Studies on the Reduction of Phosphorus Trichloride with Copper Powder in Non or Less Polar Solvents

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(Received June 20, 1961)

It has been reported in former papers[1-3] that chlorides and oxychlorides of arsenic, vanadium and phosphorus can be partially reduced with copper, and that this reduction leads to the formation of compounds of the chlorides with copper, the chlorides or their lower chlorides with cuprous chloride, and of these elements with copper. Recently, arsenic trichloride[4] and vanadium tetrachloride and oxychloride dissolved in titanium tetrachloride[5] have been studied for their reduction with copper. Little knowledge, however, has been obtained on the reduction of the chlorides of the group V element with copper; the behavior of phosphorus trichloride is particularly unclear,

In the present work the reduction of phosphorus trichloride with copper is studied in non or less polar solvents such as carbon tetrachloride, cyclohexane, silicon tetrachloride, chloroform and tetrachloroethane.

Experimental

Materials.—The solvents and the phosphorus trichloride were purified by normal procedure and stored in a desiccator. The water contents of these solvents was less than 1 mg. per 50 ml. Electrolytic copper powder used, of a purity more than 99.5%, was stored in another desiccator. It passed through a standard sieve of 250 mesh.

Procedure.—In a 100 ml. flask, 0.5 ml. of the trichloride was dissolved in 50 ml. of each solvent or dissolved in a mixture of 5 ml. of silicon tetrachloride and 50 ml. of carbon tetrachloride. The solution of the trichloride was refluxed with 10 or 20 g. of copper powder while being stirred. In another case, 10 ml. of the solution was heated with 4 g. of copper powder in an autoclave with a 20 ml. inner tube of "Teflon", while being shaken. After being cooled, a portion of the supernatant, 2 or 5 ml., was pipeted from the resulting solution and hydrolyzed in a conical flask containing 100 ml. of distilled water by cooling with ice water. The aqueous solution thus obtained, without removing the small amount of the organic phase, was half-saturated with sodium chloride and then titrated with a N/10 sodium hydroxide solution, in the presence of methyl orange and phenolphthalein as indicators, to determine the phosphorous acid and hydrochloric acid derived from the phosphorus chlorides. The procedure of the titration is almost the same as that used for the determination of phosphoric acid in the presence of hydrochloric acid. Another analytical method for chlorine, including chloride other than phosphorus chloride, and phosphorus was also used: An aqueous, hydrolyzed solution was treated with an excess of N/10 silver nitrate, the silver chloride precipitated was filtered off, and the filtrate obtained was titrated with N/10 ammonium thiocyanate after the addition of ferric alum solution as an indicator. Another aqueous, hydrolyzed solution was evaporated to nearly dryness in the presence of nitric acid on a water bath, and the residue obtained was dissolved in water and titrated with a N/10 sodium hydroxide solution as described above. In this method the aqueous solution also was subjected to analyses without removing the small amount of the organic phase. The silicon tetrachloride solution also was hydrolyzed, and the resulting solution was heated with hydrofluoric acid in the presence of perchloric acid and evaporated to nearly dryness; then the residue obtained was analyzed for phosphorus by titration with sodium hydroxide solution.

In these experiments the sampling of the trichloride, solvent, etc., was made in a dry box, and precaution was taken to exclude any effect of water vapor.

Results

Figures 1—4 represent the results of the reflux treatment at 20~140°C, where analyses were made only by the titration with sodium hydroxide. The treatment leads to a decrease in the phosphorus content of the solution and of the ratio of Cl/P, which represents the atomic ratio of chlorine to phosphorus in the solution. This reaction is rather rapid even at a lower temperature, as is shown in Figs. 2 and 3, from which it can be observed that the reaction reaches an equilibrium state within one hour. The percentage of decrease in the phosphorus content depended slightly on the preperty of the solvents and on the temperature of the treatment, although its value in every solution was about 40~50%

1) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. VIII, (1928), pp. 1016, 1025.
2) Gmelins Handbuch der Anorganischen Chemie, 8. Aufl. Nr. 17, Arsen (1952), p. 378.
3) Ibid,. Nr. 60, Kupfer, Teil B (1958), p. 225.
4) W. Rudorff and J. Gelinek, *Chem. Ber.*, **90**, 2654 (1957).
5) P. Ehrlich and W. Siebert, *Z. anorg. u. allgem. Chem.*, **302**, 275 (1959).

