

Br^- and FeBr^{++2}) were used with the results shown in Table II.

Four independent samples lead to an average value for λ of -35.3 ± 1.0 kcal./mole. This gives -62.8 ± 1.0 kcal./mole for the heat of formation of $\text{FeBr}_3(\text{s})$ at 25° . The difference between the heats of formation of $\text{FeBr}_3(\text{s})$ and $\text{FeBr}_2(\text{s})$ obtained in this work is in good agreement with that found from equilibrium studies,⁶ 4.1 ± 1.2 kcal. and 4.0 ± 0.3 kcal., respectively.

The somewhat greater scatter of data for FeBr_3 as compared with those for the chloride is thought to be due largely to the greater difficulty of purifying the bromide. Solutions gave negative tests for Fe^{++} , however.

Iron(III) Monobromodichloride.—This substance was prepared by bromination of FeCl_2 .¹⁰ Its thermal instability makes purification difficult and varying amounts of Fe^{++} were found in the solutions following thermal measurements. The Fe^{++} ion was assumed to represent FeCl_2 in the original sample and the heat of solution corrected for the amount present as determined by analysis. Interpretation of results was carried out as for the other iron(III) compounds. The fraction of iron in the form of FeBr^{++} predicted in these solutions is very small; hence only FeOH^{++} and FeCl^{++} were considered. Results are shown in Table III, where m' represents the molality of FeCl_2 in the solution and λ is again defined as ΔH° for the reaction $\text{FeBrCl}_2(\text{s}) = \text{Fe}^{+++}(\text{aq}) + \text{Br}^-(\text{aq}) + 2\text{Cl}^-(\text{aq})$. An average value for λ of -37.4 ± 0.3

kcal./mole is obtained; this leads to -82.9 ± 0.3 kcal./mole for the heat of formation of FeBrCl_2 which agrees well with -83 kcal. obtained from equilibrium studies of the thermal dissociation of FeBrCl_2 into FeCl_2 and bromine.¹⁰

Values for heats of formation of substances involving bromine are based on the liquid Br_2 as the standard state.

TABLE III
HEATS OF SOLUTION FOR FeBrCl_2

Molality	Molality m'	α	β	Exptl. heat of solution, kcal./mole	λ , kcal./mole
0.00585	0.00212	0.38	0.10	-31.8	-37.3
.00420	.00100	.46	.07	-30.9	-37.2
.00197	.00037	.63	.03	-29.5	-37.5
.00125	.00013	.73	.02	-28.6	-37.8

Conclusions.—Whereas several assumptions are involved in the interpretation of measured heats of solution of the iron halides in order to estimate heats of formation, the agreement of the values obtained with those from independent methods offers some support to the validity of the treatment.

A linear relation between the heats of formation of FeCl_3 , FeBrCl_2 and FeBr_3 and the number of Cl or Br atoms per atom of iron is observed which is not apparent if one uses the higher value for the heat of formation of FeCl_3 previously reported. This relationship also applies to the heats of solution (λ) and might be anticipated from the close similarity in structure of the mixed halide to FeCl_3 and FeBr_3 as discussed in an earlier paper.¹⁰

SEATTLE 5, WASHINGTON

(10) N. W. Gregory, *This Journal*, **73**, 5433 (1951).

{CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STATE UNIVERSITY OF IOWA}

Spectrophotometric Study of the Phosphorus-Interhalogen Complexes in Carbon Tetrachloride and Acetonitrile¹

BY ALEXANDER I. POPOV AND EDWARD H. SCHMORR

RECEIVED FEBRUARY 14, 1952

Spectrophotometric study of phosphorus hexachloroiodide and phosphorus hexabromoiodide reveal that in carbon tetrachloride solutions the complexes dissociate into component molecules $\text{PCl}_6\text{I} \rightleftharpoons \text{PCl}_5 + \text{ICl}$; $\text{PBr}_6\text{I} \rightleftharpoons \text{PBr}_5 + \text{IBr} + \text{Br}_2$. In polar solvents, like acetonitrile, the dissociation is ionic: $\text{PCl}_6\text{I} \rightleftharpoons \text{PCl}_5^+ + \text{ICl}_2^-$ and $\text{PBr}_6\text{I} \rightleftharpoons \text{PBr}_5^+ + \text{IBr}_2^-$. Phosphorus pentabromide-carbon tetrachloride complex $\text{PBr}_5 \cdot 2\text{CCl}_4$ is prepared by a new method, and its decomposition point is determined.

