[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Dissociation Constant of Propionic Acid from 0 to 60°

BY HERBERT S. HARNED AND RUSSELL W. EHLERS

In two recent communications,[1] we have shown how it is possible to determine the dissociation constant of a weak acid with a high degree of accuracy from measurements of cells without liquid junction. In addition, accurate values of the dissociation constant of acetic acid from 0 to 60° at five degree intervals were obtained. The present study is concerned with a similar determination of the dissociation constant and related properties of propionic acid.

Measurements of the Cells $H_2 | HP(m_1), NaP(m_2), NaCl(m_3) | AgCl | Ag$.—The propionic acid was fractionated three times, and only the middle portion which constituted one-third the amount of the distillate was retained each time. Carbonate-free sodium hydroxide solution was titrated against hydrochloric acid which had been standardized by gravimetric analysis. The standardized hydroxide solution was titrated against a propionic acid solution of convenient strength.

A stock solution of 0.1 *M* HP, 0.1 *M* NaP and 0.1 *M* NaCl was first made by adding equivalent amounts of the acid and hydroxide solutions, adding the required amount of sodium chloride and diluting to the required strength. From this solution, the cell solutions were made by dilution. All other details of procedure were the same as those previously described by us.

The first half of Table I contains the experimental electromotive forces corrected to 1 atm. hydrogen pressure. The equation for the electromotive force of the cell is

$$E - E_0 + \frac{RT}{F} \ln \frac{m_{HP} m_{Cl}}{m_P} = -\frac{RT}{F} \ln \frac{\gamma_H \gamma_{Cl} \gamma_{HP}}{\gamma_H \gamma_P} - \frac{RT}{F} \ln K \qquad (1)$$

E_0 is the normal potential of the cell, K the dissociation constant of propionic acid, and the "*ms*" and "γs" are the molal concentrations and activity coefficients of the species denoted by subscripts. As previously described, we let the right side of the equation equal $-(RT/F) \ln K'$, compute K', and then plot this quantity against μ. At zero μ, K' equals K. Examples of the extrapolation at 0, 25, 45 and 60° are shown in Fig. 1. The values of E_0 were taken from our recent determinations, and are given in the second column of Table II. The third column contains the experimental values of K.

The plots in Fig. 1 are typical of this extrapolation. All the plots are straight lines. The sensitivity of these plots is very great when we consider that 0.1 millivolt corresponds to an error of 7 in the third decimal place and that only a very few of the most widely scattered individual results

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(1) Harned and Ehlers, THIS JOURNAL, **54**, 1350 (1932); **55**, 652 (1933).

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS: $H_2 | HP(m_1), NaP(m_2), NaCl(m_3) | AgCl | Ag$

$m_1 = m_2 = m_3$	E'_0	E_5	E_{10}	E_{15}	E_{20}	E_{25}	E_{30}	E_{35}	E_{40}	E_{45}	E_{50}	E_{55}	E_{60}
0.004899					0.64353	0.64758	0.65161	0.65565	0.65692				
.005354									.65617	0.66113	0.66496	0.66888	0.67274
.005571									.65621	.66012	.66392	.66776	.67148
.005918					.63851	.64249	.64643	.65037	.65426			.66513	.66890
.006111									.65376	.65750	.66131		
.006442	0.62046	0.62446	0.62854	0.63258	.63670								
.006722	.61956	.62356	.62762	.63158	.63563								
.007055	.61823	.62219	.62622	.63108	.63416								
.008117					.63410	.63798	.64185	.64572	.64950				
.008716					.62896	.63275	.63654	.64033					
.009225	.61191	.61585	.61973	.62362	.62752								
.009630					.62640	.63014	.63386	.63759	.64128				
.010525									.63888	.64251	.64607	.64973	.65331
.010592									.63888	.64244	.64600	.64956	.65307
.010812	.60825	.61205	.61590	.61966	.62349								
.011181	.60723	.61097	.61483	.61865	.62251								
.012812					.61926	.62286	.62645	.63006	.63356				
.013388									.63246	.63596	.63941	.64291	.64637
.013393	.60291	.60660	.61036	.61404	.61781								
.013933									.63138	.63487	.63833	.64176	.64525
.015012									.62935	.63283	.63624	.63966	.64307
.015819									.62799	.63145	.63486	.63830	.64170
.016054					.61340	.61692	.62041	.62393	.62741				
.016431					.61297	.61651	.62000	.62349	.62699				
.016600	.59814	.60180	.60544	.60903	.61267								
.017153					.61185	.61538	.61876	.62227	.62568				
.018070									.62440	.62778	.63115	.63453	.63788
.018106					.61052	.61401	.61743	.62086	.62442				
.018669					.60964	.61311	.61655	.61994	.62334				

TABLE I (*Concluded*)

$m_1 = m_2 = m_3$	E'_0	E_5	E_{10}	E_{15}	E_{20}	E_{25}	E_{30}	E_{35}	E_{40}	E_{45}	E_{50}	E_{55}	E_{60}
0.018882	0.59491	0.59846		0.60554									
.021153	.59241	.59595	0.59958	.60305	0.60661								
.021258									0.61932	0.62268	0.62593	0.62919	0.63239
.021977					.60559	0.60901	0.61237	0.61576	.61908				
.022736	.59046	.59399	.59757	.60095	.60446								
.023284									.61748	.62073	.62397	.62718	.63041
.025546					.60178	.60522	.60851	.61190	.61514				
.026480					.60086	.60423	.60750	.61078	.61399				
.026833	.58669	.59012	.59360	.59698	.60038								
.027217									.61347	.61663	.61975	.62284	.62597
.028469									.61211	.61529	.61850	.62166	.62476
.030666	.58355	.58695	.59037	.59367	.59716								
.031078	.58317	.58660	.59001	.59332	.59660								
.031126					.59665	.60001	.60321	.60644	.60856				
.031553									.60934	.61248	.61557	.61860	.62159
.031793					.59621	.59958	.60281	.60624	.60915				
.035686					.59335	.59664	.59981	.60300	.60606				
.045243									.59959	.60262	.60557	.60852	.61143

