

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

Trifluoromethyl Hypofluorite: Its Decomposition and its Reaction with Carbonyl Fluoride to Form Perfluorodimethyl Peroxide¹BY ROGER S. PORTER² AND GEORGE H. CADY

RECEIVED MAY 4, 1957

When an electric spark is passed through trifluoromethyl hypofluorite (CF_3OF), the gas decomposes. Elevated temperatures also cause the gas to decompose. In this case the reaction is reversible and the equilibrium for the change, $\text{CF}_3\text{OF} \rightleftharpoons \text{COF}_2 + \text{F}_2$, has been studied over the temperature range, 367 to 467°. From equilibrium constants, the value of ΔH for the reaction has been calculated to be 27.7 kcal. per mole of CF_3OF . The energy of the OF bond in CF_3OF has been estimated to be 47 kcal. per mole. At temperatures between about 250 and 300° the reaction $\text{COF}_2 + \text{CF}_3\text{OF} = \text{CF}_3\text{OOCF}_2$ takes place. Perfluorodimethyl peroxide also has been formed by combining fluorine with either carbon monoxide or carbonyl fluoride.

In their original studies of trifluoromethyl hypofluorite, Kellogg and Cady³ found that the gas could be passed through a copper tube held at about 450° without being destroyed. This indicated either that the substance did not decompose at this temperature or that the decomposition, if it occurred, was reversible. The decomposition is now known to be reversible. In addition to studying the thermal decomposition in this research, the effect of an electric spark upon CF_3OF was examined.

Decomposition of CF_3OF in an Electrical Discharge

In a Glass System.—A cold-glow electrical discharge from a "leak tester" of the Tesla-coil type was passed through a stream of gaseous CF_3OF as it flowed at about 1 cm. pressure through a Pyrex glass capillary. Two millimoles of the gas were passed four different times through the discharge, during which time the glass capillary became badly etched. About 5% of the CF_3OF remained unchanged. The products recognized by analysis were CF_4 , CO_2 , O_2 , and SiF_4 . A gas which condensed to an orange colored solid when cooled to liquid air temperatures was observed, but because of its instability it was not identified.

In Metallic Vessels.—Since the above experiment indicated that glass was attacked badly, a fluorine resistant apparatus was constructed from copper, brass, nickel, and silver solder. The spark jumped between two copper rods placed parallel to each other and separated by a gap of about 3 mm. The electrodes were not seriously attacked. The copper rods were located within a vessel of nearly 1.5 liters capacity and were fastened to an assembly which could be removed easily from the vessel. One electrode was grounded to the vessel, the other was passed through an electrical insulator made from a small piece of aluminum metaphosphate glass. At first the vessel was equipped with a window of Kel-F plastic (polymeric $\text{C}_2\text{F}_5\text{Cl}$) through which the spark could be observed. A small diaphragm valve was used to separate the metallic part of the apparatus from the part made of glass. The glass line included a mercury manometer and traps and bulbs used for analysis of the reaction products. Stopcocks and standard taper ground joints were lubricated with Kel-F grease. As a run was in progress, the electrical discharge was stopped at intervals. After waiting a few minutes in each case the nickel valve was opened and the pressure was measured using the mercury manometer. Before sparking was resumed the nickel valve was again closed. A low energy, high frequency spark was used. It was produced either by a small spark coil or by a "leak tester."

Before successful runs were made, the apparatus failed several times in interesting ways. Most of the trouble involved the insulator on the electrode. At first this was a Teflon plug. After passing a spark for a few minutes the Teflon plug ignited spontaneously as the result of reacting with a very active substance (perhaps fluorine atoms) in the gas. An insulator of Pyrex glass was then tried. This was

eaten away rapidly and also was not satisfactory. Finally success was achieved with an insulator of glass composed mostly of aluminum metaphosphate. This contained only a little silica and the rate of attack was low. After this problem was solved, the Kel-F window failed. While a spark passed through F_2 gas, the window took fire and burned. It was replaced with a fluorinated copper plate. This window was located on the same level as the spark but at about 5 cm distance.

