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

Studies on the Chemistry of Halogens and of Polyhalides. VII. The Addition of Bromine to Phosphorus Trichloride[1]

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The reaction of phosphorus trichloride with bromine was investigated under different experimental conditions. Spectrophotometric measurements in carbon tetrachloride and nitrobenzene gave no evidence for the formation of mixed halides in solution. Direct reaction of the two components resulted in an unstable aggregate with the empirical formula $PCl_3Br_{5.7}$, which, when subjected to reduced pressure formed a stable mixed halide with the empirical formula $PCl_{4.67}Br_{0.33}$. Further thermal treatment of this mixed halide resulted in a new crystalline modification of phosphorus pentachloride. This new form of phosphorus pentachloride can also be obtained by sublimation of ordinary phosphorus pentachloride. Powder X-ray diffraction studies show that the mixed halide $PCl_{4.67}Br_{0.33}$ has a face-centered cubic cell with $a = 12.38$ Å., $U = 1897$ Å.^{3}, $D_x = 2.34$ g./cc., with cell contents of $P_{12}Cl_{56}Br_4$.

Introduction

While the mixed halides of phosphorus have been the subject of numerous investigations, these efforts have not been successful in elucidating the chemical nature and the properties of the resulting compounds. A survey of the literature shows that there is no agreement as to the chemical composition of the compounds formed on the addition of bromine to phosphorus trichloride. The product has been identified as phosphorus pentabromide,[2] as a mixture of bromochlorides such as $PCl_{3.15}Br_{1.89}$,[3] as PCl_3Br_8, PCl_2Br_7 and PCl_3Br_4[4] or as a series of compounds of the general formula PCl_3Br_n[5] with $n = 4, 5, 6, 7, 8$ and 10. In a later publication reaction products were reported to be $PCl_{4.05}Br_{0.95}$, $PCl_{4.21}Br_{0.85}$ and $PCl_{4.23}Br_{0.83}$.[6] Other mixed halides where the total halogen to phosphorus ratio was equal to 5/1 have been reported by Renc.[7]

Recently the question of the interaction between phosphorus trichloride and bromine was reinvestigated by Fialkov and Kuz'menko[8] who have studied the melting point diagram, the specific conductance and the viscosity of the PCl_3–Br_2 system. They reported the existence of compounds PCl_3Br_4, PCl_3Br_8 and PCl_3Br_{18}. The ion transference measurements in nitrobenzene led them to suggest that the structure of these compounds was $(PCl_3Br)^+(Br(Br_2)_n)^-$.

It can be seen readily from the above summary that the question of the exact nature of phosphorus polyhalides and mixed halides has not been unambiguously answered and it has been decided to reinvestigate this problem under carefully controlled experimental conditions.

Materials and Methods

Reagents.—C.P. phosphorus trichloride was distilled in an anhydrous atmosphere into a series of small glass ampules which were sealed until needed. The b.p. was 74.5–75.5° at 747 mm.; the literature value gives 75.7° at 749 mm.

C.P. bromine was purified according to the method of Daniels.[9]

Carbon tetrachloride was purified by refluxing with alkaline potassium permanganate, washing with water and drying with barium oxide. The solvent was then twice fractionally distilled from phosphorus pentoxide. The b.p. was 76.2° at 750 mm. Literature value is 76.74° at 760 mm.

Nitrobenzene was fractionally distilled three times under reduced pressure (2–6 mm.) from barium oxide. The purity was checked by measuring the specific conductance of the product, which was found to be less than 1×10^{-8} ohm^{-1} cm.$^{-1}$ given in the literature.

The source and the purification of acetonitrile were given in a previous publication.[10]

Spectrophotometric Measurements.—All spectrophotometric measurements were made on a Cary recording spectrophotometer Model 11. Stoppered silica cells of 1.00 ± 0.01 cm. path length were used. The measurements were made at room temperature of approximately 25°.

