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The Vapor-Phase Association of Acetic and Trimethylacetic Acids

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Introduction

Although there is no lack of evidence that paraffin acid vapors are extensively dimerized through the formation of hydrogen bonds, there are still major uncertainties in our knowledge of the molecular state of such systems. The available data, summarized in Table I, are too few and too discordant to permit any generalizations about the dependence of the polymerization process on the acid strength and/or length and character of the hydrocarbon portion of the paraffin acids. The more difficult question about the status of polymers higher than the dimer is almost completely unresolved, but even so basic a datum as the heat of dimerization is uncertain in some cases and unknown in most.

TABLE I

DATA ON THE VAPOR-PHASE ASSOCIATION OF CARBOXYLIC ACIDS

Acid	Investigator	Ref.	Heat of association. ΔH (kcal.) Dimer	Trimer	Tetramer
Formic	Ramsperger and Porter	1	−14.1[a]		
Formic	Coolidge	2	−14.125		
Formic	Herman	7	−12.4[b]		
Formic[d]	Herman	7	−12.8[b]		
Acetic	Fenton and Garner	3	−14.5[c]		
Acetic	MacDougall	4	−16.4[e]		
Acetic	Ritter and Simons	9	−14.5		27.0
Acetic[d]	Herman and Hofstadter	5	−15.9[b]		
Propionic	MacDougall,	8	−18.5[f]	24.0[f]	
Propionic[d]	Herman and Hofstadter	6	−14.1[b]		
Butyric[d]	Herman	7	−13.8[b]		
Heptoic	Fenton and Garner	3	− 7.8[c]		

[a] At 50°. [b] Infrared spectrophotometric method. [c] Calculated from Q_v by formula $\Delta H = Q_v + \Delta nRt$, T taken as 373°K. [d] Deutero-substituted carboxyl group. [e] At 25 to 40°. [f] At 45 to 65°.

The two most recent determinations of the heat of dimerization of acetic acid[4,9] differ by 12%. Although the measurements were made in different ranges of temperature, neither investigator reports evidence for the large variation of ΔH with temperature required to explain so great a difference. For formic acid the heats of dimerization obtained from two determinations of vapor density[1,2] are in good agreement with each other, but differ by 12% from a value derived from infrared spectroscopy.[7] The discrepancy might be attributed to the varying effects of higher polymerization on the results of the two methods, a possibility rendered more plausible by electron diffraction studies,[10] but Coolidge particularly examined and abandoned the hypothesis that higher polymers exist in formic acid vapors.

Evidence for the occurrence of higher polymers in related systems has been developed in two recent papers. On the basis of vapor density determinations, MacDougall[8] reports a trimer as a third component of propionic acid vapor, and Ritter and Simons[9] suggest a tetramer as the third species in acetic acid vapor. It is difficult to understand why such closely related compounds yield higher polymers of different orders.

In the present study of carboxylic acid vapors an attempt has been made to secure an accurate evaluation of the thermodynamics of the polymerization processes; and, with such information, to clarify the status of higher polymers—the extent to which they are formed, their nature and structure. To provide the refined data required for such an investigation a new method for the precise determination of vapor densities has been devised. This can be rendered entirely free of adsorption effects, it requires no direct or indirect measurement of the total weight of material in the gas phase, and it is essentially different from the previously employed methods which, as we have seen, have not provided concordant data.

Apparatus and Procedure

The instrument designed for the vapor density determination is a magnetically compensated aerostatic balance based on an apparatus described by Stock and Ritter.[11] The adaptation of such an instrument to vapor density studies conducted over wide ranges of temperature and long periods of time required special attention to constructional details which will be described elsewhere. The over-all design of the instrument is shown in Fig. 1. The balance (and its supporting structure) is made of quartz; it pivots on tungsten needle points borne in quartz cups; and its oscillations are followed with the aid of an optical lever, reflected from mirror M to a scale outside the air thermostat in which the balance is housed. The counterpoise C is a perforated bulb somewhat smaller than the buoyancy globe B; and to the extent that the surface areas of C and B are equivalent and the two bodies are equidistant from the beam's axis of rotation, this arrangement permits perfect automatic compensation for adsorption effects.

Whatever may be the ambient vapor density, this bal-

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* Harvard University Ph.D. 1949.

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(1) H. C. Ramsperger and C. W. Porter, THIS JOURNAL, **48**, 1267 (1926).

(2) A. S. Coolidge, *ibid.*, **50**, 2166 (1928).

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

(4) F. H. MacDougall, THIS JOURNAL, **58**, 2585 (1936).

(5) R. C. Herman and R. Hofstadter, *J. Chem. Phys.*, **6**, 534 (1938).

(6) R. C. Herman and R. Hofstadter, *ibid.*, **7**, 460 (1939).

(7) R. C. Herman, *ibid.*, **8**, 252 (1940).

(8) F. H. MacDougall, THIS JOURNAL, **63**, 3420 (1941).

(9) H. L. Ritter and J. H. Simons, *ibid.*, **67**, 757 (1945).

(10) (a) J. Hengstenberg and L. Bru, *Anal. soc. espan. fis. quim.*, **30**, 341 (1932); see *C. A.*, **26**, 4217 (1932). (b) O. Bastiansen, C. Finbak and O. Hassel, *Tids. Kjemi, Bergvesen Met.*, **4**, No. 9, 81 (1944).

(11) A. Stock and G. Ritter, *Z. physik. Chem.*, **119**, 333 (1926).

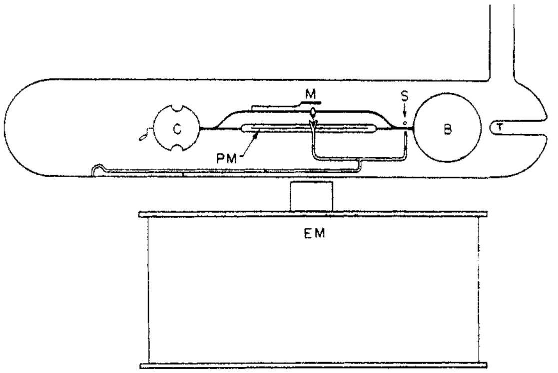

Fig. 1.—Magnetically-operated vapor density balance: B, sealed bulb; C, adsorption-compensating bulb; PM, permanent magnet; EM, electromagnet; M. mirror; S. beam stops; T, thermocouple well.

ance may be restored to symmetrical oscillation about some arbitrary fiducial position by variation of the current in an external electromagnet EM, the field of which interacts with the small permanent magnet which is sealed into the balance beam. The current required to restore the beam to its reference position depends on the extent of the initial unbalance of the moving system, which is in turn a function of the density of the vapor by which bulb B is buoyed. At any temperature this "restoring current" is a substantially linear function of the vapor density. The relationship between "restoring current" and density is easily and quantitatively established by calibration trials with a material of known vapor density. If the instrument is calibrated and used in precisely the same fashion, there is a tendency toward cancellation of indeterminate errors in what is, essentially, a vapor density *comparison* method.

