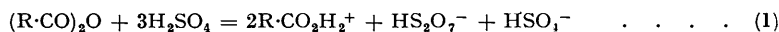


121. *Solutions in Sulphuric Acid. Part XVIII.* A Conductometric Investigation of the Ionisation of some Carboxylic Acid Anhydrides.*

By R. FLOWERS, R. J. GILLESPIE, and S. WASIF.

The electrical conductivities of dilute solutions of acetic, benzoic, succinic, and phthalic anhydrides in sulphuric acid, and of acetic and benzoic acids in dilute oleum, have been investigated. The results have been correlated with Leisten's recent cryoscopic measurements,¹ some older cryoscopic work, and the results of our own new measurements of the freezing-point depression produced by phthalic anhydride in sulphuric acid. Our results support Leisten's conclusion that acetic and benzoic anhydrides ionise completely according to equation (1) and also show that succinic and phthalic anhydrides are incompletely ionised.

LEISTEN¹ has recently concluded, from cryoscopic measurements, that acetic anhydride and benzoic anhydride ionise in sulphuric acid according to equation (1)



to form the corresponding carboxylic acidium ions and not according to equation (2) to form a carboxylic acidium ion and an acyl ion as previously suggested by Gillespie.²

This paper presents the results of conductivity measurements on solutions of acetic, benzoic, succinic, and phthalic anhydrides in 100% sulphuric acid and of acetic and benzoic acids in oleum. These results support Leisten's conclusion that acetic and benzoic anhydrides ionise according to equation (1) by removing water from the solvent to form acidium ions and that acyl ions are not formed in detectable amounts. Our results also

* Part XVII, *J.*, 1956, 80.

¹ Leisten, *J.*, 1955, 298.

² Part VIII, Gillespie, *J.*, 1950, 2997.

show that the ionisation of succinic and phthalic anhydrides, whose nature has not yet been clearly established, is incomplete.

Specific conductances of solutions of the anhydrides in 100% sulphuric acid are given in Table 1.

TABLE 1. *Specific conductances of acetic, benzoic, succinic, and phthalic anhydride solutions at 25°.*

Acetic anhydride		Acetic anhydride		Benzoic anhydride		Benzoic anhydride	
<i>c</i> (M)	100κ	<i>c</i> (M)	100κ	<i>c</i> (M)	100κ	<i>c</i> (M)	100κ
0.0000	1.043	0.0000	1.043	0.0000	1.043	0.0000	1.043
0.0229	1.125	0.0108	1.062	0.0236	1.117	0.0090	1.058
0.0391	1.242	0.0384	1.195	0.0388	1.216	0.0407	1.233
0.0570	1.386	0.0669	1.421	0.0684	1.456	0.0561	1.354
0.0757	1.559	0.0884	1.624	0.0912	1.645	0.0824	1.571
0.0931	1.693	0.1114	1.818	0.1330	1.974	0.1070	1.771
0.1160	1.888	0.1401	2.055	0.1701	2.238		
0.1390	2.074	0.1703	2.288	0.2229	2.560		
Succinic anhydride		Succinic anhydride		Phthalic anhydride		Phthalic anhydride	
<i>c</i> (M)	100κ	<i>c</i> (M)	100κ	<i>c</i> (M)	100κ	<i>c</i> (M)	100κ
0.0000	1.043	0.0000	1.043	0.0000	1.043	0.0000	1.043
0.0122	1.067	0.0314	1.151	0.0124	1.046	0.0112	1.044
0.0438	1.188	0.0763	1.352	0.0465	1.057	0.0462	1.052
0.0694	1.297	0.1036	1.463	0.0979	1.080	0.0922	1.070
0.1051	1.441	0.1557	1.647	0.1619	1.114	0.1382	1.091
0.1498	1.598	0.2205	1.837	0.2266	1.150	0.2231	1.136
0.2194	1.803	0.2963	2.020	0.2936	1.188	0.3090	1.182
0.2762	1.944			0.3892	1.240	0.3929	1.226