Analytical Techniques.—Solid mixed halides obtained in this investigation were analyzed in the following manner. The sample was first hydrolyzed with dilute ammonia in a stoppered flask. Considerable heat was evolved during the initial stages of hydrolysis, and acid fumes were given off. However, since the reaction took place in a closed system, there was no danger of loss of the halogens during hydrolysis.

An excess of a standard silver nitrate solution was then added and after digesting, filtering and washing the precipitate, excess silver in the combined filtrate and washings was titrated with standard thiocyanate. From the weight of the mixed silver halides obtained and from the total amount of silver used, it was possible to calculate the percentages of chlorine and of bromine present in the sample. This method of analysis was found to be superior to the electrometric method recently described by Fort.[11] Phosphorus was determined by the volumetric phosphomolybdate method. In the spectrophotometric part of this investigation phosphorus trichloride solutions were hydrolyzed with dilute ammonia and the chlorine was determined by the Volhard method. Bromine solutions were standardized by an iodometric titration with a standard sodium thiosulfate solution.

X-Ray Diffraction Studies.—X-Ray powder diagrams were obtained using a Debye–Scherrer type powder camera, Straumanis film mount, with a radius of 5.73 cm. Samples were packed in thin-walled glass capillaries about 0.3 mm. in diameter and were exposed to Ni filtered Cu Kα radiation (1.5418 Å.).

Use of Dry Box.—Since all compounds studied in this project are extremely hygroscopic, all transfers, preparation of stock solutions, loading of capillaries, etc., were done in a dry box in dry nitrogen atmosphere.

Experimental Results

I. Preparation of Mixed Halides

Attempted Preparation of PCl_3Br_4.—Attempt was made to prepare PCl_3Br_4 according to the method outlined by

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[1] From the M.S. Thesis of David H. Geske, State University of Iowa, June, 1955.

[2] J. H. Gladstone, *Phil. Mag.*, [3] **35**, 345 (1849).

[3] A. Michaelis, *Ber.*, **5**, 9 (1872).

[4] M. Prinvault, *ibid.*, **5**, 324 (1872).

[5] T. Milobedzki and J. Tomasewski, *Sprawozdania Pozn. Tow Przyjiaciol Nauk*, **1**, 22 (1927).

[6] T. Milobedzki and S. Krakowiecki, *Roczniki Chem.*, **8**, 563 (1928); **10**, 158 (1930).

[7] A. Renc, *ibid.*, **13**, 454, 509, 569 (1933); **14**, 69 (1934).

[8] Ya. A. Fialkov and A. A. Kuz'menko, *Zhur. Obshchei Khim.*, **21**, 433 (1951); **22**, 1290, 1335 (1952); A. A. Kuz'menko, *Ukrain. Khim. Zhur.*, **18**, 589 (1952).

[9] W. H. Bauer and F. Daniels, THIS JOURNAL, **56**, 378 (1934).

[10] A. I. Popov and N. E. Skelly, *ibid.*, **76**, 5309 (1954).

[11] R. Fort, *Chim. anal.*, **34**, 143 (1952).

Fialkov and Kuz'menko[8]; 25 ml. of bromine was mixed with 50 ml. of phosphorus trichloride (46 mole % bromine). The mixture separated into two liquid layers. The lower layer was removed and solidified by cooling in Dry Ice-acetone bath. The solid product was dissolved at room temperature in carbon tetrachloride and upon cooling the solution, fine orange-red crystals precipitated out. The solution was filtered through a sintered glass filter and dry nitrogen at room temperature was passed over the crystals. The latter appeared to lose bromine rapidly leaving a residue of yellow powder. Various modifications of the technique described above were used in an attempt to separate the crystals from the carbon tetrachloride solution without subsequent decomposition, but they were all unsuccessful.

