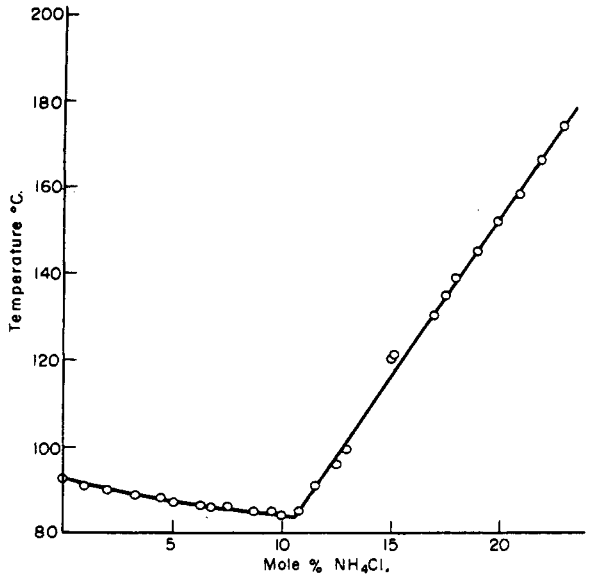

Fig. 2.—Part of the system $NH_4Cl-N_2H_5Cl$.

consist in placing the molten mixture in a test-tube which is whirled in a centrifuge during crystallization. The crystals of ammonium chloride being heavier than the melt should sink to the bottom of the tube during the centrifugation. Thus, when the melt is completely solidified there should be a gradation in composition from top to bottom, the bottom section being richer in ammonium chloride and the top section in hydrazine hydrochloride. Some simple experiments to test this procedure were carried out as follows.

Mixtures of hydrazine hydrochloride and ammonium chloride were melted, thoroughly mixed and then centrifuged until solidification was complete. The glass tube container was then carefully broken and the solidified mass carefully divided into four segments which were analyzed for hydrazine hydrochloride. The results of three such experiments are listed in Table III.

TABLE III

	N_2H_5Cl, %		
	Expt. 1	Expt. 2	Expt. 3
Top quarter	76.0	84.0	88.8
Third quarter	45.3	43.4	39.4
Second quarter	40.6	40.7	39.3
Bottom quarter	37.5	48.2	38.8

These results show that separation does occur. In fact, in expt. 3 the composition of the top quarter approaches the theoretical limit indicated by the eutectic composition. It is also apparent that by controlling the rate of cooling and increasing the force of centrifugation, the separation could be improved.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Spectrophotometric Study of Phosphorus Pentabromide in Various Solvents[1,2]

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Spectrophotometric studies of phosphorus pentabromide and bromine solutions in carbon tetrachloride, ethylene dichloride and carbon disulfide have shown that in the 300–600 mμ region a large fraction of the absorption can be ascribed to the undissociated "complex" $PBr_3 \cdot Br_2$. This observation invalidates the usually accepted value of the dissociation constant of PBr_5 in these solvents, which was determined colorimetrically, on the assumption that bromine is the only absorbing species. An approximate value for the molar absorbancy index of $PBr_3 \cdot Br_2$ "complex" has been determined and the correspondingly approximate values of the dissociation constant of this compound have been calculated for carbon tetrachloride and ethylene dichloride solutions. Similar study on phosphorus pentachloride shows that it does not undergo appreciable dissociation in the solvents used.

Introduction

The degree of dissociation of phosphorus pentabromide in carbon tetrachloride and in carbon disulfide was determined colorimetrically in 1899.[3] It was at that time assumed that the color of the solution was due entirely to the free bromine present as a dissociation product. A 90% dissociation was reported in the carbon tetrachloride and 100% dissociation in carbon disulfide; however, it was observed that the addition of an excess of phosphorus tribromide to the carbon disulfide solutions decreased the color intensity. If this was due to the repression of the dissociation, the observation was obviously incompatible with a 100% dissociation.

Popov and Schmorr[4] reported that the absorption spectrum of phosphorus pentabromide solution in carbon tetrachloride was identical to that of bromine in the same solvent, but with a somewhat lower molar absorbancy index[5]; thus the results of previous investigators were apparently confirmed.

However, it was observed that additions of excess of phosphorus tribromide resulted in a dissociation suppression which was usually greater than the one calculated on the assumption of a 90% dissociation. Likewise, the absorbancy variations on dilution were incompatible with the predicted ones. It seemed that a more detailed investigation of this problem was needed.

Experimental Part

The absorption curves reported in this investigation were obtained with a Cary recording spectrophotometer model 11. When the measurements involved determinations of absorbance at a single wave length, a Beckman DU spectrophotometer was used.