Introduction

Although a large number of phosphorus-halogen complexes have been reported in the literature, it seems that relatively little work has been done on the elucidation of their structure and their physical and chemical properties.

In recent years Fialkov and Kuz'menko² have studied the addition of iodine, iodine chloride and iodine bromide to phosphorus tri- and pentahalides. It was found that stable solid complexes, phosphorus hexachloroiodide (PCl_6I) and phosphorus hexa-

bromoiodide (PBr_6I) can be obtained by the simple addition of iodine chloride and iodine bromide to the respective phosphorus pentahalides. Likewise Fialkov and Kuz'menko have verified the reaction reported by Baudrimont³ in which phosphorus hexachloroiodide is formed by the addition of iodine to phosphorus pentachloride.

A study was made on the electrical conductivity of these complexes in various organic solvents.^{2d} It was found that while acetonitrile, nitrobenzene, ethyl bromide and chloroform yield conducting solutions—benzene, toluene, carbon tetrachloride and dioxane solutions do not. These results were based on a study of saturated solutions of these complexes in the respective solvents, and it must be noted that in the case of non-conducting solutions

(1) Abstracted from a thesis presented by Edward H. Schmorrr to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Master of Science, February, 1952.

(2) (a) Ya. A. Fialkov and A. A. Kuz'menko, *J. Gen. Chem. (U.S.S.R.)*, **19**, 812 (1949); (b) **19**, 997 (1949); (c) **21**, 433 (1951); (d) A. A. Kuz'menko and Ya. A. Fialkov, *ibid.*, **21**, 473 (1951).

(3) M. E. Baudrimont, *Ann. chim. phys.*, [4] **2**, 8 (1864).

the solubility was usually very small. To account for the different behavior of the solutions of these complexes, Fialkov and Kuz'menko postulated that in conducting solvents the compounds dissociate into $\text{PCl}_4^+ + \text{ICl}_2^-$ and $\text{PBr}_4^+ + \text{IBr}_2^-$ ions, respectively. It seemed that spectrophotometric study of these complexes in various solvents would clarify the state in which they exist in solutions.

Experimental

Reagents.—Mallinckrodt C.P. phosphorus pentachloride and Kodak phosphorus tribromide were used without further purification. Iodine was purified by sublimation, and bromine, by distillation from phosphorus pentoxide, then from potassium bromide.

Iodine chloride was prepared by the method of Cornog and Karges.⁴ After several fractional crystallizations the melting point of the product was 27.2°. Iodine bromide was prepared by placing a weighed amount of iodine in a slight excess of bromine and allowing the mixture to stand overnight. The product obtained was purified by fractional recrystallization until the m.p. of 41.9° was reached.

The purity, and especially the dryness of the solvents, was quite critical for spectrophotometric work. Carbon tetrachloride was refluxed for 24 hours with alkaline potassium permanganate, washed with water, refluxed with barium oxide, distilled, and then kept over fresh barium oxide and distilled over as needed. The boiling point was 76.0° at 760 mm.

Acetonitrile was purified in essentially the same manner, except that the treatment with permanganate was omitted. Its boiling point was 81.0° at 760 mm.

