XC.—*The Heats of Association of Acetic and Heptoic Acids in the Vapour State.*

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THE work of Ramsay and Young on the vapour pressures and vapour densities of acetic acid (*Sci. Proc. Roy. Dublin Soc.*, 1910, **12**, 374; J., 1886, **49**, 790) showed that this substance was associated in the vapour state, and that the degree of association decreased with increase in temperature. It is possible to calculate an approximate value for the heat of association from their data by means of the equation $d \log K_c/dT = -Q_v/RT^2$. We have now repeated this work and our results are in better concordance with one another than are those of the above authors; the values of Q_v found from the two investigations are 12,420 and 13,790 cals. per g.-mol., respectively.

The primary object of the present investigation was to determine Q_v for acids with longer chains, with a view to obtain evidence as to the nature of the linkage between the molecules of acids. The heat of vaporisation of acetic acid at 110° is less than one-half of Q_v (5,170 cals.; Young), which indicates that the forces holding the molecules together are greater than those causing condensation from the vapour to the liquid state. If the attachment is by means of the two carboxyl groups to give double molecules, then Q_v should approach a practically constant value as the homologous series of monobasic acids is ascended, and it would be expected that this constant value would be reached when the length of chain exceeded five or six carbon atoms. If, on the other hand, the association occurs by linking through the methylene groups, then the heat of association should increase with increasing length of chain.

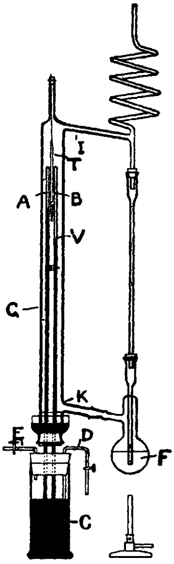
Accordingly, heptoic acid has been studied, and shown to be about 10% associated at its boiling point. A value for Q_v has been determined, *viz.*, 7,050 cals. per g.-mol., but on account of the low degree of association, this is much less accurate than that of acetic acid. Thus the heat of association decreases with increase in chain length, a result which is in accord with the view that linking occurs through the carboxyl groups, and not through the hydrocarbon chains, and that the residual affinity of the carboxyl group decreases with increasing chain length. Acids with shorter chains must, however, be investigated before this conclusion can be substantiated.

EXPERIMENTAL.

Apparatus.—The modified form of Ramsay and Young's apparatus used in the present series of experiments consists of two Pyrex-glass tubes A and B, about 90 cm. long, standing in a gas-jar C containing mercury (Fig. 1) and bound together by copper wire, a short asbestos pad being inserted to keep them vertical. C is closed by a rubber bung which carries two other tubes, D and E. D is bent twice at right angles and serves to remove the excess mercury introduced during the setting up of the apparatus. E is connected by means of a piece of glass tubing (fitted with a tap) to a water pump.

A and B were heated by the vapour from liquid boiling in the flask F, which is connected by a ground-glass joint to the cylindrical glass jacket G. The top of G has a side tube I connecting with a glass spiral open to the air and a tube leading back to the bottom of F. A spiral of nichrome wire is wound round the tube G, which is heated by an electric current. The wire is wound on strips of asbestos so placed as to leave a window in the back and front of the tube. G rests in a glass trough containing mercury, which consists of the top of a wide-mouthed bottle cut off near the top, the mouth being closed by a rubber bung through which A and B pass.

FIG. 1.



The whole apparatus from I to K is enclosed in an asbestos-lined box, to protect it from draughts, which has glass windows back and front, the front window consisting of a calibrated glass scale. A fine mark was etched near each end of A, and the volume between these two marks determined for each cm. length of tube.

The thermometers used were either standard or had been checked against standards, at or near the temperatures of the vapours used in the tube G.

Materials.—Kahlbaum's acetic acid was used, and its purity was determined by titration with *N*/10-sodium hydroxide which had been standardised against pure crystallised succinic acid. The acid was found to be 99·2% pure, and was then partly (about two-thirds) frozen, and the liquid separated. This process was repeated, and the solidified acid used for the experiment. The weights of acid used were approximately 0·1, 0·07, and 0·08 g. in three series of experiments.

Preparation of Tubes for Vapour-density Determination.—The tubes A and B were left for 24 hours full of freshly made chromic acid solution, and then repeatedly rinsed with distilled water and dried by a current of hot air. Dry mercury was poured into them to a depth of 5—6 cm. at a time, and each portion was boiled to expel any air trapped between the mercury and the walls. The two tubes (which had previously been pushed through the two bungs) were inserted in the gas-jar full of mercury and a weighed quantity of acetic acid contained in a small Victor Meyer bottle was introduced into the calibrated tube. The bung was then pushed firmly into the gas-jar C, the excess mercury being run out through the side tube D. The gas-jar was then anchored by copper wire to the sides of the tray in which the apparatus stood and a forked support attached to a heavy retort-stand was pushed under the bung closing the mercury seal. The tube E was connected to the pump and the apparatus was made gas-tight by means of melted gutta-percha at the glass–rubber connexion.

