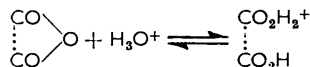


416. *Cyclic Anhydrides in Sulphuric Acid.*

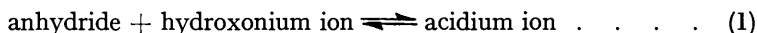
By J. A. LEISTEN.

It is shown that in the phthalic, maleic, and succinic systems the equilibrium:



is critically balanced in the region of 100% sulphuric acid, and that this finding is potentially important in the fundamental study of sulphuric acid. For the glutaric system the equilibrium lies far to the right even in the presence of a small excess of sulphur trioxide. Succinic anhydride is found to be a stronger base than phthalic and maleic anhydrides. Solvent mixtures are described which greatly increase the power of the cryoscopic method to solve problems of solute behaviour in sulphuric acid.

At the outset of this work it was known that open-chain anhydrides extract water from 100% sulphuric acid and from dilute oleums.¹ Phthalic anhydride on the other hand was known from cryoscopic²⁻⁴ and conductimetric⁴ measurements largely to retain its identity in 100% sulphuric acid. (It was in fact the only weak base in this solvent to have been found among compounds composed of carbon, hydrogen, and oxygen.) It was not clear whether succinic anhydride ionises as a base or extracts water from the solvent;⁴ and there was disagreement in the cryoscopic results reported for both phthalic acid and maleic acid.^{2,5,6} Nevertheless it appeared from these results that cyclic anhydrides and the related dicarboxylic acids do not always give the same products when dissolved in sulphuric acid. Either there are kinetic restrictions on the interconversion of the acid and anhydride in this solvent or the equilibrium



is critically balanced in that small range of concentration (99.5–100% sulphuric acid) in which cryoscopic measurements are made.

Cryoscopic results for phthalic, succinic, glutaric, and maleic acids and anhydrides are given below in terms of the van't Hoff *i*-value, which provides an estimate of the number of particles produced by each solute molecule in solution. Thus expressed, the results can be interpreted in broad outline. A finer analysis, though possible,⁷ has not been attempted for a reason which appears later; but the freezing points and molalities of all the solutions are listed. The *i*-values for successive additions of a solute are calculated from the increments of molality and freezing-point depression. Where the carboxylic acid or anhydride is added to 100% sulphuric acid no *i*-value is calculated from the first addition, for this is the one most subject to error through the self-dissociation of the solvent. It should be remembered that this error can only reduce the *i*-value.

¹ Leisten, *J.*, 1955, 298.

² Hantzsch, *Z. phys. Chem.*, 1907, **61**, A, 257.

³ Oddo and Casalino, *Gazzetta*, 1917, **47**, II, 232.

⁴ Flowers, Gillespie, and Wasif, *J.*, 1956, 607.

⁵ Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, p. 47.

⁶ Oddo and Casalino, *Gazzetta*, 1917, **47**, II, 200.

⁷ Bass, Gillespie, and Robinson, *J.*, 1960, 821.

Phthalic Acid and Anhydride.—Expt. 1 confirms the results of Hantzsch² and of Oddo and Casalino,⁶ but not those of Hammett,⁵ and it appears that, in anhydrous sulphuric acid, phthalic acid accepts rather more than one proton per molecule. The first additions of phthalic anhydride to aqueous sulphuric acid (Expt. 2) give *i*-values about 1.8 units