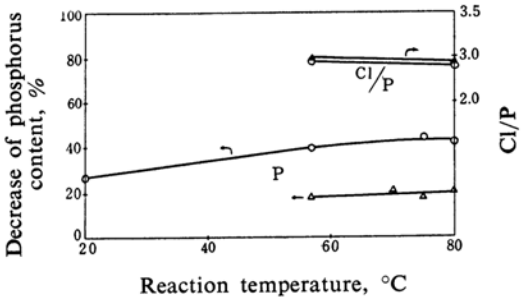

Fig. 1. Temperature dependence of the decrease of the phosphorus content and the value of Cl/P in CCl_4 soln. by the reflux treatment for 1 hr. Reaction temperature represents the temperature of a water bath in which reaction flask is heated.
○ Cu, 20 g. △ Cu, 10 g.

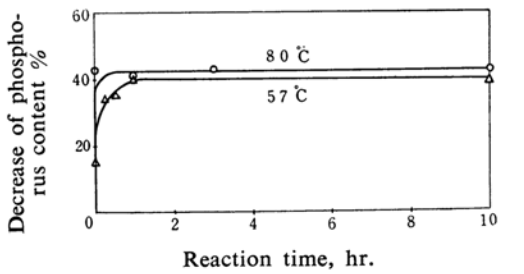

Fig. 2. Reaction time dependence of the decrease of the phosphorus content of CCl_4 soln. by the reflux treatment. Cu, 20 g.

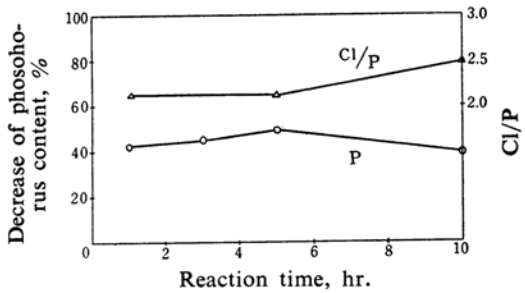

Fig. 3. Reaction time dependence of the decrease of the phosphorus content and the value of Cl/P of $CHCl_3$ soln. by the reflux treatment at 57°C. Cu, 20 g.

under these experimental conditions, whereas the value of Cl/P depended on the property of the solvent, and the values for carbon tetrachloride, chloroform and tetrachloroethane were about 3, 2.2~2.5 and 1.2~1.4 respectively. Cyclohexane, whose graphical representation is omitted, behaved like carbon tetrachloride regarding the percentage of decrease in the phosphorus content and the value of Cl/P, which were 39.6% and 2.96 respectively at 57°C.

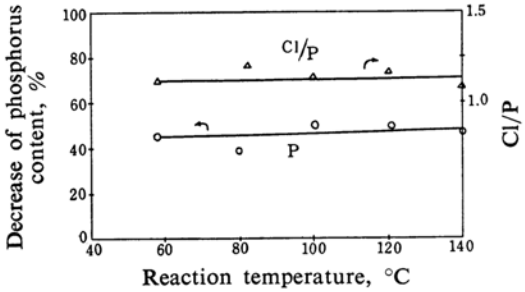

Fig. 4. Temperature dependence of the decrease of phosphorus content and the value of Cl/P of $C_2H_2Cl_4$ soln. by the reflux for 1 hr. Cu, 20 g.

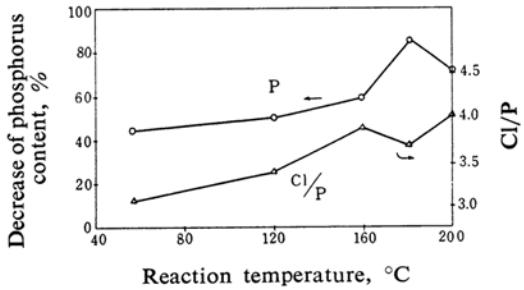

Fig. 5. Temperature dependence of the decrease of the phosphorus content and the ratio of Cl/P of CCl_4 soln. by the autoclave treatment for 1 hr.

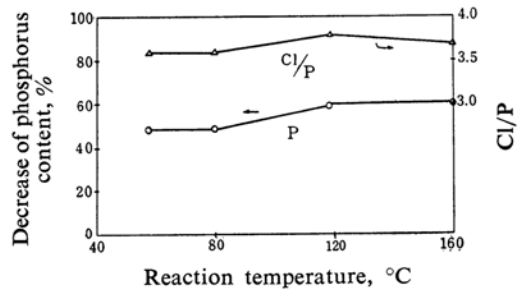

Fig. 6. Temperature dependence of the decrease of the phosphorus content and the ratio of Cl/P of $CHCl_3$ soln. by the autoclave treatment for 1 hr.