The absorbance scales of both spectrophotometers were calibrated against standardized filters supplied by the National Bureau of Standards and appropriate corrections were applied whenever necessary. Corex, stoppered cells with path length of 1.00 ± 0.01 cm. were used and all measurements were made at the room temperature of approximately 25°.

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[1] Presented before the 122nd Meeting of the American Chemical Society, Atlantic City, N. J., September 14, 1952.

[2] Abstracted in part from the M.S. thesis of Norman E. Skelly, S.U.I., February, 1953.

[3] J. H. Kastle and L. O. Beatty, *Am. Chem. J.*, **21**, 392 (1899).

[4] A. I. Popov and E. H. Schmorr, THIS JOURNAL, **74**, 4672 (1952).

[5] Symbols and nomenclature used in this paper follow the recommendations of the National Bureau of Standards, Letter Circular LC-857 (1947).

Phosphorus tribromide (C.P., Eastman Kodak) was used without further purification. Bromine was refluxed for six hours with potassium bromide and then distilled twice from anhydrous barium oxide.[6]

The purity and the dryness of the solvents were of paramount importance in this investigation because of the ease with which the halogen solutions can be decomposed by traces of water and impurities. Carbon tetrachloride and ethylene dichloride were purified by methods outlined in previous publications.[7,8]

Carbon disulfide was purified by shaking it for three hours with potassium permanganate solution (5 g./l.), for two hours with mercury and then with a solution of mercuric sulfate (2.5 g./l.). It was then dried over phosphorus pentoxide and distilled from barium oxide. The purified solvent had a boiling point of 46.5° at 760 mm.

Phosphorus Pentabromide.—Phosphorus pentabromide could not be prepared by a simple addition of bromine to phosphorus tribromide since any local excess of bromine over the stoichiometric proportions leads to the formation of solid phosphorus heptabromide. The reaction likewise could not be carried out in a carbon tetrachloride solution, because of the solvate complex formed.[4] However, it was found that if the reaction is carried out in carbon disulfide, the precipitate formed is quite pure.

A solution containing 50 g. of bromine in 50 ml. of carbon disulfide was added slowly, with constant stirring, to a solution of 90 g. of phosphorus tribromide in 50 ml. of carbon disulfide. Phosphorus pentabromide precipitated out, and after decantation of the supernatant liquid the crystals were transferred to a sintered glass filter where they were then washed with chloroform and immediately transferred to glass vials which were evacuated and sealed.

The yields were low (10–20%) mainly because of the high solubility of phosphorus pentabromide in carbon disulfide, and the necessity of having an excess of the tribromide in order to prevent the formation of the phosphorus heptabromide. The analysis gave 92.35% Br and 7.27 % P as compared with the theoretical 92.81% Br and 7.19% P.

Solutions.—All solutions were prepared in a dry-box to avoid absorption of atmospheric moisture. Concentrations of phosphorus pentabromide and phosphorus tribromide solutions were calculated from the weight of the dissolved solute. In the mixed solvent the volume of added phosphorus tribromide was carefully measured and the weight was calculated from its known density.

An attempt was made to titrate the phosphorus pentabromide solutions iodometrically. Although upon the addition of potassium iodide solution some iodine is liberated, the amount titrated was not reproducible and was invariably less than one equivalent per mole of phosphorus pentabromide. The results may be due to the reaction of liberated iodine with phosphorous acid formed by hydrolysis.

The bromine solutions were prepared by the addition of the halogen to the purified solvents. Their concentrations were determined iodometrically.

Cary absorption cells containing phosphorus pentabromide and bromine solutions were exposed to ordinary light for as long as 6 hours. No appreciable change in absorption was detected during that period. It is, therefore, believed that light has no appreciable effect on the absorption spectra of these solutions.

All the absorption measurements were made on freshly prepared solutions.

Results and Discussion

The absorption spectra of phosphorus pentabromide and of bromine in carbon tetrachloride are given in Fig. 1; similar curves were obtained in the other two solvents. The apparent dissociation of phosphorus pentabromide was then calculated from the value of the molar absorbancy indices at the maximum, with the assumption that the absorption is due entirely to free bromine. The results are shown in Table I.

Varying amounts of phosphorus tribromide were then added to each solution and the absorbance at the maximum was measured again. The variations of the molar absorbancy index in carbon tetrachloride and in ethylene chloride are shown in Fig. 2.

