The Behaviour of Acetic Anhydride and Benzoic Anhydride in Sulphuric Acid.

By J. A. LEISTEN.

[Reprint Order No. 5695.]

Acetic and benzoic anhydride have been shown to extract water from sulphuric acid, and from dilute oleum, to form the corresponding acidium ions, $Me{\cdot}CO_2H_2^+$ and $Ph{\cdot}CO_2H_2^+$. The bearing of this result on the mechanism of the hydrolysis of esters by sulphuric acid is discussed.

THE solutes acetic anhydride and benzoic anhydride in sulphuric acid of maximal freezing point were found by Gillespie (*J.*, 1950, 2997) to give approximately four-fold depressions of the freezing point. The suggested explanation of these results is given by equation (1) (R = Me or Ph throughout this paper). An alternative explanation summarised by equation (2), was rejected on the grounds that it required an improbable mechanism.

$$(R{\cdot}CO)_2O + 2H_2SO_4 = R{\cdot}CO^+ + R{\cdot}CO_2H_2^+ + 2HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$(R{\cdot}CO)_2O + 3H_2SO_4 = 2R{\cdot}CO{\cdot}HSO_4 + H_3O^+ + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It was subsequently shown that the electrical conductivities of solutions of these anhydrides in sulphuric acid correspond more closely to the formation of one than of two hydrogen sulphate ions per molecule of anhydride, supporting equation (2) rather than (1); it was concluded that the mode of ionisation of the anhydrides had not been established (Gillespie and Wasif, unpublished experiments; Gillespie and Leisten, *Quart. Reviews*, 1954, **8**, 40).

It has recently been found that phthalic anhydride produces a less-than-unit depression of the freezing point of aqueous sulphuric acid, indicating that this anhydride extracts water from the solvent (Brayford and Wyatt, personal communication). It thus becomes necessary to consider a third explanation of the four-fold freezing-point depression of acetic acid and benzoic anhydride in 100% sulphuric acid :

$$(R{\cdot}CO)_2O + 3H_2SO_4 = 2R{\cdot}CO_2H_2^+ + HS_2O_7^- + HSO_4^- \quad . \quad . \quad . \quad . \quad (3)$$

Ionisation according to equation (3) produces only one hydrogen sulphate ion per molecule of anhydride and is thus consistent with the conductivity data. Equation (3) may be considered as the sum of (4) and (5)

$$(R{\cdot}CO)_2O + 3H_2SO_4 = 2R{\cdot}CO_2H_2^+ + 2HSO_4^- + SO_3 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$SO_3 + HSO_4^- = HS_2O_7^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Expression (4) represents the extraction of water from the solvent by the anhydride, and the addition of protons to the carboxylic acid formed. Equation (5) follows from the work of Brand (*J.*, 1946, 880) and of Gillespie (*J.*, 1950, 2516), who showed that hydrogen sulphate ions are largely converted into hydrogen disulphate ions in dilute oleum.

The present work shows that both anhydrides react with 100% sulphuric acid according to equation (3); and that although the overall equation differs if the solvent is aqueous sulphuric acid, or if the solvent is dilute oleum, yet in all cases the behaviour is essentially the same : water is extracted from the solvent, and carboxylic acidium ions are formed.

EXPERIMENTAL

Materials.—" AnalaR " acetic anhydride was fractionally distilled and the fraction of b. p. 139·0—139·5° was collected. Benzoic anhydride was precipitated three times from benzene solution by the addition of light petroleum : it had m. p. 42—43°. The acetic acid used was a fresh " AnalaR " sample, and the benzoic acid had m. p. 121·5—122°. " AnalaR " ammonium sulphate was dried at 130° for 2 hr. The materials were stored over phosphoric anhydride.

Freezing-point Measurements.—The cryoscopic technique and the method of computing results were similar to those used by Gillespie and Leisten (*J.*, 1954, 1).

RESULTS

TABLE 1. *Freezing-point measurements in aqueous sulphuric acid.*

Acetic anhydride				Benzoic anhydride			
Δm	F. p.	$\Delta\theta$	*i*-Factor	Δm	F. p.	$\Delta\theta$	*i*-Factor
—	8·640°	—	—	—	8·758°	—	—
0·0672	7·800	0·840°	2·08	0·01224	8·605	0·153°	2·08

TABLE 2. *The addition of water to anhydride solutions in* 100% *sulphuric acid.*

Acetic anhydride (0·161*m*)				Benzoic anhydride (0·0423*m*)			
Molality of H_2O (Δm)	Increment of Δm	F. p.	*i*-Factor *	Molality of H_2O (Δm)	Increment of Δm	F. p.	*i*-Factor
—	—	6·815°	—	—	—	9·559°	—
0·160	0·160	6·716	0·10	0·0359	0·0359	9·594	−0·16
0·210	0·050	6·264	1·51 †	0·0522	0·0163	9·512	—
—	—	—	—	0·0815	0·0293	9·223	1·64 †

* The *i*-factors are computed for *increments* of molality and freezing-point depression.

