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The Compound of Cuprous Chloride with Phosphorus Trichloride¹

BY TENNEY L. DAVIS AND PERCY EHRLICH

More than fifty years ago in a series of brilliant papers Schutzenberger,² and Schutzenberger and Fontaine,³ described the preparation of carbonyl derivatives of platinous chloride and reported that phosphorus trichloride displaced carbon monoxide from these substances to form compounds which retained their essential structure through a variety of chemical transformations. Their experiments, demonstrating the chemical equivalence of carbon monoxide and phosphorus trichloride in complex formation, suggest that phosphorus trichloride may perhaps in general displace carbon monoxide from the carbonyls and that it may in general combine with the elements and compounds with which carbon monoxide enters into direct combination. The interesting possibilities do not appear to have been investigated.

Cuprous chloride forms complex compounds with ammonia and with carbon monoxide. Tropsch and Mattox⁴ have recently reported that it combines with ethylene in which, it may be noted, the two valences available for coordination are on different atoms. Phosphorus trichloride, like ammonia and carbon monoxide, has two available valences on its central atom. We find that it also combines directly with cuprous chloride. When phosphorus trichloride is poured upon a quantity of cuprous chloride in a test-tube, the solid immediately commences to swell, heat enough is evolved to produce incipient boiling, and at the end of two hours the solid material occupies two or three times its original volume. On standing overnight, if an excess of phosphorus trichloride is present, the material swells still further, but the reaction appears to be complete after twenty-four hours. In certain experiments in which bottles were used, the material formed hard cakes which by their swelling broke the bottles. Some samples of cuprous chloride reacted more readily than others. When purified cuprous

chloride was used, the complex was procured as a white powder having a strong odor of phosphorus trichloride. Washed with benzene or with some other inert solvent, warmed in a stream of carbon dioxide or left to itself in a vacuum desiccator, the compound lost much of its phosphorus trichloride.

The complex is attacked by atmospheric moisture, and cannot be weighed in the ordinary manner because of its high dissociation pressure. Samples for analysis were secured by allowing cuprous chloride undersaturated with phosphorus trichloride to take up more of that material from the vapor phase, and by allowing cuprous chloride oversaturated with phosphorus trichloride to give up a portion of that material through the vapor phase to other cuprous chloride and by introducing samples of the resulting materials into weighing tubes at the temperature of dry ice. The results of analysis showed that the complex has the composition $(\text{CuCl})_2 \cdot \text{PCl}_3$.

The dissociation pressures of the complex at various temperatures were determined by the static method which has been used in this Laboratory for determining the dissociation pressures of metal pyridine thiocyanates, etc.⁵ The measurements were rendered difficult by the circumstances (1) that the phosphorus trichloride attacked the mercury of the manometer, and (2) that the rate of dissociation of the complex when it was warmed was much greater than the rate of re-association of the components when they were cooled together. The first difficulty was met to some extent by working rapidly, but the second difficulty became more important when the work was rapid. The experimental results were plotted, a smooth curve drawn, and the figures for the dissociation pressures at the even temperatures were read from the curve and found to be 16 mm. at 0°, 28 mm. at 10°, 47 mm. at 20°, 73 mm. at 30°, 117 mm. at 40° and 170 mm. at 50°. These data plotted on a semilogarithmic chart, $\ln p$ vs. $1/T$, gave a straight line practically parallel with the straight line corresponding to Regnault's⁶ data

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(2) Schutzenberger, *Bull. soc. chim.*, **14**, 97, 178 (1870); *Compt. rend.*, **70**, 1414, 1287 (1870).

(3) Schutzenberger and Fontaine, *Bull. soc. chim.*, **17**, 386, 482 (1872); **18**, 148, 529, 1287 (1872).

(4) Tropsch and Mattox, *THIS JOURNAL*, **57**, 1102 (1935).

(5) Davis and Batchelder, *ibid.*, **52**, 4069 (1930); Davis and Ou, *ibid.*, **56**, 1061, 1064 (1934).

(6) Regnault, *Jahresber.*, **65** (1863). Other data by Antoine, *Compt. rend.*, **36**, 676 (1853); **167**, 681, 778, 836 (1888).

for the vapor pressure of phosphorus trichloride, a fact which shows that the affinity which holds the phosphorus trichloride in combination with the cuprous chloride is practically constant over the temperature range 0 to 50°.