In the most successful run, the starting pressure of CF_3OF was 10 cm. As the spark passed the pressure rose rather rapidly at first and then at a diminishing rate. The run was terminated after 24 hours when it was apparent that no further change from a pressure of 17 cm. was to be expected. For each mole of CF_3OF originally present the gas was found to contain these substances in the molar amounts indicated: 0.20 CF_3OF , 0.38 COF_2 , 0.37 F_2 , 0.31 CF_4 , 0.30 CO_2 , 0.08 SiF_4 , 0.06 O_2 , 0.01 other. The mass spectrum showed trace amounts of fluorocarbons or fluorinated derivatives containing more than one carbon atom per molecule. Since this analysis indicated a small increase in the number of gram atoms of carbon and oxygen, it follows that these elements as well as silicon must have been added from the walls of the apparatus. The most likely source for carbon was the Apiezon wax used remotely to hold the aluminum metaphosphate glass insulator and to make a gas-tight seal. The added oxygen and silicon could have come either from the insulator or from the glass line leading to the manometer.

Reversible Thermal Dissociation of CF_3OF

Apparatus.—A cylindrical reaction vessel was constructed from $\frac{1}{8}$ inch nickel sheet. The seams of the vessel and the $\frac{1}{4}$ inch Monel metal inlet tube were nickel welded. The inside diameter of the vessel was approximately 12.7 cm. and the volume was 1.71 liters. Upon the outside of the top, bottom and side of the vessel three Chromel-Alumel thermocouples were brazed with a nickel alloy having a remelting temperature above 1000°K. A fourth thermocouple was calibrated at the boiling points of water, sulfur and mercury, and was then placed next to the nickel vessel without brazing. Thermocouple voltages were measured with a potentiometer. The nickel reactor was surrounded by a copper jacket of 6.3 mm. wall thickness. An air space of about 3 mm. separated the two metals and the space was maintained by a few porcelain spacers. The thermocouple wires and the Monel metal inlet tube passed through holes in the copper jacket.

Heating was accomplished with several 5-ohm Calrods spaced regularly over the outer faces of the copper jacket. A Hoke No. 413 diaphragm valve of nickel was placed between the reactor inlet and the Pyrex glass vacuum manifold. A Booth-Cromer pressure transmitter was connected to the inlet tube. This instrument was operated by automatically balancing air pressure in an external manometer against the pressure of gas in the metallic system.⁴ The transmitter allowed pressures to be measured in an all-metal system.

Results.—Pressure and temperature measurements were taken during the slow and carefully controlled heating and cooling of samples of CF_3OF . The data, some of which are

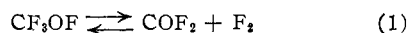
(1) Presented at the Atlantic City Meeting of the American Chemical Society, September 18, 1956. From the Ph.D. thesis of R. S. Porter, University of Washington, 1956.

(2) California Research Corporation, Richmond, California.

(3) K. B. Kellogg and G. H. Cady, *THIS JOURNAL*, **70**, 3986 (1948).

(4) S. Cromer, "The Electronic Pressure Transmitter and Self-Balancing Relay," Atomic Energy Commission, declassified 3/20/47 (MDDC), Columbia University, New York, 6/20/41.

represented in Fig. 1 by lines, show that between 300 and nearly 600°K. CF_3OF behaved as an ideal gas within the limits of measurement. Between 600 and 740°K., however, CF_3OF decomposed reversibly, as indicated by the abnormally large changes in pressure which accompanied increments of temperature. The substances formed by this dissociation were identified by analysis of rapidly cooled samples removed from the nickel vessel while held at temperatures ranging between 600 and 825°K. These samples contained carbonyl fluoride and elementary fluorine together with trifluoromethyl hypofluorite. As long as the temperature of the gas remained below about 750°K., the curves shown in Fig. 1 were reproduced either by increasing or decreasing the temperature. The abnormal change in pressure with temperature was caused by the reaction



As work progressed, numerous samples of gas were allowed to react with potassium iodide solution, and the resulting iodine was titrated. At temperatures below 750°K. the gas retained its ability to liberate iodine and lost little or none of this capacity over a period of several hours. This was clearly shown by measurements with the gas held at 700°K. and later at 740°K. At 750°K. there was a slow loss of the ability to liberate iodine and at 775°K. the rate was greater. After 21 hours at the latter temperature the gas had lost about 72% of its capacity for oxidizing iodide ion.