Finally the solidified lower layer was analyzed without any attempts at purification. The analysis showed the following composition: P, 5.2%; Br, 76.4%; Cl, 17.8%. Instead of expected composition of PCl_3Br_4, the analysis corresponds to the empirical formula $PCl_3Br_{5.7}$. The melting point of this phase was 36.8–38°. When this material was kept for several days in an evacuated glass tube at 30°, it was transformed into large clear red crystals. The analysis of these crystals as well as numerous other preparations obtained in a similar manner gave chlorine/bromine ratios ranging from 3/5.7 to 3/5.1. In no case was the rato $^3/_4$ obtained. Spectrophotometric study of this compound is given in Part II of this paper.

Investigation of the Yellow Powder.—The yellow powder left after the decomposition of the polybromide appeared to be quite stable in dry atmosphere. It can be readily prepared by placing the red crystals of $PCl_3Br_{5.7}$ into a flask and evacuating to approximately 5 mm. at room temperature for several hours until no further change in the residue is visible. Analysis of the products obtained under varying conditions of preparation gave from 13.3 to 14.4% bromide, 71.4–72.0% chlorine and 13.1 to 13.2% phosphorus which corresponds approximately to the empirical formula $PCl_{4.8}$-$Br_{0.2}$

This powder was sealed into an evacuated glass tube which was then partially immersed in a constant temperature bath maintained at approximately 50°. The protruding end of the tube was jacketed and cold water was circulated through the jacket. After one week the material had completely sublimed from the lower end of the tube and transparent yellow crystals were formed in the middle portion of the tube with some orange-red material deposited on the cold portion. Analysis of the yellow crystals gave the following results: P, 13.3_0%; Cl, 73.8_2%; Br, 11.6_9%. Calculated values for $PCl_{4.67}Br_{0.33}$ are: P, 13.89%; Cl, 74.17%; Br, 11.94%. It is seen from the above results that the powder represents a mixed pentahalide of phosphorus in which the ratio of the chlorine/bromine atoms is 14/1. Consideration of X-ray diffraction and density data indicates that the unit cell contents of the crystalline material are $P_{12}Cl_{56}Br_4$, hence, it is not a non-stoichiometric compound as the empirical formula might indicate.

The compound melted in a sealed tube at 145–148°. The change of phase is reversible. Refractive index was determined by observing the "Becke line" through a microscope when the crystals were immersed in various mixtures of α-bromonaphthalene and *n*-butyl phthalate and was found to be 1.64_7. Optical properties of the crystals as observed through a polarizing microscope showed them to be isometric and therefore belonging to the cubic system. The density of the crystals determined by the flotation method in mixtures of bromoform and methyl iodide was found to be 2.37.

When the mixed pentahalide of phosphorus was subjected to vacuum sublimation at 80° a white powdery material was observed to condense on the cold portion of the tube. The analysis gave 84.8% chlorine and 14.9% phosphorus with a small trace of bromine. This compared reasonably well with the composition of phosphorus pentachloride which is 85.22% chlorine and 14.88% phosphorus. Subsequent X-ray studies showed it to be a hitherto unknown crystalline modification of phosphorus pentachloride (see below). This same new form of phosphorus pentachloride can be obtained by rapid sublimation under reduced pressure of the ordinary tetragonal form of phosphorus pentachloride. The density and the melting point remain unchanged.

II. Spectrophotometric Studies

Behavior of the PCl_3–Br_2 System in Carbon Tetrachloride.—The absorption curve of bromine in carbon tetrachloride solutions was measured; the solutions were found to be stable for at least 24 hours. Addition of phosphorus trichloride (which does not absorb in the region 275–650 mμ) to the bromine solution in carbon tetrachloride did not produce any change in the absorption spectrum of the halogen. This behavior was opposite to the one observed upon the addition of phosphorus tribromide to bromine solution in the same solvent.[12] A continuous variation study[13] was made on the PCl_3–Br_2 system but no evidence of interaction was obtained.