† The solute water produces a depression which is slightly less than two-fold in pure sulphuric acid, and considerably less than two-fold in solutions containing a high concentration of hydrogen sulphate ion (Gillespie, *J.*, 1950, 2493).

TABLE 3. *Freezing point of solutions of acetic anhydride and of benzoic anhydride in oleum.*

Acetic anhydride		Benzoic anhydride	
Initial molality of $H_2S_2O_7$ = 0·1363		Initial molality of $H_2S_2O_7$ = 0·1328	
Molality of $(Me{\cdot}CO)_2O$	F. p.	Molality of $(Ph{\cdot}CO)_2O$	F. p.
—	9·460°	—	9·487°
0·0131	9·301	0·0092	9·373
0·0423	8·867	0·0228	9·183
0·0600	8·557	0·0424	8·860
0·0793	8·214	0·0598	8·549

TABLE 4. *Freezing point of oleum solutions containing acetic acid.*

$Me{\cdot}CO_2H$ (*m*)	$H_2S_2O_7$ (*m*)	F. p.	$Me{\cdot}CO_2H$ (*m*)	$H_2S_2O_7$ (*m*)	F. p.	$Me{\cdot}CO_2H$ (*m*)	$H_2S_2O_7$ (*m*)	F. p.
—	0·1420	9·420°	—	0·1822	9·136°	—	0·2273	8·812°
0·0262	0·1158	9·353	0·0348	0·1474	9·065	0·0527	0·1746	8·688
0·0592	0·0828	9·233	0·0663	0·1159	8·956	0·0926	0·1347	8·535
0·1147	0·0273	8·915	0·1067	0·0755	8·761	0·1246	0·1027	8·385
—	—	—	0·1596	0·0226	8·420	0·1557	0·0716	8·211

TABLE 5. *Freezing point of oleum solutions containing benzoic acid.*

$Ph{\cdot}CO_2H$ (*m*)	$H_2S_2O_7$ (*m*)	F. p.	$Ph{\cdot}CO_2H$ (*m*)	$H_2S_2O_7$ (*m*)	F. p.	$Ph{\cdot}CO_2H$ (*m*)	$H_2S_2O_7$ (*m*)	F. p.
—	0·1012	9·708°	—	0·1611	9·288°	—	0·2047	8·975°
0·0163	0·0849	9·663	0·0217	0·1394	9·232	0·0113	0·1934	8·945
0·0321	0·0691	9·599	0·0566	0·1045	9·095	0·0340	0·1707	8·885
0·0545	0·0467	9·483	0·0863	0·0748	8·945	0·0607	0·1440	8·786
0·0912	0·0100	9·235	0·1133	0·0478	8·772	0·0975	0·1072	8·604
—	—	—	—	—	—	0·1523	0·0524	8·269

TABLE 6. *Freezing point of oleum solutions containing ammonium sulphate.*

Molality of $NH_4HS_2O_7$	—	0·0371	0·0791	0·1143
Molality of $H_2S_2O_7$ *	0·1152	0·0781	0·0361	0·0009
F. p.	9·610°	9·513	9·317	9·079

* Uncorrected for sulphuric acid formed as in eqn. (13).

It is shown in Table 1 that, in slightly aqueous (99·8%) sulphuric acid, acetic and benzoic anhydrides give two-fold depressions of the f. p. No anhydride could be isolated or detected when the solutions were diluted with water. These results appear to have only one reasonable interpretation : that in aqueous sulphuric acid, the anhydrides are hydrolysed as follows.

$$(R{\cdot}CO)_2O + H_2SO_4 + H_3O^+ = 2R{\cdot}CO_2H_2^+ + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The cryoscopic results are consistent with expression (6), because although three particles are produced per molecule of anhydride, a hydroxonium ion is at the same time removed from the aqueous solvent.