After a sample of CF_3OF had been heated to 1000°K. (see curve C in Fig. 1) the only gas remaining was carbonyl fluoride. Thus, the marked drop in pressure with rising temperature shown in curve C appeared to result from the reaction of elementary fluorine with nickel. A similar drop was observed when the vessel contained only fluorine, and reaction also set in at about 750°K. The dashed portion of curve C represents the pressures observed as the resulting COF_2 was cooled from 1000°K.

The equilibrium represented by equation 1 was studied by pressure measurements. The assumption was made that below 750°K. the pressures of COF_2 and of F_2 were equal. Separate measurements on pure COF_2 and F_2 gave linear plots of pressure *versus* temperature in the region 300 to 740°K., therefore, at temperatures of 740°K. or below, the equilibrium constants for reaction (1) were calculated from pressure *versus* temperature data such as those graphed in Fig. 1. If a sample of CF_3OF had remained undissociated between 600 and 740°K., its pressure P_1 at any temperature T in this range would have been represented by a point on the linear extrapolation of its pressure-temperature line from 300 to 600°K. At this temperature T there is a measured pressure, P_0 . For the dissociation of CF_3OF at temperature T , the pressures of COF_2 and of F_2 are each equal to $(P_0 - P_1)$, and the pressure of CF_3OF is $(2P_1 - P_0)$. The equilibrium constant, K , at any temperature T , between 600 and 740°K., may be evaluated as

$$K = \frac{(P_{\text{COF}_2})(P_{\text{F}_2})}{(P_{\text{CF}_3\text{OF}})} = \frac{(P_0 - P_1)^2}{(2P_1 - P_0)} \quad (A)$$

Calculated K 's derived from experimental data demonstrated that the equilibrium constants for reaction (1) were not pressure dependent. Constants obtained for different samples and pressures of CF_3OF were mutually consistent. The average deviation among experimental constants ranged from 15% at around 650°K. to less than 5% at temperatures above 720°K. Experimentally evaluated constants represented fractions of trifluoromethyl hypofluorite dissociation between 4 and 25%.

The average values of the constants for reaction (1) based upon the six most precise experiments are given in column 2 of Table I. A single run was made in which both CF_3OF and F_2 were introduced into the reactor system. At 300°K. the pressure of CF_3OF was 100 mm. and that of fluorine 19 mm. The presence of fluorine suppressed the dissociation of CF_3OF , and values for the equilibrium constants calculated on the basis of added fluorine are seen, in Table I, to agree rather well with those from CF_3OF alone. Equilibrium constants were calculated from observed pressures at 10° intervals and the constants were averaged at each temperature. By plotting $\log K$ (average) *vs.* $1/T$ from 630 to 750°K., the points gave a good straight line. Values taken from this line are listed in column 4 of Table I. This table also gives constants for reaction (1) derived at 10° intervals

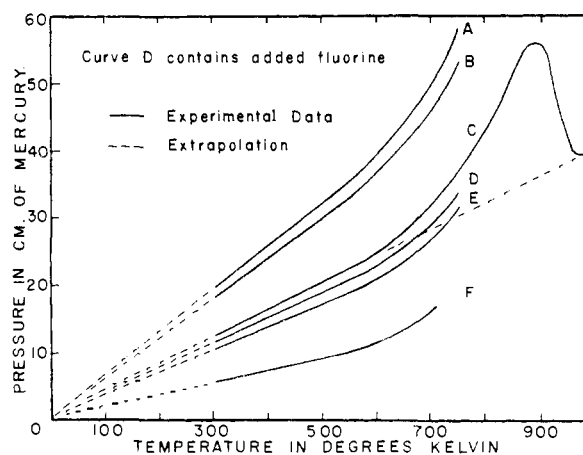


Fig. 1.—Heating curves for CF_3OF .

over the region 670 to 740°K. for a linear relationship such that the quantity (measured constants - derived constants)² is a minimum.

