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The Vapor Phase Dissociation of Some Carboxylic Acids. II. Formic and Propionic Acids[1,2]

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The vapor phase dissociation of formic and acetic acids has been studied in the pressure range below one-tenth atmosphere and the temperature range of 50–150°. The data are summarized by the equations $\log_{10} K = -3083/T + 10.743$ (formic acid); $\log_{10} K = -3316/T + 10.834$ (propionic acid). The data for formic acid agree with the results obtained by Coolidge. The data for propionic acid yield a heat of dissociation much lower than that reported by MacDougall. These data combined with those previously published for acetic acid suggest that the hydrogen bond strength in the acids considered increases in the order $HCOOH << CH_3COOH < C_2H_5COOH$. It is suggested that the strength levels off and remains essentially constant beyond propionic acid. Other data are summarized which support this order.

A knowledge of the variation of hydrogen bond strength with structure should lead to a better understanding of the factors involved in the formation of the hydrogen bond. Many studies have been conducted for the purpose of gaining such knowledge for the simple fatty acids.[3] The precision of the numerous quantitative results obtained does not permit the unique establishment of the order of bond strength in the simple carboxylic acids. Even investigations employing similar experimental techniques lack close accordance. This investigation was initiated for the purpose of studying a sufficient number of carboxylic acids with sufficient precision, to permit one to establish the order of variation of bond strength with length of carbon chain.

Experimental

The apparatus, method of analysis, procedure of measurement and method of calculation have been discussed elsewhere.[4] In all studies of formic acid and some of propionic acid the pressure P_0, at 0°, of the undissociated dimer was ascertained by the method of approximations.[5] The precision of this method was increased because the temperature range selected for study covered nearly the whole range of dissociation of the acids (10–90%). Formic acid had to be studied by this procedure because it underwent slight decomposition producing a permanent gas which prevented its quantitative removal, by condensation, from the line for analysis. This dissociation was apparently too small to exert an appreciable effect on the equilibrium.

Purification of Materials.—The starting material was Eastman Kodak Co., white label, formic acid which analysis proved to be 99.5% pure. Drying over B_2O_3 raised the assay value to 99.9%.[6] The acid was further purified by vacuum distillation in an all-glass vacuum line and a middle fraction with an assay value of 100.1 was used in the studies. The following vapor pressures were obtained for the pure sample: solid at 0°, 8.52 mm.; liquid at 0°, 10.95 mm.; liquid at triple point, 17.72 mm. The corresponding values reported by Coolidge[7] are 8.46, 11.16 and 17.94. The acid was kept frozen during its investigation to minimize decomposition.[8]

Eastman Kodak Co. white label propionic acid proved to be 99.4% pure. The acid was purified in a Todd fractionating column and a fraction boiling at 141.1° (cor.) was transferred to the vacuum line. After fractionation a portion was selected which analyzed 100.0% propionic acid.

Results and Discussion

In this investigation the results from four out of six complete vapor phase dissociation studies for formic acid and fourteen out of fifteen similar studies for propionic acid all below 0.1 atm. pressure and over the temperature range of 50–150° are reported. Heats of dissociation data were obtained from plots of log K *versus* $1/T$ which yielded straight lines, in all cases, similar to those reported in the acetic acid study.[4]

Generally measurements were made over the range 50 to 150° at intervals of 10°.[9] Pertinent values computed from these data are shown in Tables I and II. One observes that the scatter of the propionic data is much wider than that for formic and acetic[4] acids. This accounts for the large number of studies on propionic acid to achieve the proper precision. MacDougall[10] likewise experienced considerable difficulty studying propionic acid. The study of formic acid was undertaken to ascertain if the present investigators could reproduce the results of Coolidge, which are generally accepted as correct. The excellent agreement of our results with his increases our belief in the significance of our findings.

TABLE I

SUMMARY OF COMPUTED DATA FOR FORMIC ACID

P_0 (mm.)	A^a	B^a	$K_{75(\text{mm.})}$	$K_{100(\text{mm.})}$	$K_{125(\text{mm.})}$	ΔH (cal.)
17.44	3034	10.611	78.53	301.3	977.3	13,884
26.25	3101	10.802	78.35	309.8	1029.0	14,190
21.34	3088	10.749	75.51	296.5	981.8	14,130
26.45	3111	10.811	74.81	297.2	990.9	14,236
			Mean			
	3083	10.743	76.80	301.2	994.8	14,110
	% P.E. =		0.9	0.7	0.8	0.4

[a] Constants for the equation $\log_{10} K = -A/T + B$.

Data which permit a comparison among the three acids are collected in Table III. Formic acid possesses, by far, the weakest hydrogen bond. Acetic and propionic acids possess bonds of nearly

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[2] Presented before the Division of Physical and Inorganic Chemistry at the Buffalo meeting of the American Chemical Society, March, 1952.

[3] M. Davis, *Ann. Reps. Progress Chem. (Chem. Soc. London)*, **48**, 6 (1946).

[4] M. D. Taylor, THIS JOURNAL, **73**, 315 (1951).

[5] H. C. Brown and M. Gerstein, *ibid.*, **72**, 2923 (1950).

