CCLXXII.—*The Solubility of the Aldehydobenzoic Acids.*

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THE investigation of the physical properties of this group of substances is of interest in view of the undoubtedly tautomeric behaviour of the ortho-compound. Not only do substitution products of this acid give two series of esters, but the relation of the dissociation constant of the acid itself to those of analogous acids shows that the free acid is largely present in water in an isomeric form (Wegscheider, *Sitzungsber. Akad. Wiss. Wien*, 1905, **104**, IIb, 765). We have therefore examined the solubility of the three isomerides in water and benzene. Although certain peculiarities of these substances prevent a complete investigation, the results are worth recording.

Preparation of Materials.—The *o*-aldehydo-acid was prepared by the method of Graebe and Trümpy (*Ber.*, 1898, **31**, 369) by the oxidation of naphthalene to phthalonic acid,* and the elimination of carbon dioxide from the latter by treatment with sodium bisulphite. The yield in the second stage was found to be increased if the bisulphite compound before acidification was heated for an hour in an oven at 120°, instead of being evaporated down on a water-bath as recommended by Graebe and Trümpy. The meta-acid was prepared by several methods: by the partial oxidation of *m*-phthalaldehyde with bromine water (Simonis, *Ber.*, 1912, **45**, 1584), from *m*-toluidine

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* This acid is remarkable for its great solubility in water as compared with organic solvents. At 15°, 100 grams of water will dissolve 115 grams of the acid: 100 grams of chloroform, only 2 grams.

through *m*-toluonitrile and its benzylidene chloride (Reinglass, *Ber.*, 1891, **24**, 2423), and from *m*-nitrobenzaldehyde through the cyanide. The para-acid was made by the direct oxidation of *p*-toluic acid with manganese dioxide or with chromic acid. None of these methods was found to give a satisfactory yield; and subsequently all three isomerides were prepared with remarkable ease by a method suggested by Dr. W. Davies, which will be described in detail in another paper. This consists in the chlorination (up to the benzylidene chloride) of the toluoyl chloride, and the complete hydrolysis of the product.

There is considerable uncertainty in the literature as to the melting points of all these acids. The ortho is stated to melt at 97°. This was found to be the case when it was recrystallised from water, but by solution in benzene and precipitation with light petroleum (b. p. 40—60°) the melting point was raised to 100·5° (corr.). The meta-acid melts according to Reinglass (*loc. cit.*) at 164—166°; according to Simonis (*loc. cit.*) at 175°. We found all pure specimens, however made, to melt at 175° (corr.). Reinglass states that the para-acid begins to melt at 285°, whilst Löw (*Annalen*, 1885, **231**, 366) gives the m. p. as 246°, and Simonis as 256°. We found that the high melting point was obtained when the acid had been dried in an oven at about 110° for an hour, but the low one when it had been dried in a desiccator at the ordinary temperature. This suggests that the high melting point may be caused by atmospheric oxidation to terephthalic acid. The acid was therefore separated by extraction with chloroform, and the melting point determined in tubes from which air had been exhausted. Under these conditions the substance, whatever its method of preparation, melted at 248—250° (corr.).

Determination of Solubility.—This was carried out in the usual manner, by enclosing weighed quantities of the acid and the solvent in small tubes, which were then sealed. The stable phase in contact with the solution is always the solid; but the ortho-acid, like salicylic acid, gives with water a metastable, two-liquid curve, which at its nearest point is only 4° below the liquid–solid curve. In benzene, the solubilities could not be measured over the whole range, except with the ortho-acid, which offered no difficulties. The meta-acid gave satisfactory results at higher concentrations (above 40 per cent.), but from more dilute solutions a small quantity of a solid separated, which did not dissolve even at the melting point of the acid (175°). At the higher concentrations, this substance was no doubt also formed, but remained in solution. We were not able to determine the nature of this product. It was not *iso*phthalic acid (formed by the oxidation of the aldehyde by the air in the tube), since (1) it was formed to the same extent when the tubes were filled with carbon dioxide, and (2) it was not produced in the experiments with water, although *iso*-

phthalic acid is almost insoluble in water. It was not an impurity in the original acid, because it was formed, on heating with benzene above 100°, from a sample of the acid which had been dissolved out of a large quantity by benzene at a lower temperature. It must therefore be produced by some reaction of the acid, possibly of the nature of a benzoin condensation. A quantity of the pure acid was heated with benzene at 140° for five hours in an atmosphere of carbon dioxide. From the product the unchanged acid (which is by far the larger part) was removed by extraction with benzene in a Soxhlet apparatus. The insoluble remainder did not melt at 280°, but it could not be obtained in a state pure enough for analysis.

With the para-acid in benzene, where the solubilities, owing to the high melting point, are very small, successive determinations with the same tube gave increasing values of the solution temperature, owing, no doubt, to the occurrence of a similar reaction; the values given in the table are those of the first determination in each case, but not much reliance can be placed on them.

The results are given in Tables I and II, and are plotted in Fig. 1 (S–L solid–liquid equilibrium: L_1–L_2 two liquids, the concentrations in both cases being expressed in weights per cent.

