the ionization constants of the maleic acids to those of the fumaric acid. A convenient way to illustrate this is by the plot of Fig. 2 which gives ΔpK values for the various acids as a function of pK_{HA}, where ΔpK is defined as $pK^D - pK^H$. The figure includes the Rule and LaMer[13] data for three other carboxylic acids. The dotted line through the latter reflects the Rule and LaMer conclusion that ΔpK increases with pK. Actually the data for the hydrogen bifumarate ion is not particularly in accord with this proposal and suggests rather that K^H/K^D for these acids is roughly constant at a value of around 2.8. But even if one considers this rather than the Rule and LaMer curve to be the normal behavior for carboxylic acids, it is clear that for maleic acid K_1^H/K_1^D is substantially larger than expected and K_2^H/K_2^D is substantially smaller. These facts are consistent with the proposal that the deutero acid ion of maleic acid is relatively less stable than the hydrogen acid ion, *i.e.*, that there is less internal H-bonding for the deutero ion. One can in fact estimate "proper" values of the K^H/K^D ratios for the maleic acids and then use these and the observed ratios to make a semiquantitative calculation of the relative H-bonding. However, a rather more satisfactory procedure is to use the values for H-bonding that result from the ester studies to calculate corrected K^H/K^D ratios for maleic acid and its acid ion.

If we assume negligible internal H-bonding for maleic acid itself, we can write the observed ionization constants for the acids as

$$\frac{(H^+)[(\overline{HA^-}) + (HA^-)]}{(H_2A)} = K_1^H \qquad (8)$$

$$\frac{(H^+)(A^=)}{(\overline{HA^-}) + (HA^-)} = K_2^H \qquad (9)$$

with similar expressions for the deutero acids. It is then reasonable to define "corrected" ionization constants, *i.e.*, for ionization of the unbonded species, by the equations

$$K_1^H\,(\text{corr.}) = \frac{(HA^-)}{(\overline{HA^-}) + (HA^-)}\,K_1^H \qquad (10)$$

and

$$K_2^H\,(\text{corr.}) = \frac{(\overline{HA^-}) + (HA^-)}{(HA^-)}\,K_2^H \qquad (11)$$

Similar equations will hold for the deuterio acids. Application of equation 2 to the data of Table III for the ionization of esters relative to that of the acids shows that 14% of the hydrogen acid ion is in the unbonded form whereas 20% of the deuterio acid ion is unbonded. These figures and the pK values of Table II lead to the following "corrected" values for ionization of the unbonded maleic acids: pK_1^H (cor.) = 2.78 and $\Delta pK_1 = 0.46$; pK_2^H (cor.) = 5.47 and $\Delta pK_2 = 0.55$. These values are plotted in Fig. 2. It is evident that the corrected values for ΔpK are quite sensibly positioned relative to the data for the other carboxylic acids listed. We conclude that the observed abnormal values of ΔpK_1 and ΔpK_2 for maleic acid give added semiquantitative support to the conclusions that there is extensive internal H-bonding of the hydrogen bimaleate ion in water and somewhat less H-bonding of the deuterium analog in deuterium oxide.

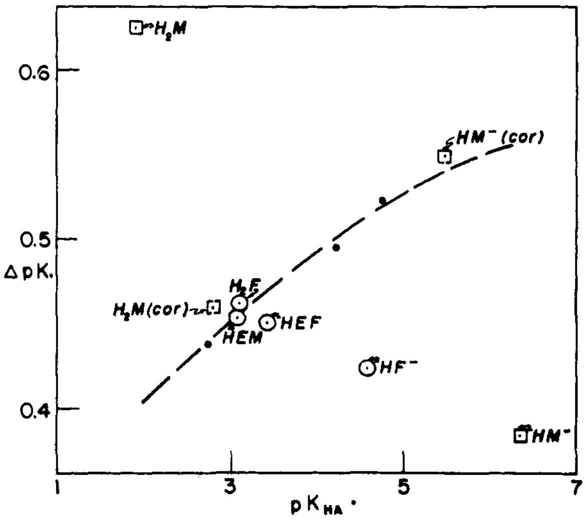


Fig. 2.—($pK^D - pK^H$) *versus* pK_{HA}. ● chloroacetic, benzoic and acetic acids (Rule and LaMer); [·] "corrected" values for maleic acid.

