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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

The Vapor Phase Association of Butyric and Heptanoic Acids

BY R. E. LUNDIN, F. E. HARRIS AND L. K. NASH

Data secured in an experimental study of the vapor densities of butyric and heptanoic acids are presented. These data indicate that the length and/or branching of the hydrocarbon substituent attached to the carboxyl group is without appreciable effect on the heats of dimerization of the paraffin acids. The presence of one or more higher polymers in the acid vapor is strongly indicated; and the experimental data are shown to be entirely consistent with the hypothesis that the predominant higher polymer is a trimeric species of substantial stability.

The results of a recent study[1] of the vapor phase association of the vapors of acetic and trimethylacetic acids have indicated that though the predominant polymeric form is the dimer, the acid vapors also contain substantial proportions of a stable trimeric species. The heat of dimerization of both acids was found to be close to −14 kcal., and in both cases the heat of trimerization was of the same order as (slightly greater than) $^3/_2$ the heat of dimerization. This suggests that the trimer bonds are of a character similar to those of the dimer. The further investigation here reported was designed: (a) to define more closely the influence on the dimerization process of the nature of the hydrocarbon substituent of the acid; and (b) to secure further evidence bearing on the trimerization postulate, which is diametrically opposed to the tetramer hypothesis advanced by Ritter and Simons.[2]

The former point is of interest because the heat of dimerization reported by Fenton and Garner[3] for *n*-heptanoic acid is but −7.8 kcal., little more than one-half the generally accepted corresponding value(s) for the lower carboxylic acids. Fenton and Garner suggest that the heats of dimerization of the paraffin acids must fall off markedly with increasing bulk of the hydrocarbon substituent. However, there is no indication of such a trend in the previously reported results for the lower paraffin acids and further work was considered desirable.

The small degree of polymerization of heptanoic acid vapor hinders the study of the dimerization, and effectively excludes the possibility of a meaningful examination of the trimerization process. It also appears[4] that heptanoic acid undergoes some decomposition at its boiling point. These circumstances suggested the desirability of limiting the work with heptanoic acid to a short series of measurements—made as rapidly and at as low temperatures as possible—while also making a more extended series of trials with a lower normal paraffin acid. *n*-Butyric acid was selected as the second subject of investigation.

Heptanoic Acid.—Heptanoic acid, twice vacuum distilled at room temperature, was found to melt at −8.7°. There is no agreement among the recently cited values for the melting point of this acid, the figures given ranging from −10.5 to −6.3°. A sample of the vacuum distilled heptanoic acid was introduced into the balance system[1] and a short series of measurements at minimum temperatures (and, necessarily, low pressures) was made as rapidly as possible. The results are given in Table I. The gas density, *d*, was determined from the balance readings, interpreted with the aid of check calibrations with carbon tetrachloride performed both before and after the trials with the acid. The values of *M*, the apparent molecular weight, were derived by making appropriate substitutions in the equation: $M = dRT/P$. The figures for $-\log K_2'$ were calculated from the following expression for K_2', the apparent dimerization constant

$$K_2' = \frac{m(M - m)}{P(2m - M)^2} \qquad (1)$$

In this expression *m* is the molecular weight of the acid monomer.

TABLE I

EXPERIMENTAL DATA AND APPARENT DIMERIZATION OBTAINED WITH BUTYRIC AND HEPATANOIC ACIDS

t (°C.)	P (mm.)	d(g./l.)	M	$-\log K_2'$
		Heptanoic acid		
227.1	277.9	1.189	133.5	4.015
200.6	256.8	1.186	136.5	3.682
218.2	198.6	0.858	132.4	3.897
189.4	244.9	1.1725	138.1	3.552
		Butyric acid		
195.5	717.5	2.479	100.99	3.553
172.7	634.4	2.468	108.17	3.220
183.2	676.4	2.484	104.50	3.381
195.2	664.7	2.280	100.20	3.556
183.0	624.2	2.272	103.55	3.384
172.7	588.7	2.267	107.05	3.227
195.3	592.6	2.007	98.95	3.568
172.8	527.9	2.001	105.42	3.239
163.4	497.6	2.003	109.61	3.066
195.7	506.2	1.690	97.59	3.573
173.0	452.8	1.685	103.55	3.245
163.0	427.1	1.686	107.36	3.077
153.7	402.6	1.687	111.54	2.911
184.8	395.5	1.360	98.21	3.432
163.1	353.2	1.360	104.79	3.088
153.0	331.4	1.356	108.74	2.919
142.8	299.7	1.311	113.45	2.723
152.8	262.1	1.044	105.84	2.919
141.4	242.7	1.041	110.90	2.712

A plot of $-\log K_2'$ against $1/T$ was linear, within the experimental error. The least-squares line fitted to the experimental points is represented by the equation

$$-\log K_2' = 9.807 - 2900/T$$

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[1] E. W. Johnson and L. K. Nash, THIS JOURNAL, **72**, 547 (1950).

