

585. *Cryoscopic Measurements in Sulphuric Acid. Part VIII. The Solutes Acetic Anhydride and Benzoic Anhydride. Cryoscopic Evidence for the Acetylium and Benzoylium Ions.*

By R. J. GILLESPIE.

Evidence for the existence of the acetylium and benzoylium ions has been provided by a cryoscopic investigation of solutions of acetic and benzoic anhydrides in sulphuric acid.

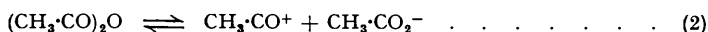
ACYLIUM ions have for some years been recognised as probable intermediates in acid-catalysed esterification and hydrolysis of carboxylic esters (cf. Ingold and Ingold, *J.*, 1932, 756; Datta, Day, and Ingold, *J.*, 1939, 838; Day and Ingold, *Trans. Faraday Soc.*, 1941, **38**, 686) and in the formation of ketones by the Friedel-Crafts reaction with acyl halides, esters, and acid anhydrides in the presence of an acid catalyst (cf. W. Hückel, "Theoretische Grundlagen der Organische Chemie," 3rd edn., 1940, Vol. I, p. 559; Fairbrother, *J.*, 1937, 503; *Trans. Faraday Soc.*, 1941, **38**, 763; Norris and Wood, *J. Amer. Chem. Soc.*, 1940, **62**, 1429). Mackenzie and Winter (*Trans. Faraday Soc.*, 1948, **44**, 159, 171, 243) have postulated the existence of the acetylium ion to account for the kinetics of the perchloric acid-catalysed Thiele acetylation of some quinones. Recently, Burton and Praill (*J.*, 1950, 1203) have shown that whereas mixtures of acetic and perchloric acids which contain the acetic acidium ion, $\text{CH}_3\cdot\text{CO}_2\text{H}_2^+$, are not acetylating agents, yet addition of acetic anhydride to such mixtures gives rise to a powerful acetylating agent, which they postulate as the acetyl ion $\text{CH}_3\cdot\text{CO}^+$, capable of rapidly converting anisole into *p*-methoxyacetophenone at room temperature. An equally powerful acetylating agent can be prepared from acetyl chloride and silver perchlorate (Burton and Praill, *J.*, 1950, 2034) and these authors suggest that this is ionised acetyl perchlorate. It has also been shown (Burton and Praill, private communication) that benzoyl perchlorate prepared in a similar way is a powerful benzoylating agent, presumably because it is ionised into benzoylium, $\text{C}_6\text{H}_5\cdot\text{CO}^+$, and perchlorate ions.

The first evidence that certain acylium ions could be obtained as stable entities under appropriate conditions and not just as transient reaction intermediates was obtained by Treffers and Hammett (*J. Amer. Chem. Soc.*, 1937, **39**, 1708), who showed that 2 : 4 : 6-trimethylbenzoic acid gives a four-fold depression of the freezing point of sulphuric acid. This can only be reasonably interpreted as meaning that this acid is converted rapidly and completely into the 2 : 4 : 6-trimethylbenzoylium ion according to the equation



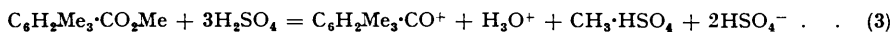
By the same method, the closely related 2 : 6-dimethyl- and 3 : 5-dibromo-2 : 4 : 6-trimethylbenzoic acids were found to undergo partial ionisation in sulphuric acid to the corresponding acylium ions.

Recent work on solutions in acetic anhydride has provided evidence for the existence of the acetylum ion as a stable entity under suitable conditions. Acetic anhydride has a small but by no means negligible electrical conductivity which can most reasonably be attributed to an ionic self-dissociation forming acetylum and acetate ions (Hall and Voge, *J. Amer. Chem. Soc.*, 1933, **55**, 239) :

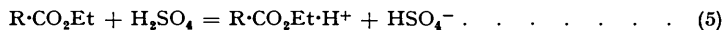
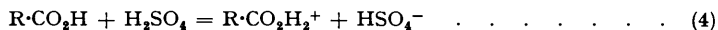