The performance of the balance in calibration and use gave no evidence of thermal hysteresis effects. Disturbances due to the conjectural magnetic hysteresis of the soft (Norway) iron core of the electromagnet were suppressed by a routine procedure designed to bring the core to a reproducible condition before each density determination. The balance was sensitive to a change of density of 0.0002 g. per liter, but the dependable long range reproducibility did not much surpass 0.001 g. per liter. Thus for vapor densities equal to or greater than 1 g. per liter, the balance readings are precise to 0.1% or better. The stability of the calibration was established by check trials over a period of five months.

The balance was mounted in an air thermostat, as shown in Fig. 2. The sample, in an ampule fitted with a breakable joint, was attached close to CB. The system was thoroughly evacuated, the ampule was fractured with a magnetically operated breaker, and its contents were distilled into CB—which was held in a Dry Ice-bath. The ampule and breaker were then pulled off under vacuum, the connection to the pump was sealed at constriction CC, and the sample was thus isolated in a glass-quartz system.

A series of measurements of vapor density as a function of temperature and pressure was now obtained. For each "point" the following coördinated data were secured.

Temperature was measured to the nearest 0.1° with a calibrated chromel-alumel thermocouple, the warm junction of which was inserted in the well next to the buoyancy bulb. Readings were made with a Leeds and Northrop Type K-2 potentiometer. The balance case was heavily sheathed with aluminum foil, and the couple was placed only a few cm. from the only vapor region—that around the buoyancy bulb—which makes any contribution to the density readings.

Pressure was measured with the aid of the quartz click gage C, patterned after the glass gage of Smith and Taylor,[12] and used in conjunction with a mercury manometer

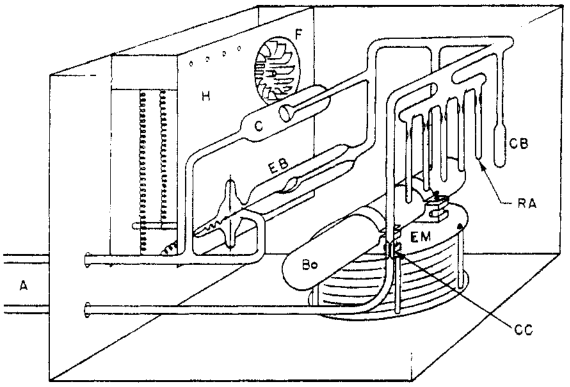

Fig. 2.—Vapor-density apparatus and thermostat: A, connections, to vacuum line; Ba, balance; C, click gage; CB, condensation bulb; CC, capillary constriction; EB, electro-bourdon gage; EM, electromagnet: F, fan; H, heater; RA, removal ampules.

read to the nearest 0.1 mm. The critical pressure differential required to produce the "click" was independent of the total pressures involved, and was reproducible to 0.1 mm. at any given temperature. A small temperature correction factor was established by calibration, and there was never any evidence of thermal hysteresis in the behavior of this gage. (The electro-Bourdon gage EB was used to follow rapid pressure changes in the system, but it displayed a large thermal hysteresis and was not used for the final measurements.)

Restoring current was controlled by rheostats and determined by measuring, with the potentiometer, the potential drop produced in a standard two-ohm resistance connected in series with the electromagnet.

In principle all the readings performed with the same "charge" in the balance case are made at essentially constant vapor density; but to avoid this unnecessary assumption, which requires that there be absolutely no adsorption effects and no temperature gradients throughout an extended system, renewed balance readings were taken at every temperature. To change the vapor density the sample was condensed in bulb CB, and a small fraction was distilled into one of the removal ampules. This ampule and CB were then immersed in Dry Ice-baths and the ampule was sealed off. A new series of determinations at lower vapor density was then secured and, with progressive removal of the "charge," a complete set of measurements was obtained. The residual sample was then condensed and the pressure in the system was checked for the presence of permanent gases. No trace of such materials has ever been detected; and it may be concluded that there is no chemical reaction between the hot acid vapors and the tungsten pivots of the balance beam.

Calibration.—The calibration of the balance with a substance of known vapor density should closely simulate the conditions of the proposed determinations; and, in particular, it should cover the entire working range of temperatures and vapor densities, so that no extrapolation of the calibration data will be required. A "standard" material with molecular weight approximating that of the heaviest vapor to be studied in practice is preferred, because complete calibration is then attainable without subjecting the balance and its auxiliary equipment to the abnormal stresses[11] of high pressures. Carbon tetrachloride (molecular weight 154) was selected as a promising "standard" and, although its equation of state is not perfectly defined, we shall see that no serious error can arise from this uncertainty.

C. P. carbon tetrachloride was repeatedly distilled *in vacuo*, and was then distributed in a number of sampling ampules. The contents of one of these was transferred to the balance system, and the determination of "restoring current" as a function of vapor density was carried out for

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(12) D. F. Smith and N. W. Taylor, This Journal, **46**, 1393 (1924).

vapor densities ranging from 0 to 3.6 g. per liter and at temperatures from 80 to 200°.

For the estimation of the vapor densities three equations of state which may be derived from the known critical constants of carbon tetrachloride have been considered. These are the relations of van der Waals, Berthelot and Joffe.[13] For the region covered in this investigation, the Joffe and Berthelot equations yield entirely concordant values for the vapor density of carbon tetrachloride; but the van der Waals equation gives appreciably different results.

If there were any reason to suppose that the true equation of state lies between the extremes defined by the van der Waals and Joffe expressions, the extent of the uncertainty with which the vapor density of carbon tetrachloride is known could be established. With this aim in mind, these equations of state have been applied to the vapors of *n*-pentane, ethyl ether and *n*-heptane, for which imperfection coefficients have been evaluated empirically.[14] In every instance, for the range of temperatures and pressures used in this work, the Joffe equation gave a slight over-correction for gaseous imperfection, while the van der Waals equation yielded undercorrected results. The Joffe value was generally the more nearly correct. This admittedly limited but fairly searching test indicates the true vapor density of carbon tetrachloride as a value intermediate between the predictions of the two theoretical equations of state. Since this range of uncertainty averages *ca.* 0.25% for our experimental conditions, it appeared that the vapor density of carbon tetrachloride could be defined closely enough for our purposes.

