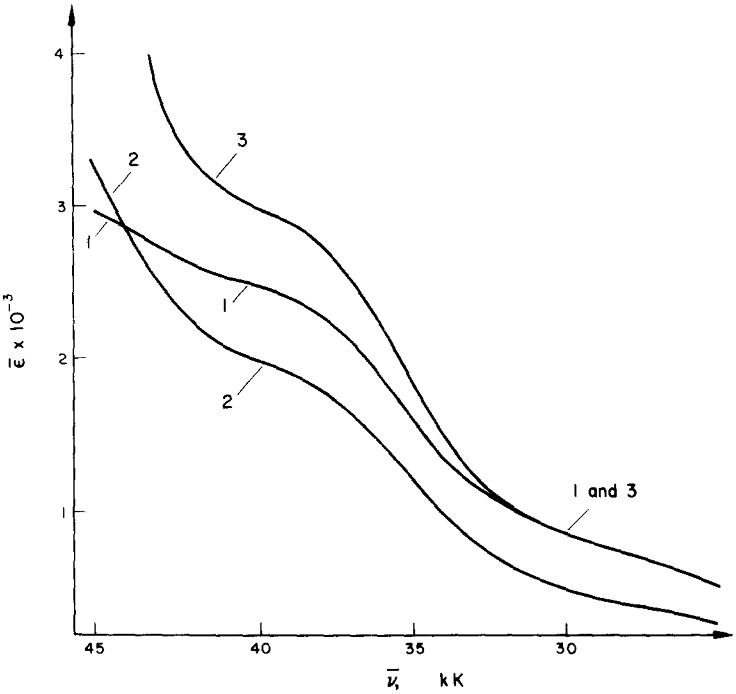

Fig. 2. Ultraviolet spectra of vanadium(V) citrato complexes: 1—$A:B = 0$; 2—$A:B = 0{\cdot}25$; 3—$A:B = 5$. All solutions containing $5{\cdot}10^{-4}$ M V(V) and 1 M sodium chloride; pH = 3·00.

Indeed, $\bar{\epsilon}$ at a given wave number is a function of the ligand concentration (Fig. 2), which supports our assumption about the stability of the citrato complexes formed in the solution.

Judging from the variation of $\bar{\epsilon}$ as a function of both A and B, it may be suggested that a number of complexes, including polynuclear ones, are formed in the solution.

University of Sofia
Department of Chemistry
Sofia 26, Bulgaria

G. ST. NIKOLOV
B. M. NIKOLOVA

J. inorg. nucl. Chem., 1968, Vol. 30, pp. 333 to 335. Pergamon Press Ltd. Printed in Great Britain

The hydrolysis of triphenylphosphine borane

(*First received* 27 *April* 1967; *in revised form* 6 *July* 1967)

HEAL and co-workers[1, 2] have reported that triphenylphosphine borane(I) could be quantitatively recovered after heating for 3 hr at 150° with 3 N HCl or after refluxing for 1 hr with 6 N HCl. Also, (I) could be recovered unchanged after passing HCl, HBr, and HI gas for 6 hr through a solution of (I) in boiling toluene[1]. In contrast to the stability of (I) under these conditions, we have found that

1. M. A. Frisch, H. G. Heal, H. Mackle, and I. O. Madden, *J. chem. Soc.* 899 (1965).
2. H. G. Heal and I. O. Madden, *Nature, Lond.* **195**, 280 (1962).

(I) was easily hydrolysed by 6 N HCl or water in diglyme at 100°. Control experiments employing diglyme alone yielded only recovered (I). Similarly, heating (I) with 6 N HCl alone (without any diglyme solvent) at 100° for 1 hr afforded only recovered (I) confirming Heal's earlier observation[2]. The relative ease of hydrolysis of (I) under these conditions probably is due to the fact that the diglyme provides a homogeneous media; whereas in aqueous solution alone, (I) appears not to be wetted and does not dissolve. Although diglyme was employed in this study, presumably any solvent which dissolves (I) will facilitate hydrolysis.

A semi-quantitative measurement of the relative rates of hydrolysis by heating (I) in acidic, basic, and neutral media at 100° in diglyme was obtained by measuring the volume of hydrogen evolved during the course of the hydrolysis reaction and this data is presented in Fig. 1. The rate of hydrolysis of the first and second B—H bond is accelerated in acid solution compared to neutral or basic hydrolysis (cf. Fig. 1). The rates of hydrolysis with water or sodium hydroxide were essentially identical, indicating base has little effect on the hydrolysis reaction. Hydrolysis with 6 N HNO_3 proceeded similarly to yield triphenylphosphine oxide.

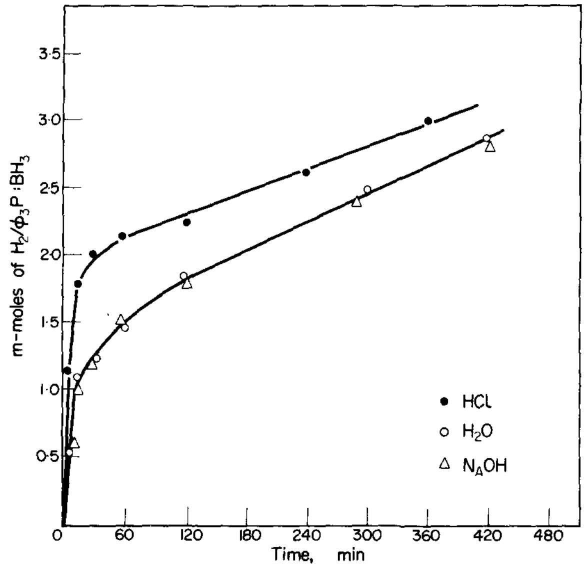

Fig. 1. Rates of hydrolysis of $(C_6H_5)_3P:BH_3$.

Since the reaction is quite exothermic and may rapidly get out of control once initiated, some caution should be exercised in carrying out the hydrolysis on a large scale.

EXPERIMENTAL

Typical experiment for measuring the rate of hydrolysis

The apparatus employed for following the rate of hydrolysis consisted of a specially constructed two-necked, round-bottom, 200 ml flask having a thermometer well and a small neck over which a rubber septum was placed. The flask was equipped with a thermometer, magnetic stirring bar, and a Dry-Ice condenser which led to a Dry-Ice trap and through a mercury–acetone bubbler to two 250 ml gas burets. The flask was charged with 2·76 g (10 m-moles) of triphenylphosphine borane and 80 ml of dry diglyme. This mixture was heated with stirring to 100°C. Then 1·0 ml of either 6 N HCl, water, or 6 N NaOH was syringed into the solution through the serum cap. The hydrogen evolved was measured at various intervals and corrected to STP. The data for these hydrolysis reactions are plotted in Fig. 1.

CONCLUSION

In diglyme solution at 100°C, triphenylphosphine borane is readily hydrolysed by aqueous hydrochloric acid, aqueous sodium hydroxide, and water to triphenylphosphine. Similar hydrolysis by aqueous nitric acid gives triphenylphosphine oxide.

Acknowledgement—This work was supported in part by a grant from the Public Health Service (GM 11809) for which grateful acknowledgement is made. F. J. M. acknowledges fellowship support by the National Institutes of Health (Fellowship No. 1-F1-GM-29, 754-01A1).

Department of Chemistry
University of Iowa
Iowa City, Iowa 52240 U.S.A.

FRANCIS J. METTILLE
DONALD J. BURTON