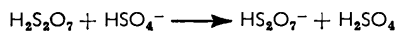
TABLE I. *Cryoscopic results.*

Expt.	Molality of		F. p.	<i>i</i> -Value	Expt.	Molality of		F. p.	<i>i</i> -Value						
1.	—	Phthalic acid		10.359°	—	2.	H ₂ O 0.0851	Phthalic anhydride							
		0.0245	10.118	—	9.591°			—							
		0.0567	9.710	2.11	9.544			0.32							
		0.1061	9.029	2.30	9.445			0.56							
		0.1612	8.256	2.34	9.194			0.77							
3.	—	Succinic acid		10.362	—	4.	0.1473	Succinic anhydride							
		0.0647	9.548					—	8.902	—					
		0.1000	9.038					2.41	8.688	0.58					
		0.1508	8.308					2.39	8.531	0.61					
7.	KHSO ₄ 0.168	—		8.446	—	5.	—	—							
		0.0156	8.329	1.25	10.365			—							
		0.0375	8.137	1.46	10.137			—							
		0.0705	7.837	1.51	10.031			1.96							
		0.1078	7.499	1.51	9.913			1.82							
8.	H ₂ O 0.064	Glutaric anhydride		9.821	—	6.	—	—							
		0.0173	9.725					0.93	10.364	—					
		0.0512	9.511					1.05	9.422	—					
9.	—	—		10.358	—	11.	0.066	Maleic anhydride							
		0.0225	10.109	—	6.855			0.48							
		0.0613	9.522	2.55	6.519			0.65							
		0.0945	9.014	2.55	9.799			—							
10.	0.180	Maleic acid		—	—			—							
		0.0514	7.863	2.18	9.389			0.68							
		0.1052	7.147	2.22	8.787			0.99							
					7.865			1.05							
							Maleic acid								
							0.0630	6.142	2.20						
Expt.	Molality of		F. p.	<i>i</i> -Value	Expt.	Molality of		F. p.	<i>i</i> -Value						
12.	0.074	KHSO ₄ 0.206	Phthalic acid *		7.373°	—	13.	0.075	0.145	Succinic acid *					
			0.0476	7.066	1.07	7.998°				—					
						7.774				1.43					
			Benzoic acid										Water		
			0.0447	6.561	1.88	0.0233				7.770	0.03				
14.	0.133	0.250	Phthalic acid		6.249	1.26			Succinic acid						
			0.0413	6.249	1.26	0.0207			7.570	1.61					
			Maleic acid								Glutaric acid				
			0.0334	6.092	1.10	0.0183			7.291	2.54					
							Water								
							0.0233	7.272	0.14						

* Molalities in this column are those for each separate addition. All other molalities in the Table are total values.

lower than those of phthalic acid: the obvious interpretation is that the anhydride forms phthalic acidium ions by removing water, whose *i*-value is about 1.8 in these concentrations,⁸ from the solvent. When the total molality of anhydride exceeds the initial molality of water in the solvent, the *i*-value for a further addition should be similar to that for an addition of the anhydride to anhydrous sulphuric acid. This is so, for the final *i*-value in Expt. 2 is 1.09, and Flowers, Gillespie, and Wasif⁴ found that phthalic anhydride gives 1.14—1.18 particles per molecule in anhydrous sulphuric acid containing potassium hydrogen sulphate to repress the self-dissociation. We shall next consider Expt. 12.

Disulphuric acid in sulphuric acid behaves as a weak acid, which can be titrated with a strong base such as a metal hydrogen sulphate:⁸



Suppose that to a sulphuric acid solution containing HS_2O_7^- and HSO_4^- in comparable amounts some phthalic acid is added. If the acidium ion is formed, as in anhydrous sulphuric acid, a similar *i*-value (of about 2.3) would be found. If however the anhydride is formed the water produced will merely convert some of the hydrogen disulphate into hydrogen sulphate, with little change in freezing point (see Expt. 13): the observed freezing-point depression will be due almost entirely to phthalic anhydride. In fact the average *i*-value for two additions is 1.16, in good agreement with the results of Gillespie and his co-workers for phthalic anhydride in anhydrous sulphuric acid containing potassium hydrogen sulphate. (An addition of benzoic acid has been made in Expt. 12 to show that a simple base^{2,6} gives the expected two-fold freezing-point depression in this solvent mixture¹).

It has now been shown that, in sulphuric acid containing a small excess of water, phthalic anhydride is converted into phthalic acidium, whilst in solutions containing a small excess of sulphur trioxide phthalic acid is converted into the anhydride. Evidently the different behaviour in 100% sulphuric acid of phthalic acid and phthalic anhydride is not due to a kinetic impediment to their interconversion. The equilibrium (1) must be balanced in the region of 100% sulphuric acid.