The specific conductances of acetic anhydride solutions are compared with those of acetic acid [which exists as the mono(hydrogen sulphate)] and potassium sulphate [which exists as the di(hydrogen sulphate)] in Fig. 1, and the specific conductances of solutions of benzoic anhydride are compared with those of benzoic acid and potassium sulphate in Fig. 2. In Fig. 3 the specific conductances of solutions of succinic anhydride and phthalic anhydride are compared with those of the strong electrolyte acetic acid, the weak electrolytes *p*-nitrotoluene and dichloroacetic acid, and the non-electrolyte sulphuryl chloride. The molar conductances of all four anhydrides are compared with those of nitric acid and potassium sulphate [existing as their di(hydrogen sulphates)] and acetic acid and benzoic acid [existing as their mono(hydrogen sulphates)] in Table 2. The conductivities of the comparison electrolytes given in Figs. 1—3 and Table 2 have been taken from Part XII³ and from some additional new measurements at the lower concentrations.

TABLE 2. *Comparison of the molar conductances of acetic, benzoic, succinic, and phthalic anhydrides with some other electrolytes.*

Electrolyte	Molarity			Electrolyte	Molarity		
	0.05	0.10	0.15		0.05	0.10	0.15
Nitric acid {(NO ₂ ⁺)(H ₂ O ⁺)(HSO ₄ ⁻) ₂ }	306	229	197	Acetic acid {(CH ₃ ·CO ₂ H ₂ ⁺)(HSO ₄ ⁻)}	244	156	129
Potassium sulphate {(K ⁺) ₂ (HSO ₄ ⁻) ₂ }	312	238	204	Benzoic acid {(Ph·CO ₂ H ₂ ⁺)(HSO ₄ ⁻)}	246	158	130
Acetic anhydride	258	172	143	Succinic anhydride	244	142	107
Benzoic anhydride	260	173	140	Phthalic anhydride	212	108	74

Conductivities of Acetic and Benzoic Anhydrides in Sulphuric Acid.—The conductivities of solutions of acetic and benzoic anhydrides are much closer to those of solutions of a mono(hydrogen sulphate) than a di(hydrogen sulphate). They are therefore consistent with ionisation according to equation (1) and not equation (2). That the conductivities are actually a little greater than for a mono(hydrogen sulphate) is to be expected for ionisation according to equation (1), since the hydrogen disulphate ion that is formed will undergo a small amount of solvolysis⁴ according to equation (3) and hence the hydrogen



³ Part XII, Gillespie and Wasif, *J.*, 1953, 221.

⁴ Part IV, Gillespie, *J.*, 1950, 2516.

FIG. 1. Comparison of the specific conductances of acetic anhydride and other electrolytes.

