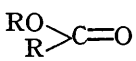
6. *The Physical Properties of the Aliphatic Acid Anhydrides.*

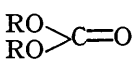
By David T. Lewis.

The surface tensions, densities, and viscosities of the aliphatic acid anhydrides have been determined in the range 15—50°. The parachor values reveal that the anhydrides exhibit a typical ester anomaly, the other parts of the molecules making a normal volume contribution. Certain parachor–viscosity relationships are discussed in the light of the present data.

The method of Rosenbaum and Walton (*J. Amer. Chem. Soc.*, 1930, **52**, 3366) is found to be unsuitable for determining the higher anhydrides, although it gives excellent results with acetic anhydride.

The parachor values of the alkyl carbonates have been determined by Bowden and Butler (J., 1939, 77), who concluded that the most suitable value for the three oxygen atoms and the double bond in these compounds is 80, the constitutive effect being thus equivalent to that observed for the esters of monobasic acids (I), the carbonates having the non-polar


(I.)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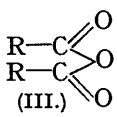

(III.)

formulation (II). The acid anhydrides (III) contain three oxygen atoms, including the ester group and an additional double bond, and the present work endeavours to establish to what extent these factors affect the anomalies existing in structures (I) and (II). Jones (J., 1928, 1193) measured the parachors of the corresponding acids, but no general study of the anhydride series has been made, though Ramsay and Shields (J., 1893, **63**, 1089), from determinations of the surface tensions of acetic anhydride by the capillary-rise method, concluded that it was a normal, unassociated liquid.

One of the major difficulties encountered in work with these substances is that of obtaining them pure, and the diverse values recorded for the density of acetic anhydride have been listed by Orton and Jones (J., 1912, **101**, 1722) and illustrate the purification

difficulties encountered by previous workers with even the simplest of these substances. The chief impurity in the anhydrides is undoubtedly the parent acid, and most methods of purification involve the careful fractional distillation of the liquids (see, *e.g.*, Kilpatrick, *J. Amer. Chem. Soc.*, 1928, **50**, 2895; Soper and Williams, J., 1931, 2297). Walton and Withrow (*J. Amer. Chem. Soc.*, 1923, **45**, 2690) purified acetic anhydride by keeping it over sodium for some days and then fractionating it over sodium and fused sodium acetate. It was found that although the anhydrides did not react with the metal at room temperature, yet they did so at higher temperatures and so this method was abandoned. (The previous authors rejected a considerable portion of the distillate owing to its curious colour.) Ultimately the method now to be recorded was adopted as being least likely to contaminate the anhydrides with traces of products produced by the slight interaction of the liquid with the purifying agent employed.

EXPERIMENTAL.

(1) *Purification of Materials.*—The anhydrides were initially fractionated through a glass-bead column until they gave a fairly constant b. p. and were relatively free from the lower-boiling acids. They were then fractionated twice over the fused sodium salt of the fatty acid and twice through a similar column under reduced pressure. The higher anhydrides slowly decompose on distillation at normal pressure, becoming light brown. Hexoic anhydride gave great difficulty and was subjected to distillation under reduced pressure until the distillate from two successive experiments gave a constant density. A slight parachor anomaly (about 1%) which seemed to increase from acetic to hexoic anhydride was traced to insufficient fractionation, but continued distillation gave fractions of a slowly increasing density which ultimately became constant within the limits of experimental error. All the anhydrides thus obtained were crystal-clear liquids.

The acetic anhydride was of "AnalaR" grade. The b. p.'s (corr.) were as follows: Acetic, 139·4—139·5°/770 mm.; propionic, 168·1—168·4°/771·9 mm., 66—67°/16 mm.; butyric, 198·1—198·7°/770·5 mm., 85—86°/18 mm.; hexoic, 246—248°/766 mm., 143—144°/18 mm.

The anhydrides distil quietly under normal pressure but tend to bump violently when the pressure is reduced, so small pieces of dry porous pot were added to facilitate ebullition. They are very resistant to the action of water, but every precaution was taken in the subsequent physical measurements to prevent access of moisture to the liquids.