Acetyl halides, acetyl thiocyanate, and acetyl benzenesulphonate all behave as acids in acetic anhydride, and can be titrated conductometrically with inorganic acetates which behave as bases, the neutralisation reaction being essentially the reverse of (2) (Jander, Rüsberg, and Schmidt, *Z. anorg. chem.*, 1948, **255**, 238; Jander, "Die Chemie in Wasserähnlicher Lösungsmitteln," Berlin, 1949; Usanovitch and Yatsimirskii, *J. Gen. Chem. Russia*, 1941, **11**, 954). Benzoyl chloride can also be titrated in the same way (Usanovitch and Yatsimirskii, *loc. cit.*), presumably because it ionises to form the benzoylium ion. Seel (*Z. anorg. Chem.*, 1943, **250**, 331) has prepared the rather unstable acetyl borofluoride, $\text{CH}_3\cdot\text{CO}\cdot\text{BF}_4$, from acetyl fluoride and boron trifluoride, and has shown that this compound and the previously known acetyl and benzoyl hexachloroantimonates have conductivities in liquid sulphur dioxide comparable with those of known binary electrolytes, such as KSbCl_6 , and are therefore presumably ionised into acetylum ions and either borofluoride or hexachloroantimonate ions. All these compounds undergo numerous reactions in sulphur dioxide solution which are consistent with this mode of ionisation (Seel, *ibid.*, 1943, **252**, 24; Seel and Bauer, *Z. Naturforsch.*, 1947, **2**, b, 397).

Whereas the 2 : 4 : 6-trimethylbenzoylium ion is formed in sulphuric acid from the corresponding carboxylic acid (mesitoic acid), which gives a four-fold depression of the freezing point of the solvent (eqn. 1), and from the methyl ester of mesitoic acid, which gives a five-fold depression of the freezing point (Newman, Kuivila, and Garrett, *J. Amer. Chem. Soc.*, 1945, **67**, 704), *i.e.*,



benzoic and acetic acids and their ethyl esters (*idem, ibid.*; Kuhn and Corwin, *J. Amer. Chem. Soc.*, 1948, **70**, 3370; Part I of this series, *J.*, 1950, 2473) give only a two-fold depression, corresponding to the following general equations :



If any acetylum and benzoylium ions are formed, it can only be in amounts too small to be detected by the cryoscopic method. Kuhn and Corwin (*loc. cit.*) have recently made an investigation of the behaviour of a number of other esters of acetic and benzoic acids, and also of anisic acid, in sulphuric acid. On the basis of cryoscopic and other evidence they concluded that acylium ions are not present in these solutions and suggested that the acetylum, benzoylium, and anisoylium ions are unstable in sulphuric acid, combining with hydrogen sulphate ions to form un-ionised acyl hydrogen sulphates.

The only previously reported cryoscopic investigation of acetic anhydride in sulphuric acid is that of Oddo and Casalino (*Gazzetta*, 1917, **47**, II, 232), who found that it gave an approximately three-fold freezing-point depression. Benzoic anhydride does not appear to have been investigated in this way before. The present work shows that both acetic and benzoic anhydride give a four-fold depression of the freezing point of sulphuric acid. This provides further evidence for the existence of the acetylum and benzoylium ions. It shows that these ions are quite stable in sulphuric acid solution; and that they are formed quantitatively or nearly quantitatively when small amounts of acetic and benzoic anhydrides respectively are dissolved in sulphuric acid.

EXPERIMENTAL.

Purification of Materials.—"AnalaR" Acetic anhydride was distilled, and the fraction of b. p. 139.0—139.5° was collected. Benzoic anhydride was twice recrystallised by dissolving it in benzene and reprecipitating it by adding light petroleum. It was stored in a vacuum-desiccator over phosphoric anhydride; it had m. p. 42—43°.

Freezing-point Measurements.—The freezing-point experiments were carried out in the same apparatus and by the same technique as previously described (see Part I, *loc. cit.*). All the measurements were carried out with sulphuric acid of maximum freezing point instead of the slightly aqueous acid generally employed by other workers and in the measurements reported in the earlier papers of this series (*J.*, 1950, 2473). This was done to avoid the complicated calculations necessary to allow for the repression of the ionisation of the water present in the solvent by the hydrogen sulphate ion formed by the added solute (cf. Parts I and II of this series, *J.*, 1950, 2473, 2493). The results of the freezing-point experiments with acetic and benzoic anhydrides as solutes are given in the following tables.