To avoid any premature assumptions, however, the calibration data have been worked up by both equations, to provide a "van der Waals calibration" and a "Joffe calibration"; and the calculations of the molecular state of acetic acid have been carried out in parallel, with vapor densities derived from each of these calibrations. The probable uncertainty of the mean of two such coördinate densities is somewhat less than 0.15% which is also the estimated over-all experimental error, so that the conduct of these parallel calculations serves in lieu of an error analysis.

Calibration served to define the terms F and j in the expression of the vapor density, d, as a function of the "restoring current," i

$$d = (i - i_0)/F + j$$

where i_0 is the restoring current required when the balance case is evacuated. The factor F was a smooth and easily established function of temperature, and the small additive term j expressed the slight deviations of the isotherms from linearity. Separate sets of values for F and j were derived from both of the equations of state previously mentioned.

Acetic Acid: Dimerization.—Reagent grade glacial acetic acid was treated in an all-glass system by the fractional freezing procedure of Ritter and Simons.[9] After twenty fractionations the melting curve of the residual material showed a well-defined plateau at 16.6°, the accepted melting point of pure acetic acid.[15] The recrystallization flask was then connected, through a breakable joint, with a vacuum system in which the acid was twice distilled, to free it of dissolved air, and then distributed among several sampling ampules.

Two complete series of trials were made, one preceding a carbon tetrachloride calibration, and the other immediately following it. Both sets of data were in good agreement. The vapor densities calculated from the "restoring currents" were converted to the corresponding apparent molecular weights defined by

$$M = \mathrm{d}RT/P \qquad (1)$$

TABLE II

EXPERIMENTAL DATA, M AND $-\mathrm{LOG}\ K_2'$ FOR ACETIC ACID

		Van der Waals calibn.			Joffe calibn.		
t, °C.	P, mm.	d (g./l.)	M	$-\log K_2'$	d (g./l.)	M	$-\log K_2'$
193.7	819.8	1.935	68.72	3.619	1.938	68.82	3.612
193.6	820.3	1.937	68.73	3.618	1.940	68.84	3.611
176.0	749.7	1.932	72.19	3.374	1.935	72.30	3.367
155.5	662.1	1.935	78.13	3.032	1.940	78.33	3.022
155.2	661.0	1.938	78.34	3.021	1.943	78.53	3.012
138.7	590.7	1.941	84.38	2.713	1.946	84.61	2.703
121.3	522.7	1.944	91.55	2.352	1.950	91.77	2.343
199.4	568.7	1.265	65.56	3.708	1.266	65.61	3.704
176.4	511.5	1.265	69.34	3.372	1.267	69.44	3.366
155.4	454.4	1.266	74.47	3.039	1.267	74.52	3.036
138.8	406.3	1.267	80.12	2.731	1.270	80.31	2.723
121.8	359.7	1.270	86.97	2.388	1.272	87.10	2.382
103.7	315.0	1.275	95.13	1.970	1.279	95.43	1.955
194.7	325.8	0.714	64.0	3.642	0.714	64.0	3.642
176.1	302.3	.714	66.2	3.377	.714	66.2	3.377
155.6	272.1	.714	70.2	3.049	.714	70.2	3.049
138.9	244.7	.711	74.7	2.760	.713	74.9	2.750
121.7	216.6	.713	81.1	2.417	.714	81.2	2.412
102.9	187.6	.711	88.9	2.023	.712	89.0	2.018
81.9	160.2	.714	98.7	1.499	.715	98.8	1.493
199.1	1131.0	2.690	70.05	3.674	2.695	70.18	3.666
198.2	1127.1	2.689	70.10	3.669	2.694	70.26	3.659
184.7	1052.3	2.690	73.00	3.477	2.696	73.16	3.469
170.7	969.7	2.690	76.79	3.257	2.699	77.05	3.245
154.6	874.8	2.692	82.09	2.980	2.702	82.40	2.967
139.1	786.3	2.699	88.25	2.673	2.709	88.58	2.659
125.9	719.2	2.701	93.48	2.404	2.715	93.94	2.383
193.8	750.6	1.760	68.28	3.611	1.763	68.40	3.602
176.2	687.8	1.762	71.79	3.357	1.764	71.87	3.352
155.5	606.3	1.760	77.60	3.017	1.764	77.78	3.009
139.3	543.8	1.765	83.49	2.714	1.768	83.63	2.708
139.1	543.0	1.764	83.52	2.712	1.767	83.67	2.706
121.5	479.6	1.769	90.78	2.349	1.774	91.05	2.337
199.8	592.1	1.324	65.95	3.690	1.325	66.01	3.685
176.7	533.1	1.323	69.62	3.373	1.325	69.73	3.366
155.6	471.8	1.324	75.04	3.027	1.325	75.10	3.024
139.2	422.8	1.325	80.60	2.728	1.328	80.77	2.720
122.1	374.3	1.321	87.00	2.403	1.325	87.27	2.392
103.5	326.9	1.326	95.29	1.979	1.330	95.58	1.965
155.6	287.8	0.760	70.6	3.045	0.760	70.6	3.045
139.3	259.8	.757	75.0	2.772	.758	75.0	2.768
122.1	229.9	.760	81.5	2.426	.761	81.6	2.421
103.4	199.3	.762	89.8	2.011	.763	89.9	2.007
92.1	182.5	.764	95.4	1.721	.766	95.6	1.711
82.4	169.9	.767	100.1	1.451	.768	100.2	1.446

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[13] J. Joffe, THIS JOURNAL, **69**, 540 (1947).

[14] J. A. Beattie, *Chem. Revs.*, **44**, 141 (1949).

[15] E. Griswold and F. V. Olson, THIS JOURNAL, **59**, 1894 (1937).

and these, together with their coördinated temperatures and pressures, are listed in Table II.

Assuming that the only molecular species present are the monomer and the dimer, and that these behave as ideal gases, then, for the association

$$2\text{HOAc} = (\text{HOAc})_2$$

it has been shown[9] that

$$K_2' = \frac{p_2}{p_1^2} = \frac{P_0 - P}{(2P - P_0)^2} = \frac{m(M - m)}{P(2m - M)^2} \quad (2)$$

where K_2' is the apparent association constant, p_1 and p_2 are the partial pressures of the monomer and dimer, respectively, P is the total pressure, P_0 is the pressure which would have prevailed had only the monomeric form been present, M is defined by equation (1), and m is the molecular weight of the monomer, 60.05 for acetic acid. The calculated values of $-\log K_2'$ are listed in Table II.

