Alkaloid.	Cc. calculated.	Cc. found.
Quinine Sulphate*	21.82	25.05
Quinine Sulphate*	21.82	24.99
Cinchonidine	10.18	10.10

* The calculations were made on the hydrated form. Upon heating to 115° the material lost in weight only about 3%, showing that we were not dealing with the hydrated form.

Curves are given for the following: Quinine, quinine sulphate, cocaine, cocaine hydrochloride, cinchonidine and strychnine. The curves were plotted by using cc. of acid or base as abscissae and millivolts as ordinates. Potential readings were taken about one-half minute after the addition of either acid or base.

This work is being continued using purer materials.

SUMMARY.

It is possible to titrate electrometrically alkaloids or their salts using a plain platinum wire. Two breaks are obtained when an excess of acid is added to the alkaloid, the first representing the excess of acid, the second the conversion of the salt to the alkaloid. The method is simpler and more rapid than that using either the hydrogen electrode or the quinhydrone electrode.

UNIVERSITY OF IOWA,
DEPARTMENT OF CHEMISTRY,
IOWA CITY, IOWA

THE ACTION OF RED PHOSPHORUS ON IODINE IN ORGANIC SOLVENTS.

BY RALPH N. TRAXLER AND FRANK E. E. GERMANN.

Gordon and Krantz in a paper entitled, "Adsorption of Iodine from Organic Solvents by Red Phosphorus and Charcoal"[1] set forth experimental results obtained by them for the adsorption of iodine from various organic solvents, using charcoal and red phosphorus as adsorbing agents. They have drawn various deductions from their own work and the work of others among which we note "when adsorption of iodine by red phosphorus is considered the absence of moisture is essential for correct results."

Adsorption isotherms are given by the authors using iodine and red phosphorus in carbon bisulphide and xylene at 30° C. and 45° C., and 30° C. and 50° C., respectively. Numerical data are given for the removal of iodine from solution by red phosphorus using 0.3, 0.2 and 0.1 Gm. of iodine and 1 Gm. dried red phosphorus in 50 cc. of toluene, xylene, chloroform, benzene, carbon tetrachloride and carbon bisulphide. The amount of adsorption is found to be quite high in all of the cases.

The present writers have investigated the action which takes place when red phosphorus is brought into contact with iodine dissolved in carbon bisulphide. The results obtained from these investigations lead to the conclusion that adsorption has little or nothing to do with the removal of the free iodine from that solvent when the solid substance used is red phosphorus.

When dry red phosphorus (as used by Gordon and Krantz) is added to a solution of iodine in purified carbon bisulphide at 22° C. under conditions which exclude

[1] Gordon and Krantz, THIS JOURNAL, Vol. 13, No. 7, p. 609–12.

moisture, and thoroughly agitated, the original violet color of the solution undergoes a change yielding a dark reddish brown solution. The depth of color depends upon the concentration of the original iodine solution. If the mixture is filtered after a few minutes of agitation and the filtrate evaporated red crystals are obtained. From the analysis of these crystals, their melting point and reaction products with water, they are found to be phosphorus triiodide. All of the iodine present in the solution is converted to phosphorus triiodide provided sufficient red phosphorus is added. It has been found that approximately 20 per cent of the red phosphorus is capable of reacting with iodine in carbon bisulphide solution.

From the above results it is quite clear as to what happens when moisture is present. The iodine and red phosphorus react just as they do when moisture is excluded, but the triiodide formed is decomposed by the water yielding hydrogen iodide and phosphorus acid. Both of these substances being quite insoluble in carbon bisulphide are precipitated out upon the remaining red phosphorus. The presence of these compounds on the red phosphorus may be shown by filtering out the solid material, washing thoroughly with carbon bisulphide and then treating with warm water. The resulting aqueous solution gives a strong test for hydrogen iodide and phosphorus acid. It is true that this process causes a considerable decrease in the intensity of the original iodine solution and may in fact under right conditions of concentration of iodine, phosphorus and water cause complete removal of the iodine color, but the disappearance of the iodine is not due to direct adsorption of the element by the red phosphorus.

A *chemical reaction not adsorption* is the phenomenon met with in considering the action of red phosphorus on iodine in carbon bisulphide. The writers have not investigated fully the action when xylene, toluene, benzene, chloroform and carbon tetrachloride are used as solvents, but from experiments performed it is evident that chemical action takes place to a marked extent in these cases also. It is a matter of surprise to the writers that the fact of chemical reaction between iodine and red phosphorus in dry carbon bisulphide should have been overlooked in the investigations of the other experimenters.

SUMMARY.

1—Gordon and Krantz have given experimental results to prove that red phosphorus adsorbs iodine from various organic solvents, including carbon bisulphide.

2—When red phosphorus and iodine are brought together in carbon bisulphide, a reaction takes place yielding phosphorus triiodide. The reaction is complete provided sufficient red phosphorus is present.

3—If moisture is present the iodide formed reacts with the water yielding hydrogen iodide and phosphorus acid both of which can later be removed from the remaining red phosphorus by washing with water.

4—The error in the work of the former experimenters rests in their failure to recognize that a chemical reaction not adsorption was the main factor in the removal of free iodine by red phosphorus from the solutions used.

Department of Chemistry,
University of Colorada,
Boulder, Colorado.