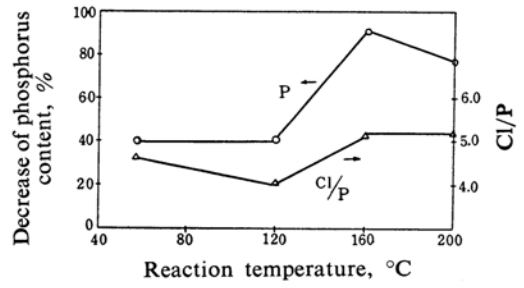

Fig. 7. Temperature dependence of the decrease of the phosphorus content and the ratio of Cl/P of $C_2H_2Cl_4$ soln. by the autoclave treatment for 1 hr.

Figures 5—7 represent the results of the treatment in the autoclave, where analyses were made by titrations with silver nitrate and sodium hydroxide. Although the phosphorus contents of the solutions treated at 56～120°C were comparable to those obtained by the reflux treatment, the ratios of Cl/P of the solution differed from those obtained by the reflux treatment and were more than 3. With an increase in the temperature of the treatment above 160°C, the phosphorus contents decreased and the ratios of Cl/P presented a particular change in every solvent. In the chloroform solutions, the treatment above 160°C gave rise to an obvious change in the quality of the solvent; the copper powder became voluminous and the volume of the liquid phase decreased. Because of this change, the treatment for the chloroform solution was not carried out above 160°C. Some darkening of the surface of copper powder was seen in the treatment at 200°C for the carbon tetrachloride solution and the tetrachloroethane solution. In Fig. 5 or 7, the irregular change in the phosphorus content and the ratio of Cl/P can be observed at 160～200°C, and this change was consistent with the change in the quality of the copper surface at that temperature range. In Figs. 1—7, it can be observed that the percentage of decrease in the phosphorus content in every solution treated by the reflux amounted to nearly the same, 40～50%, whereas the percentage of decrease in the phosphorus content in the carbon tetrachloride solution and the tetrachloroethane solution treated by autoclave at 160 or 180°C amounted to about 85 and 90% respectively, while those treated at 200°C amounted to about 70 and 80% respectively. The value of Cl/P in the former solution treated at 200°C was about 4, and that of the latter solution was about 5.

TABLE I. Cl/P RATIO OF SOLUTION TREATED WITH COPPER FOR ONE HOUR

	Refluxed at 57°C Analyzed by		Autoclaved at 200°C Analyzed by	
Solvent	NaOH	$AgNO_3$, NaOH	NaOH	$AgNO_3$, NaOH
CCl_4	2.97	ca. 3.0	3.30	4.02
$CHCl_3$	.142	3.26	—	3.68[6]
$C_2H_2Cl_4$	1.18	4.75	—	5.15

Table I represents the values of Cl/P in the solutions subjected to the treatments. In Table I it is clear that the values of Cl/P, obtained only by titrations with sodium hydroxide, of the solutions subjected to the reflux treatment were less than 3; this difference afforded a measure of the degree of the reduction, which was higher in more polar solvent. When the estimation of the value of the same solution was made by titration with silver nitrate and sodium hydroxide, the value of every solution became more than 3 and the solution of a more polar solvent took a larger value. The silver nitrate herein used reacts not only with the chloride ion produced by the hydrolysis of phosphorus chloride, but also with cuprous chloride in a solid state and with some others. The Cl/P ratio larger than 3 obtained by this analytical method, therefore, presumably implies the presence of cuprous chloride in the solvent and, in consequence, the reduction of phosphorus trichloride. Such facts were observed for the value of Cl/P in the solutions subjected to the autoclave treatment at 200°C, where the value was larger than 3 even in the case of titration with only sodium hydroxide. In connection with the action of silver nitrate, it also was found qualitatively that the solutions of a more polar solvent subjected to these treatments contained a greater amount of copper compound.