These conclusions suggested two questions: Is this tendency for a relatively smaller amount of H-bonding by deuterium a general effect? And is it a property of isolated molecules or is it rather a reflection of different H-bonding by the solvents H_2O and D_2O? Turning to the first question, evidence for two additional systems suggests that the phenomenon is fairly common, at least for OH—O bonding in water. Korman and LaMer[17] reported a K^H/K^D ratio of 4.1 for salicylic acid ($pK^H = 3.0$) in H_2O relative to 92% D_2O. Salicylate ion is commonly assumed to be extensively H-bonded. Hence the high K^H/K^D ratio is consistent with the proposal that the H-bonding is smaller for the anion as present in deuterium oxide. Nachod[24] and Long and Watson[25] report that the equilibrium constant for the enolization of methylacetylacetone is 35% larger for enolization in water than for the analogous reaction in deuterium oxide. The usual explanation for the relatively large amount of enolization of β-diketones is H-bonded stabilization of the enol. These data thus imply a smaller amount of H-bonding for the deutero enol in deuterium oxide.[26]

A somewhat more speculative piece of evidence which points in a different direction is that Hermans and Scheraga[27] find for the equilibrium be-

---

ratio implies a 280 calorie greater heat of reaction for the internal bonding in H_2O than for the same reaction in D_2O.

(24) F. C. Nachod, *Z. physik. Chem.*, **182A**, 193 (1938).

(25) F. A. Long and D. Watson, *J. Chem. Soc.*, 2019 (1958).

(26) There are indications from Nachod's work that solvent can play a substantial role in determining the relative extent of internal H-bonding. He reports these values for various solvents:

Ketone	Solvent	$K^H = C_{Enol}/C_{Ket}$	K^H/K^D
Acetylacetone	H_2O *vs.* D_2O	0.244	1.8
Acetylacetone	CH_3OH *vs.* CH_3OD	3.98	1.02
Methylacetylacetone	H_2O *vs.* D_2O	0.0373	1.47
Methylacetylacetone	CH_3OH *vs.* CH_3OD	0.515	1.17

(27) J. Hermans, Jr., and H. A. Scheraga, *Biochim. et Biophys. Acta*, **36**, 534 (1959). See also M. Calvin, J. Hermans, Jr., and H. A. Scheraga, THIS JOURNAL, **81**, 5048 (1959).

tween the helical and random coil forms of ribonuclease that the helical form is relatively less stable in water than it is in deuterium oxide. Since the helical form presumably owes most of its stability to internal H-bonding, this result indicates less extensive internal H-bonding for the hydrogen compound in water. However, this protein transformation is relatively more complex than the previous example and interpretation is correspondingly more difficult.

Very little definite information is available on the role of the solvent in establishing the observed ratios of relative H-bonding. General zero-point energy arguments lead to the prediction that for isolated gaseous molecules internal hydrogen bonding by deuterium would be greater than that by hydrogen. In agreement with this Potter, Bender and Ritter[28] find the heat of dimerization of gaseous acetic acid-d_4 to be 300 calories greater than that of ordinary acetic acid and, at temperatures below about 140°, this leads to greater dimerization of the deuterium compound. However, there is also a measurable entropy difference for the two dimerizations so that zero-point energy considerations do not tell the whole story.

We know of no measurements of relative internal H-bonding in the gas state. But tentatively we can assume that, as with acetic acid dimerization, the bonding by deuterium will be slightly stronger. The implication of the present work then is that the H-bonding of the *solvent* deuterium oxide can be enough greater than that of water to reverse the normal prediction for internal H-bonding. Some direct studies of this proposal are in progress.

(28) A. E. Potter, Jr., P. Bender and H. L. Ritter, *J. Phys. Chem.*, **59**, 250 (1955).

ITHACA, N. Y.