When the values of $-\log K_2'$ were plotted against $(1/T)$ a family of almost parallel and approximately rectilinear curves was obtained. Each of these lines was an isometric—all the values of $-\log K_2'$ determined at different temperatures, but with a given density, falling on a distinct curve. When the figures for $-\log K_2'$ were reduced to a series of "standard" temperatures by very limited algebraic (not graphical) interpolations, a more useful expression of the isothermal density dependence of K_2' could be secured by a plot of $-\log K_2'$ against density. Such graphs were prepared from data based on both the Joffe and the van der Waals calibrations, that obtained in the former instance being shown in Fig. 3. In both cases isotherms which were linear within experimental error were obtained. Similar rectilinear isotherms were also derived from our results for trimethylacetic acid; and identical behavior was also observed in the recalculation of Coolidge's formic acid data,[2] which were the product of an entirely different kind of vapor density determination. No theoretical explanation of this regularity, which does not appear to have been noted previously, is assigned at this time.

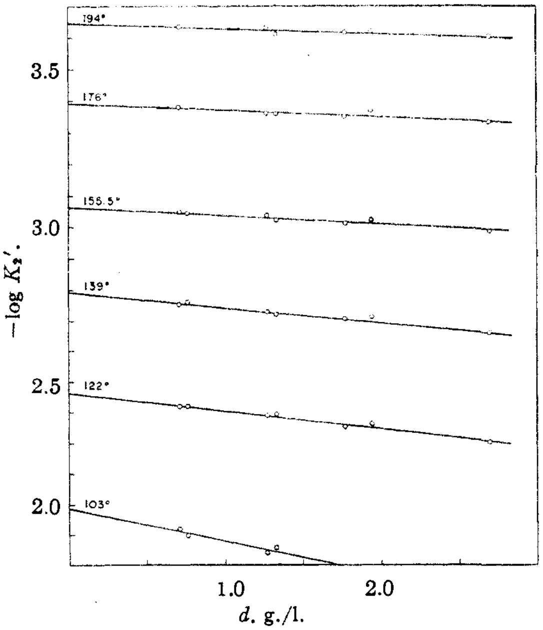

Fig. 3.—Variation of $-\log K_2'$ with density for acetic acid, using Joffe carbon tetrachloride calibration.

Extrapolation along these approximately linear isotherms, to find the limiting values of $-\log K_2'$ at zero density, is much more satisfactory than were extrapolation attempted by the usual method —along a plot of K_2' against pressure which displays a pronounced curvature. The ideal or thermodynamic association constant, K_2, may be defined as

$$K_2 = K_2'{}_{\text{lim. d.} \to 0} \quad (3)$$

and in Fig. 4 the values of $-\log K_2$ obtained by extrapolation of the isotherms of Fig. 3 are plotted against $(1/T)$. Within experimental error the points define a straight line with equation

$$-\log K_2 = 10.108 - (3018/T) \quad (4)$$

from which ΔH_2 for the dimerization is calculated as $-13{,}820$ cal., estimated as accurate to ±100 cal.

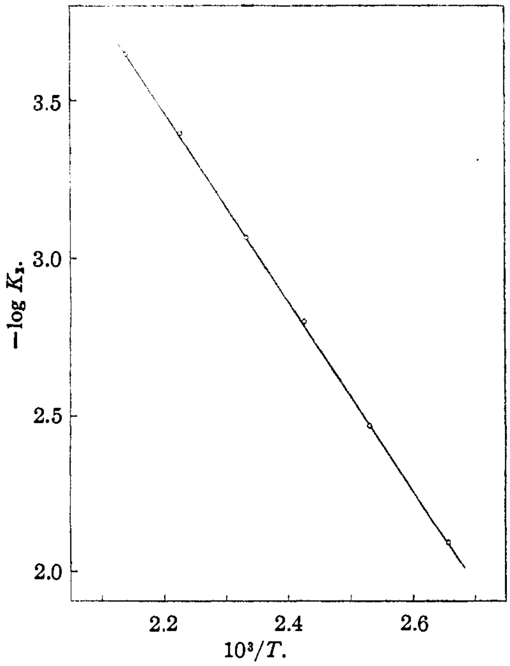

Fig. 4.—Variation of $-\log K_2$ with temperature for acetic acid, Joffe calibration.

A substantially identical equation, with experimental constants agreeing with those of equation (4) to 0.2%, was obtained from a similar treatment of the data based on the van der Waals calibration. Such concordance is only to be expected inasmuch as errors due to imperfect estimation of the equation of state of the calibration vapor should, like the discrepancies due to the non-ideality of the acid vapor(s), drop out in the extrapolation to zero density. The evaluation of K_2 and ΔH_2 is, therefore, insensitive to the uncertainties regarding the equation of state of the calibrating substance.

Higher Polymers.—The pronounced dependence of K_2' on isothermal variations in density (or pressure), as indicated in Fig. 3, has been remarked by other investigators of this system,[4,9] and signifies a breakdown of the assumptions on which the calculation of K_2' was based. The trend of the values of K_2' is of such a magnitude and direction that it may be viewed either as due to the failure to treat the monomer and dimer as non-ideal gases, or as due to neglect of the possible presence of polymers higher than the dimer. Actually it is questionable whether these should be regarded as two independent possibilities. Although a distinction is usually drawn between the deviations of a vapor from ideality and the chemical association of its molecules, the two cases are qualitatively intimately related. Under the experimental conditions prevailing in this investigation the principal imperfection term in the equation of state of a vapor (*e. g.*, *a* in the van der Waals equation) is a measure of the intermolecular attractions. According to a proposal of Fowler and Guggenheim which has been further developed by Hirschfelder, *et al.*,[16] the deviation from ideality in such cases may be construed as a measure of the extent of molecular association. Considered from this point of view the variation of K_2' with density is an unequivocal indication of the presence in acetic acid vapor of aggregates higher than the dimer.

Whether these aggregates are of the general type formed in all vapors by random inelastic collisions, or whether they should be classified, like the dimer, as distinct molecular species, must now be determined. Lacking a clear-cut qualitative distinction between these alternatives, a quantitative differentiation must be developed. The experimental data may be subjected to two independent but complementary modes of analysis, which should yield concordant results. In one, the gaseous imperfections are assayed on the assumption that there is no higher polymerization; in the second, the higher polymerization is evaluated on the assumption that there are no gaseous imperfections.

If α, the second virial coefficient of an imperfect gas, is defined by the equation: $PV = RT(1 - \alpha P)$, this coefficient is a function of temperature alone and serves as a measure of the prevailing intermolecular attractions. Assuming that a carboxylic acid vapor contains only monomeric and dimeric species, Coolidge has demonstrated[2] that

$$K_2 = \frac{m[M - m(1 + \alpha_1 P)]}{P[2m(1 + \alpha_2 P) - M]^2[1 - (\alpha_1 + \alpha_2)P]} \quad (5)$$

where α_1 and α_2 are the second virial coefficients of the monomer and dimer, respectively. In his study of formic acid vapor Coolidge estimated values for α_1 and α_2 from empirical data for suitable "model" compounds; and was then able to show that the calculated values of K_2 were substantially independent of isothermal variations in pressure. We have preferred a treatment which, though more laborious, permits a more straightforward comparison of the coefficients of the acid species with a wider variety of model compounds. In this procedure values of α_1 and α_2 are calculated directly from the empirical data for the acid vapor, and only then are they referred to the model compounds.