TABLE I
EQUILIBRIUM CONSTANTS FOR THE THERMAL DISSOCIATION OF TRIFLUOROMETHYL HYPOFLUORITE, $\text{CF}_3\text{OF} = \text{COF}_2 + \text{F}_2$

Temp. in °K.	Av. K , cm. exptl.	K , cm., added F_2 run	K , cm., from graph	K , cm., from least squares
630	0.062	0.082	0.061	
640	.092	.100	.086	
650	.119	.134	.121	
660	.170	.188	.167	
670	.229	.246	.225	0.220
680	.309	.308	.305	.299
690	.398	.393	.410	.407
700	.528	.503	.540	.537
710	.707	.667	.720	.720
720	.945	.875	.940	.938
730	1.25	1.13	1.23	1.22
740	1.62	1.49	1.58	1.59
750	2.03	1.80	2.02	

Discussion

Using a form of the van't Hoff equation

$$\Delta H^0 = -4579 \frac{d \log K}{d(1/T)} \quad (B)$$

ΔH^0 for reaction (1) has been calculated to be 27.7 ± 1.5 kcal. per mole of CF_3OF at 700°K. To calculate ΔH^0 at 298°K. it was necessary to use the specific heats of the three gases involved. Calculated heat capacities were known for fluorine and carbonyl fluoride.^{5,6} Since the heat capacity of CF_3OF was not known, it was assumed to be the same as that of CF_2I over the range 298 to 740°K.⁷ Using these data the value of ΔH^0_{298} was calculated to be 26.9 kcal. per mole.

The equilibrium constant for the reaction at 298°K. was estimated to be 2.2×10^{-14} atmospheres. This corresponded to $\Delta F^0 = 18.6$ kcal. for the molar free energy of dissociation. A calculation using the Gibbs-Helmholtz equation gave the standard entropy of dissociation, $\Delta S^0 =$

(5) L. G. Cole, M. Farber and G. W. Elverum, Jr., *J. Chem. Phys.*, **20**, 586 (1952).

(6) R. J. Lovell, C. V. Stephenson and E. A. Jones, *ibid.*, **22**, 1953 (1954).

(7) E. Gelles and K. S. Pitzer, *This Journal*, **75**, 5259 (1953).

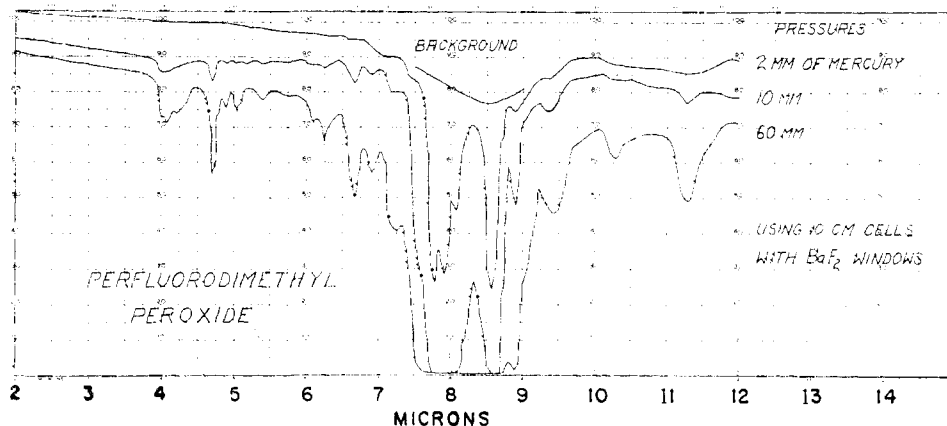


Fig. 2.—Infrared spectrum of CF_3OOCF_3 .

28 E.U./mole. To estimate the heat of formation of CF_3OF from the elements, the molar heat of formation of COF_2 was taken to be -150.35 ± 0.5 kcal.⁸ This gave $\Delta H_{298}^0 = -177.3$ kcal. for the molar heat of formation of CF_3OF from the elements in their standard states. With this value and thermodynamic data published by the U. S. Bureau of Standards,⁹ the molar heat of formation of CF_3OF at 298°K. from gaseous atoms was calculated to be $\Delta H^0 = -481.4$ kcal.