Phosphorus Hexachloroiodide.—Phosphorus hexachloroiodide was prepared essentially by the method employed by Fialkov and Kuz'menko.² Approximately unimolar solutions of iodine monochloride and phosphorus pentachloride were prepared in carbon tetrachloride. Iodine monochloride solution was then slowly added to that of phosphorus pentachloride and the solution was rapidly stirred. Orange needles of the complex separated immediately. The suspension was filtered on a sintered glass crucible and the precipitate was repeatedly washed with purified carbon tetrachloride, care being taken not to expose the precipitate to air. The washed precipitate was transferred to glass vials which were then evacuated to less than 1 mm. pressure in order to remove the adhering solvent. To facilitate the removal of solvent the vials were heated, during evacuation, to about 50°. The vials were sealed with a blowtorch, and the product could be kept without decomposing until the time of use. The purity of the preparation was checked by iodometric titration, and the compound was found to be approximately 99% pure.

Solutions of phosphorus hexachloroiodide in carbon tetrachloride and in acetonitrile were prepared by breaking the weighed vial under the appropriate solvent, dissolving the precipitate and diluting the solution to the desired volume. The concentration of the solutions was obtained from the original weight of the sample, and it was again checked iodometrically. The agreement was always satisfactory if the solvent was anhydrous. The average concentration of these solutions was approximately $10^{-3}M$. Solutions of iodine chloride and iodine bromide were prepared in both solvents and their concentration was likewise determined iodometrically.

Phosphorus Pentabromide.—An attempt was made to prepare phosphorus pentabromide by mixing equimolar solutions of phosphorus tribromide and bromine in carbon tetrachloride. An orange yellow precipitate was obtained which was subsequently treated in the way described above for the PCl_2I . However, gravimetric analysis of the precipitate gave only 55.4% of bromine, instead of 92.8% for PBr_5 . It was noticed that on dissolving the precipitate in dilute aqueous ammonia, a few drops of immiscible liquid resulted, which disappeared on heating the solution. The droplets were removed with a capillary pipet, dried with barium oxide, and distilled in a micro-distilling apparatus. Upon purification they were identified as carbon tetrachloride.

Phosphorus pentahalide complexes with carbon tetrachloride, $2\text{PCl}_2\cdot\text{CCl}_4$ and $\text{PBr}_5\cdot 2\text{CCl}_4$, were reported in 1930 by Krakowiecki.⁵ They were obtained in crystalline form on cooling hot saturated solutions of the pentahalides in carbon tetrachloride. The pentabromide complex should contain 54.1% bromine. No description of their physical or chemical properties was given in the above quoted article.

Apparently the complex is quite stable at room temperature and is only slowly hydrolyzed by air moisture. It does not have a sharp melting point, but begins to decompose at about 86°.

Phosphorus Hexabromoiodide.—This compound was prepared in essentially the same way as phosphorus hexachloroiodide. A ruby-red precipitate was obtained in carbon tetrachloride solution which was treated in essentially the way described above. The bromine complex proved to be considerably more hygroscopic than its chlorine analog. To avoid decomposition all solutions were prepared in a dry-box. Iodometric titration of different preparations of this complex gave rather erratic results, and in all cases the amount of halogen titrated was less than the theoretical. It was evident that the compound obtained was contaminated with carbon tetrachloride, the amount of which varied from preparation to preparation. However, when a similar reaction was carried out using carbon disulfide as a solvent, a pure product, uncontaminated with the solvent, was obtained.

Apparatus.—A Beckman model DU spectrophotometer was used for the absorption work. Below 320 $m\mu$, silica stoppered cells of path-length 1.000 ± 0.001 cm. were used. Corex cells of the same path-length were used for higher wave length regions. All measurements were made at room temperature, which was approximately 25°.

Results and Discussion

In carbon tetrachloride solution, the absorption curves of phosphorus hexachloroiodide and iodine chloride are practically identical (Fig. 1, curves 1 and 2). They both have maxima at 460 $m\mu$ and a molar absorptancy index of 144. Evidently the absorbing molecule in both cases is iodine chloride, and since in this wave length region phosphorus pentachloride does not absorb, the complex must be entirely dissociated into phosphorus pentachloride and iodine chloride.