Equation (5) may be rewritten in the form

$$K_2 = K_2' \left\{ \frac{1 - m\alpha_1 P/y}{[1 + 2m\alpha_2 P/x]^2[1 - (\alpha_1 + \alpha_2)P]} \right\} \quad (6)$$

where $x = 2m - M$; $y = M - m$; and K_2' is defined by equation (2). The linear isotherms observed in a plot of $-\log K_2'$ against density (see Fig. 3) may each be represented by the equation

$$\log K_2' = \log K_2 + Ad$$

which is equivalent to

$$\frac{K_2'}{K_2} = e^{2.3Ad} = e^{2.3APM/RT} = e^{BPM} \quad (7)$$

where $B = 2.3\ A/RT$. From equations (6) and (7) we find

$$\frac{[1 + 2m\alpha_2 P/x]^2[1 - (\alpha_1 + \alpha_2)P]}{1 - m\alpha_1 P/y} = e^{BPM} \quad (8)$$

Since the second virial coefficient is a function of temperature but independent of pressure we may also write

$$\alpha_2/\alpha_1 = q \quad (9)$$

at any given temperature. If, now, various arbitrary but plausible values of q (*e. g.*, 1.5, 2.0, 2.5, etc.) are assumed, equations (8) and (9) constitute two independent equations from which solutions for the two unknowns, α_1 and α_2, can be made by a method of successive approximations. The calculations have been carried out with several values of q, with data based on both the Joffe and van der Waals calibrations, and for the highest and lowest densities measured at each temperature.[17] The values of α_1 and α_2 so computed were compared with the specific imperfections of a variety of model compounds, including methyl ethyl ether and butyl acetate (the models selected by Ritter and Simons for the acetic acid monomer and dimer, respectively) as well as ethyl ether, *n*-pentane, *n*-heptane, etc.

In every instance the α_1 and α_2 values of acetic acid displayed an extraordinarily great temperature dependence. At the higher temperatures α_1 and α_2 were of the same order of magnitude as

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[16] J. O. Hirschfelder, F. T. McClure and I. F. Weeks, *J. Chem. Phys.*, **10**, 201 (1942).

[17] E. W. Johnson, Ph.D. Thesis, Harvard University, 1949.

the corresponding coefficients of the model compounds; but where between 200 and 100° the coefficients of the model compounds increased by factor of *ca.* 2, α_1 and α_2 increased by a factor of *ca.* 10. This accentuated temperature dependence and the abnormally large values of α_1 and α_2 at low temperatures constitute a strong indication that the higher aggregates, whose presence in acetic acid vapor was suggested by the pronounced density dependence of K_2', are not of the general type formed in "normal" non-ideal vapors; but, rather that they are relatively stable higher polymers.

The second method of analyzing the data substantiates this conclusion by providing, through an evaluation of their heats of formation, a quantitative measure of the stability of the higher polymers. On the basis of the formulation presented by Ritter and Simons, and assuming that all the species in the acid vapor behave ideally, we may represent x_1, the mole fraction of the monomeric species, as

$$x_1 = \frac{1}{PK_2}\left\{\left[1 + PK_2\left(3 - \frac{M}{m}\right)\right]^{1/2} - 1\right\} \qquad (10)$$

If it is further assumed that polymers higher than the trimer are absent, K_3, the association constant of the trimer, may be expressed as

$$K_3 = [1 - x_1(1 + x_1PK_2)]/P^2x_1^3 \qquad (11)$$

Table III

Variation of Log K_3 and Log K_4 for Acetic Acid with Density (Joffe Calibration)

d, g./l. → t, °C.	0.71	0.76	1.27	1.94	2.70
		$-\log K_3$			
194	7.98				7.92
176	7.43				7.56
155.5	7.07			7.02	7.02
139			6.47		6.50
122	6.02				6.02
103	5.50		5.33		
82	4.70	4.51			
		$-\log K_4$			
194	10.47				10.84
176	10.08				10.61
155.5	9.55			10.00	10.00
139			9.24		9.39
122	8.40				8.30
103	7.79	7.66	7.71		
82	6.75	6.60			

The calculations of K_3, which are excessively tedious, were carried out for a selection of points considered as representative of the data, and the values so secured are listed in Table III. Near one temperature (155.5°), however, K_3 was calculated for all the available data, to provide some estimate of the density dependence of this function. In general the density dependence is unpronounced and is no greater than is to be expected from the inaccuracies of the primary experimental data. The somewhat larger dependence at the lowest temperatures may, however, reflect the presence of traces of aggregates still higher than the trimer. A plot of $-\log K_3$ as a function of $(1/T)$ is shown in Fig. 5. The best straight line that can be drawn through the points is represented by the equation

$$-\log K_3 = 18.59 (4960/T) \qquad (12)$$

from which ΔH_3, for trimerization, is calculated as −22,700 cal.

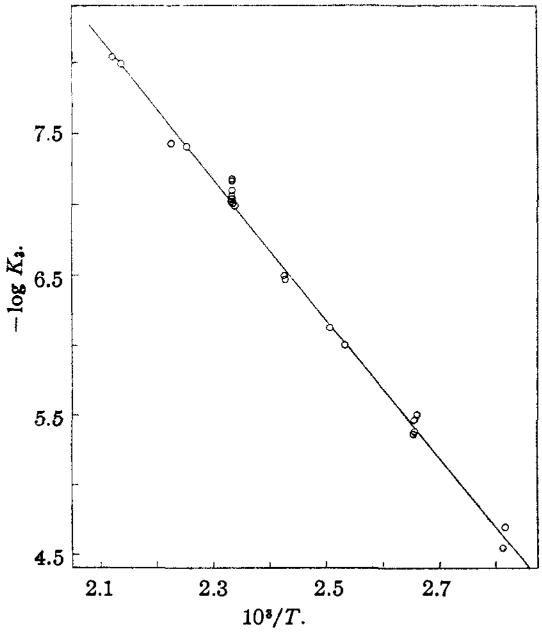

Fig. 5.—Variation of log K_3 with $1/T$ for acetic acid, using Ritter and Simons formula and Joffe calibration.