Table 2 shows the effect of adding water to solutions of the anhydrides in 100% sulphuric acid. The addition of an amount of water equimolecular to that of the anhydride has no significant effect on the f. p. of the solution; subsequent additions produce freezing-point depressions that are normal for the solute water. These results are consistent with equations (1) and (3) but not with equation (2). For supposing that the ionisation in 100% sulphuric acid is according to (1), or (2), or (3), the reaction with an equimolecular amount of water must, in view of the experiments in aqueous sulphuric acid, be represented by equations (7), or (8), or (9), respectively.

$$\mathrm{R{\cdot}CO^+ + H_2O = R{\cdot}CO_2H_2^+} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

$$\mathrm{R{\cdot}CO{\cdot}HSO_4 + H_2O = R{\cdot}CO_2H_2^+ + HSO_4^-} \quad . \; . \; . \; . \; . \; . \; . \quad (8)$$

$$\mathrm{HS_2O_7^- + H_2O = H_2SO_4 + HSO_4^-} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

The reactions (7) and (9) cause no change in the total number of solute particles. But (8) would lead to a unit depression of the f. p.; moreover, by comparing equations (2) and (8) it is seen that the addition of a further equimolar quantity of water should also produce a unit depression of the f. p. Equation (2) is therefore excluded as an explanation of the cryoscopic behaviour of the anhydrides in 100% sulphuric acid : the remaining results distinguish between (1) and (3).

FIG. 1. *Freezing point of solutions of acetic anhydride in oleum.*

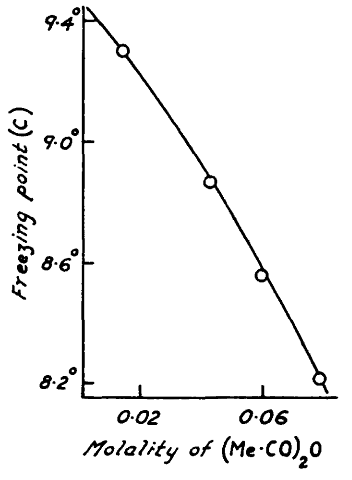
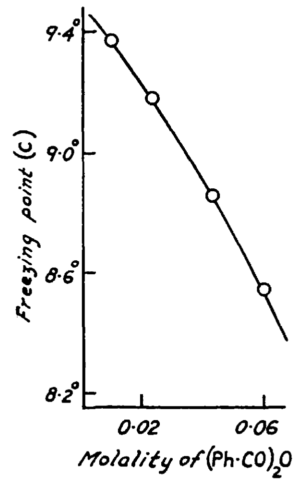


FIG. 2. *Freezing point of solutions of benzoic anhydride in oleum.*



In Fig. 1, the curve shows the changes of f. p. that would occur if amounts of acetic acid were added to, and half the molar amounts of water were subtracted from, an oleum solvent. Such additions and subtractions are stoicheiometrically equivalent to additions of acetic anhydride. The experimental points in Fig. 1 relate to actual additions of acetic anhydride (Table 3). Similar results are shown for benzoic anhydride in Fig. 2.

The derivation of the curve in Fig. 1 will be illustrated by calculating one point on it. Suppose that the oleum solvent, in which the molality of disulphuric acid is 0·1363, is made 0·1000*m* with respect to acetic acid. On subtracting a 0·0500 molal quantity of water from this solution, the molality of disulphuric acid will become approximately 0·1863, in accordance with the equation : $\mathrm{2H_2SO_4 - H_2O = H_2S_2O_7}$. This molality is approximate because the removal of water from the solvent to form disulphuric acid decreases the amount of sulphuric acid in the solution. The exact molality of disulphuric acid will be 0·1881, and that of the acetic acid 0·1010. The f. p. of this solution may be found by interpolation, using the results in Table 4 on the f. p.s of acetic acid solutions in oleum and Gillespie's data on the f. p.s of solutions of disulphuric acid in sulphuric acid (*loc. cit.*). The required f. p. is 8·754° : this is plotted against 0·0500 on the abscissa.

The coincidence of the experimental points and the curve shows that acetic acid and acetic anhydride form identical solutions in oleum solvents, provided that the stoicheiometrical compositions of the solutions are identical. The same conclusion may be drawn for benzoic acid and benzoic anhydride (Fig. 2, Table 5). The following demonstration of the mode of ionisation of acetic and benzoic acids in oleum will therefore apply also to the anhydrides.

Acetic and benzoic acids behave as monoacid bases in aqueous sulphuric acid. Similar behaviour in oleum would lead to expression (10), because the relative strengths of sulphuric acid and disulphuric acids are such that the equilibrium (11) lies to the right-hand side (Brand, *loc. cit.*; Gillespie, *J.*, 1950, 2516).

$$\mathrm{R{\cdot}CO_2H + H_2S_2O_7 = R{\cdot}CO_2H_2^+ + HS_2O_7^-} \quad \ldots\ldots \quad (10)$$

$$\mathrm{H_2S_2O_7 + HSO_4^- = HS_2O_7^- + H_2SO_4} \quad \ldots\ldots\ldots \quad (11)$$

In oleum solution, however, there is the possibility of ionisation (12):

$$\mathrm{R{\cdot}CO_2H + 2H_2S_2O_7 = R{\cdot}CO^+ + HS_2O_7^- + 2H_2SO_4} \quad \ldots\ldots \quad (12)$$

These two possibilities cannot be distinguished by direct determination of the i-factors because of complicating equilibria in the oleum solvent (Gillespie, *loc. cit.*); a comparative procedure was therefore employed, using the solute ammonium sulphate as a standard.