[2] H. L. Ritter and J. H. Simons, *ibid.*, **67**, 757 (1945).

[3] T. M. Fenton and W. E. Garner, *J. Chem. Soc.*, 694 (1930).

[4] W. O. Pool and A. W. Ralston, *Ind. Eng. Chem.*, **34**, 1105 (1942).

from which the apparent heat of dimerization of heptanoic acid is calculated as −13.4 kcal. The accuracy of this determination is not extremely high because: (1) the possibility of slight decomposition of the specimen cannot be completely excluded; (2) the proportion of association at the high temperatures and low pressures used is meager; and (3) no corrections can be made for effects introduced by higher polymerization. However, the possible error(s) associated with point (3) must be very small, since—in view of the low degree of dimerization and the low working pressures—the extent of the higher polymerization must be quite minute.

Considering the substantial error that may attach to the evaluation of the heat of dimerization of heptanoic acid, as defined above, this figure is in satisfactory agreement with the corresponding results secured with the lower paraffin acids. This evaluation of the heat of dimerization of heptanoic acid cannot, however, be reconciled with that reported by Fenton and Garner.[3] The present results, taken together with those, reported below, for butyric acid, indicate that the length and/or branching of the hydrocarbon substituent attached to the carboxyl group is without appreciable effect on the heats of dimerization of the paraffin acids. There is little indication of the strong trend, suggested by Fenton and Garner, toward lower heats of dimerization with increasing size of the hydrocarbon substituent.

Butyric Acid.—Eastman Kodak Co. "White Label" *n*-butyric acid was purified by vacuum distillation through a 40-plate column. Recent reports of the melting point of *n*-butyric acid are exceedingly various, ranging from −7.9 to −5.37°.[5] The material obtained in the present work melted sharply at −5.3 to −5.2°, and was adjudged to be of adequate purity. The results obtained are shown in Table I. When plotted as a function of $1/T$, the values of $-\log K_2'$ yielded a series of almost rectilinear and parallel isometrics. The $-\log K_2'$ values were reduced to a series of "standard" temperatures; and a set of isothermal plots, shown in Fig. 1, of $-\log K_2'$ as a function of density was prepared. As in the work previously reported from this Laboratory, the isotherms were best represented by a series of straight lines, with slopes that become progressively more negative in passing from the high temperature to the low temperature isotherms. The lines were fitted to the points by the method of least squares. The density dependence of the apparent dimerization constant strongly suggests the presence of aggregates higher than the dimer. A limiting value of $-\log K_2'$, free of the effects of higher aggregation, may be obtained by extrapolating the isotherm to zero density. The extrapolated values of $-\log K_2'$ should serve as close preliminary approximations to the corresponding figures for $-\log K_2$, where K_2 is the ideal or thermodynamic dimerization constant. However, to minimize the uncertainties arising from poor definition of the shape of the isotherms, the final evaluation of $-\log K_2$ has been based on a different treatment of the data, which is an outgrowth of the calculations relating to higher polymerization.

In considering the higher polymerization, calculations were made on two hypotheses: a trimer hypothesis, which considers the vapor as containing only monomeric, dimeric and trimeric species; and a tetramer hypothesis, which postulates a vapor containing only monomeric, dimeric and tetrameric species. If the trimer hypothesis is accepted, the association constant of the trimeric species is given by the expression

$$K_3 = \frac{1 - X_1(1 + PK_2X_1)}{P^2X_1{}^3} \qquad (2)$$

where X_1, the mole fraction of the monomeric species in the vapor, is given by the equation

$$X_1 = \frac{1}{PK_2}\left\{\left[1 + PK_2\left(3 - \frac{M}{m}\right)\right]^{1/2} - 1\right\}$$