A parallel calculation has also been carried out with the more general expression of MacDougall.[8] In principle this is somewhat less exact since it is an infinite series expression of which only the first few terms are evaluated. However, the calculations are relatively simple, and provide a convenient opportunity to estimate the uncertainties introduced into the trimer determination(s) by the indefiniteness of the equation of state of carbon tetrachloride.

There appears to have been an algebraic slip in the derivation of the formula given by MacDougall,[18] and his equation (7), carried out to one more term, should read

$$K_2' = K_2 + 2K_3P + 3K_4P^2 + 2(K_3^2 - K_2K_4)P^3 + \ldots \qquad (13)$$

Since both K_2 and K_2' have been calculated from the Joffe and van der Waals calibration data, this equation is readily solved for K_3 if it is assumed, as above, that polymers higher than the trimer are absent or present only in negligible concentration (*i. e.*, that K_4 may be set equal to zero). From the Joffe data are obtained values

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[18] Confirmed by private communication from F. H. MacDougall.

for $-\log K_3$ which, when plotted against $(1/T)$, fall closely on the line represented by the equation

$$-\log K_3 = 18.58 - (4930/T) \quad (14)$$

from which ΔH_3 is calculated as $-22{,}600$ cal. The van der Waals data yield an analogous plot represented by

$$-\log K_3 = 18.95 - (5030/T) \quad (15)$$

from which ΔH_3 is calculated as $-23{,}000$ cal.

The agreement of equations (14) and (12) is quite satisfactory; the discrepancy between equations (14) and (15) indicates the extent of the uncertainties introduced into these expressions by choice of one or the other equation of state for carbon tetrachloride. It is plain that no significant inaccuracy in ΔH_3 springs from this source (*i. e.*, the two lines are substantially parallel); but since one line is displaced from the other, there is some uncertainty in the evaluation of the standard entropy change associated with trimerization. Our estimation of the most probable equation of state of carbon tetrachloride, together with equations (12), (14) and (15), suggest the following "most probable" expression for the trimerization constant, K_3

$$-\log K_3 = 18.63 - (4960/T) \quad (16)$$

from which ΔH_3 is calculated as $-22{,}700$ cal.

Uncertainties arising from our ignorance of the true equation of state of carbon tetrachloride are thus localized and delimited, and it is noteworthy that they are not of major magnitude. Indeed, it is probable that the assumption of ideal gas behavior involved in the formulation and application of equations (10) and (13) introduces rather greater errors. Thus, for example, although the value of ΔH_3 is essentially independent of the choice of equation of state for the calibration substance, the intensification of the non-ideal behavior of the acid vapor(s) at lower temperatures produces a net tendency to increase the slope of the plot of $-\log K_3$ against $(1/T)$. Consequently, the figure for ΔH_3 which has been derived must be regarded as a maximum value.

Although the experimental data have been shown to be entirely consistent with the hypothesis that the acid vapor contains monomeric, dimeric and trimeric species, we have also considered the possibility suggested by Ritter and Simons—that the vapor consists of monomeric, dimeric and tetrameric species. Values of the tetramerization constant, K_4, may be calculated from an expression similar to equation (11), which is derived on the assumption that K_3 is zero. The figures obtained for $-\log K_4$ are listed in Table III. These indicate that K_4 has a substantial density dependence, particularly at the four highest temperatures. The direction of this dependence is just the reverse of that which could be explained in terms of the breakdown of the ideal gas assumption implicit in equation (10). A trend of the latter type may be seen in the values of $-\log K_3$, but it is conspicuously reversed in the case of $-\log K_4$. Moreover, a plot of the values of $-\log K_4$ against $(1/T)$ exhibited a curvature not apparent in the similar plot of $-\log K_3$. It was concluded, therefore, that the experimental data are not consistent with the idea that the acid vapor consists of monomeric, dimeric and tetrameric species. They are, on the contrary, entirely in harmony with the hypothesis that the vapor is almost exclusively composed of monomeric, dimeric and trimeric species. This general consistency, taken with the high heat of formation of the trimer, provides full confirmation of the provisional statement, based on the accentuated temperature dependence of the acid's apparent virial coefficients, that one or more definite polymers higher than the dimer exist in the acid vapor.

Although the possible occurrence of some tetramer cannot be excluded, the density dependence of K_3, even at low temperatures, is too small to signify more than a trace of such a species. A better estimation of this "trace" might be secured by extrapolation of isothermal plots of log K_3 against density (as in the case of log K_2'); but the accuracy of any data presently available is an order of magnitude removed from that which would be required to sustain such a treatment.

Trimethylacetic Acid.—Data for trimethylacetic acid were secured and treated by the same methods used with acetic acid, and only a brief description of the work with this compound is necessary. Since the selection of an equation of state for carbon tetrachloride had no notable effect on the main results obtained with acetic acid; and inasmuch as the trimethylacetic acid data were secured at generally higher temperatures, where the imperfection of the calibrating gas introduces even smaller uncertainties, only the Joffe calibration was used in the work with trimethylacetic acid.

Eastman Kodak Co. "White Label" trimethylacetic acid was subjected to thirty fractional freezings and two vacuum distillations before its introduction into the system. Two complete series of measurements were secured. The data are given in Table IV together with values of M calculated from equation (1) and values of $-\log K_2'$ calculated from equation (2) with m as 102.13, the molecular weight of trimethylacetic acid.

A plot of $-\log K_2'$ against $(1/T)$ again yielded a series of almost linear isometrics. Values of $-\log K_2'$ reduced to a series of "standard" temperatures were then plotted against density, and linear isotherms were again obtained. Extrapolation to zero density provided values of $-\log K_2$ which were, in turn, plotted against $(1/T)$, as shown in Fig. 6. The equation of the line so defined was

$$-\log K_2 = 9.978 - (3063/T) \quad (17)$$

which yields a value for ΔH_2 of $-14{,}030$ cal., estimated as accurate to ±200 cal.