- A, K_2SO_4
- B, $(CH_3 \cdot CO)_2O$
- C, $CH_3 \cdot CO_2H$

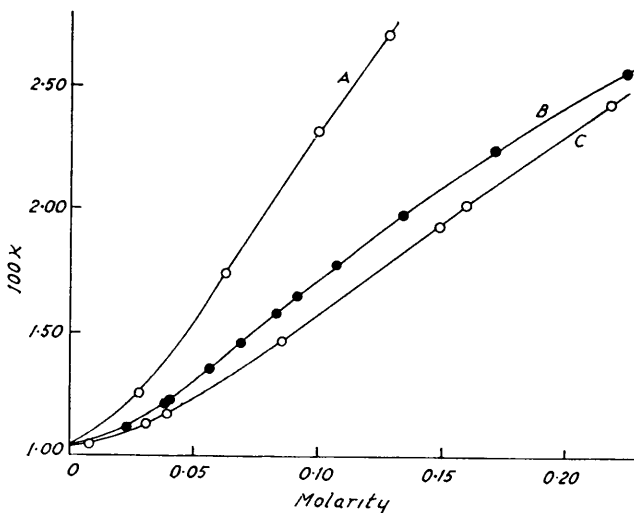
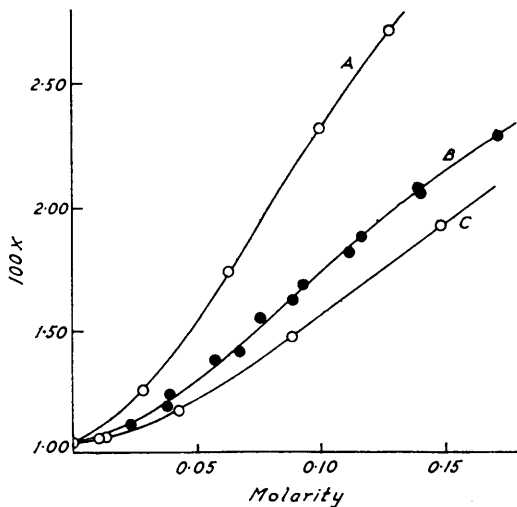
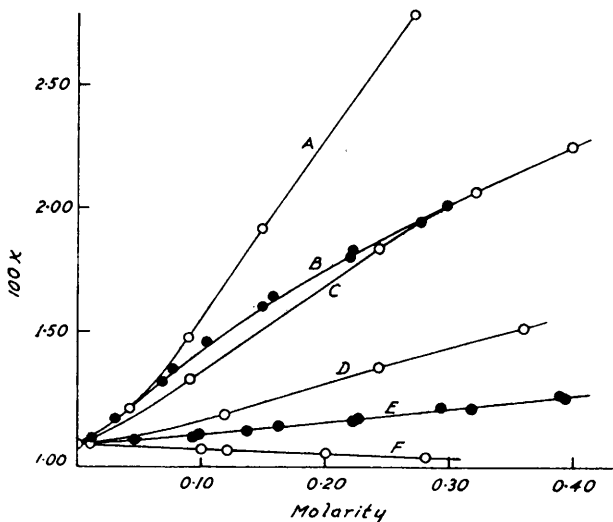


FIG. 2. Comparison of the specific conductances of benzoic anhydride and some other electrolytes.

- A, K_2SO_4
- B, $(Ph \cdot CO)_2O$
- C, $Ph \cdot CO_2H$

FIG. 3. Comparison of the specific conductances of succinic and phthalic anhydrides and some other electrolytes.

- A, $Me \cdot CO_2H$
- B, $\begin{array}{c} CH_2 \cdot CO \\ | \\ CH_2 \cdot CO \end{array} \begin{array}{c} O \\ \diagup \end{array}$
- C, $CH_3 \cdot \text{C}_6\text{H}_4 \cdot NO_2$
- D, $CHCl_2 \cdot CO_2H$
- E, $\begin{array}{c} CO \\ \diagup \end{array} \begin{array}{c} O \\ \diagdown \end{array}$
- F, SO_2Cl_2



sulphate ion concentration will be slightly increased resulting in a slightly greater conductivity. From the equilibrium constant for the above reaction, $K_b[\text{HS}_2\text{O}_7^-] = 0.008 \text{ mole kg.}^{-1}$, it may be shown that at 10° the HS_2O_7^- ion is solvolysed to the extent of approximately 12% in a 0.1M-solution. The value of the equilibrium constant is not known at 25° , but it does not appear unreasonable that the specific conductivities of acetic and benzoic anhydrides at this concentration exceed those of a monohydrogen sulphate by approximately 10%.

Conductivities of Acetic and Benzoic Acids in Dilute Oleums.—The conductivities of solutions of acetic and benzoic acids in dilute oleums were measured. The results are given in Table 3 and Fig. 4. The specific conductance decreases on the addition of acetic or benzoic acid to an oleum, passes through a minimum and then begins to rise again before

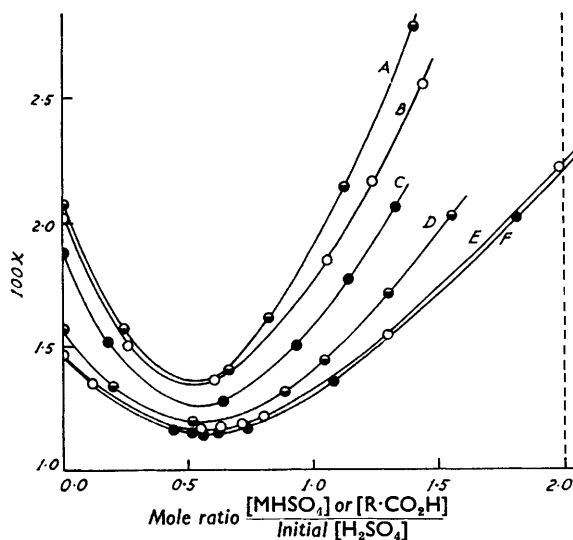


FIG. 4. Specific conductances of acetic and benzoic acids and ammonium and potassium hydrogen sulphates in oleum solutions.