TABLE I.

Solubility in Water.

Ortho.			Meta.		Para.	
Weight per cent.	Temp. S–L.	Temp. L_1–L_2.	Weight per cent.	Temp. S–L.	Weight per cent.	Temp. S–L.
100	100·5°	—	100	175·0°	100	250·0°
91·66	75·0	—	86·76	140·0	79·40	191·5
87·20	64·5	—	81·88	132·9	49·60	181·5
81·50	58·1	—	70·72	121·5	32·46	158·9
59·48	53·2	39·2°	58·87	116·6	19·08	150·9
40·83	51·8	44·0	49·45	114·6	10·24	142·3
29·20	49·9	45·75	40·28	113·5		
20·00	48·92	43·3	29·97	112·3		
9·38	46·1	21·1	19·87	110·7		
			11·22	107·5		
			4·94	99·7		

TABLE II.

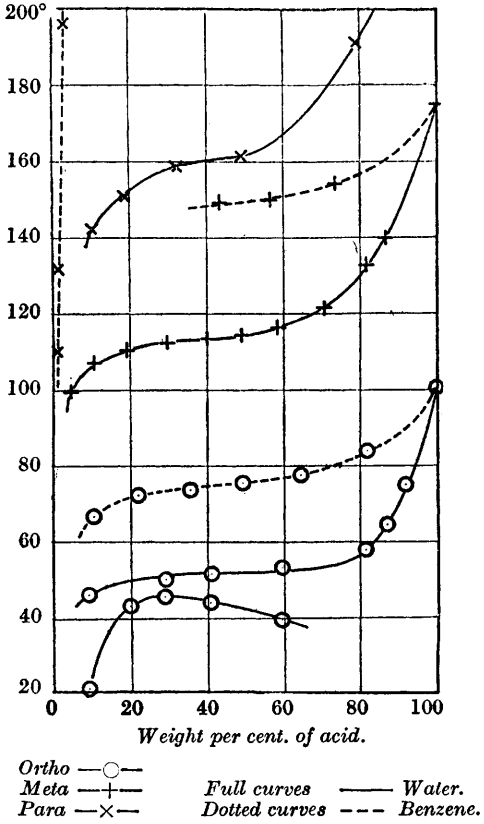
Solubility in Benzene.

Ortho.		Meta.		Para.	
Weight per cent.	Temp.	Weight per cent.	Temp.	Weight per cent.	Temp.
100	100·5°	100	175·0°	100	250·0°
81·84	84·0	73·36	154·5	2·40	196·0
64·09	77·8	56·98	149·9	1·41	131·9
49·50	75·7	43·84	149·7	0·96	110·0
35·88	73·9				
21·87	72·3				
10·16	66·7				

Discussion of Results.—The solubility curves show that this group of isomerides is undoubtedly abnormal, and also that it has peculiarities of its own. The behaviour with water is in many ways unusual.

FIG. 1.

Solubility of aldehydobenzoic acids in water and benzene.



We find, as we do with the hydroxybenzoic and the hydroxytoluic acids (T., 1921, **119**, 979), that the ortho-acid alone is capable of forming two liquid layers, although only (as with salicylic acid) in the metastable region. Flaschner and Rankin (*Sitzungsber. Akad. Wiss. Wien*, 1909, **118**, IIb, 695) found in such cases an empirical relation between the slope of the curve (*dc*/*dt*, the increase in weight per cent. at the flattest part of the curve for 1° rise in temperature) and the smallest distance in degrees between the two curves, the product of these two factors being approximately constant. In twelve examples of substituted benzoic acids which they quote, this product E only varies between 189 and 520, the mean value being 330. *o*-Aldehydobenzoic acid gives the abnormally low value for E of 76. This may be connected with the tautomeric behaviour of the acid, but the uncertainty makes it impossible to use this quantity to calculate the critical solution temperatures of the other two acids. The curve for the meta-acid is very nearly as flat as that for the ortho, and an attempt was made to supercool the solution to the point of separation into two liquid layers; but this point could not be reached. The values of dc/dt, the slope of the curve at its flattest, are: ortho 19, meta 15, para 3·4. From the behaviour of other acids of the abnormal type we should expect the meta- and para-curves to have a similar and considerable slope (a small value of dc/dt), and the ortho to be much flatter; if the acids were normal, all three curves should have about the same inclination.

The heats of solution in benzene were calculated from the solubility curves, as far as these go, and gave the following results (Table III).

TABLE III.

Nominal Heats of Solution in Benzene.

Mean mols. per cent.	Heat in kgr.-cal.		Mean mols. per cent.	Heat in kgr.-cal.	
	Ortho.	Meta.		Ortho.	Meta.
95	3·97	7·05	45	32·0	39·7
85	5·83	7·68	35	57·9	128·1
75	8·34	8·68	25	74·9	—
65	12·5	16·1	17·5	62·4	—
55	17·3	22·6	12·5	32·0	—

As we should expect, the increase in the heat of solution is greater for the para-acid; but the difference is unusually small, and the increase for the ortho-acid is much larger than has been observed for any other ortho-substituted benzoic acid in benzene.

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