The complex reacts violently with a small quantity of water and goes entirely into solution. With a solution of aniline in benzene its reaction is vigorous enough to cause the benzene to boil. It reacts vigorously with methyl and ethyl alcohols, less vigorously with isopropyl, *n*-butyl and isoamyl alcohols, and with phenol in benzene solution only very slowly in the cold and more strongly on warming. The product of the reaction with methyl alcohol is a mixture of cuprous chloride with a compound having the formula $\text{CuCl}\cdot\text{P}(\text{OCH}_3)_3$, m. p. 216–217°, crystals from acetone or methyl alcohol, identical with the material prepared by Arbusow⁷ by the direct combination of cuprous chloride with methyl phosphite. Arbusow reported m. p. 190–192°. He reported complexes of cuprous chloride, bromide and iodide with a number of alkyl phosphites, complexes generally having the formula $\text{CuX}\cdot\text{P}(\text{OR})_3$, but in a few cases the formula $\text{CuX}\cdot[\text{P}(\text{OR})_3]_2$. In our experiments with alcohols other than methyl, no solid products except cuprous chloride could be isolated from the reactions of $(\text{CuCl})_2\cdot\text{PCl}_3$ with the alcohols.

The white crystalline compound $\text{CuCl}\cdot\text{P}(\text{OCH}_3)_3$ oxidizes slowly in the air, turning green and finally black, but appears to be otherwise stable and odorless. The tendency toward its formation is so great that powdered cuprous chloride added to an ether solution of methyl phosphite wholly deprives it of its offensive odor. The compound dissolves in ammonia water to yield a colorless solution which quickly turns blue in the air, and it produces at the same time an extremely offensive carbylamine-like odor. It dissolves in warm aniline or dimethylaniline without the production of any odorous substance, and the solution on boiling deposits a copper-colored material. It hisses with strong nitric acid. On pyrolysis the compound does not decompose into cuprous chloride and methyl phosphite as might be expected, but leaves a residue which contains metallic copper, and produces methyl chloride and volatile compounds of phosphorus. The latter are now being studied further in this Laboratory.

(7) Arbusow, *Ber.*, **38**, 1121 (1905).

Experiments

Analysis of the Complex $(\text{CuCl})_2\cdot\text{PCl}_3$.—Although it was not found possible to procure the complex in a state of complete purity, satisfactory indications of its composition were secured by approaching the equilibrium from both sides and analysing the resulting materials. A quantity of freshly purified, finely powdered cuprous chloride was introduced into a short tube open at the top and this was placed within a wide tube which contained some liquid phosphorus trichloride; the wide tube was stoppered and allowed to remain in the refrigerator for ten days. A similar arrangement was set up with cuprous chloride in the outer tube and cuprous chloride plus an excess of phosphorus trichloride in the inner one. After ten days the smaller tubes which contained the complex were removed and cooled in dry ice. Samples of the complex were introduced quickly into previously weighed small glass tubes which had also been cooled in dry ice. These tubes were immediately sealed at the blast lamp, weighed again and marked with identifying marks. In making the analyses, the tubes were scratched with a file, warmed at the scratch with a blowpipe flame and dropped into strong ammonia water, whereupon they cracked open and the contents dissolved in the liquid. Chlorine was determined in the usual way by precipitation as silver chloride in the presence of dilute nitric acid. The samples to be analyzed for copper and phosphorus were evaporated to dryness; concd. nitric acid was added and the mixtures were again evaporated to dryness, the residues were taken up in dilute nitric acid, and the copper in them was determined electrolytically. Phosphorus was determined in the residual solution by precipitation as magnesium ammonium phosphate and the ignition of this material to magnesium pyrophosphate. The results of the analyses, indicated in Table II, correspond fairly closely to the composition, two molecules of cuprous chloride and one of phosphorus trichloride, and differ widely from the composition, one molecule of each of the two.

TABLE I
ANALYSIS OF THE COMPLEX, $(\text{CuCl})_2\cdot\text{PCl}_3$

	Found, %				
					Average
Chlorine	51.88	53.91	51.02	49.75	51.39
Copper	36.33	35.80	40.52	40.79	38.36
Phosphorus	9.71	9.00	8.13	8.23	8.77
	Calcd. for				
	$(\text{CuCl})_2\cdot\text{PCl}_3$				$\text{CuCl}\cdot\text{PCl}_3$
Chlorine	52.89				59.99
Copper	37.88				26.88
Phosphorus	9.23				13.13