	Initial $\text{H}_2\text{S}_2\text{O}_7$ concn.
A, NH_4HSO_4	0.2668m
B, $\text{Me}\cdot\text{CO}_2\text{H}$	0.2387m
C, $\text{Ph}\cdot\text{CO}_2\text{H}$	0.1961m
D, KHSO_4	0.1177m
E, $\text{Me}\cdot\text{CO}_2\text{H}$	0.0937m
F, $\text{Ph}\cdot\text{CO}_2\text{H}$	0.0951m

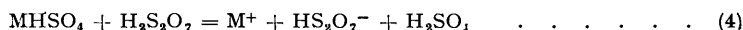
one mole of carboxylic acid has been added for each mole of disulphuric acid originally present, and continues to rise after this composition has been reached.

TABLE 3. Specific conductances of solutions of acetic and benzoic acids in dilute oleums at 25° .

Acetic acid						Benzoic acid					
<i>m</i>	Mole ratio	100κ	<i>m</i>	Mole ratio	100κ	<i>m</i>	Mole ratio	100κ	<i>m</i>	Mole ratio	100κ
Initial $\text{H}_2\text{S}_2\text{O}_7$ concn. = 0.0937m			Initial $\text{H}_2\text{S}_2\text{O}_7$ concn. = 0.2387m			Initial $\text{H}_2\text{S}_2\text{O}_7$ concn. = 0.0951m			Initial $\text{H}_2\text{S}_2\text{O}_7$ concn. = 0.1961m		
0.0000	0.0000	1.462	0.0000	0.0000	2.018	0.0000	0.0000	1.468	0.0000	0.0000	1.875
0.0116	0.1239	1.350	0.0626	0.2623	1.504	0.0425	0.4466	1.160	0.0354	0.1803	1.518
0.0517	0.5519	1.166	0.1444	0.6051	1.366	0.0489	0.5142	1.149	0.1268	0.6466	1.277
0.0591	0.6306	1.170	0.2520	1.0557	1.847	0.0524	0.5514	1.147	0.1832	0.9342	1.502
0.0666	0.7108	1.184	0.2950	1.2359	2.164	0.0591	0.6219	1.150	0.2233	1.1387	1.770
0.0753	0.8032	1.212	0.3441	1.4416	2.558	0.0695	0.7304	1.172	0.2606	1.3289	2.064
0.1219	1.3010	1.546				0.1030	1.0825	1.358			
0.1855	1.9793	2.215				0.1727	1.8156	2.020			

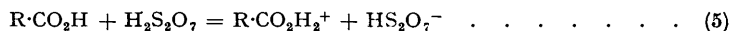
* Stoichiometric mole ratio = moles of solute : initial moles of $\text{H}_2\text{S}_2\text{O}_7$.

The conductivities of solutions of ammonium and potassium hydrogen sulphate in oleum⁵ are also given in Fig. 4 for comparison; the conductivities of these solutions are closely similar to those of acetic and benzoic acids in oleums of approximately the same initial concentration. Metal hydrogen sulphates ionise according to equation (4) and it



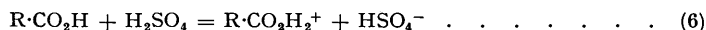
⁵ Part XIII, Gillespie and Wasif, *J.*, 1953, 964.

may be reasonably concluded that acetic and benzoic acids ionise in an analogous manner [eqn. (5)] and this agrees with Leisten's conclusions from his cryoscopic measurements.¹