TABLE IV

EXPERIMENTAL DATA, M, AND $-\log K_2'$ FOR TRIMETHYLACETIC ACID

t, °C.	P, mm.	d, g./l.	M	$-\log K_2'$
201.8	482.0	1.857	114.12	3.505
186.5	447.8	1.859	119.01	3.276
170.9	410.7	1.863	125.64	3.024
159.0	380.9	1.863	131.82	2.819
154.7	370.0	1.861	134.2	2.743
201.8	344.4	1.296	111.5	3.492
186.5	322.5	1.296	115.2	3.283
170.7	297.0	1.296	120.8	3.036
155.2	270.3	1.296	128.1	2.772
141.2	245.1	1.294	136.4	2.508
190.2	171.8	0.6465	108.8	3.359
172.6	159.7	.648	112.7	3.092
155.3	145.4	.646	118.7	2.798
139.6	131.9	.642	125.4	2.537
132.3	125.1	.643	130.0	2.383
121.4	115.4	.645	137.5	2.152
115.3	98.1	.5655	139.7	2.027
200.9	777.6	3.176	120.8	3.452
185.6	717.1	3.180	126.9	3.228
169.9	639.4	3.116	134.7	2.967
201.7	654.9	2.611	118.1	3.473
186.3	605.9	2.613	123.6	3.253
170.3	550.7	2.615	131.3	2.992
201.8	435.5	1.666	113.3	3.498
186.6	406.2	1.669	117.8	3.277
170.5	371.8	1.668	124.1	3.026
155.1	337.1	1.667	132.1	2.758
171.2	227.0	0.957	116.8	3.063
155.5	207.6	.958	123.4	2.795
139.6	186.4	.957	132.2	2.497
133.0	177.5	.957	136.6	2.362

A pronounced variation of K_2' with density again indicated the presence in the acid vapor of aggregates higher than the dimer. The data were subjected to the same mathematical analysis previously applied to the results for acetic acid; and it was concluded that, again, the aggregates were not of the familiar type formed in all "normal" non-ideal vapors. Calculations of K_3 and K_4 were undertaken, and the values of $-\log K_3$ so obtained were plotted against $(1/T)$, as in Fig. 7. Some experimental scattering is apparent, but the points suffice to define a line with equation

$$-\log K_3 = 18.29 - (5070/T) \qquad (18)$$

from which ΔH_3 is calculated as −23,200 cal. The computed values of K_4 were badly scattered, and again manifested an accentuated density dependence.

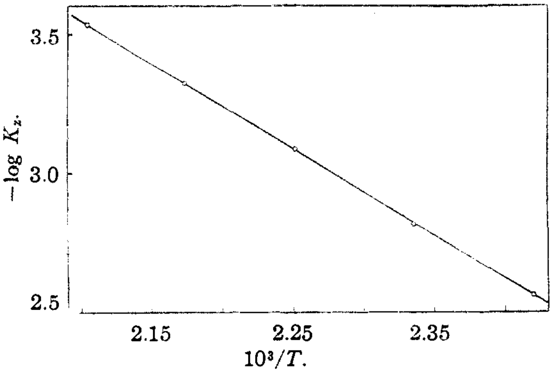

Fig. 6.—Variation of $-\log K_2$ with reciprocal temperature for trimethylacetic acid.

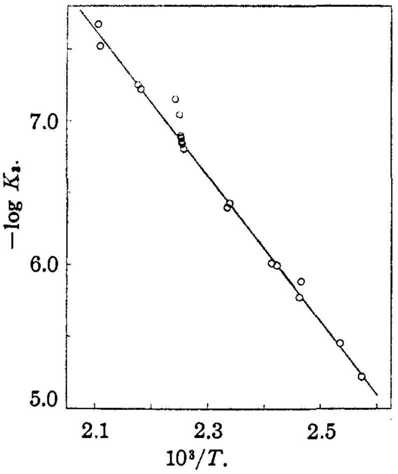

Fig. 7.—Variation of $\log K_3$ with $1/T$ for trimethylacetic acid.

On the basis of these results it was concluded that here, as in the case of acetic acid, there is definitely higher polymerization, and the predominant species so formed is the trimer.

Discussion

The chief numerical results secured in this research are summarized in Table V; and a comparison of these findings with those listed in Table I suggests the following considerations.

TABLE V

CHARACTERISTICS OF VAPOR-PHASE ASSOCIATION

	Acetic acid	Trimethylacetic acid
$-\log K_2(T)(\text{mm. Hg})^{-1}$	$10.108-3018/T$	$9.978-3063/T$
$-\Delta H_2$ (cal. mole^{-1})	13,820	14,030
$-\log K_3(T)(\text{mm. Hg})^{-2}$	$18.63-4960/T$	$18.29-5070/T$
$-\Delta H_3$ (cal. mole^{-1})	22,700	23,200

Dimerization Equilibrium.—The heat of dimerization of acetic acid deduced from this investigation is lower than any previously reported value, though it does not differ from that of Ritter and Simons by so large a margin as the latter differs from MacDougall's figure. Since our experimental conditions coincided quite closely with those of Ritter and Simons, their data have been re-examined. The experimental scatter of these data, particularly those for high temperatures and low pressures, is not inconspicuous. The values of $\log K_2$ which were calculated from these experimental results also show a not inappreciable scattering when plotted against $(1/T)$, and the best straight line that can be drawn through these "points" is not defined with high precision. Actually the higher value of ΔH_2 reported by Ritter and Simons was not derived from these data alone, but from a composite of their results with those of MacDougall—who, working at lower temperatures and, apparently, without any corrections for adsorption effects—had calculated a value of ΔH_2 which is some 2000 cal. higher than that reported by Ritter and Simons. There is, in fact, no incompatibility between the value of ΔH_2 presently reported and the slope of a line which is fairly representative of a plot of Ritter and Simons own values of log K_2, graphed as a function of $(1/T)$.

The heat of dimerization reported by Fenton and Garner[8] for heptoic acid suggests some major change in bond character from that prevailing in the lower paraffin acids. However, the variation of the heat of dimerization with increasing size of the hydrocarbon substituent of the lower paraffin acids is relatively inconspicuous and, if anything, a trend in the opposite direction is indicated. The value for the highly branched pentanoic acid—trimethylacetic acid—appears to be slightly greater than that for acetic acid. This is in line with MacDougall's report of a higher heat of dimerization for propionic than for acetic acid; but it is the reverse of the trend, observed by infrared spectrophotometry, in the deutero-substituted paraffin acids.

Higher Polymers.—Our experimental data are entirely consistent with the hypothesis that the vapors of acetic and trimethylacetic acids contain monomeric, dimeric and trimeric species, the latter in small but appreciable concentrations. Some tetramer may be present, but not in any readily perceptible proportion. This is in accord with MacDougall's opinion on the vapor state of propionic acid; but it reflects a behavior different from that assigned by Coolidge to formic acid, and by Ritter and Simons to acetic acid. Since, to the extent that association occurs through the carboxyl group, there should be certain common elements in the behavior of the paraffin acids, these apparent contradictions suggest a closer examination of the conflicting statements.