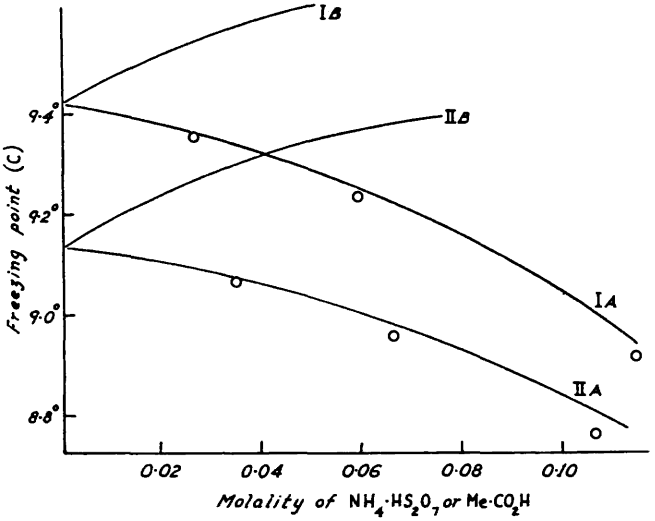


FIG. 3. *Freezing points of solutions of ammonium sulphate and acetic acid in oleum.*

Initial molality of $H_2S_2O_7$; $I = 0{\cdot}1420$, $II = 0{\cdot}1822$.

Added solute: $A = (NH_4)_2SO_4$, $B = (NH_4)_2SO_4 + H_2O$ (1 : 2). ○ = acetic acid (experimental points).

Fig. 3 shows the results of such a comparison, in two different oleum solvents, for the case of acetic acid. The curves *A* describe the change of f. p. when ammonium sulphate is added to oleum solvents. [Ammonium sulphate is expressed as ammonium hydrogen disulphate: see expression (13).] Ammonium sulphate ionises in oleum according to (13) (*idem, loc. cit.*).

$$\mathrm{\tfrac{1}{2}(NH_4)_2SO_4 + H_2S_2O_7 = NH_4^+ + HS_2O_7^- + \tfrac{1}{2}H_2SO_4} \quad \ldots\ldots \quad (13)$$

This equation is cryoscopically similar to (10), if we neglect the small diluting effect of the sulphuric acid formed in reaction (13). The curves *B* show the change of f. p. when the solute is a mixture of ammonium sulphate and water in the molecular ratio of 1 : 2.

$$\mathrm{[\tfrac{1}{2}(NH_4)_2SO_4 + H_2O] + 2H_2S_2O_7 = NH_4^+ + HS_2O_7^- + 2\tfrac{1}{2}H_2SO_4} \quad \ldots\ldots \quad (14)$$

Expression (14) is cryoscopically similar to (12), the effect of the sulphuric acid formed being again neglected. Comparison of the experimental points with the curves indicates that acetic acid ionises in oleum solutions according to equation (10) and not according to (12); the fact that the points do not exactly coincide with the curves *A* may be attributed to small differences in the cryoscopic properties of the ammonium and the acetic acidium ions. The possibility that a small but cryoscopically significant proportion of acetic acid ionises according to expression (12) can be discounted by a comparison of the results for the two oleum solvents. For if reaction (12) were significant in the weaker oleum (*I*) we should expect it to be more prominent in the stronger oleum (*II*): the experimental points should then be further below curve *A* in the case of *I* than in the case of *II*. This is the opposite of what is observed. Qualitatively similar results are obtained with benzoic acid, but the experimental points lie somewhat further below the curves than with acetic acid.

The derivation of the curves in Fig. 3 is similar to that in Figs. 1 and 2. It is necessary to find the f. p.s of certain mixtures of ammonium sulphate, disulphuric acid, and sulphuric acid: this was done by interpolation, with Gillespie's data on the f. p. of solutions of disulphuric acid in sulphuric acid (*J.*, 1950, 2493), and of ammonium sulphate in oleum solvents (*ibid.*, p. 2516, Table 1, Expts. 10 and 104), supplemented by the results in Table 6. The acetic and benzoic acid results are in Tables 4 and 5.