Studies in Nitrobenzene and Acetonitrile Solutions.—The behavior of the PCl_3–Br_2 system in nitrobenzene was of special interest because of the electrical conductance study carried out by Fialkov and Kuz'menko.[8] However, since nitrobenzene is opaque below 420 mμ, spectrophotometric measurements had to be made at higher wave lengths rather than at the bromine absorption maximum.

Values of the molar absorbancy indices determined for bromine in carbon tetrachloride and in nitrobenzene are, respectively, 425 mμ, 201 and 215; 450 mμ, 160 and 164; 500 mμ, 94 and 72. These results contradict the statement of Joseph[14] that the bromine color is about half as intense in nitrobenzene as in carbon tetrachloride, but agree with the spectra reported by Child and Walker.[15]

The value of 209 for the molar adsorbancy index at 430 mμ was found to be entirely reproducible and all subsequent measurements were done at this wave length.

Equimolar solutions of phosphorus trichloride and bromine were prepared in nitrobenzene and analyzed as described above. The total concentration was 1×10^{-2} *M* and the mole ratio of the two components was varied from 9:1 to 1:9. A decrease in absorbance compared with that calculated for bromine alone was observed, but the solutions were found to be unstable and the absorption decreased rapidly with time even when extreme precautions were taken to assure seemingly completely anhydrous conditions. It seems doubtful that this change in the absorption spectrum is due to interaction between bromine and phosphorus trichloride.

Bromine solutions in acetonitrile were found to be unstable and spectrophotometric measurements showed the presence of the tribromide ion.

Spectrophotometric Study of the Mixed Halides.—The mixed halide of the empirical composition $PCl_3Br_{5.7}$ was dissolved in carbon tetrachloride and its absorption spectrum was measured. It was found to be identical to that of bromine in the same solvent and the concentration of the bromine as calculated from the absorption maximum at 416 mμ agreed to within 0.5% with the bromine determined gravimetrically.

When dissolved in acetonitrile the compound gave immediately the characteristic absorption spectrum of the tribromide ion with a maximum at 269 mμ and an apparent molar absorbancy index of 2.7×10^4. The bromine peak at 392 mμ was not observed.

The absorption spectrum of the mixed pentahalide crystals in the same solvent is given in Fig. 1. In the region above 360 mμ, it is in all respects identical with the absorption curve of bromine. However, below 360 mμ it indicates the presence of another absorbing species whose absorption maximum apparently lies below the transmission limit of the carbon tetrachloride (dotted line indicates absorption spectra of bromine below 360 mμ). Absorption curve of phosphorus pentachloride was then run in the same solvent and the molar absorbancy indices of the pentachloride were determined in the 300–330 mμ range. Knowing the con-

Table I

Absorption Data for the Mixed Pentahalide

Wave length, mμ	A_s	a_m-(Br_2)	$A_s(Br_2)$	$A_s(PCl_5)$	a_m-(PCl_5)	(PCl_5) $\times 10^2$
300	1.160	4	0.016	1.144	87	1.31
310	0.825	2	.008	0.817	61	1.34
320	.530	1	.004	.526	39	1.35
330	.300	2	.008	.292	22	1.33

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(12) A. I. Popov and N. E. Skelly, This Journal, **76**, 3916 (1954).

(13) P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

(14) A. F. Joseph, *J. Chem. Soc.*, **107**, 1 (1915).

(15) C. L. Child and O. J. Walker, *Trans. Faraday Soc.*, **34**, 1506 (1938).