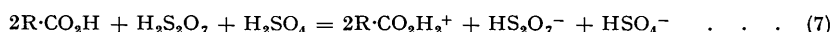


According to equation (5) the highly conducting $H_3SO_4^+$ ions resulting from the ionisation of the disulphuric acid are replaced by the poorly conducting carboxylic acidium ions and hence the conductivity decreases at first. Although the conductivity begins to increase before the stoichiometric mole ratio $R \cdot CO_2H : H_2S_2O_7 = 1 : 1$ is reached the actual value of the specific conductance at this composition is very small, certainly very much smaller than that of a mono(hydrogen sulphate) at the same concentration. This is consistent with equation (5) which indicates that at this composition the solution contains the electrolyte $R \cdot CO_2H_2^+, HS_2O_7^-$ both of whose ions have a very small mobility. The rise in the conductivity before this composition is reached can again be attributed to solvolysis of the hydrogen disulphate ion according to equation (3) which gives rise to a small amount of the highly conducting hydrogen sulphate ion.

Comparison of the Conductivities of Acetic and Benzoic Anhydrides in Sulphuric Acid with Acetic and Benzoic Acids in Dilute Oleums.—Further addition of acid up to, and beyond, the stoichiometric mole ratio $R \cdot CO_2H : H_2S_2O_7 = 2 : 1$ causes an increase in the

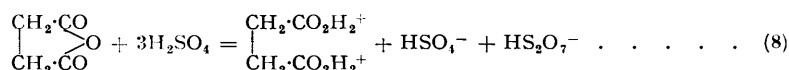


conductivity which may be attributed to the ionisation (6). At the composition corresponding to this mole ratio the overall reaction may be written

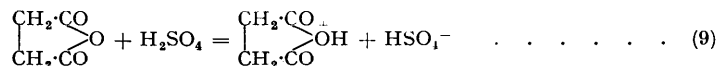


and comparison with equation (1) shows that a solution of a carboxylic acid in oleum having a composition corresponding to the mole ratio 2 : 1 should be identical with a solution of half the concentration of the corresponding anhydride in 100% sulphuric acid. That the conductivities of such solutions are in fact the same may be seen from the results given in Tables 1 and 3. Thus a solution of 0.1874m-acetic acid in an oleum whose initial concentration of disulphuric acid was 0.0937m had a specific conductance of 0.0224 ohm⁻¹ cm.⁻¹. This may be compared with the specific conductance of 0.0937m-acetic anhydride in 100% sulphuric acid which was 0.0220 ohm⁻¹ cm.⁻¹. Similarly 0.1902m-benzoic acid in an oleum whose initial concentration was 0.0951m had a specific conductance of 0.0220 ohm⁻¹ cm.⁻¹ compared with 0.0220 ohm⁻¹ cm.⁻¹ for 0.0951m-benzoic anhydride in 100% sulphuric acid.

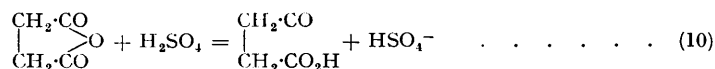
Succinic Anhydride.—The results of our measurements on succinic anhydride given in Tables 1 and 2 and in Fig. 3 show that it produces rather less than one hydrogen sulphate ion per molecule of anhydride. Its specific conductance is quite close to that of *p*-nitrotoluene, which has been shown by cryoscopic measurements to be approximately 70% ionised in a 0.1m solution.⁶ Its mode of ionisation cannot be unambiguously established on the basis of our conductivity measurements alone. Thus our observations are consistent with a partial ionisation according to an equation analogous to equation (1), *i.e.*, (8), or



equally with an incomplete simple protonation according to equation (9) or with the

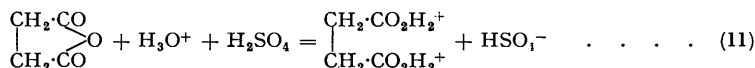


incomplete formation of an acyl ion [equation (10)] or with a combination of any two or all three of these ionisations.

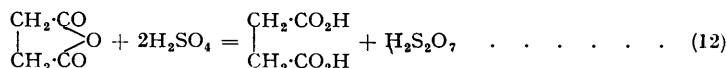


⁶ Part VII, Gillespie, *J.*, 1950, 2542.