The Complex Methyl Ester $\text{CuCl}\cdot\text{P}(\text{OCH}_3)_3$.—When the complex $(\text{CuCl})_2\cdot\text{PCl}_3$ was treated with absolute methyl alcohol, a violent reaction ensued, clouds of hydrogen chloride were evolved and a heavy, white, crystalline powder remained in the bottom of the vessel. Extraction of the solid with boiling methyl alcohol, ethyl acetate or acetone yielded liquids which on cooling deposited white prismatic crystals of the crude complex ester. Acetone is the best solvent which we have found; on cooling it deposited, sometimes in handsome needles, about one-

half of the material which it dissolved at boiling temperature. In methyl alcohol or ethyl acetate solution the methyl ester tended to oxidize readily and to turn green. The crude ester melted at about 180–190° and did not appear to decompose at this temperature. At distinctly higher temperatures it decomposed to yield a red residue and to produce a very offensive odor. Recrystallization from acetone or methyl alcohol raised the melting point of the material, 197–202°, 202–207°, 203–209°, etc., and in one instance 216–217°. The latter material showed almost no red color when heated to its melting point.

Chlorine was determined by dissolving a sample of the ester in ammonia water and precipitating as silver chloride in the presence of dilute nitric acid. Copper was determined electrolytically in the solution which resulted from treating the ester with concd. nitric acid and diluting with water. The residual liquid gave no test for phosphate with ammonium molybdate, for the trivalent phosphorus had not been oxidized by the cold concd. nitric acid. Experiment showed that evaporation to dryness with concd. nitric acid, or evaporation to fuming with concd. sulfuric acid, would not accomplish the result. Satisfactory phosphorus determinations were finally made by evaporating the sample with a mixture of nitric and sulfuric acids until fumes of sulfuric acid were given off, or by evaporating with fuming sulfuric acid until the liquid

boiled freely, and then diluting with water, precipitating as magnesium ammonium phosphate, etc.

Anal. Calcd. for $\text{CuCl}\cdot\text{P}(\text{OCH}_3)_3$: Cl, 15.89; Cu, 28.49; P, 13.91. Found: Cl, 15.36, 16.26, 16.00; Cu, 28.69, 28.63; P, 13.60, 13.59, 14.22, 13.87, 13.41.

Summary

Phosphorus trichloride combines directly with cuprous chloride to form the compound $(\text{CuCl})_2\cdot\text{PCl}_3$.

The dissociation pressure of this compound has been measured from 0 to 50°. The affinity which holds the phosphorus trichloride in combination with the cuprous chloride is practically constant over that temperature range.

The complex reacts with methyl alcohol, losing one of its molecules of cuprous chloride and forming a complex ester $\text{CuCl}\cdot\text{P}(\text{OCH}_3)_3$.

The pyrolysis of the complex ester yields metallic copper, methyl chloride and volatile compounds of phosphorus which we have not yet identified.

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Metal Pyridine Complex Salts. V.¹ Volume Change During Formation of Cyanates and Thiocyanates

BY TENNEY L. DAVIS AND ALBERT V. LOGAN

The fact that cobaltous thiocyanate forms compounds only with two and with four molecules of pyridine, while cobaltous cyanate forms compounds with two, with four, and with six molecules, has suggested that the affinity of pyridine for the metal in complex thiocyanates is probably less than it is in the complex cyanates. Experiments reported in the second and third papers of this series showed that cobaltous, cupric and nickelous pyridine cyanates have lower dissociation pressures than the corresponding thiocyanates containing the same number of pyridine molecules—and support the conclusion that the pyridine coordinately attached to the metal is held in the complex cyanates by a stronger affinity than it is held in the complex thiocyanates. The substitution of an oxygen atom in place of a sulfur at the remote end of the electrovalently connected acid radical considerably increases the residual affinity of the metal atom available for

combination with pyridine through its coordination valence.

We now find that the greater forces of affinity at work in the complex cyanates, by pulling the parts of the molecules more closely together, produce greater contractions than do the forces which hold together the complex thiocyanates. The proportionate decrease in volume when the complex cyanate is formed from the simple salt plus pyridine is greater than when the complex thiocyanate is similarly formed. The cyanate radical, then, exhausts to a less extent than the thiocyanate radical the total affinity of the metal atom, and leaves more of it available for holding the pyridine with those internal forces which reduce both the dissociation pressure and the volume of the resulting compounds.²

The fact that water and all organic liquids (ex-

(1) Earlier papers of this series: I, Davis and Logan, *THIS JOURNAL*, **50**, 2493 (1928); II, Davis and Batchelder, *ibid.*, **52**, 4089 (1930); III and IV, Davis and Ou, *ibid.*, **56**, 1061, 1064 (1934).

(2) Compare the ideas of T. W. Richards on compressible atoms developed in his Faraday Lecture, delivered before the Chemical Society of London June 14, 1911, and in his Presidential Address to the American Chemical Society, published in *THIS JOURNAL*, **36**, 2417–2439 (1914), where a bibliography of his papers on the subject is also printed.