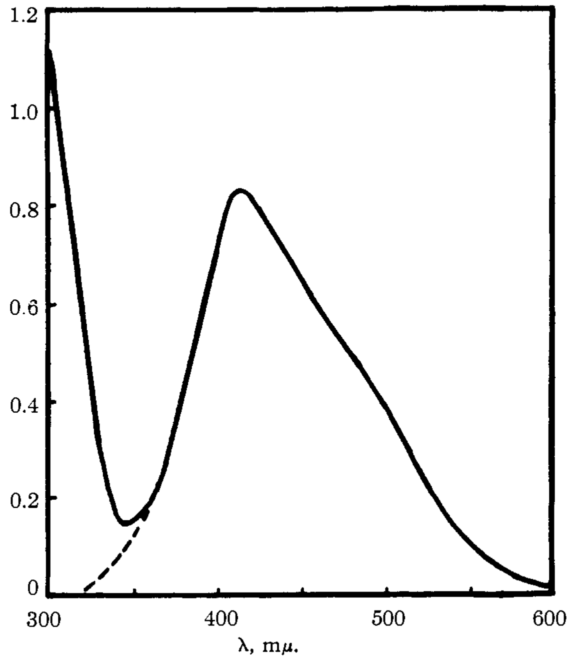

Fig. 1.—Absorption spectrum of 2.1×10^{-2} M $PCl_{4.67}Br_{0.33}$ in carbon tetrachloride at 25°, 1 cm. cell. Dotted line shows absorption of bromine below 360 mμ.

centration of bromine and its molar absorbancy indices in the same region it is possible to calculate the apparent concentration of phosphorus pentachloride in the solution of the mixed pentahalide. Table I gives the results of these calculations. From the constancy in the calculated value of (PCl_5) it can be reasonably concluded that the absorption below 360 mμ is due to phosphorus pentachloride and therefore that the mixed pentahalide dissociates in carbon tetrachloride into phosphorus pentachloride and bromine.

III. X-Ray Diffraction Studies

Powder X-ray diffraction diagrams were obtained for phosphorus pentabromide, phosphorus pentachloride, sublimed pentachloride, the mixed halide $PCl_{4.67}Br_{0.33}$ and $PCl_3Br_{5.7}$. The powder diagrams of phosphorus pentachloride and phosphorus pentabromide were found to agree with the cell dimensions reported for them in the literature.[16,17] The sublimed phosphorus pentachloride X-ray diagram differs considerably from that of the ordinary phosphorus pentachloride. A line comparison diagram of the two substances is given in Fig. 2. The sublimed pentachloride when melted and solidified gives the powder diagram of the ordinary pentachloride.

The X-ray powder diagram of $PCl_{4.67}Br_{0.33}$ shows it to be a unique single phase and not a mixture of different crystalline components. All the lines on the powder diagram arise from a face-centered cubic unit cell with a = 12.38 Å., U = 1897 Å.^{3}, D_x = 2.34 g./cc. (calculated from cell contents of $P_{12}Cl_{56}Br_4$). A structure determination based on powder data alone obtained fair agreement for an arrangement of 8 PCl_4^+ ions, 4 PCl_6^- ions and 4 Br^- ions closely related to the CsCl type structure.

Because some discrepancies in the intensity agreement exist, it is quite likely that the true structure differs slightly from this simple arrangement. A complete structure determination based on single crystal data will be reported later. The powder diagram of the sublimed phosphorus pentachloride resembles the diagram of $PCl_{4.67}Br_{0.33}$, so that its structure will probably be closely related to that of $PCl_{4.67}Br_{0.33}$. Again, single crystal data will be necessary for the solution of the structure.

Powder diagrams of $PCl_3Br_{5.7}$ were very complex with rather broad lines which indicated that it might be a mixture of crystals with related structures but slightly differing cell dimensions. The pattern did not appear to represent mixtures of phosphorus pentabromide and phosphorus pentachloride.