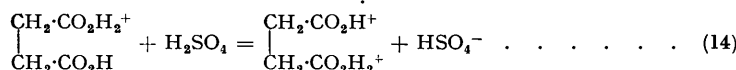
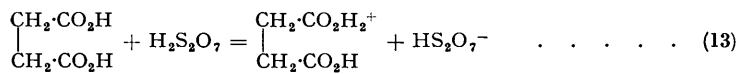
By means of cryoscopic measurements in slightly aqueous sulphuric acid, Oddo and Casalino ⁷ found that succinic anhydride had an *i*-factor increasing from approximately 1.2 to 1.8 with increasing concentration of the anhydride. This suggests that equation (8) most nearly represents the ionisation of succinic anhydride, the low *i*-factors and their dependence on concentration being due to the reaction of the anhydride with the water initially present in the solvent [equation (11)].



It has been shown by cryoscopic measurements ^{7,8,9} that succinic acid has an *i*-factor of approximately 2.5, which suggests, although it does not prove, that it undergoes simple protonation, the second stage of ionisation being incomplete; this is consistent with our conclusion that if, as seems likely, the ionisation of succinic anhydride occurs according to equation (8), it is incomplete. It may be regarded as occurring in three stages: (a) the removal of water from the solvent to form the acid [eqn. (12)], (b) monoprotection of the



acid by disulphuric acid, which is essentially complete [eqn. (13)], (c) incomplete diprotection of the acid by the solvent [eqn. (14)].



Further cryoscopic and conductivity measurements are, however, needed before any firm conclusions concerning the ionisation of succinic anhydride can be reached.

Phthalic Anhydride.—Our results on phthalic anhydride (Tables 1 and 2, Fig. 3) indicate that it is considerably less ionised or, more exactly, produces considerably less hydrogen sulphate ion, than succinic anhydride. It is probably ionised only to the extent of 10% or less. Again we cannot decide on the mode of ionisation on the basis of conductivity results alone.

In order to obtain some further information we measured freezing-point depressions produced by phthalic anhydride in sulphuric acid, using sulphuric acid containing a little potassium sulphate to repress the autoprotolysis; the results are given in Table 4. Column

TABLE 4. *Freezing-points of solutions of phthalic anhydride in sulphuric acid.*

m_2	F. p.	$\Delta\theta$	ν'	m_2	F. p.	$\Delta\theta$	ν
Molality of K_2SO_4 (m_3) = 0.0656				Molality of K_2SO_4 (m_3) = 0.0544			
0.0000	8.875°	—	—	0.0000	9.180°	—	—
0.0372	8.645	0.230	1.03	0.0115	9.100	0.080	1.15
0.0677	8.413	0.462	1.14	0.0293	8.975	0.205	1.16
0.0880	8.268	0.607	1.15	0.0489	8.832	0.348	1.18
0.1080	8.134	0.741	1.14	0.0675	8.714	0.464	1.14

4 of this table gives ν' , the approximate value of the number of moles of particles produced in solution by one mole of the solute, calculated by means of the equation $\Delta\theta/m_2 = 6.12 \nu' (1 - 0.0039\theta)[1 + (m_2 - 6m_3)/2m_1]$, where m_1 and m_2 are the molalities of sulphuric acid and solute respectively, which is an extended and slightly modified form of equation 2 of Part XIX ¹⁰ which allows for the presence of the second electrolyte potassium sulphate ($\nu_3 = 4$, $s_3 = 1$. Cf. equation 4 of Part I ¹¹). The mean value of ν' is 1.15,

⁷ Oddo and Casalino, *Gazzetta*, 1917, **47**, II, 232.

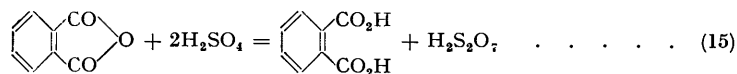
⁸ Wiles, *J.*, 1953, 986

⁹ Hantzsch, *Z. phys. Chem.*, 1907, **61**, A, 257.

