563. *Solutions in Sulphuric Acid. Part XXV.* Cryoscopic Measurements on Some Phenols.*

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It is concluded from cryoscopic measurements that when dissolved in sulphuric acid at room temperature phenol and *p*-cresol are rapidly sulphonated and esterified, *o*- and *m*-nitrophenol are rapidly esterified but not sulphonated, *p*-nitrophenol is partly esterified and partly sulphonated, and 2 : 4-dinitrophenol is partially protonated.

CRYOSCOPIC and conductometric measurements have shown that methyl and ethyl alcohols give stable solutions of methyl and ethyl hydrogen sulphates respectively when dissolved in sulphuric acid:

$$ROH + 2H_2SO_4 = RHSO_4 + H_3O^+ + HSO_4^-$$

Many other alcohols show a similar initial behaviour but the solutions of their hydrogen sulphates are not stable; oxidation and other reactions occur.[1] Some aryl-substituted alcohols give the corresponding carbonium ion, *e.g.*,

$$Ph_3C{\cdot}OH + 2H_2SO_4 = Ph_3C^+ + H_3O^+ + 2HSO_4^-$$

With the exception of picric acid, which cryoscopy has shown to be a non-electrolyte,[2] no previous cryoscopic or conductometric measurements have been made on solutions of phenols in sulphuric acid. The most probable of the possible modes of ionisation or reaction that phenols might undergo in sulphuric acid and the corresponding values of ν,

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* Part XXIV, *J.*, 1958, 667.

[1] See, *e.g.*, Gillespie and Leisten, *Quart. Rev.*, 1954, **8**, 40.

[2] Brayford and Wyatt, *J.*, 1955, 3453; Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1933, **55**, 1900.

the total number of moles of ions and molecules produced by one mole of the phenol, would appear to be the following:

(1) Protonation

$$C_6H_5{\cdot}OH + H_2SO_4 = C_6H_5{\cdot}OH_2^+ + HSO_4^- \quad \nu = 2$$

(2) Esterification

$$C_6H_5{\cdot}OH + 2H_2SO_4 = C_6H_5{\cdot}HSO_4 + HSO_4^- + H_3O^+ \quad \nu = 3$$

(3) (*a*) Mono-sulphonation

$$C_6H_5{\cdot}OH + 2H_2SO_4 = HSO_3{\cdot}C_6H_4{\cdot}OH + HSO_4^- + H_3O^+ \quad \nu = 3$$

(*b*) Di-sulphonation

$$C_6H_5{\cdot}OH + 4H_2SO_4 = (HSO_3)_2C_6H_3{\cdot}OH + 2HSO_4^- + 2H_3O^+ \quad \nu = 5$$

(4) Carbonium-ion formation

$$C_6H_5{\cdot}OH + 2H_2SO_4 = C_6H_5^+ + 2HSO_4^- + H_3O^+ \quad \nu = 4$$

(5) Protonation and sulphonation

$$C_6H_5{\cdot}OH + 3H_2SO_4 = HSO_3{\cdot}C_6H_4{\cdot}OH_2^+ + 2HSO_4^- + H_3O^+ \quad \nu = 4$$

(6) Esterification and sulphonation

$$C_6H_5{\cdot}OH + 4H_2SO_4 = HSO_3{\cdot}C_6H_4{\cdot}HSO_4 + 2HSO_4^- + 2H_3O^+ \quad \nu = 5$$

Water is produced in all of these reactions except (1), and because it has a ν value of slightly less than 2 the observed ν values are expected, in these cases, to be slightly less than the integral values given above.[3]

Cryoscopic results for solutions of phenol, *p*-cresol, *o*-, *m*-, and *p*-nitrophenols, 2 : 4-dinitrophenol, and potassium *p*-nitrophenyl sulphate in sulphuric acid are given in the Table.

o- and *m*-Nitrophenol both give rather stable solutions whose freezing points decrease very slowly with time and have ν values of slightly less than 3. This suggests that either esterification (2) or mono-sulphonation (3*a*) occurs rapidly, *i.e.*, in the 10—15 minutes elapsing between the addition of the solute and the measurement of the freezing point of the solution, to give products which undergo little further reaction under the experimental conditions. Simple mono-sulphonation, which would leave an unchanged and unprotonated OH group, seems less likely than esterification. This is partly confirmed by the fact that the nitrophenol can be recovered by pouring the sulphuric acid solution on ice. Rapid hydrolysis of the phenyl hydrogen sulphate seems to be much more likely than rapid desulphonation under these conditions.