[6] Small bubbles were observed forming in the acid as it stood over B_2O_3 at room temperature.

[7] A. S. Coolidge, THIS JOURNAL, **52**, 1874 (1930).

[8] A. S. Coolidge, *ibid.*, **50**, 2166 (1928).

[9] For complete data order Document 3611 from American Documentation Institute, 1719 N Street, N.W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

[10] F. H. MacDougall, THIS JOURNAL, **63**, 3420 (1941).

TABLE II

SUMMARY OF COMPUTED DATA FOR PROPIONIC ACID

P_0 (mm.)	A[a]	B[a]	K_{75}(mm.)	K_{100}(mm.)	K_{125}(mm.)	ΔH (cal.)
23.97	3306	10.851	22.59	97.73	352.4	15,128
13.88	3333	10.796	16.63	72.95	265.5	15,252
18.40	3304	10.785	19.63	84.92	306.2	15,119
15.22	3316	10.795	18.58	80.72	291.7	15,174
15.62	3221	10.489	17.22	71.78	250.0	14,739
16.19[b]	3368	10.958	19.19	85.31	314.8	15,412
16.42	3407	11.153	23.23	105.00	393.6	15,590
23.72	3299	10.786	20.37	87.90	315.5	15,096
22.22	3296	10.770	20.00	86.30	309.7	15,082
13.90[b]	3318	10.856	21.09	91.83	331.9	15,183
11.02	3250	10.675	21.83	92.05	324.3	14,872
25.49[b]	3340	10.925	21.38	93.97	342.8	15,284
29.58[b]	3314	10.873	22.54	97.95	353.2	15,165
36.02[b]	3356	10.958	20.75	91.83	337.3	15,357
Mean =	3316	10.834	20.36	88.59	320.6	15,175
	% P.E. =		1.7	1.8	2.0	0.3

[a] Constants for the equation $\log_{10} K = -A/T + B$. [b] P_0 obtained by direct analysis.

TABLE III

DATA FOR COMPARING FORMIC, ACETIC AND PROPIONIC ACIDS

			Constants			
Acids	A	B	K_{100}(mm.)	ΔF_{100}(cal.)	ΔS_{100}(cal).	ΔH(cal.)
Formic	3083	10.743	301.2	686	36.0	14,110
% P. E. =			0.7	0.7	0.4	0.4
Acetic	3347	10.932	92.0	1570	36.7	15,270
% P. E. =			0.8	0.8	0.2	0.2
Propionic	3316	10.834	88.6	1594	36.4	15,175
% P. E. =			1.8	1.8	0.3	0.3

equal strength. On the basis of ΔF_{100}, the bond appears to be slightly stronger in propionic acid. The authors believe that the hydrogen bond strength differs very little among the fatty acids beyond formic, perhaps increasing very slightly with chain length. This conclusion is in accord with the findings of other investigators. Gillette[11] obtained the following order of decreasing hydrogen bond strength based on the frequency shift of the band at 1721 cm.$^{-1}$; trimethylacetic > diethylacetic > dimethylacetic > acetic acid. Pohl, Hobbs and Gross[12] obtained a similar order of decreasing hydrogen bond based on electric polarization, *viz.*, trimethylacetic > butyric > propionic > acetic > formic. Nash[13] obtained the order trimethylacetic > butyric > acetic. Infrared studies,[14] however, indicate the order $CH_3COOD > C_2H_5COOD > C_3H_7COOD > HCOOD > HCOOH$. Foz[15] finds from $P-V-T$ data that acetic acid possesses a lower heat of dissociation, 13.8 kcal. mole^{-1}, than formic acid, 14.5 kcal. mole^{-1}. In all cases cited, differences among acids higher than formic scarcely exceed experimental error.

In the low pressure range where these acids were investigated the data seem to obey the simple gas and equilibrium laws so it was not necessary to postulate higher polymers than the dimer. The equilibrium constants varied only slightly with pressure over a threefold variation in sample size in the case of propionic acid. Similar results have been reported for acetic acid.[4] Other investigators[10,13,16] found evidence for higher polymerization at higher pressures. It is believed that even if the constants reported in this paper prove not to be the true thermodynamic ones, their determination by the same investigator with the same apparatus renders them quite reliable for comparing the relative order of hydrogen bond strengths in the carboxylic acids. For these reasons the authors believe that the order proposed above has a high degree of probability.

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(11) R. H. Gillette, THIS JOURNAL, **58**, 1143 (1936).

(12) A. Pohl, M. Hobbs and P. Gross, *J. Chem. Phys.*, **9**, 408 (1941).

(13) E. W. Johnson and L. K. Nash, THIS JOURNAL, **72**, 547 (1950); L. K. Nash, private communication to M. Taylor.

(14) R. Hofstadter and R. C. Herman, *J. Chem. Phys.*, **6**, 534 (1938); **7**, 460 (1939); **8**, 252 (1940).

(15) O. R. Foz and J. Morcillo, *C. A.*, **44**, 8716 (1950).

(16) H. L. Ritter and J. H. Simons, THIS JOURNAL, **67**, 757 (1945).