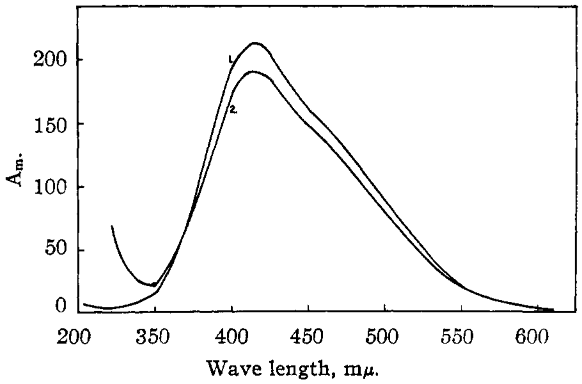

Fig. 1.—Absorption spectra of: 1, bromine; 2, phosphorus pentabromide in carbon tetrachloride. Concentration of bromine, 4.38 × 10^{-3}; concentration of PBr_5, 5.45 × 10^{-3}.

TABLE I

APPARENT DISSOCIATION OF PHOSPHORUS PENTABROMIDE

Solvent	Concn. PBr_5	a_mPBr_5	a_mBr_2	Per cent. app. dissn.
$C_2H_4Cl_2$	3.88 × 10^{-3}	198	218	90.8
CCl_4	3.31 × 10^{-3}	197	213	92.5
CS_2	3.59 × 10^{-3}	352	390	90.3

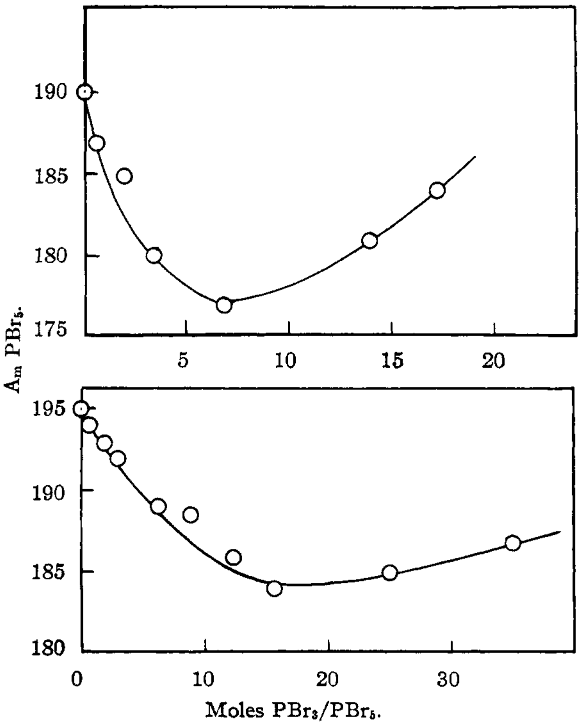

Fig. 2.—Variation of the molar absorbancy index of phosphorus pentabromide upon addition of phosphorus tribromide. Measurements taken at the absorption peaks. PBr_5 in CCl_4 is 1.20 × 10^{-2} *M;* in $C_2H_4Cl_2$, 1.41 × 10^{-2} *M.*

If bromine was the only absorbing species present in solution, the addition of phosphorus tribromide should produce a steady decrease in absorb-

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(6) F. Daniels, THIS JOURNAL, **56**, 378 (1938).

(7) A. I. Popov and J. J. Mannion, *ibid.*, **74**, 222 (1952).

(8) R. E. Buckles, J. P. Yuk and A. I. Popov, *ibid.*, **74**, 4379 (1952).

ance. However, in both solvents the absorbancy actually increased after an initial slight drop. In carbon disulfide, in which the molar absorbancy index of bromine is much higher than in the other two solvents, there is a definite change in the rate of decrease of absorbance when the excess of phosphorus tribromide is approximately 100-fold.

A solution of phosphorus pentabromide in phosphorus tribromide was then prepared. The solution was red in color and its absorption spectrum is given in Fig. 3. The maximum is at 418 mμ and the molar absorbancy index is 253. It seems reasonable to suppose that in the phosphorus tribromide medium the concentration of free bromine would be quite small, and could not account for the observed absorption. The latter must then be due to "solvated" bromine, either in the form $PBr_3 \cdot Br_2$, or, more likely, $(PBr_3)_n \cdot Br_2$. The upturn of the absorption curves 2 (Fig. 1) and 3 (Fig. 3) can be explained by increasing absorption of phosphorus tribromide below this wave length (see curve 2, Fig. 3).