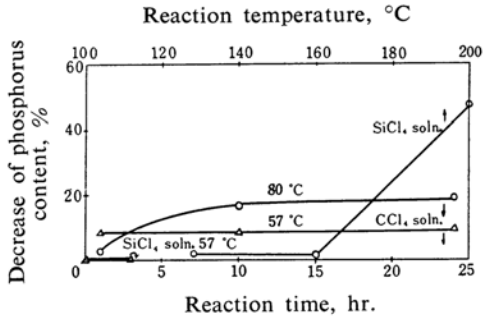

Fig. 8. Effect of $SiCl_4$ on the decrease of phosphorus content. CCl_4 soln. and $SiCl_4$ soln. represents a soln. of PCl_3: $SiCl_4$: CCl_4=1 : 10 : 100 in volume and PCl_3: $SiCl_4$=1 : 100 respectively, Cu, 20 g. in reflux; 4 g. in autoclave.

Figure 8 represents the effect of silicon tetrachloride. A slight decrease in the phosphorus content by the treatment was obtained with the mixed solution of phosphorus trichloride and silicon tetrachloride in carbon tetrachloride. Such facts were observed in the silicon tetrachloride solutions of the trichloride at lower temperatures. Although the phosphorus content presented a marked decrease as a result of the treatment at 200°C, the percentage of decrease was only about 50%, smaller than that in the case of other solvents.

Discussion

From the above results it was considered that the phosphorus trichloride in the solution

6) Representation of the treatment at 160°C.

is primarily decreased by its adsorption on the surface of copper powder; then the trichloride on the surface and in the solution is reduced by another reaction, in which the solvents themselves are dechlorinated[7] with copper and then such dechlorinated products are chlorinated with phosphorus trichloride and with its lower chloride produced by the reduction. This reaction of copper powder yields cuprous chloride, which is insoluble in water and many solvents. The values of Cl/P smaller than 3 were obtained by titration with sodium hydroxide. The values greater than 3, however, were obtained by titration with silver nitrate and sodium hydroxide. These facts suggest that a certain part of the cuprous chloride has been dissolved in the solvents and that this cuprous chloride reacts with silver nitrate. This suggestion contradicts the expectation derived from the solubility of cuprous chloride described above. Thus, it was assumed that cuprous chloride partly reacts with solvents and forms certain complexes, which are soluble in the solvents but only with difficulty soluble in water; such complexes then react with silver nitrate in the aqueous phase in contact with the solvent during analytical procedure. With an increase in the treatment temperature by the autoclave, the compounds of phosphorus trichloride with copper powder are probably transformed into a more reduced form, ultimately into copper phosphides, and this change of the compounds is followed by the darkening of the surface of copper above 140~160°C. Thus, a greater amount of cuprous chloride is produced above this temperature range. The cuprous chloride herein produced is not necessarily in the form of a complex with a solvent, but a part of it may be in the form of another complex which has an ionic property. Such a complex is possibly hydrolyzed during the analytical procedure, thereby leading to the formation of chloride ion and, in consequence, to a greater value of Cl/P, as is shown in the carbon tetrachloride solution at 200°C, in which the value is larger than 3 even in the case of titration only with sodium hydroxide.

Silicon tetrachloride inhibits the reaction of phosphorus trichloride with copper powder. This inhibiting action may be due either to the adsorption of the tetrachloride on the surface of copper powder or to the solvation of phosphorus trichloride with silicon tetrachloride, or it may be due to both the effect of the adsorption and the solvation.

7) Cf. Gmelins Handbuch der Anorganischen Chemie, 8 Aufl. Nr. 60, Kupfer, Teil A (1955), p. 1277.

Summary

A phosphorus trichloride solution in non or less plar solvents was subjected to reaction with copper powder in a flask equipped with a reflux condenser or in an autoclave with an inner tube of "Teflon", and the resulting solution was examined with respect to the phosphorus content and the ratio of Cl/P. By these treatments the phosphorus trichloride was partially reduced with copper powder, and the phosphorus content decreased by the formation of a certain compound of phosphorus trichloride or its lower chloride or phosphorus with copper or cuprous chloride. The degree of the reduction depends on the property of the solvent and on the temperature of the treatment, whereas the decrease in the phosphorus content slightly depends on the property of the solvent. Silicon tetrachloride inhibits the reaction even at 200°C. This action may be due either to the adsorption of silicon tetrachloride on the surface of copper powder or to the solvation of phosphorus trichloride with silicon tetrachloride, or it may be due to the effects of both the adsorption and the solvation.

The author wishes to express his sincere thanks to Mr. Seiichi Ujiie for his helpful co-operation.

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