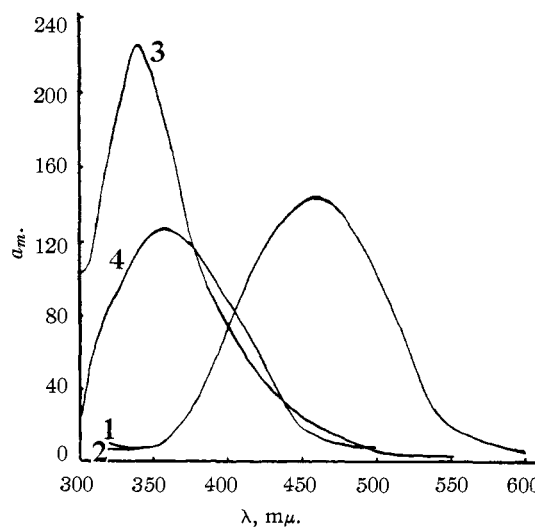


Fig. 1.—Absorption spectra of PCl_2I and ICl in carbon tetrachloride and acetonitrile: curve 1, ICl in CCl_4 ; curve 2, PCl_2I in CCl_4 ; curve 3, PCl_2I in CH_3CN ; curve 4, ICl in CH_3CN .

The non-existence of the complex in undissociated form is not surprising in view of the tendency of the

(4) J. Cornog and R. A. Karges, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 165.

(5) S. Krakowiecki, *Rocz. Chem.*, **10**, 197 (1930).

solvent to form stable complexes with phosphorus pentahalides.

In acetonitrile, on the other hand, the two absorption curves are quite distinct, as shown by Fig. 1, curves 3 and 4. The phosphorus hexachloroiodide maximum at 341 $m\mu$ is very similar to the 340 $m\mu$ peak of the ICl_2^- ion in polar solvents found by Gilbert, Goldstein and Lowry,⁶ and recently confirmed by the study of the absorption spectra of tetramethylammonium dichloroiodide.⁷

In the case of phosphorus hexachloroiodide, the results are somewhat different. The absorption curve of $PBr_5 \cdot 2CCl_4$ in carbon tetrachloride is given by Fig. 2, together with the absorption curve of bromine (curves 1 and 2). It is seen that the two curves are practically identical except that the molar absorptivity index of the complex is lower by about 7% (see Table I). This agrees with the observations of Kastle and Beatty⁸ that phosphorus pentabromide dissociates in carbon tetrachloride solution into PBr_3 and Br_2 to the extent of 90–95%.

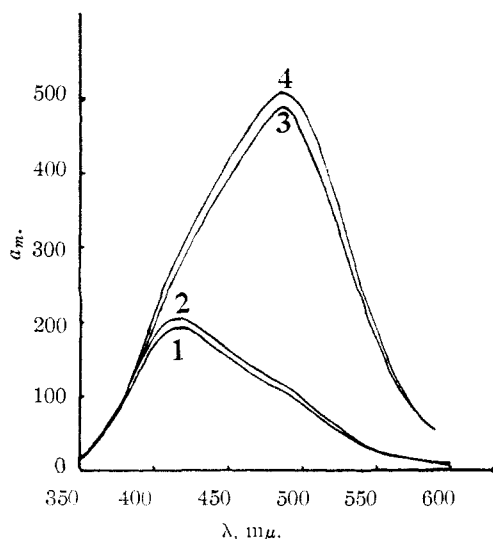


Fig. 2.—Absorption spectra of Br_2 , PBr_5 and PBr_5I in CCl_4 : curve 1, PBr_5 ; curve 2, Br_2 ; curve 3, PBr_5I ; curve 4, $IBr + Br_2$.