Coolidge secured a satisfactory correlation of his experimental data for formic acid on the assumption that no polymeric forms higher than the dimer were present, but that the monomeric and dimeric species behaved as non-ideal gases with imperfection coefficients approximating those of "normal" non-associating vapors. However, it has already been suggested that for systems such as these a correction for gaseous imperfection is the qualitative equivalent of a correction for the formation of higher aggregates in the vapor. Consequently, it should be possible to substantiate Coolidge's conclusions by subjecting his data to our second mode of analysis. This considers the vapor species as behaving ideally, but recognizes the possible existence in the vapor of aggregates higher than the dimer, and it provides some estimate of the stability of such aggregates. Recalculating Coolidge's data for the temperature range 60 to 156°, values of log K_2 were secured by extrapolation along the linear isotherms of a plot of log K_2' against density. A graph of log K_2 against $(1/T)$ defined a straight line whose equation agreed with that reported by Coolidge. Values of K_3 were then determined with the aid of equation (11), and a plot of $-\log K_3$ against $(1/T)$ was constructed. The points fell quite closely on a rectilinear curve with equation

$$-\log K_3 = 15.72 - (3520/T)$$

from which ΔH_3 is calculated as $-16{,}150$ cal.

The straightness of this line indicates that Coolidge's results are compatible with the idea that formic acid vapor contains an aggregate higher than the dimer; but the small value of ΔH_3 suggests that this aggregate is not, like the formic acid dimer, a substantially stable species. Thus, although the value of ΔH_3 should be viewed as a maximum figure (*vide supra*), a comparison of this amount with the heat of dimerization (14,100 cal.) shows that at most 2000 cal. are evolved in the formation of a trimer from a dimer and a monomer. Thus the conjectural formation of a trimer must be a radically different process from dimerization and, it is doubtful that a formic acid trimer exists as anything but a transient collision complex. This is in essential agreement with Coolidge's conclusion.

If, from the present work on acetic and trimethylacetic acids, a comparison is made between the values of ΔH_2 and those for ΔH_3, the heat of trimerization is seen to be at least as great as, and possibly even greater than, 3/2 the heat of dimerization. Thus, in these cases, the bonding in the trimer appears to be of the same order of strength and character as that in the dimer, and in this respect the trimer has every claim to consideration as a distinct molecular species.

Ritter and Simons rejected the trimeric form not only because it did not seem to be an entirely adequate explanation for one part of their experimental data (*i. e.*, the 120° isotherm); but also because of their belief that a layer-structured tetramer, shown in Fig. 8, would be a peculiarly stable resonant aggregate, which could be formed without the rupture of any exothermic bonds.

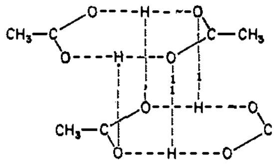

Fig. 8.—Tetramer of acetic acid, as postulated by Ritter and Simons.

Believing that the steric requirements for such a configuration could be met only under conditions of severe strain, we have submitted the proposed structure to an indirect empirical test.

In trimethylacetic acid the methyl group of acetic acid is replaced by the much more bulky *t*-butyl group; and the formation of the postulated tetramer would be considerably more difficult, if not impossible, in this instance. If it may be assumed that the higher polymerization of the paraffin acids follows the same general course, and if we accept Ritter and Simons' suggestion that the lamellar tetramer is the predominant higher polymeric species, then trimethylacetic acid ought to display a sharply reduced tendency toward higher polymerization, as compared with acetic acid. Actually, in a comparison using the same experimental and mathematical procedures, higher polymerization was found to be of the same order of magnitude in both instances and, if anything, trimethylacetic acid formed higher polymers more readily than acetic acid, under comparable conditions. This observation inclines us to view with considerable scepticism the postulated tetramer and, with it, one of the main arguments advanced for a tetrameric as against a trimeric species.

The structure of the trimer cannot now be decided with any degree of certainty. The heats of polymerization per mole of monomer indicate that there are three hydrogen bonds in the trimer, each of which is at least as strong as a dimer bond. Furthermore, the higher polymer structure whatsoever does not appear to suffer in stability from the presence of large hydrocarbon substituents to the paraffin acids: on the basis of the results for acetic and trimethylacetic acids, the *t*-butyl group may even enhance the higher association. This is in harmony with the observation that in formic acid, which is structurally unique in that there is no hydrocarbon substituent to the carboxyl group, a stable higher polymeric species does not appear to exist.

A trimer structure meeting these requirements might be a non-planar 12-membered ring with three hydrogen bonds. Realistic molecular models of these polymeric configurations are difficult to construct because of their effective requirement for divalent hydrogen, trivalent oxygen and very short O–H distances. To the extent that we have been able to realize these conditions in our models, we find that the trimer is as easily constructed as, and under no more strain than, the dimer.

Summary

A new method for the precise determination of the vapor densities has been applied in a study of the vapors of acetic and trimethylacetic acids. An accurate evaluation of the thermodynamics of the polymerization processes in these vapors has been secured. There is strong evidence for the formation of stable polymeric forms higher than the dimer—most notably, a trimeric species.

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[CONTRIBUTION FROM THE DIVISION OF FUEL TECHNOLOGY, THE PENNSYLVANIA STATE COLLEGE]

Pyrolysis of Humic Acids Prepared from Oxidized Bituminous Coal

BY MOFIZUD-DIN AHMED[1] AND CORLISS R. KINNEY*

Pyrolysis of the humic acid-like substances obtained from bituminous coal by oxidation has been studied particularly in connection with the constitution of these acids and indirectly the constitution of the coal from which they were made. Preliminary tests were made to isolate, if possible, any volatile aromatic fragments which might be expected if the humic acids have an aromatic structure[2] and an average molecular weight of about 250.[3] However, no aromatic substances or tar were obtained and consequently no provision was necessary for analyzing for such products. The volatile substances identified were water, carbon dioxide and monoxide, ammonia, hydrogen, methane, nitrogen and oxides of nitrogen. No diminution in the gas volume was observed with fuming sulfuric acid, indicating an absence of unsaturated hydrocarbons as well as aromatics. Likewise, no hydrogen sulfide, sulfur dioxide, nitric oxide or oxygen was detected.

Experimental

The humic acids used were a part of a sample prepared previously for other studies,[4,5] and were stored under nitrogen. Analyses of the coal, the humic acids and the pyrolytic residue at 950° are given in Table I.

TABLE I

ANALYSES, MOISTURE-FREE BASIS

	Raw coal, %	Humic acids, %	Residue at 950°, %
Ash	7.7	1.5	3.3
C	79.5	62.4	90.4
H	5.0	2.8	0.7
N	1.4	4.5	2.2
S	1.8	0.5	0.3
O	4.6	29.3	3.1

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* Harvard University Ph.D. 1925.

(1) Present address: University of Dacca, Dacca, E. Pakistan.

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(3) Smith and Howard, THIS JOURNAL, **57**, 512 (1935); Belcher, *J. Soc. Chem. Ind.*, **67**, 213 (1948).

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