

BORIC ACID AND THE O-HYDROXY-CARBONYL COMPOUNDS; MELTING POINT CURVES

It is well-known that boric acid exerts remarkable effects on the optical rotation and electrical conductivity of aqueous solutions of polyhydric alcohols, phenols and hydroxy acids such as malic, tartaric and salicylic acids. As an explanation, compound formation has been assumed by van't Hoff, Boeseken and others but complete and satisfactory evidence for this view has been lacking, the chief difficulty being isolation of compounds which undergo hydrolysis very readily. Bancroft and Davis¹ explain the well-known increase in acidity, of an aqueous solution of boric acid on the addition of glycerine, as due to an increase in the ionisation, the ionising power of aqueous glycerine being greater than that of water. For a critical account of the large amount of literature on the subject, the paper by these authors may be referred to.

Of the large number and wide variety of o-hydroxy-carbonyl compounds available, only salicylic acid has received attention so far in this connection. There is evidence to show that boric acid reacts with o-hydroxy carbonyl compounds in the presence of a dehydrating agent, producing complex chelate structures

lost. Stackelberg, *et al.*⁷ report 170° C. for the ortho-acid. Mehta and Kantak⁸ recently calculated the melting point of the ortho-acid from the data obtained by them for melting points of mixtures with glucose, galactose and tartaric acid. Their values are 169.5, 170.5 and 160.9° C. respectively. The considerably low value obtained in the last case is ascribed to compound formation. By melting the boric acid in a corked test-tube and determining the m.p. of the powdered melt we obtained 177° C.

Mixtures of boric acid and the organic compound in known proportions were prepared by weighing the two components in ignition tubes, sealing off the tubes and heating the tubes gradually in a sulphuric acid or glycerol bath. In all cases excepting 2-acetyl-1 naphthol, there was an initial lowering of the melting point of boric acid. The melts were quickly powdered and the melting points taken.

In the following table, the maxima temperatures and molecular ratios corresponding to them read out from the graphs constructed are shown.

Surprisingly enough the last compound caused an initial rise in the melting point of boric acid instead of the usual lowering on addition of the substance. Evidence for compound formation is indicated in the curves. The molecular ratios, however, indicate that the matter

TABLE I

Serial No.	Compound	M.P. °C.	Maxima °C.	Molecular ratios	
				Boric acid	Compound
1	Resacetophenone	143	196	4	1
2	Gallacetophenone	171	195	4	1
			182	2	3
3	Resorcylic aldehyde	135	199	3	1
4	2-Acetyl-1-naphthol	102	220	3	1

which exhibit prominent colour changes or fluorescence. Mention may be made of the work of Dimroth,² Feigl,³ Neelakantam⁴ and others. The present authors have, therefore, undertaken systematic investigation of compound formation with them.

As the first part of the investigation, the melting point curves of boric acid in the presence of some o-hydroxy-carbonyl compounds, which were synthesised for this purpose, have been constructed. The determination of the melting point of boric acid itself is complicated by the fact that it readily undergoes dehydration. Apparently this is responsible for some contradictions in literature regarding its stability and melting point. Philbrick and Holmyard⁵ state that at 100° C. or a little over, boric acid forms the meta-acid, at 140° C. the pyro-acid and the anhydride is obtained only by strong heating. Hackspill and Kieffer,⁶ on the other hand, state that the ortho-acid is stable only up to 90° C., at 100° C., the decomposition is explosive and 95 per cent. of the water is lost forming boric anhydride with a little water of adsorption and at 250° C. all the water is

is more complicated. Further investigation is in progress.

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December 21, 1946.

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