

The formation of molecular complexes containing the borazine nucleus is not necessarily indicative of its 'aromatic nature'. Theoretically, borazines could form complexes with Lewis acids if the  $\pi$  electrons were either localized on the nitrogen atom (I) or if they were partially delocalized (II) as in benzene. In the former case borazine would be formulated as a cyclic triamine and it would be expected to act as a Lewis base. It is well established that amines form molecular complexes with some of the same donors which interact with aromatic systems, for example, sulphur dioxide and iodine. In addition, several strong donors, for example, hydrogen chloride, bromine, and chlorine, are known to add to adjacent boron and nitrogen atoms in the borazine nucleus to form the corresponding analogues of *cyclohexane*. The solids which separate from mixtures of picric acid and the borazines may have been formed by a similar addition.

We thank the Robert A. Welch Foundation for supporting this investigation.

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<sup>1</sup> Sheldon, J. C., and Smith, B. C., *Quart. Rev.*, **14**, 200 (1960).

<sup>2</sup> Champion, N. G. S., Foster, R., and Mackie, R. K., *J. Chem. Soc.*, 5060 (1961).

<sup>3</sup> Mellon, E. K., and Lagowski, J. J., in Emeleus and Sharpe's *Advances in Inorganic and Radiochemistry* (Academic Press, Inc., New York) (in the press).

## Dissolution of Glass at Elevated Temperatures

THE finite solubility of glass containing vessels has long been the concern of chemists interested in the properties of solutions and hence in preparing solutions of accurately controlled composition. By the use of certain types of glass or of silica this problem can, to a large extent, be eliminated at temperatures near ambient. However, recently, certain experimental results have been obtained which have brought to our notice the high solubility of a hard borosilicate glass at elevated temperatures.

An attempt to use glass feed tubes in a boiler operating at 200° C was unsuccessful owing to the high rate of solution of the glass. A stout tube of wall thickness of more than 1 mm was reduced to paper thinness after exposure to oxygenated sea water at 200° C for 16 weeks. Even when exposed for some time to salt solutions boiling at atmospheric pressure, glass beakers have been found to undergo marked etching rendering them partially opaque.

A more striking example of the errors which can be introduced by neglecting glass solubility has recently been obtained during an investigation of the dissolution of zinc in millimolar sodium chloride at elevated temperatures in glass-lined autoclaves. The product obtained was generally found by X-ray analysis to consist of zinc oxide or an unknown compound giving a diffraction pattern identical with one of a series found by Gilbert<sup>1</sup> and designated by the letter *E* (Fig. 1). This compound was found to be insoluble in acids and further examination of the product and comparison of its diffraction pattern with those of the *A.S.T.M. Index* proved it to be a well-crystallized specimen of zinc pyrosilicate hydrate ( $Zn_4(OH)_2 \cdot Si_2O_7 \cdot H_2O$ , hemimorphite) (Fig. 1). Samples of this material could be prepared at 80° C, 140° C and 200° C by exposure of the zinc to the above oxygenated solution for several hours. In Gilbert's experiments this compound was formed at atmospheric pressure after exposure of zinc

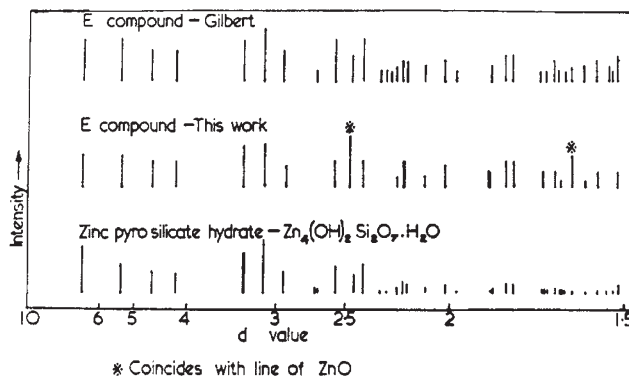


Fig. 1

or zinc hydroxide to distilled water at 85° C for periods of 35 days and upwards. It is quite clearly associated with dissolution of silica in some form from the glass container and interaction with the zinc corrosion product to give the silicate. In a separate experiment the dissolution rate of a borosilicate glass liner was found by loss of weight to be 0.22 mg/dm<sup>2</sup>/day at 140° C. This agreed closely with the amount of silica found by analysis in the millimolar chloride solution used.

The fact that the dissolution of glass is appreciable in distilled water and dilute salt solutions at temperatures as low as 80° C is noteworthy and should be borne in mind in chemical tests and, in particular, in dissolution tests on metals since silicates are well-known corrosion inhibitors.

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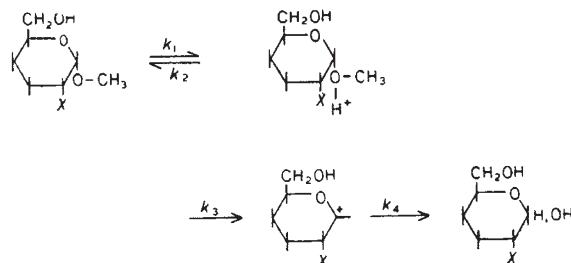
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<sup>1</sup> Gilbert, P. T., *J. Electrochem. Soc.*, **99**, 16 (1952).

## Rates of Acid Hydrolysis of 2-substituted Methyl Glucopyranosides

THE hydrolysis of methyl glycosides probably proceeds through the formation of an oxonium salt as intermediate<sup>1-3</sup>. The steps involved in the reaction of water with a methyl glycoside may thus be represented:



where  $k_3$  represents the rate constant for what is generally believed to be the rate-controlling step.

Shafizadeh<sup>4</sup> has stressed how the inductive effect of a hydroxyl group at C-2 (*X*) may be used to explain the difference in the rates of acid hydrolysis of the methyl glucopyranosides of *D*-glucose and of 2-deoxy-*D*-glucose. He has further pointed out the similarity in the effect of a  $\beta$ -hydroxyl group on the stability in acid between these methyl glucopyranosides and the corresponding diethyl acetals.

I wish to indicate how the effect of a C-2 substituent on the rate of hydrolysis of a methyl glucopyranoside may be related in a quantitative way to the  $pK$  value of the corresponding substituted acetic acid.