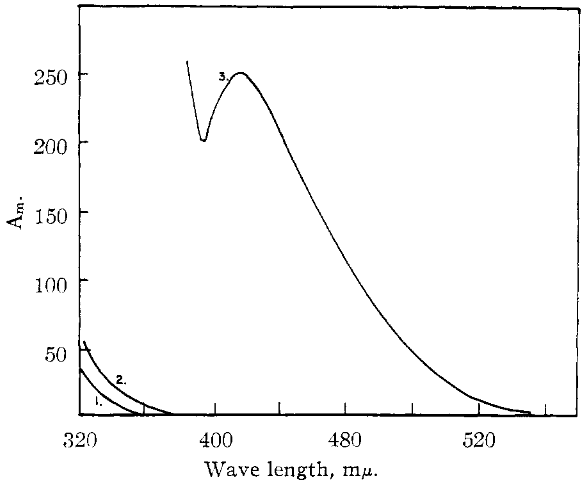

Fig. 3.—Curve 1, absorption spectrum of 7.65×10^{-3} *M* phosphorus pentachloride in carbon tetrachloride. Curve 2, absorption spectrum of 1.17×10^{-1} *M* phosphorus tribromide in carbon tetrachloride. Curve 3, absorption spectrum of 1.20×10^{-2} *M* phosphorus pentabromide in phosphorus tribromide.

Since such complex or complexes have a strong absorption in the wave length region studied, then the previous assumptions that the color is due only to the free bromine are in error, and the color of the phosphorus pentabromide *solutions* (Fig. 1, curve 2) is actually due to the absorption by both chemical species, free bromine and the $PBr_3 \cdot Br_2$ complex.

In order to establish the validity of the above assumptions a current of pure dry nitrogen was first passed through a 3×10^{-3} *M* solution of phosphorus pentabromide in carbon tetrachloride and then through an aqueous solution of potassium iodide. The gas was bubbled for 10 minutes and by the end of this period a considerable amount of free iodine was liberated in the KI solution. Thus the presence of free bromine in carbon tetrachloride was established. The experiment was repeated, under identical conditions, with a 3×10^{-3} *M* phosphorus pentabromide solution to which an approximately 30-fold excess of phosphorus tribromide was added, and then with a 3×10^{-3} *M* solution of phosphorus pentabromide in phosphorus tribromide. This time only a trace of free iodine was detected in the first solution, and none at all in the second. The tests for phosphorus were negative showing that the substance carried over by nitrogen was free bromine and not phosphorus pentabromide.

Since the molar absorbancy indices of the two phosphorus pentabromide solutions in carbon tetrachloride described above at 415 mμ do not differ by more than 5% (Fig. 2), the results seem to justify the conclusion that the color in solutions containing a large excess of phosphorus tribromide is due mainly to the undissociated phosphorus pentabromide.

In order to determine the degree of dissociation of phosphorus pentabromide in the solvents used, it is necessary to evaluate its molar absorbancy index at the given wave length. The common spectrophotometric practice in such cases, is to add sufficient amount of one of the reaction products so as to suppress the dissociation and to obtain a constant value for absorbance.[7,9] In this instance, however, upon the addition of an excess of phosphorus tribromide, the absorbancy index does not become constant (Fig. 2). The initial decrease of absorbance can be explained readily by the decrease in the dissociation of the phosphorus pentabromide. The subsequent increase is probably due either to a further solvation of the $PBr_3 \cdot Br_2$ complex by phosphorus tribromide, or to the gradual change of the refractive index of this solution with increasing mole fraction of phosphorus tribromide.[10]

In either case, the abrupt change in the value of the molar absorbancy index at the minimum at least roughly indicates that the dissociation of phosphorus pentabromide is practically suppressed. Therefore the absorbance at this point should correspond to that of the undissociated $PBr_3 \cdot Br_2$ complex, and the approximate value of its molar absorbancy index can be calculated.

Figure 4 represents the variation of the molar absorbancy index of phosphorus pentabromide as a function of the mole fraction of phosphorus tribromide, in the carbon tetrachloride–phosphorus tribromide mixtures. It is seen that the change in slope occurs at a very small fraction of phosphorus tribromide after which the molar absorbancy index is gradually approaching the one observed in pure phosphorus tribromide. Similar results were obtained in the other two solvents. These results indicate that the assumption as to the value of the molar absorbancy index of phosphorus pentabromide is a reasonable one.

Since phosphorus tribromide does not absorb at the wave lengths used, the absorption of the phosphorus pentabromide solutions is due to the bromine and to the phosphorus pentabromide. If additivities of absorbancies are assumed, the total absorption is given by

$$A_{s(\text{tot.})} = a_{m(\text{PBr}_5)}bC_{\text{PBr}_5} + a_{m(\text{Br}_2)}bC_{\text{Br}_2} \qquad (1)$$

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[9] G. Chalot and R. Gauguin, "Les Methodes d'Analyse des Reactions en Solution," Masson et Cie, Paris, 1951, p. 83.