Solute : Acetic anhydride.

| Molality Ac ₂ O, Δ <i>m</i> ₂ . | F. p. | Δ <i>θ</i> ₁ * Corr. | Δ <i>θ</i> ₂ * ν. | Molality Ac ₂ O, Δ <i>m</i> ₂ . | F. p. | Δ <i>θ</i> ₁ * Corr. | Δ <i>θ</i> ₂ * ν. |
|-------------------------------------------------------------|---------|------------------------------------|---------------------------------|-------------------------------------------------------------|---------|------------------------------------|---------------------------------|
| Experiment No. 132. | | | | Experiment No. 133. | | | |
| — | 10·351° | — | — | — | 10·352° | — | — |
| 0·01089 | 10·187 | — | — | 0·04222 | 9·499 | 0·853° | 0·136° |
| 0·01752 | 10·043 | 0·308° | 0·109° | 0·05542 | 9·198 | 1·154 | 0·142 |
| 0·03452 | 9·675 | 0·676 | 0·131 | 0·07651 | 8·715 | 1·637 | 0·147 |
| 0·05430 | 9·226 | 1·125 | 0·142 | 0·09740 | 8·251 | 2·101 | 0·150 |
| 0·05430 † | 9·232 | 1·119 | 0·142 | 0·1083 | 7·988 | 2·364 | 0·150 |

* Δ*θ*₁ and Δ*θ*₂ are respectively the observed and the corrected f. p. depressions.
 † This measurement was made 16 hours after the preceding one; otherwise it was a repetition.

Solute : Benzoic anhydride.

| Molality Bz ₂ O, Δ <i>m</i> ₂ . | F. p. | Δ <i>θ</i> ₁ | Corr. | Δ <i>θ</i> ₂ | ν. | Molality Bz ₂ O, Δ <i>m</i> ₂ . | F. p. | Δ <i>θ</i> ₁ | Corr. | Δ <i>θ</i> ₂ | ν. |
|-------------------------------------------------------------|---------|-------------------------|--------|-------------------------|------|-------------------------------------------------------------|---------|-------------------------|--------|-------------------------|------|
| Experiment No. 134. | | | | | | Experiment No. 136. | | | | | |
| — | 10·357° | — | — | — | — | — | 10·352° | — | — | — | — |
| 0·02615 | 9·858 | 0·499° | 0·124° | 0·623° | 3·98 | 0·02030 | 9·983 | 0·369° | 0·114° | 0·483° | 3·98 |
| 0·04360 | 9·457 | 0·900 | 0·137 | 1·037 | 3·98 | 0·03798 | 9·576 | 0·776 | 0·133 | 0·909 | 4·01 |
| 0·06396 | 8·958 | 1·399 | 0·145 | 1·544 | 4·03 | 0·05361 | 9·213 | 1·139 | 0·142 | 1·281 | 4·00 |
| 0·07938 | 8·601 | 1·756 | 0·148 | 1·904 | 4·01 | 0·06306 | 8·992 | 1·360 | 0·145 | 1·505 | 4·00 |
| 0·09432 | 8·232 | 2·125 | 0·150 | 2·275 | 4·03 | | | | | | |

The observed freezing-point depressions, Δ*θ*₁, are corrected in each case to allow for the incomplete depression, by the formed hydrogen sulphate ion, of the autoprotolysis of the solvent. This can readily be done by using the value given in Parts II and IV of this series (*J.*, 1950, 2493, 2516) for the autoprotolysis constant

$$K_{sp} = [H_3SO_4^+][HSO_4^-] = 0.00017$$

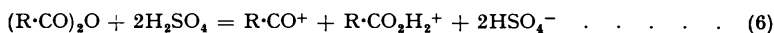
The concentration of autoprotolytic ions remaining in the solution with any given concentration of added solute can be calculated by using this value of the autoprotolysis constant, and knowing the concentration of hydrogen sulphate ions formed by the solute. The freezing-point depression corresponding to this concentration of autoprotolytic ion can then be calculated by the usual equation, and the difference between two such values calculated for the appropriate solute concentrations is the correction to be applied to the observed freezing-point depressions. Such corrections are listed in column 4 of both tables, and the corresponding corrected freezing-point depressions, Δ*θ*₂, are given in column 5. The values of ν (the number of particles produced in solution by one solute molecule) given in column 6 of the tables have been calculated from the appropriate form of equation (5) of Part I (*loc. cit.*). With the substitution of *s*₂ = 2 and ν₂ = 4, and the assumption (in the absence of any information on the subject) that the formed ions are unsolvated, and *s*₃ = ν₃ = *m*₃ = 0 (since the concentration of water in the solvent is zero or at least quite negligible), this equation reduces to the form