Analysis of the Anhydrides.—Acetic anhydride, as determined by the method of Rosenbaum and Walton (*J. Amer. Chem. Soc.*, 1930, **52**, 3366), was 99·9% pure. The anhydrous oxalic acid was prepared by means of the automatic separator apparatus of Hultman, Davis, and Clarke (*ibid.*, 1921, **43**, 366), and the "AnalaR" pyridine catalyst was dried over potassium hydroxide and redistilled. This method had not been applied to the higher anhydrides and was tested during the present work. It was found that, although reaction occurred according to the scheme $(CO_2H)_2 + (R{\cdot}CO)_2O = CO + CO_2 + 2R{\cdot}CO_2H$, yet the organic acids produced were oxidised by hot permanganate and prevented satisfactory determination of the excess of oxalate. The higher anhydrides were therefore estimated by refluxing about 1 g. with excess of standard sodium hydroxide and titrating with standard acid. The best samples obtained showed the following purities: propionic, 99·98%; butyric, 99·54%; hexoic, 98·81%, and were used in this investigation. Despite the low figure for hexoic anhydride, the analysis is regarded as satisfactory owing to the extreme resistance of this substance to hydrolysis. The above figure was obtained after 4 days' refluxing and some loss is suspected. The indicator was added after refluxing, for if placed in the flask before this operation it became rather insensitive.

Surface-tension Measurements.—The apparatus employed was of the Sugden type (J., 1924, **125**, 27) having a ground glass neck 2 in. deep which was lubricated with a little of the anhydride. The manometer contained purified alcohol tinted with a trace of methylene-blue, and its temperature was thermostatically controlled to prevent error due to fluctuating room temperature. The radius of the larger tube was 0·1385 cm., and the apparatus was calibrated with pure benzene: $\gamma_{20°} = 28{\cdot}88$ dynes/cm. The Sugden constant A for the instrument had the value 0·003963.

The densities of the pure liquids were determined by using an 8 c.c. pyknometer in an electrically controlled thermostat, and the values corrected for buoyancy are given below, together with the observed surface tensions, γ (in dynes/cm.), and the parachor values, P. The values given in Beilstein's Handbuch (Band 2, p. 167) for the densities of acetic anhydride are much lower than those here determined, *e.g.*, $D_{4°}^{15°}$ 1·0797 as compared with $D_{4°}^{15°}$ 1·0870, though the latter value is in good agreement with that of Orton and Jones (*loc. cit.*), $D_{4°}^{15°}$ 1·0876, and careful fractionation failed to give a higher value. Another sample of the anhydride which was

some months old gave $D_{4°}^{20°}$ 1·08097 after purification, in good agreement with the value given below.

Temp.	$D_{4°}^{t°}$.	γ.	P.
Acetic anhydride, $C_4H_6O_3$.			
15°	1·0870	33·14	225·4
20	1·0810	32·56	225·6
25	1·0749	31·90	225·5
30	1·0690	31·24	225·7
35	1·0629	30·76	225·9
40	1·0567	30·05	226·1
45	1·0505	29·57	226·5
50	1·0443	29·00	226·6
Theoretical P = 225·0		Mean = 225·9	

Temp.	$D_{4°}^{t°}$.	γ.	P.
Propionic anhydride, $C_6H_{10}O_3$.			
15°	1·0163	30·86	301·6
20	1·0110	30·30	301·8
25	1·0057	29·70	301·8
30	1·0003	29·19	302·2
35	0·99503	28·59	302·2
40	0·98974	28·13	302·6
45	0·98442	27·52	302·6
50	0·97913	27·07	302·8
Theoretical P = 303·0		Mean = 302·2	

Butyric anhydride, $C_8H_{14}O_3$.			
20	0·96677	28·93	379·2
25	0·96199	28·44	379·4
30	0·95714	27·90	379·6
35	0·95240	27·36	379·6
40	0·94758	26·79	379·6
45	0·94256	26·40	380·2
50	0·93745	25·89	380·3
Theoretical P = 381·0		Mean = 379·7	

Hexoic anhydride, $C_{12}H_{22}O_3$.			
20	0·92016	28·26	536·8
25	0·91605	27·90	537·3
30	0·91189	27·35	537·1
35	0·90778	26·94	537·5
40	0·90347	26·54	537·9
45	0·89930	26·04	538·0
50	0·89519	25·55	537·9
Theoretical P = 537·0		Mean = 537·6	