The freezing-point depression for phthalic anhydride is 10—15% higher than that expected for a non-electrolyte.^{4,9} This can be explained either by a small degree of protonation, or by a fractional conversion into phthalic acidium. These two possibilities are distinguished by Expt. 12, for the hydrogen disulphate should reduce any tendency to form acidium ions that phthalic anhydride might have in the less water-deficient solvent used by Gillespie and his co-workers. The similarity of the cryoscopic results suggests that phthalic anhydride ionises as a base in each solution to a similar extent. This is reasonable since, by the equilibrium $\text{B} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{HB}^+ + \text{HSO}_4^-$ where B is any base, the acidity of concentrated sulphuric acid solutions is determined only by the concentration of bisulphate ion, which is approximately the same in the two solutions.

Succinic Acid and Anhydride.—In both aqueous sulphuric acid¹⁰ and anhydrous acid (Expt. 3) succinic acid appears to accept about 1.5 protons per molecule. In the aqueous solvent (Expt. 4) succinic anhydride has an *i*-value about 1.8 units less than that of succinic acid, and it seems clear that water is removed from the solvent as in the case of phthalic anhydride. The behaviour of the anhydride in 100% sulphuric acid is less simple (Expt. 5 and 6). The observed *i*-values vary from 1.96 to 1.45. High *i*-values and a high rate of change of the *i*-value with total molality are obtained for small additions; and lower *i*-values, and a low rate of change, for larger additions. Evidently some equilibrium, either equilibrium (1) or the acid-base equilibrium, is being suppressed by increasing the anhydride concentration. The change of *i*-value with molality must be due to a shift

⁸ Gillespie, *J.*, 1950, 1493.

⁹ Brayford and Wyatt, *J.*, 1955, 3453.

¹⁰ Wiles, *J.*, 1953, 996.

in the acid-base equilibrium, since the effect is not observed (Expt. 7) in anhydrous acid containing a moderate concentration of bisulphate ion (added as the potassium salt), which has a lowering and buffering effect on the acidity but does not appreciably alter the water affinity. In this solution *i*-values of about 1.5 are obtained even for small additions, and, as with the phthalic system, similar *i*-values are found in sulphuric acid containing potassium hydrogen disulphate and potassium hydrogen sulphate. The results are consistent with these conclusions: that succinic anhydride does not form acidium ions in 100% sulphuric acid; that in the presence of a moderate concentration of bisulphate ion the anhydride is about half ionised as a base; and that succinic acid forms the anhydride in solutions containing excess of sulphur trioxide. The position of equilibrium (1) is similar to that in the phthalic system.

Glutaric Acid and Anhydride.—Wiles¹⁰ gives the *i*-value of glutaric acid in aqueous sulphuric acid as 2.6. Similar values are found for the anhydride in 100% sulphuric acid (Expt. 9), and for glutaric acid in sulphuric acid containing potassium hydrogen disulphate and potassium hydrogen sulphate (Expt. 13). The *i*-values for the anhydride in aqueous acid are about 1.7 units lower (Expt. 8). The results are explained by assuming that glutaric acid accepts about 1.6 protons per molecule, and that the anhydride forms the acidium ion under all the conditions tried. (An alternative interpretation, that the anhydride exists as a polyacid base in the water-deficient solvents is rejected because phthalic and succinic anhydrides are only weak monoacid bases.)

Maleic Acid and Anhydride.—The results obtained in experiments 10, 11, and 14, are almost indistinguishable from the results for phthalic acid and anhydride. The interpretation is the same.

Some Useful Cryoscopic Mixtures.—Cryoscopic measurements in pure or aqueous sulphuric acid are seldom sufficient to establish the behaviour of a solute, as the present examples suggest. The reason for this is that acid-base reactions, and reactions which take water from the solvent (as in various types of solvolysis) or produce water (as in sulphation and sulphonation), are common in sulphuric acid, and they often occur together. Abstraction of water by anhydrides is a specific problem of this kind, and it is evident that some of the conclusions would not have been reached without the use of the solvent mixture $\text{H}_2\text{SO}_4\text{-KHS}_2\text{O}_7\text{-KHSO}_4$.

The characteristics of this and three other solvent mixtures are summarised in Table 2.