The parallel expressions secured on the basis of the tetramer hypothesis are

$$K_4 = \frac{1 - X_1(1 + PK_2X_1)}{P^3X_1{}^4} \qquad (3)$$

and

$$X_1 = \frac{3}{4PK_2}\left\{\left[1 + \frac{8PK_2}{9}\left(4 - \frac{M}{m}\right)\right]^{1/2} - 1\right\}$$

In using these equations the extrapolated values of $-\log K_2'$—listed, in parenthesis, under the coördinated temperatures in the first column of Table II—were used in estimating the corresponding figures for $-\log K_2$. The values of $-\log K_3$ and $-\log K_4$ so obtained for all the experimental points are listed in the third and fourth columns of Table II.

TABLE II

HIGHER POLYMERIZATION OF BUTYRIC ACID

t (°C.) ($-\log K_2'$ lim $d \rightarrow 0$)	d (g./l.)	$-\log K_3$	$-\log K_4$	$-\log K^2$ (from $-\log K_3$)	$-\log K_2$ (from $-\log K_4$)
195.4	1.69	7.61	10.38	3.611	3.608
	2.00	7.68	10.60	3.616	3.621
(3.604)	2.27	7.68	10.65	3.612	3.626
	2.48	7.61	10.55	3.612	3.635
	Avg.	7.64	10.54	3.613	3.623
183.4	1.36	7.48	10.26	3.437	3.431
	2.27	7.49	10.39	3.439	3.440
(3.439)	2.48	7.45	10.39	3.435	3.441
	Avg.	7.47	10.35	3.437	3.437
172.8	1.69	7.24	10.03	3.281	3.274
	2.00	7.30	10.13	3.286	3.283
(3.289)	2.27	7.25	10.14	3.280	3.284
	2.48	7.23	10.13	3.277	3.284
	Avg.	7.25	10.12	3.281	3.281
163.1	1.36	6.96	9.63	3.136	3.128
	1.69	6.97	9.66	3.133	3.134
(3.124)	2.00	6.89	9.69	3.124	3.135
	Avg.	6.94	9.66	3.131	3.132
153.2	1.04	6.64	9.17	2.970	2.963
	1.36	6.71	9.28	2.980	2.978
(2.963)	1.69	6.65	9.31	2.964	2.981
	Avg.	6.67	9.25	2.971	2.974
142.2	1.04	6.34	8.83	2.780	2.777
(2.793)	1.36	6.33	8.88	2.780	2.787
	Avg.	6.335	8.855	2.780	2.782

The calculations involved in the assessment of the higher polymerization constitute a heavy strain of the primary experimental data, and some variations in the values of $-\log K_3$ and $-\log K_4$ at a given temperature are certainly to be expected. The observed variations in $-\log K_3$ may well spring from this source and/or the perfect gas assumption that is implicit in the formula from which K_3 is calculated. Some part of the isothermal density dependence of $-\log K_4$ may be similarly produced, but the somewhat greater dependence here displayed suggests that the basic assumption of the tetramer hypothesis may be at fault.

The averages of the calculated values of K_3 at each temperature were then resubstituted in equation (2), to permit a new calculation of the coördinated values of K_2. This led to the figures for $-\log K_2$ that are listed in the fifth column of Table II. Average values of the figures for K_4 were similarly

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(5) Donald Belcher, THIS JOURNAL, **60**, 2745 (1938).

employed in a parallel evaluation of K_2 from equation (3), and the values of $-\log K_2$ so secured are listed in the sixth column of Table II. Aside from a small experimental scatter, the new values of $-\log K_2$ should manifest no appreciable density dependence since, unlike the values for $-\log K_2'$ plotted in Fig. 1, they have already been corrected for the effects of higher polymerization. The figures for $-\log K_2$ calculated from the corresponding average values of $-\log K_3$ are, indeed, gratifyingly free of any marked density dependence. Contrariwise, the values of $-\log K_2$ calculated from the corresponding average values of $-\log K_4$ display a systematic density dependence. The variation with density is in a sense opposite to that originally observed in the figures for $-\log K_2'$, and is too large to be explained in terms of the finite volume of the molecules, corresponding to a van der Waals *b* term.