The jacket and flasks were then fitted on, and the electrical heating was adjusted so that the temperature was about 10—20° below the boiling point of the jacketing liquid. The liquid in the flask was then boiled until steady circulation of the vapour occurred. The temperature was measured by means of three standardised thermometers suspended at intervals between the two experimental tubes.

The pressure was obtained from the difference between the levels of the mercury in the two tubes. Since the temperature of the two tubes was the same, the vapour pressure of mercury and the density of the liquid mercury in the tubes were identical. The difference in level, multiplied by the density of mercury, therefore gave the pressure of the vapour of acetic acid.

To read the mercury level, a diffuse light was placed behind the apparatus so that the meniscus showed black against it. The telescope was first adjusted so that the cross-wires touched the top of the meniscus, and then readjusted until the glass scale was in focus, whereupon the scale reading was taken, decimals of a millimetre being determined by means of a vernier on the cathetometer. The volume was calculated from the height of mercury in the experimental tube and allowance was made for the volume of the

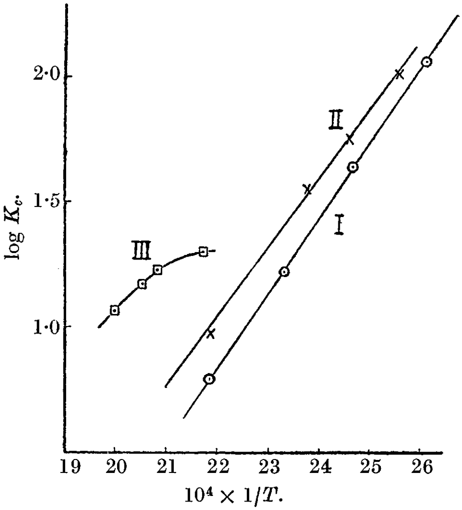
Victor Meyer bottle. The volume correction for expansion of the glass tube is negligible for the range of temperatures used.

From these measurements the ratio of the apparent to the real molecular weight was determined by the formula

$$R = \frac{w}{M} \cdot \frac{22{,}400}{v} \cdot \frac{T}{273} \cdot \frac{760}{p} \cdot \frac{13{\cdot}6}{\delta},$$

where w = weight of acid introduced, M = molecular weight of acid, v = volume (in c.c.), p = observed pressure (in mm.), T = absolute temperature of experiment, and δ = density of mercury at $T°$ Abs.

FIG. 2.



I. *Acetic acid (authors).* II. *Acetic acid (Young).*
III. *Heptoic acid.*

Assuming that the association of acetic acid is due to the reaction, $2CH_3{\cdot}CO_2H \rightleftharpoons (CH_3{\cdot}CO_2H)_2$, we have for the equilibrium constant, $K_p = p_{A_2}/p_A^2$, where p_{A_2} is the partial pressure due to double molecules and p_A that due to single molecules; therefore $K_p = (R - 1)/p(2 - R)^2$.

In Table I are collected the data for acetic acid (under the symbols defined above) together with the average value of K_c calculated from $K_c = K_p \,.\, 760 \,.\, T \,.\, 22{\cdot}4/273$.

The plot of log K_c both for our results and for Young's (J., 1886, **49**, 790) is given in Fig. 2, and it will be seen that, although both sets lie on straight lines, the two curves are not coincident.

The average values of K_c are employed in the calculation of the heat of reaction at constant volume in the usual way and give the results shown in Table II.

TABLE I.

Data for acetic acid.

No. of expts.	Series.	v.	p.	$T-273°$.	R.	$K_p \times 10^5$.	Mean K_c.
1	1	67·255	499·980	131·03°	1·380	197	44·16
1	1	67·469	499·868	130·0	1·379	197	
1	2	60·575	425·724	132	1·320	163	
1	2	69·561	374·403	132	1·307	171	
1	2	70·785	369·460	132	1·301	167	
1	2	60·774	424·661	132	1·319	162	
4	2	61·265	416·139	131·9	1·335	181	
2	2	63·642	402·825	131·9	1·328	180	
1	3	57·632	463·490	131·93	1·339	167	
1	3	58·004	460·481	131·8	1·339	168	
4	3	57·979	460·210	131·9	1·341	170	
1	1	74·292	550·836	154·9	1·209	64·2	16·86
3	2	64·224	475·852	155·73	1·185	58·5	
2	2	66·385	458·374	155·73	1·190	63·2	
2	2	68·199	448·378	155·73	1·184	61·8	
4	2	63·992	473·474	155·73	1·195	63·7	
4	3	62·438	505·594	156·05	1·206	64·8	
2	3	63·068	500·575	156·05	1·206	65·3	
3	2	68·753	517·218	183·83	1·089	20·6	6·296
5	2	69·131	512·222	183·83	1·093	21·0	
4	2	70·544	500·467	184·2	1·097	23·9	
4	2	69·012	511·432	183·8	1·097	23·2	
3	3	66·911	556·007	183·9	1·099	21·8	
2	3	66·900	553·190	183·9	1·099	22·2	
1	3	67·240	552·257	183·9	1·095	21·1	
1	1	66·741	554·844	183·9	1·098	21·8	
1	1	63·974	453·390	110·11	1·514	480	117·00
1	1	63·157	454·285	110·1	1·531	506	
1	1	63·688	453·659	110·1	1·520	496	
1	1	65·867	438·050	110·1	1·522	522	
3	2	71·227	306·000	110·5	1·444	469	
2	2	64·580	331·850	110	1·468	436	
2	2	55·373	379·600	110·8	1·499	524	