Phenol and *p*-cresol both give ν values of approximately 5, which suggests either esterification and sulphonation (6) or disulphonation (3*b*). Since we have concluded that *o*- and *m*-nitrophenol are esterified it seems reasonable to conclude that phenol and *p*-cresol are esterified and, in addition, sulphonated. The further very slow decrease in the freezing point is probably due to disulphonation.

The ν-values for *p*-nitrophenol increase from approximately 2·6 to 3·0 in a few hours and to approximately 4·0 in about 24 hr., thereafter showing only a very slight increase over a period of several days or more. *p*-Nitrophenol thus behaves rather differently from the *ortho*- and the *meta*-isomer. The initial reaction giving $\nu = 3{\cdot}0$ cannot be simply esterification since potassium *p*-nitrophenyl sulphate initially gives the expected $\nu = 3{\cdot}0$ which only increases to 3·3 during two days,

$$NO_2{\cdot}C_6H_4{\cdot}OSO_3K + H_2SO_4 = K^+ + HSO_4^- + NO_2{\cdot}C_6H_4{\cdot}OSO_3H$$

indicating that *p*-nitrophenyl hydrogen sulphate does not undergo any extensive further reaction in contrast to the product of the initial reaction of *p*-nitrophenol with sulphuric acid. It seems probable, therefore, that *p*-nitrophenol sulphonates more rapidly than the *ortho*- and the *meta*-isomer and this reaction thus competes with the esterification reaction producing a mixture of *p*-nitrobenzenesulphonic acid and *p*-nitrophenyl hydrogen sulphate. Any such mixture would give the initially observed ν-value of 3·0. The

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[3] Gillespie, *J.*, 1950, 2493.

p-nitrobenzenesulphonic acid then esterifies slowly and the value of ν increases correspondingly, while the *p*-nitrophenyl hydrogen sulphate remains essentially unchanged. If the mixture formed initially contained approximately equal amounts of the hydrogen sulphate and the sulphonic acid then the esterification of the sulphonic acid would cause the value of ν to increase to 4·0, as observed. The probably more rapid rate of sulphonation of *p*-nitrophenol is of interest. Because of the conjugation between the nitro- and the hydroxyl group in *p*-nitrophenol it seems probable that it is less extensively protonated than the *ortho*- and the *meta*-isomer and is therefore correspondingly less deactivated towards sulphonation.

Freezing points of solutions of 2 : 4-dinitrophenol change very slowly with time and the ν-value obtained is about 1·3. It seems most likely that it is a weak base, *i.e.*, is partially protonated (1), and also undergoes either very slow esterification or sulphonation, or both. 2 : 4 : 6-Trinitrophenol has been shown to be a stable non-electrolyte in sulphuric acid.[2]

EXPERIMENTAL

Apparatus.—The apparatus and general procedure for cryoscopy have been described.[4]

Materials.—Sulphuric acid, prepared as previously described,[5] was adjusted to maximum freezing point before each experiment. Phenol and *p*-cresol were twice redistilled and had