$$\nu = \Delta\theta_2[5.98\{1 - 0.0035 \bar{\theta}\}\Delta m_2]^{-1}$$

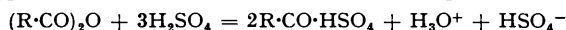
where $\bar{\theta}$ is the mean freezing-point depression over the range of solute concentration Δ*m*₂.

DISCUSSION.

The value of ν is approximately 4 for both acetic and benzoic anhydride, and this can only be reasonably interpreted * by assuming that they form acylium and acidium ions according to the general equation



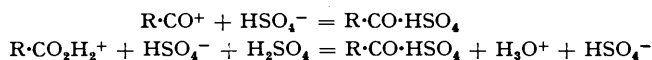
* The only other apparently reasonable interpretation is that expressed by the equation



This is excluded by the two-fold freezing-point depression given by acetic and benzoic acids. For if this interpretation were correct it would imply that the reaction

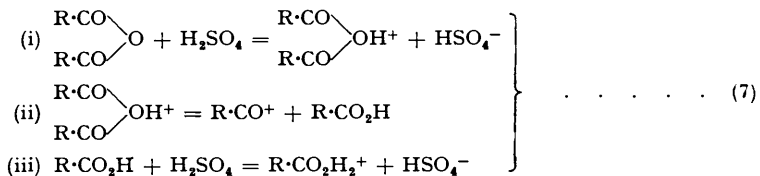


goes to completion, *i.e.*, that both of the reactions



go to completion. This in turn would require a three-fold freezing-point depression by benzoic and acetic acids.

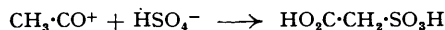
This can be visualised as occurring in the following stages



It has been shown previously that the carboxylic acid formed in (ii) ionises further (iii) in the case of acetic and benzoic acids to give the corresponding acidium ion (cf. Part I, *loc. cit.*; Newman, Ruivila, and Garrett, *loc. cit.*).

It can be seen from the relevant table that the mean value of ν for benzoic anhydride is 4.00 and the individual values do not, within the experimental error, change either with time or with the solute concentration. It can be concluded therefore that benzoic anhydride is completely ionised according to equation (6), forming the benzoylum ion and the benzoic acidium ion.

The values of ν for acetic anhydride are sufficiently close to 4 to indicate that ionisation occurs largely according to equation (6). The difference between the observed values of ν and the integral value of 4 is, however, significant; and the observed values appear, moreover, to decrease very slightly with increasing concentration, and with time. It is not yet possible to give a definite interpretation of this slight discrepancy. Perhaps the acetic anhydridium ion $(\text{R}\cdot\text{CO})_2\text{OH}^+$ is not completely split up into acetylium ion and acetic acid [equation 7(ii)]. This would imply that in a sulphuric acid solution of acetic anhydride there is a small quantity of the acetic anhydridium ion, whose existence and acetylating properties have recently been postulated by Burton and Praill (*loc. cit.*). Alternatively, there may be some slight combination between acetylium and hydrogen sulphate ions to form un-ionised acetyl hydrogen sulphate. Or, again, the formation of a small amount of sulphoacetic acid, which would be expected to be a weak electrolyte in sulphuric acid solution, would equally well account for the slightly low observed values of ν . This substance is known to be formed at a measurable rate in acetic anhydride solutions of sulphuric acid at 40° (Murray and Kenyon, *J. Amer. Chem. Soc.*, 1940, **62**, 1230) :



This latter interpretation receives some support from the slight decrease in the observed freezing point when a solution of acetic anhydride was set aside for some hours (see table).

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[Received, June 27th, 1950.]