It has now been shown that acetic and benzoic acids and anhydrides dissolve, both in dilute oleums and in aqueous sulphuric acid, to give carboxylic acidium ions. It is therefore concluded that similar behaviour occurs is 100% sulphuric acid, and that the ionisation of the anhydrides in this solvent is given by expression (3).

DISCUSSION

The mechanism of the hydrolysis of acetic and benzoic anhydride by sulphuric acid is probably that suggested by Gillespie (*J.*, 1950, 2997), but with an additional stage (iv), the extraction of water from the solvent by the acyl ion. This stage (iv), which implies

$$\text{(i)}\quad (R{\cdot}CO)_2O + H_2SO_4 = (R{\cdot}CO)_2OH^+ + HSO_4^-$$

$$\text{(ii)}\quad (R{\cdot}CO)_2OH^+ = R{\cdot}CO_2H + R{\cdot}CO^+$$

$$\text{(iii)}\quad R{\cdot}CO_2H + H_2SO_4 = R{\cdot}CO_2H_2^+ + HSO_4^-$$

$$\text{(iv)}\quad R{\cdot}CO^+ + H_2O = R{\cdot}CO_2H_2^+$$

that acetyl and benzoyl ions are unstable in sulphuric acid, solves a problem that has arisen as a result of experiments on the hydrolysis of esters by sulphuric acid. Ingold ("Structure and Mechanism in Organic Chemistry," G. Bell and Sons Ltd., London, 1953, p. 771) has adduced evidence that certain esters are hydrolysed in sulphuric acid by a mechanism ($A_{AC}1$) of which the rate-determining stage is, for the example of methyl benzoate:

$$Ph{\cdot}CO_2MeH^+ = Ph{\cdot}CO^+ + MeOH$$

If the benzoyl ion were stable, methyl benzoate when fully "hydrolysed" should thus produce a five-fold depression of the freezing point:

$$Ph{\cdot}CO_2Me + 3H_2SO_4 = Ph{\cdot}CO^+ + MeHSO_4 + H_3O^+ + 2HSO_4^-$$

Semiquantitative experiments (Newman, Craig, and Garnett, *J. Amer. Chem. Soc.*, 1949, **71**, 869) indicated that the freezing-point depression corresponding to complete hydrolysis is in fact only three-fold. This result, which has been confirmed quantitatively (Leisten. unpublished experiments), leads to the conclusion that the hydrolysis produces the benzoic acidium ion:

$$Ph{\cdot}CO_2Me + 2H_2SO_4 = Ph{\cdot}CO_2H_2^+ + MeSO_4H + HSO_4^-$$

The apparent contradiction between this conclusion, the then accepted stability of the benzoyl ion, and the $A_{AC}1$ mechanism, led to the suggestion of an alternative mechanism (Gillespie and Leisten, *Quart. Reviews*, 1954, **8**, 40); the acceptance of stage (iv), however, removes this objection to the $A_{AC}1$ mechanism, and the alternative mechanism now appears improbable. The mechanism for the hydrolysis of certain esters put forward by Kuhn and Corwin (*J. Amer. Chem. Soc.*, 1948, **70**, 3370) also appears improbable in the light of the present work, for it supposes the existence in sulphuric acid of acyl hydrogen sulphate molecules.

The demonstration that the acetyl and benzoyl ions do not exist in cryoscopically detectable amounts in sulphuric acid or in dilute oleum, is without prejudice to the existence of these ions in other systems, or as reaction intermediates. In fact the volume of evidence for these acetyl ions (see Gillespie, *loc. cit.*) suggests that the equilibrium $R{\cdot}CO_2H_2^+ + H_2S_2O_7 \rightleftharpoons R{\cdot}CO^+ + 2H_2SO_4$ is a significant one, and that by increasing the proportion of disulphuric acid to sulphuric acid in solutions of the anhydrides, the acidium ions could be converted into the acyl ions. This conversion, which might be detected spectroscopically, appears more probable when it is considered that certain acids (*e.g.*, mesitoic acid) are known to form acyl ions in aqueous sulphuric acid, and that others (*e.g.*, 3 : 5-dibromo-2 : 4 : 6-trimethylbenzoic acid) probably yield a mixture of acyl and acidium ions in the same solvent (Treffers and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 1758).

The writer thanks Dr. P. A. H. Wyatt for valuable discussions, and Dr. R. J. Gillespie and Dr. Wyatt for commenting on the manuscript.

THE UNIVERSITY, SHEFFIELD, 10.

[*Received, September 2nd*, 1954.]