Time (hr.)	10^2m	F. p.	ν
	Phenol		
—	0·000	10·365°	—
—	1·440	10·106	4·61
—	2·449	9·831	4·71
—	3·955	9·408	4·73
—	5·453	8·976	4·75
—	7·265	8·446	4·76
—	8·149	8·213	4·72
0·0	10·078	7·684	4·68
30·0	10·078	7·614	—
—	0·000	10·365	—
—	3·085	9·670	4·64
—	6·929	8·568	4·71
—	8·683	8·054	4·73
—	11·146	7·374	4·69
	o-*Nitrophenol*		
—	0·000	10·365	—
—	3·451	9·927	2·81
—	5·916	9·513	2·84
—	8·618	9·044	2·87
—	14·243	8·020	2·92
—	16,889	7·546	2·92
—	0·000	10·365	—
—	4·173	9·829	2·74
—	5·596	9·588	2·79
—	9·447	8·911	2·83
—	10·556	8·715	2·86
—	12,609	8·346	2·88
—	13·921	8·125	2·87
—	0·000	10·365	—
0·0	5·391	9·631	2·76
168·0	5·391	9·575	2·92
	m-*Nitrophenol*		
—	0·000	10·365	—
—	4·080	9·820	2·84
—	7·515	9·232	2·87
—	11·071	8·617	2·87
—	13·081	8·251	2·89
—	15·214	7·892	2·87
—	0·000	10·365	—
—	3·573	9·558	2·89
—	6·434	9·186	2·88
—	8·820	8·754	2·92
—	11·380	8·321	2·90
—	13·760	7·918	2·88
0·0	16·310	7·510	2·85
24·0	16·310	7·483	2·88
—	0·000	10·365	—
—	3·066	10·006	2·74
—	5·078	9·657	2·83
—	8·349	9·092	2·87
—	10·451	8·717	2·88
—	12·916	8·239	2·94
0·0	14·891	7·957	3·01
21·0	14·891	7·953	3·01
	p-*Nitrophenol*		
—	0·000	10·365	—
0·18	8·644	9·160	2·63
0·43	8·644	9·154	2·64
1·90	8·644	9·107	2·74
3·22	8·644	9·017	2·90
4·1	8·644	8·964	3·00
5·0	8·644	8·796	3·32
24·5	8·644	8·415	4·05
27·7	8·644	8·372	4·15
96·0	8·644	8·340	4·19
428·0	8·644	8·332	4·21
—	0·000	10·365	—
0·13	6·619	9·497	—
2·95	6·619	9·468	2·66
5·60	6·619	9·311	3·05
20·8	6·619	8·933	3·86
313·0	6·619	8·967	3·91
	p-*Cresol*		
—	0·000	10·365°	—
—	1·586	10·016	5·16
—	3·218	9·542	5·10
—	5·531	8·868	5·00
0·0	7·007	8·458	4·91
96·0	7·007	8·399	5·04
	2 : 4-*Dinitrophenol*		
—	0·000	10·365	—
—	10·309	9·795	1·25
—	14·267	9·438	1·31
—	18·796	9·138	1·26
—	24·537	8·746	1·22
0·0	31·902	8·238	1·20
36·6	31·902	8·018	1·31
	Potassium p-*nitrophenyl sulphate*		
—	0·000	10·365	—
—	3·237	9·604	3·10
—	6·362	9·076	3·01
—	9·289	8·540	3·03
0·0	1·275	7·916	3·02
17·5	1·275	7·677	3·32
—	0·000	10·365	—
0·4	5·560	9·232	2·97
3·0	5·560	9·222	3·10
25·8	5·560	9·138	3·24
50·5	5·560	9·134	3·25

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[4] Gillespie, Hughes, and Ingold, *J.*, 1950, 2473.

[5] Gillespie and Oubridge, *J.*, 1956, 80.

b. p.s 179—181° and 203—205° respectively. *o*-Nitrophenol was recrystallised from alcohol-water and had m. p. 43·4—44·4°; *m*- and *p*-nitrophenol were recrystallised from dilute hydrochloric acid, m. p.s 95·0—95·5° and 112—113° respectively; 2 : 4-dinitrophenol was recrystallised from water, m. p. 112—112·5°. A sample of potassium *p*-nitrophenyl sulphate was kindly provided by Mr. C. A. Vernon.

Procedure.—In most cases, the solutions were not completely stable and their freezing points decreased slowly with time. However, except for *p*-nitrophenol this change was very slow and reasonably constant values of ν were obtained if the measurements were completed within a few hours. After a set of additions of solute the freezing point of the solution was followed over a period of time (often several days) to see if it eventually reached a constant value.

Calculations.—Values of ν, the number of moles of ions and molecules formed from one mole of the solute, were calculated from the equation

$$\nu = \theta\,(1 + 0{\cdot}002\theta)/(6{\cdot}12m - m_d/m)$$

where θ is the freezing-point depression calculated from the freezing point of hypothetical undissociated sulphuric acid (10·615°), m is the molality of the solute, and m_d is the molality of the products of the self-dissociation of the solvent.[6]

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[*Received, March* 31*st*, 1958;
Revised, April 28*th*, 1959.]

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[6] Bass, Gillespie, and Robinson, Part XXVII, to be published.