TABLE 2. *Some useful cryoscopic mixtures.*

Essential constituents (in addition to H_2SO_4)	Acidity (relative to pure acid)	Water affinity (relative to pure sulphuric acid)	Change in <i>i</i> -value associated with: *		
			transfer of a proton to the solute	extraction of a water molecule from the solute	addition of a water molecule to the solute
HS_2O_7^- , HSO_4^- ...	less	greater	+1	0	0
$\text{H}_2\text{S}_2\text{O}_7$, HS_2O_7^- ...	greater	greater	0	-1	+1
H_3SO_4^+ †	greater	similar	-1	0	+1
H_3SO_4^+ , † H_3O^+ ...	greater	less	-1	0	0

* The contribution from the solute species is excluded. Thus, *e.g.*, to determine the *i*-value for a solute to which a proton is added and from which a water molecule is extracted, add the values appropriate to the solvent mixture in the fourth and fifth columns; and add 1 for the solute fragment.

† Produced by the reaction $\text{H}_3\text{BO}_3 + 3\text{SO}_3 + 2\text{H}_2\text{SO}_4 \longrightarrow \text{H}_3\text{SO}_4^+ + \text{B}(\text{HSO}_4)_4^-$ (see reference 11).

Gillespie's fundamental work on the cryoscopy of sulphuric acid is the basis of all four solvent mixtures, but the application of this knowledge to the examination of solutes appears to be new. The first mixture has been successfully used in studying the behaviour of certain phenols in sulphuric acid,¹² and the third and fourth have been of value in a

¹¹ Flowers, Gillespie, and Oubridge, *J.*, 1956, 1925.

¹² Leisten, unpublished experiments.

study of nitriles.¹³ The second has not yet been used. (It could be applied in the present problem to prove that glutaric anhydride does not exist as a polyacid base, a possibility that was rejected in an earlier section by analogy alone.) An examination of Table 2 will suggest that the four solutions are complementary. Together they form a versatile and powerful addition to the cryoscopic method. The solutions also have potentialities in the field of reaction mechanisms.

The Anhydride-Acidium Ion Equilibrium.—The conclusion that the six-membered ring has a greater tendency to split in sulphuric acid than the five-membered ring is not unexpected: but no explanation is offered for the fact that succinic anhydride is a stronger base than phthalic and maleic anhydrides, although it is probably significant that in the last two the carbonyl groups are conjugated. One aspect of the results requires comment. The constitution of sulphuric acid has had much recent attention and in matters of detail is still under discussion.^{7,14} Sulphuric acid gives rise to a number of dissociation products, of which the hydroxonium ion is certainly one, and any method of determining the concentration of the hydroxonium ion in sulphuric acid and sulphuric acid solutions that is independent of theories of self-dissociation has potential value for the study of this system. Now in the case of phthalic, succinic, and maleic anhydride, it has been shown that the ratio [acidium ion]/[anhydride] changes sharply in the region of 100% sulphuric acid. From the equilibrium (1) this ratio must be proportional to the hydroxonium-ion concentration:

$$[\text{H}_3\text{O}^+] = K \frac{[\text{acidium ion}]}{[\text{anhydride}]}$$

By measuring the ratio of acidium ion to anhydride concentration we can in principle determine the variation of the hydroxonium-ion concentration in the important region around 100% sulphuric acid.

It was considered unprofitable to use the cryoscopic results for this purpose. One reason is that the necessary computations require a knowledge of the position of equilibrium (1), which was the very problem under investigation. Fortunately phthalic anhydride in sulphuric acid absorbs at longer wavelengths in the near ultraviolet region than does the phthalic acidium ion. This gives the prospect of a method of analysis which is independent of the concentrations of other species and of the values of self-dissociation constants, and which has the further advantage that the anhydride can be used in indicator concentrations. Further work is in progress.

Experimental.—The materials were carefully purified and melted sharply. The cryoscopic method has been previously described.¹⁵

The writer thanks Mr. J. R. Brayford and Mr. M. C. W. Cottrill for carrying out the experiments 1 and 2, and 8 and 9, respectively.

THE UNIVERSITY, SHEFFIELD, 10.

[Received, November 18th, 1960.]

¹³ Leisten and Wright, unpublished experiments.

¹⁴ Wyatt, *Trans. Faraday Soc.*, in the press.

¹⁵ Leisten, *J.*, 1956, 1572.