[CONTRIBUTION FROM THE LOW TEMPERATURE LABORATORY, DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING UNIVERSITY OF CALIFORNIA, BERKELEY]

Phosphoryl Chloride. Entropy. Low Temperature Heat Capacity. Heats of Fusion and Vaporization. Vapor Pressure[1]

BY J. B. OTT AND W. F. GIAUQUE

RECEIVED SEPTEMBER 15, 1959

The heat capacity of phosphoryl chloride has been measured from 13 to 304°K. The heat of fusion at the triple point, 274.33°K., was determined as 3132 cal. mole^{-1}. The heat of vaporization at 298.15°K. and a pressure of 3.092 int. cm. was found to be 9220 cal. mole^{-1}. The calorimetric data were used to calculate the entropy of the ideal gas at 1 atm. and 298.15° K. as 77.75 gibbs mole^{-1}. A selected assignment of the fundamental frequencies of $POCl_3$ was used to calculate a value of 77.77 gibbs mole^{-1}.

This paper describes a low temperature calorimetric investigation of phosphoryl chloride, $POCl_3$, for the purpose of determining its entropy. This molecule is a somewhat unsymmetrical tetrahedron, and while it was expected that the crystal would attain perfect order at low temperatures, there was at least a small possibility of the type of disorder found[2] in perchloryl fluoride, ClO_3F.

Calorimetric Apparatus and Temperature Scale.—The measurements were made in Gold Calorimeter V. This designation is used for the rebuilt calorimeter IVA.[2] The calorimeter is similar to the one described by Giauque and Egan.[3] The bottom, in which a welding crack had developed, was replaced, and a new gold resistance thermometer-heater was wound on the outside surface. The calorimeter weighed 453.2 g. before the resistance thermometer was added. The capacity to the top of the small platinum access tube was 135.37 cm.^{3} at 20°. The platinum tube was 1.4 cm. long, 0.24 cm. i.d. The standard thermocouple was attached by means of a detachable thermocouple well, as described by Busey and Giauque.[4]

The standard copper-constantan thermocouple No. 102 was compared with the triple (13.94° K.) and boiling (20.36° K.) points of hydrogen, and the triple (63.15° K.) and boiling (77.34° K.) points of nitrogen. Appropriate corrections were made for the deviations. 0° was taken as 273.15° K.

Sample of Phosphoryl Chloride.—Reagent grade Baker and Adamson phosphoryl chloride was selected as a starting material. The label specified 0.01% sulfate and 0.001% iron. It probably would also contain some hydrogen chloride and phosphoric acid from hydrolysis with moisture. This material was put in a vacuum jacketed distillation column and refluxed for two days. Air was removed by pumping a small amount of the material through a capillary during the initial refluxing. The material remaining was distilled at a reflux ratio of 125:1. Of 400 cc. distilled, the central 150 cc. fraction was used for the calorimetric measurements. The column has been described by Koehler and Giauque.[2] The condensation coil at the top was maintained at 20°. This held the distillation pressure of $POCl_3$ inside the calorimeter at about 2.5 cm.

Premelting heat capacity measurements indicated that the material contained 0.02 mole % of liquid soluble-solid insoluble impurity.

Heat Capacity of Phosphoryl Chloride.—The heat capacities were measured in the usual manner. 202.187 g. corrected to *vacuo* were distilled into the calorimeter. The molecular weight was taken as 153.346. One atmosphere of helium was added at 10° to purge the filling tube and to essentially prevent later diffusion into it. The helium also provided good heat transfer within the calorimeter. One defined calorie was taken as 4.1840 absolute joules. Two series of measurements were made on the solid. The resistance thermometer-heater showed evidence of strain for about 50° below the melting point. The standard thermocouple was used for temperature observations in this region. The data are given in Table I. The values are

---

(1) This work was supported in part by the National Science Foundation.

(2) J. K. Koehler and W. F. Giauque, THIS JOURNAL, **80**, 2659 (1958).

(3) W. F. Giauque and C. J. Egan, *J. Chem. Phys.*, **5**, 45 (1937).

(4) R. H. Busey and W. F. Giauque, THIS JOURNAL, **74**, 4443 (1952).