In view of the fact that the absorption spectrum of phosphorus pentabromide is due to bromine, it seemed reasonable to expect that phosphorus hexabromoiodide would dissociate, in carbon tetrachloride solutions, into phosphorus tribromide, bromine and iodine bromide. Comparison of the absorption curves of the solutions of the complex with that of an equimolar mixture of bromine and iodine bromide (Fig. 3) shows that this supposition is correct since phosphorus tribromide does not absorb in this wave length region. The molar absorptivity index of the complex is somewhat lower than that of the corresponding mixture, but this is probably due to incomplete dissociation of phosphorus pentabromide.

(6) F. L. Gilbert, R. R. Goldstein and T. M. Lowry, *J. Chem. Soc.*, 1092 (1931).

(7) A. I. Popov, D. H. Meyer and R. E. Buckles, to be published.

(8) J. H. Kastle and L. O. Beatty, *Am. Chem. J.*, **21**, 398 (1899).

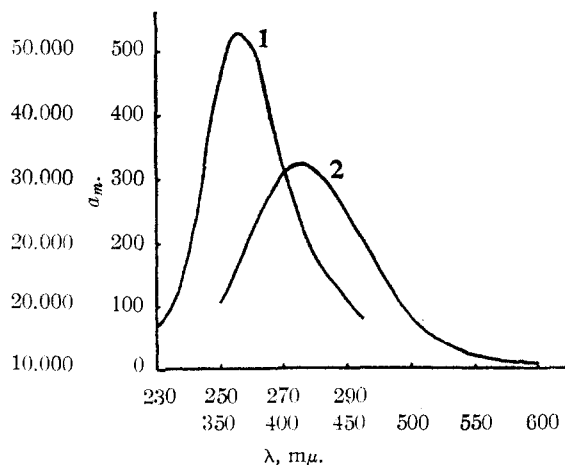


Fig. 3.—Absorption spectra of PBr_5I and IBr in CH_3CN : curve 1, PBr_5I ; curve 2, IBr . Left-hand ordinate in upper abscissa is for curve 1.

In acetonitrile, phosphorus hexachloroiodide, gave an absorption peak in the ultraviolet, with a maximum at 256 $m\mu$ (Fig. 3, curve 1). Gilbert, Goldstein and Lowry⁶ report a peak at 260 $m\mu$ for the IBr_2^- ion in alcohol. They have also found another peak for this ion with a maximum at 390 $m\mu$, which could not be reproduced in this work. However, since tetramethylammonium dibromoiodide likewise gives only the 256 $m\mu$ peak in acetonitrile and the 390 and 256 $m\mu$ peaks in ethylene chloride,⁷ it seems safe to assume that in acetonitrile, phosphorus hexachloroiodide dissociates ionically into PBr_4^+ and IBr_2^- . Absorption of iodine bromide in acetonitrile is given by curve 2, Fig. 3.

The results of the absorption work are summarized in Table I.

TABLE I
ABSORPTION CHARACTERISTICS OF IODINE HALIDES AND PHOSPHORUS-HALOGEN COMPLEXES IN CARBON TETRACHLORIDE AND ACETONITRILE

Compound	Solvent	Maximum, $m\mu$	a_m
PCl_6I	CCl_4	460	144
ICl	CCl_4	460	144
PCl_5I	CH_3CN	341	225
ICl	CH_3CN	358	128
Br_2	CCl_4	416	208
PBr_5	CCl_4	416	195
IBr	CCl_4	495	392
$IBr + Br_2$	CCl_4	486	508
PBr_5I	CCl_4	486	490
IBr	CH_3CN	416	323
PBr_5I	CH_3CN	256	52,500

Conclusions

Phosphorus halogen complexes are unstable in carbon tetrachloride solutions, and dissociate quantitatively into corresponding phosphorus halides and interhalogen compounds. In acetonitrile, they are much more stable and dissociate ionically into the positive phosphorus tetrahalide cation and trihalide anion.

IOWA CITY, IOWA