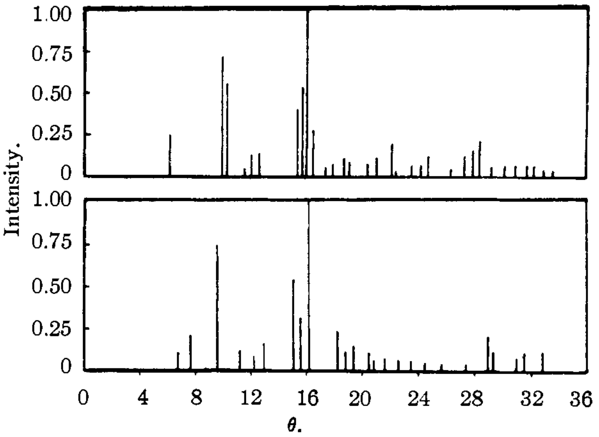

Fig. 2.—Line comparison diagram of ordinary phosphorus pentachloride (top) and sublimed phosphorus pentachloride (bottom).

Discussion and Conclusions

In general, the results outlined above indicate that in all probability the addition of bromine to phosphorus trichloride results initially in the formation of a non-stoichiometric aggregate of approximate formula $PCl_3Br_{5.7}$ in which the chlorine/bromine ratio may vary over a rather considerable range of values. Compounds containing more than five equivalents of halogens for one equivalent of phosphorus are unstable and tend to lose bromine readily, under reduced pressure. However, the decomposition reaction does not represent the reversal of the formation reactions since the halides apparently undergo disproportionation and yield phosphorus pentachloride as the ultimate product. Such results are not surprising in view of the disproportionation of phosphorus dibromotrifluoride as observed by Moissan[18] in which phosphorus pentafluoride and pentabromide are formed.

$$5PF_3Br_2 \longrightarrow 3PF_5 + 2PBr_5$$

It can be suggested tentatively that in the case of phosphorus trichloride and bromine the reaction occurs in two or more steps, involving PCl_3Br_2 as an intermediary product. This compound is highly unstable and disproportionates at room temperature and reduced pressure to a stable phase $PCl_{4.67}Br_{0.33}$ which at higher temperature goes to phosphorus pentachloride, and presumably either phosphorus tribromide or phosphorus pentabromide. According to this hypothesis, the over-all reactions would be

$$PCl_3Br_{5.7} \longrightarrow PCl_3Br_2 + 1.85Br_2$$
$$5PCl_3Br_2 \longrightarrow 3PCl_5 + 2PBr_5$$

Comparison of the absorption spectra of the $PCl_3Br_{5.7}$ aggregate and the mixed pentahalide $PCl_{4.67}Br_{0.33}$ shows that phosphorus pentachloride appears in solution only for the latter. This lends support to the suggestion that the disproportiona-

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(16) D. Clark, H. M. Powell and A. F. Wells, *J. Chem. Soc.*, 642 (1942).

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(18) H. Moissan, *Compt. rend.*, **100**, 1348 (1885).

tion reaction takes place upon evacuation of the $PCl_3Br_{6.7}$ aggregate and not before.

The X-ray evidence unambiguously indicates that the mixed halide $PCl_{4.67}Br_{0.33}$ is a true monophasic crystal and not a microcrystalline mixture of the respective phosphorus pentahalides.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

A Kinetic Study of the Reaction of Decaborane with Alcohols

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The reaction of decaborane with low molecular weight alcohols to yield borate esters and hydrogen has been found to be consistent with the general concepts of the absolute and statistical kinetic theories. Specific bimolecular rate constants, energies of activation and Arrhenius frequency factors are given for several alcohols and relative rate constants are given for the reaction in several solvents of varying dielectric constant. For the reaction involving primary alcohols, the observed increase in rate constant as the number of carbon atoms increased from two to five and the effect of the dielectric constant of the medium, was found to be consistent with the application of Kirkwood's formula to the absolute theory of reaction rates. It is shown that a reasonable correlation between the observed heats of activation with the energy of the boron hydrogen bond and with the ionization energies of the alcohols is possible, thereby indicating that the boron hydrogen bond and the electrons on the alcohol are probably involved in the rate-determining step. The relative values of the entropies of activation are found to be in reasonable accord with the concept of a decrease in activation entropy with increasing complexity of the molecules concerned. The existence of intermediates in the alcoholysis reaction was not shown by the kinetic data, so that the point of attack of the alcohol on the decaborane was not determined. The results did not lead to any information concerning the nature of the reaction course involved in the formation of products from the activated complex.