TABLE II.

K_{c_1}.	K_{c_2}.	T_1.	T_2.	Q_v.
44·16	16·86	404·68	428·70	13,800
44·16	6·296	404·68	456·91	13,690
117·00	44·16	383·24	404·68	14,000
16·86	6·296	428·70	456·91	13,580
117·00	16·86	383·24	428·70	13,900
117·00	6·296	383·24	456·91	13,790
			Mean	13,790

X-Ray evidence shows that, in the solid state, the carboxyl groups of adjacent molecules of monobasic acids are attached to one another, and it is not unlikely that the molecules of acetic acid are attached in a similar manner in the vapour state. On this view, the heat of association of acetic acid would be the heat of association of carboxyl groups, and the high value of this heat may be ascribed to an atomic rearrangement occurring between these groups on association.

Determination of the Heat of Association for Heptoic Acid.—The heptoic acid, obtained by repeated fractionation of a specimen from Kahlbaum, had been employed in a determination of heats of crystallisation, and melted at − 7·5°; its purity was found by titration to be 98·79%.

The mode of heating the tube G was modified slightly, since, for the higher temperatures, the fall of temperature along the tube was about 5° when the vapour was distilling through it. The wiring was therefore readjusted until the electrical heating by itself gave a fall of only 6°; with the circulating vapour, this gave a satisfactorily constant temperature with a fall of about 1°, and the average temperature was taken. The three jacketing vapours used were aniline, benzyl alcohol, and methyl salicylate. The weights of acid used were 0·06 and 0·03 g. approximately. Table III gives the results obtained at four temperatures. Partly owing to the difficulty of maintaining constant temperatures at 200° and above, and partly owing to the low degree of association of heptoic acid, the values of K_p are much less concordant than those obtained for acetic acid; and the corresponding values of Q_v (Table IV) do not

TABLE III.

No. of expts.	Series.	v.	p.	$T - 273°$.	R.	$K_p \times 10^6$.	Mean K_c.
3	1	47·838	292·626	230·5°	1·084	350	11·59
6	1	46·861	293·936	227	1·093	384	
1	2	39·163	203·481	225·5	1·067	379	
2	2	53·974	136·330	213·75	1·063	525	14·93
2	2	37·733	192·684	213·75	1·076	459	
2	1	43·554	292·806	206·3	1·130	587	17·06
2	1	51·840	252·525	206·3	1·098	479	
2	1	57·739	226·530	206·3	1·099	541	
2	1	43·560	292·659	206·3	1·128	576	
2	2	41·851	168·673	207·12	1·091	650	
2	2	52·255	137·391	207·8	1·074	629	
2	2	36·508	195·660	210·5	1·084	527	
2	1	53·189	227·199	186·2	1·136	804	20·17
2	1	62·637	197·001	185·2	1·101	604	
2	1	64·352	189·424	185·2	1·124	851	
2	2	34·902	192·599	187·75	1·096	612	
2	2	57·963	118·746	187·77	1·071	687	
2	2	34·964	193·021	191·00	1·100	640	

TABLE IV.

K_{c_1}.	K_{c_2}.	T_1.	T_2.	Q_v.
17·06	11·59	480·23	500·66	9,030
14·93	11·59	486·75	500·66	8,820
17·06	14·93	480·23	486·75	9,470
20·17	11·59	460·19	500·66	6,260
20·17	17·06	460·19	480·23	3,670
20·17	14·93	460·19	486·75	5,040

possess much value by themselves. Nevertheless, the results indicate that the heat of association of heptoic acid is decidedly lower than that of acetic acid. An investigation into the behaviour of acids of intermediate chain length would appear desirable.

Summary.

Acetic and heptoic acids have been shown to be associated in the vapour state and the heats of association have been calculated. For acetic acid, $Q_v = 13{,}790$ cals. per g.-mol. over the temperature range 110—184°. For heptoic acid, Q_v appears to vary with temperature; the average value between 185° and 230° is 7,050 cals. per g.-mol. Since the heat of evaporation of acetic acid is only 5,570 cals. per g.-mol., it is concluded that the double molecules are held together by forces analogous to those of chemical combination.

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[*Received, December 18th,* 1929.]