[10] M. G. Mellon, "Analytical Absorption Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 96.

where $a_{m(PBr_5)}$ and $a_{m(Br_2)}$ are the molar absorbancy indices of phosphorus pentabromide and bromine, respectively, at the maximum, C_{PBr_5} and C_{Br_2} are their respective equilibrium concentrations, and b is the path length.

If C is the original concentration of phosphorus pentabromide and α is the degree of dissociation, eq. 1 can be written as

$$A_{s(tot.)} = a_{m(PBr_5)}b(1 - \alpha)C + a_{m(Br_2)}b\alpha C \qquad (2)$$

It is now possible to calculate the degree of dissociation from the measured absorption of a phosphorus pentabromide solution. Since all the solutions used were dilute ($\approx 10^{-3}M$) the equilibrium constant was calculated from the Ostwald dilution law. At least five independent measurements were made in each solvent. The results are given in Table II.

TABLE II

DISSOCIATION CONSTANTS FOR THE REACTION $PBr_3{\cdot}Br_2 \rightarrow PBr_3 + Br_2$ IN CARBON TETRACHLORIDE AND ETHYLENE CHLORIDE AT 25°

Expt.	$C_{PBr_5} \times 10^2$, M	A_s	α	$K \times 10^3$, M
I. Carbon tetrachloride; molar absorbancy index of PBr_5 = 177 (Fig. 2); molar absorbancy of Br_2 = 213				
1	0.331	0.652	0.556	2.30
2	.545	1.07	.528	3.22
3	.572	1.12	.528	3.38
4	1.17	2.21	.333	1.95
5	1.28	2.42	.332	2.13
II. Ethylene chloride; molar absorbancy index of PBr_5 = 184 (Fig. 2); molar absorbancy index of Br_2 = 218				
1	0.388	0.768	0.412	1.12
2	.785	1.59	.544	5.09
3	.865	1.73	.471	3.62
4	.905	1.79	.412	2.60
5	1.41	2.75	.324	2.19

It must be noted that the above results depend upon the accuracy of the value taken for the molar absorbancy index of phosphorus pentabromide in the respective solvents. Since the latter cannot be accurately determined, *no great accuracy can be claimed for the K values.* However, it is believed that they at least indicate the correct order of magnitude, and show that the dissociation of phosphorus pentabromide is considerably smaller than previously reported.

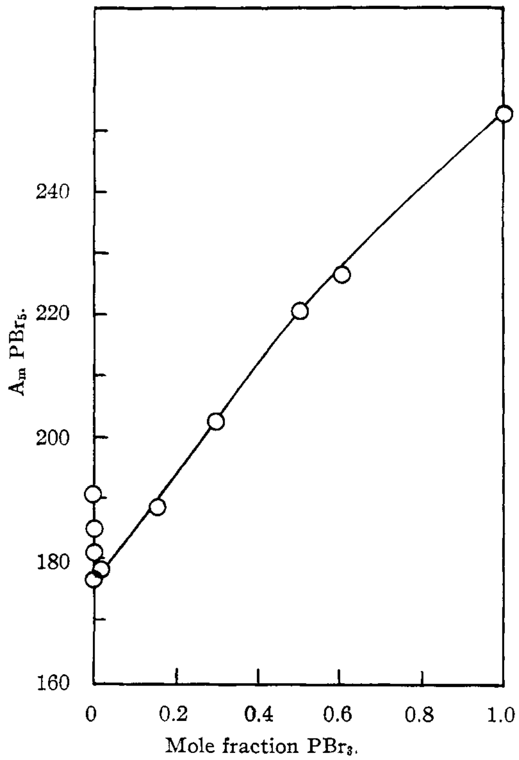

Fig. 4.—Molar absorbancy index 5.33×10^{-3} M solution of phosphorus pentabromide in CCl_4–PBr_3 mixtures at the absorption maximum.

Since the molar absorbancy index of phosphorus pentabromide solution in carbon disulfide is higher than that in phosphorus tribromide, the estimation of the dissociation constant is more uncertain and no attempt was made to evaluate it.

An attempt was made to determine the extent of dissociation of phosphorus pentachloride. Its solution in carbon tetrachloride did not show any appreciable absorption at 332 mμ where chlorine has maximum absorption (Fig. 3). Likewise the presence of free chlorine could not be detected by extraction with an aqueous solution of potassium iodide and starch. Evidently phosphorus pentachloride does not dissociate in carbon tetrachloride solutions.

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