

Quantitation of the PVA-Borate-Iodine Complex

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While the PVA-borate-iodine complex is shown to be suitable for the qualitative determination of boric acid, attempts to adapt this to a colorimetric procedure were of no avail. A possible explanation is suggested as a dilution phenomenon.

IN A PREVIOUS publication (1), it was reported that the PVA-borate-iodine reaction was suitable for the detection of boric acid in urine. At the same time it was inferred that this test might be adaptable to a quantitative determination of boric acid, on the basis of the fact that the authors were able to detect as little as 0.3 mg. of that substance. The fact that this reaction involved the development of a color as an end point might also lead one to believe that variation in the color produced by different concentrations of boric acid could be used as the basis for a colorimetric assay.

In a series of experiments conducted along those lines in these laboratories, the following facts were ascertained.

(a) Simple dilution with water caused the typical blue-black color to be discharged. The resultant color was either yellow or red-brown. The intensity of the dilute color could not be related to differences in the concentration of any of the components of the reaction mixture. Colorimetric determinations were carried out using a Spectronic 20 colorimeter.

(b) The discharge of color could not be attributed to alteration in pH. It was determined that an optimum pH of 4.0 was necessary for initial color development, but that subsequent dilution caused the color to discharge even though the optimum pH was maintained throughout the series of dilutions.

(c) A variety of water-miscible, organic solvents was tested to determine whether the discharge of color could be caused by the available excess hydroxyl or hydronium ions. A spectrum of glycols and alcohols caused color discharge. In addition, color loss was also noted with the addition of dioxane, acetone, and ethyl acetate. This seems to indicate that the change in color from blue to yellow is a dilution phenomenon not related to either excess hydroxyl or hydronium ions.

(d) In the case of dilution with absolute ethyl alcohol, it was noted that the yellow color which developed could be related to the concentration of boric acid. Using a Beckman model DB recording spectrophotometer, a linear relationship was established for concentrations of boric acid down to 10.0 mg. Below this concentration, only erratic readings were obtained. The developed color was discharged on standing. Decoloration was hastened when heat was applied. It was shown subsequently that the yellow color represented an excess of iodine.

(e) The above observations lead us to believe that this test, in all probability, will have to remain qualitative.

It must be concluded that the color developed in the PVA-borate-iodine reaction is dependent upon the optimum concentration of reactants in an optimum volume of solvent. The nature of the solvent is important to the extent that all reactants must be mutually soluble in it. The initial color is probably not due to a production of a color pigment in the complex formation, but rather to the ability of that specific concentration of substances to exhibit spectral absorbance within the blue range.

REFERENCES

- (1) Monte-Bovi, A. J., Sciarra, J. J., and Lynch, V. deP., *J. Pharm. Sci.*, **53**, 1278(1964).

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Preparation of Some Cyanoalkylpiperidines

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Selective conversion of the pyridine ring was accomplished without attack of the nitrile group when some alkyl cyanoalkylpyridinium halides were hydrogenated in the presence of platinum oxide or rhodium on carbon catalyst.

CATALYTIC hydrogenation of a ring system is more difficult to achieve than reduction of a functional group. In the pyridine series the difficulty is due to the poisoning effect of the ring nitrogen or

more likely to the effect of the resultant more basic piperidine nitrogen atom. Nevertheless, a number of examples have been cited where the ring was preferentially attacked when a methylene bridge separated it from a ketone group (1). In general this took place when the ring was quaternized. There are only a few examples of selective conversion when the carbonyl group is adjacent to the ring. Lyle and Warner converted 3-benzoylpyridine hydrochloride and methyl 3-benzoylpyridinium iodide to the corresponding benzoylpiperidines in 35-40% yield (2); Freifelder obtained 70% of 3-acetyl-1,4,5,6-tetrahydropyridine and 7% of 3-acetyl-piperidine

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