A second complete cycle of calculations was carried out, taking as a starting point the results obtained from the first cycle. That is, in place of the extrapolated $-\log K_2'_{\lim d \rightarrow 0}$ figures used in beginning the first cycle, the second cycle was begun by substituting in equations (2) and (3), respectively, the average $-\log K_2$ figures given in the fifth and sixth columns of Table II. The values for the equilibrium constants secured in the second cycle of calculations proved to be essentially the same as those found in the first cycle and, therefore, the trimer hypothesis maintained an appreciable margin of superiority.

An important by-product of this consideration of the higher polymerization process is a superior evaluation of the dimerization constant. The analytically determined values of $-\log K_2$ listed in the fifth column of Table II can be averaged directly, without any necessity for extrapolation. When plotted as a function of $1/T$, the figures so obtained were found to lie very closely on the straight line fitted to them by the method of least squares. The equation of this line is

$$-\log K_2 = 10.100 - 3040/T$$

from which the heat of dimerization of butyric acid calculated as −13.9 kcal. This figure is almost exactly the same as that recently reported[1] for the heat of dimerization of trimethylacetic acid, and it should be remarked also that these two acids boil at almost exactly the same temperature (164°). It is therefore of interest to observe that, despite these similarities, the two acids have, at any given temperature, dimerization constants that are quite appreciably different.

The plot against $1/T$ of the averaged values of $-\log K_3$ at each temperature shows some scatter but, as has already been remarked, this is only to be expected in view of the character of the calculations from which these values are derived. The equation of the least-squares line fitted to the trimerization data is

$$-\log K_3 = 18.45 - 5020/T$$

from which the heat of trimerization is calculated as −23 kcal.

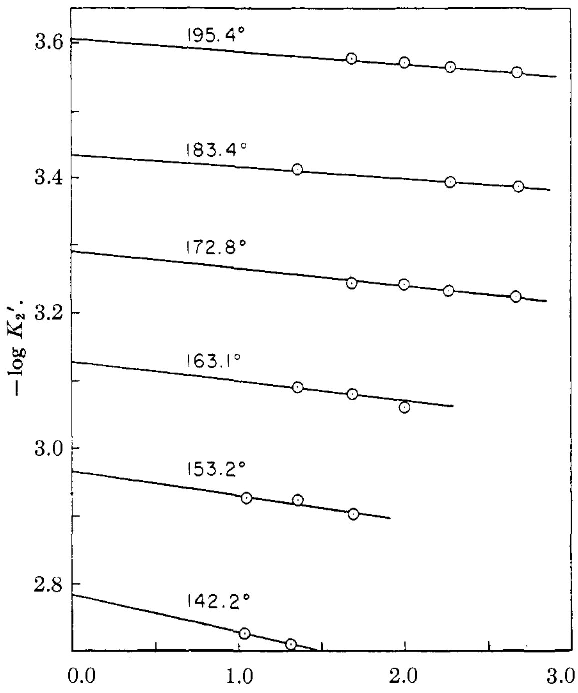

Fig. 1.—Variation of log K_2' with density for butyric acid.

The situation with regard to the existence in butyric acid vapor of aggregates higher than the dimer can now be summarized. That some such aggregates definitely do exist is indicated by the slope of the isotherms shown in Fig. 1. If it be assumed that these aggregates are predominantly trimeric, a fully satisfactory interpretation of the experimental data is possible. That is, at any given temperature there are unique values of K_2 and K_3 with which the vapor density data can be closely fitted. (In our experience, these data cannot be as well fitted with unique values of K_2 and K_4 derived on the tetramer hypothesis.) Furthermore, the trimer hypothesis yields plots of $-\log K_2$ and $-\log K_3$ against $1/T$ that are satisfactorily linear, as well as acceptable estimates of the slopes of the isotherms, of $-\log K_2'$ against density, that are plotted in Fig. 1. Thus the trimer hypothesis is found to be entirely compatible with the available data. It is not unlikely that aggregates still higher than the trimer exist, in relatively minute concentrations, in the acid vapor. However, the present analysis of the butyric acid data, taken with the previously indicated[1] steric insensitivity of the polymerization process, indicates that a special tetrameric state[2] is not favored; and that the trimer is probably the major higher aggregate. That this is a well-defined polymeric form, and not simply a collision complex, is indicated by the fact that the heat of trimerization is at least as great as $^3/_2$ the heat of dimerization (*i.e.*, it is indicated that there are three hydrogen bonds in the trimer, corresponding to the two in the dimer.)

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