In this table the theoretical parachor values have been computed on the basis of a typical ester anomaly, the other parts of the molecule making a normal parachor contribution, and the mean values obtained for the parachors are in good agreement with those calculated. The parachor values appear to increase by some 0·3% with temperature over the range studied. The International Critical Tables give for acetic anhydride $\gamma_{15°}$ 33·3, $\gamma_{50°}$ 29·2, which, with the densities previously given, yield parachor values of 225·6 and 227·3 respectively, the increase being greater than that in the present results. Small traces of the associated acids would contribute to this anomaly, as the parachors of these substances increase slowly with temperature (Sugden, "The Parachor and Valency," 1931, p. 46). In general, however, the anhydrides may be regarded as normal ester derivatives, for in no case is the difference between the calculated and observed values greater than the 1% variation usually observable (cf. Hammick and Wilmut, J., 1933, 207). Moreover, should there be any pronounced tendency for abnormality during the ascent of the series, it should be shown by hexoic anhydride, but the parachor of this substance is undoubtedly normal.

Viscosity Measurements.—The viscosities of acetic and propionic anhydride have been determined over an extensive temperature range by Thorpe and Rodger (*Phil. Trans.*, 1895, **185**, 397) but no data are available for the higher anhydrides. Gartenmeister (*Z. physikal. Chem.*, 1890, **6**, 524), Drucker and Kassel (*ibid.*, 1911, **76**, 367), and de Heen (*Bull. Acad. roy. Belg.*, 1891, **21**, 11) have given values for the viscosity of acetic anhydride which are some 1—3% higher than those of Thorpe and Rodger. Such differences are appreciable and may depend on the purity of the substance used, though Andrade (*J. Inst. Chem.*, 1939, 197) has pointed out that recorded viscosities for a number of other liquids exhibit divergences of this order and that it is important to apply a kinetic-energy correction.

Bowden and Butler (*loc. cit.*) found that the author's parachor–viscosity relation (J., 1938, 1063), which takes the form $\log P\eta = (A \log M)/T - C$, where M is the molecular weight, expressed their results for the alkyl carbonate series with accuracy, though the methyl derivative exhibited some divergence. In order further to test the application of this relation, the viscosities of the higher anhydrides have now been determined.

Method.—The viscometer used was of the Ostwald type and the design incorporated Barr's recommendations ("Monograph of Viscometry," Oxford Univ. Press, 1931). The limbs of the instrument were connected by means of an H-piece carrying three taps so that measurements could be carried out in a dry, enclosed system. It was set vertically in a glass thermostat and viewed with a plumb-line from two directions mutually at right angles, the times of flow being observed on a standardised stopwatch.

A kinetic-energy correction was applied to the viscometer (Barr, *op. cit.*) by means of the equation $\eta = D(Ct - B/t)$, where the calibrating constants C and B were determined by using two liquids of very different kinematic viscosity. The standard liquids used were water, ether,

and benzene, the organic liquids being dried over sodium and distilled from phosphoric oxide. For the range 15—25°, the combination ether–water was used, and for the higher range, benzene–water. The viscosity values used in the calculations are those given in the International Critical Tables (Vol. V, 10 and 11). Both B and C were found to change slightly with temperature, though the change in C was inappreciable.