The chemistry of the boron hydrides has been of increasing interest in the past few years.[2] This work is an attempt to add to the knowledge of these compounds by a kinetic study of the reaction of decaborane with several representative alcohols. Some of the properties of the activated complex were deduced from a study of the influence of solvent character and of the alcohol nature on the rate constant. Heats of activation and frequency factors were obtained for several alcohols. Application of the generally accepted theories of chemical kinetics to the observations yielded a consistent interpretation of the results of the experimental work. In analogy with the reaction of the lower boron hydrides with alcohols,[2-4] decaborane reacted with alcohols[5] to form alkyl borates and hydrogen according to equation 1

$$30ROH + B_{10}H_{14} \longrightarrow 10B(OR)_3 + 22H_2 \qquad (1)$$

This reaction was studied with a specific effort to obtain any information on a kinetic basis for the presence of intermediates, either of a substituted decaborane nature or of a substituted borine nature,[3,4] but there was no indication in the kinetic pattern that any of these were formed.

Experimental

Materials.—In this study decaborane of 98% purity was further purified by vacuum sublimation and by recrystallization from pentane and subsequent removal of the pentane by storing in a vacuum desiccator over $CaCl_2$ to protect from moisture. The melting point of decaborane purified by either method (99.5°) was found to agree well with the value found by Stock for carefully purified samples.[6] Storage of this material in an unevacuated desiccator resulted in an unexplained increase in the observed rate constant after a few days, so the purified product was stored under vacuum. Stock also observed a similar phenomenon in his samples.[6]

The alcohols and solvents used in this study were dried either with metallic calcium or with calcium sulfate and distilled twice from a dry flamed all glass distilling flask equipped with a Vigreux column, and small middle fractions were taken for the kinetic experiments. The higher boiling branched alcohols were distilled under reduced pressure from the same apparatus. The boiling points and refractive indices agreed with those listed in the literature.[7] All materials were stored in a desiccator and repurified once more near the end of a set of experiments and the kinetics results remeasured and compared with the previous runs.

Method.—The reaction of decaborane with alcohols was found to yield hydrogen and the corresponding borate ester in good yield, even in two cases where the alcoholysis of BCl_3 or B_2O_3 gave no borate esters.[8] The following yields based on equation 1 were reported to us by Schar[9]: *n*-propyl, 95%; *n*-butyl, 98%; *sec*-butyl, 93%; *t*-butyl, 85–90%; *t*-amyl, 92%. These values showed that equation 1 was followed and that the reaction, under our experimental conditions, was subject to only minor side reactions, if any. A check of the hydrogen liberated under experimental conditions was found to yield 95–100% of the amount calculated by this equation.

The rates of alcoholysis were measured by studying the rate of hydrogen evolution according to equation I. Several runs were made for *n*-butyl alcohol and decaborane with the decaborane at a concentration of about 0.1 mole/liter and the alcohol concentration at about 0.1 mole/liter (equimolar quantity) and at about 3.0 mole/liter (equivalent quantity). Both alcohol concentrations gave analogous bimolecular relative rate constants except for the dielectric effect described later. Since no evidence for any intermediates was obtained, it was assumed that the rate of decaborane disappearance was $-1/22$ of the rate of appearance of the hydrogen gas evolved.

The increase in hydrogen pressure was measured with a Barcroft–Warburg[10] apparatus consisting of a small mercury

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[1] Taken in part from the thesis submitted by Thrygve R. Meeker to the University of Delaware in partial fulfillment of requirements for the degree of Doctor of Philosophy.

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