deviate as much as this from the plots. We believe that K has been estimated from these graphs to within ±0.003. This is somewhat greater than the estimated error due to making up the solutions. Like acetic acid K increases with T to 20°, passes through a maximum at about this temperature and then decreases. The graphs in Fig. 1 have slopes which in passing from the lower to the higher temperatures decrease regularly, change sign, reach a maximum at about 25°. At temperatures above this the slope gradually decreases but does not again change sign. The whole system of graphs is consistent in this respect as shown by the values of the slopes given in the last column of Table II. At 25° our value of 1.336×10^{-5} is somewhat higher than 1.32×10^{-5} which has been recorded in the "International Critical Tables."[2]

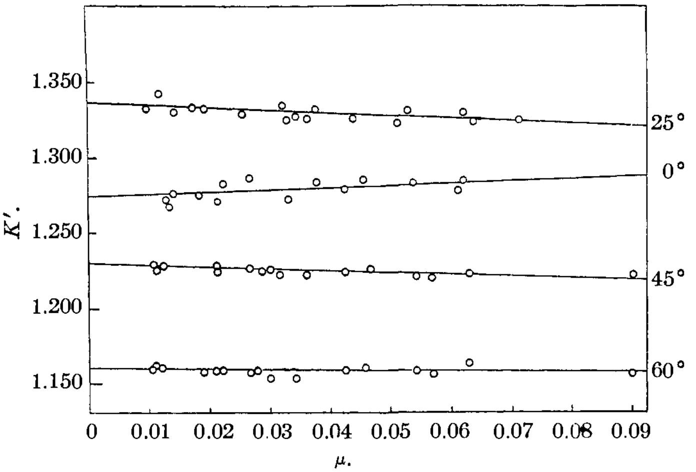

Fig. 1.

In order to calculate the heat of ionization, ΔH, we employed the equation.

$$\Delta H = a + bT + cT^2 \qquad (2)$$

Upon substitution of this value of ΔH in the van't Hoff equation, and integrating, we obtain

$$\log K = -\frac{a}{2.303RT} + \frac{b}{R}\log T + \frac{c}{2.303R}\,T + d \qquad (3)$$

By substituting the experimental values of K and T in this equation, thirteen equations were obtained from which the constants a, b, c and d were evaluated by the method of least squares. The equation for K was found to be

$$\log K = -\frac{1274.95}{T} - 1.31574 \log T - 0.012843\,T + 6.48708 \qquad (4)$$

that for ΔH was

$$\Delta H = 5837.6 - 2.6163\,T - 0.058806\,T^2 \qquad (5)$$

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(2) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, Vol. 6, p. 264.

and the equation for the difference in specific heat of the ions and undissociated molecules, ΔC_p, was

$$\Delta C_p = -2.6163 - 0.11761\,T \qquad (6)$$

The values of these quantities computed by the corresponding equations are given in the fourth, sixth and seventh columns of Table II. The agreement between the experimental values of K and those computed by equation (4) is good as shown by the deviations given in the fifth column of the table. The greatest deviation is 5 in the third decimal place which corresponds to 0.07 of a millivolt. Eight of the thirteen results lie within ±1 in the third decimal place. This agreement gives us considerable confidence in the calculated values of the heat content and specific heat of the reaction under consideration. The calculated maximum in K occurs at 20.6°. The values of ΔH differ little from similar values obtained by us for the heat of dissociation of acetic acid.

TABLE II

DISSOCIATION CONSTANT AND HEAT OF IONIZATION OF PROPIONIC ACID

t, °C.	E_0	$K \times 10^{-5}$ (obs.)	$K \times 10^{-5}$ (Equation 4)	ΔH	ΔC_p	$\frac{K - K^1}{\mu}$
0	0.23632	1.274	1.275	737	−34.7	−0.12
5	.23391	1.305	1.303	562	−35.3	− .06
10	.23130	1.326	1.323	384	−35.9	.00
15	.22851	1.336	1.335	203	−36.5	+ .06
20	.22554	1.338	1.339	19	−37.1	+ .10
25	.22239	1.336	1.336	− 168	−37.7	+ .16
30	.21908	1.326	1.327	− 358	−38.3	+ .18
35	.21561	1.310	1.311	− 551	−38.9	+ .16
40	.21200	1.284	1.289	− 746	−39.4	+ .14
45	.20825	1.257	1.261	− 945	−40.0	+ .12
50	.20436	1.229	1.230	−1147	−40.6	+ .10
55	.20033	1.195	1.194	−1351	−41.2	+ .08
60	.19620	1.160	1.155	−1559	−41.8	+ .06

Summary

1. From measurements of the cells, $H_2|HP(m_1)$, $NaP(m_2)$, $NaCl(m_3)|AgCl|Ag$, the dissociation constant of propionic acid has been determined from 0 to 60° at 5° intervals.

2. The dissociation constants at any temperature between 0 and 60° may be computed by equation (4) with a high order of accuracy.

3. By means of equations (5) and (6) the heat of ionization, ΔH, and the difference in specific heats of the ions and undissociated molecule, ΔC_p may be accurately computed.

NEW HAVEN, CONNECTICUT

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