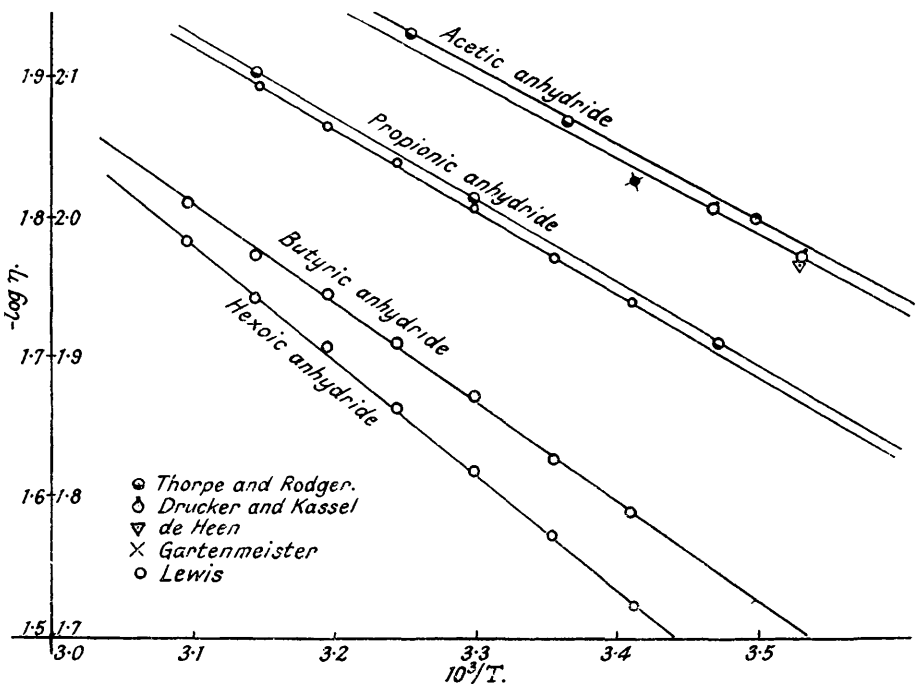
In order to compensate for liquid expansion, with consequent diminution of hydrostatic head, the anhydride and a standard 10 c.c. pipette were kept in a closed tube immersed in the thermostat, and quantities transferred rapidly to the viscometer after filling the pipette by external suction through a sealed-on tap. The viscosity results are given in the following table and are expressed in centipoises.

Temp.	20°	25°	30°	35°	40°	45°	50°
η, $(CH_3{\cdot}CO)_2O$ *	0·9120	0·8511	0·7962	0·7447	0·7015	0·6592	0·6209
η, $(C_2H_5{\cdot}CO)_2O$	1·144	1·061	0·9776	0·9057	0·8531	0·8004	0·7511
η, $(C_3H_7{\cdot}CO)_2O$	1·615	1·486	1·340	1·228	1·133	1·063	0·9754
η, $(C_5H_{11}{\cdot}CO)_2O$	2·990	2·671	2·398	2·163	1·953	1·802	1·647

* Interpolated from the results of Thorpe and Rodger by means of the equation $\log \eta = 527/T - 3{\cdot}838$.

Discussion.

The viscosities of the anhydrides increase regularly as the series is ascended. It has already been remarked that Drucker and Kassel's values for acetic anhydride (*loc. cit.*) are slightly higher than those of Thorpe and Rodger, and similarly the values obtained during the present investigation for propionic anhydride are also slightly higher than the results of the latter authors. The general differences in the recorded values for the viscosities are illustrated on the accompanying graph, which has been drawn to a large scale so that the



divergences are much accentuated. Andrade's linear equation $\log \eta = A/T - C$ has been employed, and it is seen that this is closely obeyed by all four substances. A determination of the viscosity of acetic anhydride gave $\eta_{20°} = 0{\cdot}009417$, which is in close agreement with the value given by Gartenmeister (*loc. cit.*), *viz.*, $\eta_{20°} = 0{\cdot}00946$, and is higher than the values of other authors mentioned above.

In the following table, the calculated values of the viscosities at 20° given by the equation $\log P^{\frac{2}{3}}\eta = (785 \log M)/T - 5{\cdot}951$ are compared with the experimental figures.

Anhydride.	P.	$(10^3 \log M)/T$.	η, obs.	η, calc.
Acetic	225·0	6·853	0·9417	0·7270
Propionic	303·0	7·213	1·144	1·141
Butyric	381·0	7·451	1·615	1·649
Hexoic	537·0	7·950	2·990	2·951

The agreement is good except for acetic anhydride, and the anomaly exhibited by the first member of the series has been commented on by many investigators (cf. Bowden and Butler, *loc. cit.*), and is undoubtedly due to the singular properties of the methyl group. Bowden and Butler's results, together with those of the present paper, give some support to the suggestion (J., 1939, 630) that the molecular weight and volume must be incorporated in any equation representing the variation of viscosity with temperature.

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