¹⁰ Part XIX, Flowers, Gillespie, and Oubridge, *J.*, 1956, in the press.

¹¹ Part I, Gillespie, Hughes, and Ingold, *J.*, 1950, 2473.

which is consistent with the small percentage ionisation found from the conductivity measurements. Both the conductivity and the cryoscopic measurements are, however, consistent with very incomplete ionisation according to equations analogous to (8), (9), or (10). Earlier work provides additional information. Hantzsch concluded from the results of both cryoscopic and conductivity measurements that phthalic anhydride is a non-electrolyte, but this was disputed by Oddo and Casalino who found that in slightly aqueous sulphuric acid phthalic anhydride had an *i*-factor which increased with increasing concentration from 0.9 to 1.2. Leisten¹ has reported an unpublished observation of Brayford and Wyatt that in sulphuric acid containing a little water phthalic anhydride gives a molar freezing-point depression that is considerably less than that for a non-electrolyte. Thus the work of Oddo and Casalino and of Brayford and Wyatt suggests that phthalic anhydride removes water from the solvent to form phthalic acid, just as succinic anhydride probably gives succinic acid, *i.e.*, that it ionises in a manner analogous to that represented by equations (8) and (11). The degree of ionisation is certainly much smaller than that of succinic anhydride, however, and even the formation of the acid must itself be very incomplete :



Phthalic anhydride must exist in sulphuric acid largely in a non-ionised form. We may note, however, that Newman and Deno¹² obtained an *i*-factor of 1.8 for naphthalene-1 : 8-dicarboxylic anhydride and claimed that the anhydride was completely recovered on dilution of the solution with water; this suggests that it ionises as a simple base as represented by equation (9).

Further work is needed on phthalic anhydride and similar anhydrides before any definite conclusions concerning their ionisation can be reached. Although acyl ions are not formed in appreciable amounts by acetic and benzoic anhydrides, the possibility of their formation by succinic and phthalic anhydrides cannot be ruled out. In cases such as phthalic anhydride, where the removal of water from the solvent to form the acid takes place only incompletely, the extent of the reaction may depend largely on the composition of the solvent, and may vary considerably from slightly aqueous acids to dilute oleum and ionisation at these compositions should be investigated.

EXPERIMENTAL

Apparatus and Procedure.—The technique and apparatus for cryoscopic measurements have been described.¹¹ Conductivity measurements were made at 25° with an improved form of the apparatus used by Gillespie and Wasif¹³ which will be fully described later.¹⁴

Materials.—Sulphuric acid and oleums were prepared as described by Gillespie and Oubridge.¹⁵ 100% Sulphuric acid was obtained by adding aqueous acid to a dilute oleum until its conductivity was a minimum (the composition of "minimum conductivity" acid differs very slightly from 100% H₂SO₄,^{14,16} but the difference is negligible for the present work).

"AnalaR" acetic anhydride was distilled and the middle fraction (b. p. 137—138°) collected. Benzoic anhydride, twice recrystallised from benzene-light petroleum (b. p. 40—60°) and dried *in vacuo* at 100° had m. p. 41.5°. Succinic anhydride, crystallised from acetic anhydride, washed with dry ether, and dried *in vacuo* at 100°, had m. p. 119.5°. Phthalic anhydride, crystallised from chloroform and dried *in vacuo* at 100°, had m. p. 132°. "AnalaR" acetic acid was purified by fractional freezing. "AnalaR" benzoic acid, recrystallised from water and dried *in vacuo* at 100°, had m. p. 122°.

We thank the Ministry of Education for a scholarship (to R. F.).

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1.

[Received, September 8th, 1955.]

¹² Newman and Deno, *J. Amer. Chem. Soc.*, 1951, **73**, 3651.

¹³ Part IX, Gillespie and Wasif, *J.*, 1953, 204.

¹⁴ Gillespie and Solomons, to be published.

¹⁵ Part XVII, Gillespie and Oubridge, *J.*, 1956, 80.

¹⁶ Kunzler and Giaouque, *J. Amer. Chem. Soc.*, 1952, **74**, 804.