Since the heat of formation of a compound from its gaseous atoms at 298°K. may be interpreted as the sum of the bond strengths, it was of interest to apportion this energy to the various bonds in CF_3OF . The strength of the C-F bond was taken as 116.3 kcal.; this was calculated from the molar heat of formation of CF_4 taken as $H_{298}^0 = -220.4$ kcal.^{10,11,12} In simple alcohols and ethers the C-O bond has an energy of about 85 kcal. When this was used as the value for the C-O bond in CF_3OF , there remained an energy difference of 47 kcal. which was attributed to the O-F bond strength in trifluoromethyl hypofluorite. This value for the hypofluorite bond energy must be considered of only qualitative merit because of the number of assumptions involved in its derivation.

The standard heat of formation of OF_2 is reported to be $\Delta H_{298}^0 = +5.5$ kcal.⁹ From this datum and other values of the U. S. Bureau of Standards,⁹ the O-F bond energy in OF_2 was calculated to be 45 kcal. The activation energy for the decomposition of trifluoroacetyl hypofluorite suggests that the energy of the O-F bond in this substance may be only about 25 kcal.¹³ Since trifluoroacetyl hypofluorite is explosively unstable, it is possible that the O-F bond strength in this compound is less than in CF_3OF .

(8) H. von Wartenburg and G. Riteris, *Z. anorg. Chem.*, **258**, 356 (1949).

(9) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Chemical Thermodynamic Properties," U. S. Bureau of Standards, 1952.

(10) R. S. Jessup, R. E. McCoskey and R. A. Nelson, *THIS JOURNAL*, **77**, 244 (1955).

(11) H. C. Duus, *Ind. Eng. Chem.*, **47**, 1445 (1955).

(12) D. W. Scott, W. D. Wood and G. Waddington, *THIS JOURNAL*, **77**, 245 (1955).

(13) R. D. Stewart and G. H. Cady, *ibid.*, **77**, 6110 (1955).

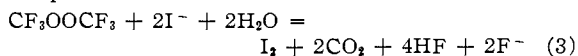
Reaction of Trifluoromethyl Hypofluorite with Carbonyl Fluoride

To test the suppression effect of COF_2 on the dissociation of CF_3OF , a mixture of the two gases was heated in the nickel vessel described above. When the temperature of the mixture rose to 510°K., the pressure unexpectedly began to decrease. By raising the temperature still higher, however, the gas pressure increased sharply, and in the range of 590 to 740°K. pressures were again about as expected for the original mixture of CF_3OF and COF_2 . Pressure versus temperature data were not reproduced during subsequent cycles of heating and cooling, and after a few such cycles in which the temperature had not risen above 740°K., it was found that nearly all of the CF_3OF had disappeared.

In another experiment, equimolar amounts of CF_3OF and COF_2 were heated together to about 560°K. in the nickel vessel and then allowed to cool to room temperature. The original pressure was 16.1 cm. at 300°K. and the final pressure was 11.1 cm. The resultant mixture was distilled and the three predominant components so obtained were identified by both physical and chemical means. The two most volatile constituents were unreacted COF_2 and CF_3OF . The least volatile substance was the product of reaction. It had measured gas densities of 169, 166 and 171 g./mole. Vapor pressures of the product yielded a linear plot of $\log P$ versus $1/T$ which placed the normal boiling point at close to -37° . The substance was colorless and it did not react with a solution of sodium hydroxide. It did react easily with dry metallic potassium. Analysis of two samples indicated the fluorine content to be 69.1% and 67.8%. For a substance of molecular weight 170, these analyses correspond respectively to 6.18 and 6.07 atoms of fluorine per molecule. For the compound CF_3OOCF_3 , the fluorine content is 67.1% by weight. On these criteria, the pressure drop accompanying the heating of COF_2 with CF_3OF was explained by the reaction



The compound perfluorodimethyl peroxide was found to be stable and non-explosive and to react slowly with aqueous iodide ion. The rate of this reaction was increased by irradiating the glass reaction flask with light from a carbon arc or other ultraviolet source. Under these conditions one mole of the gas liberated one mole of iodine as shown in equation 3.



This reaction and the original preparation of perfluorodimethyl peroxide were described in 1933 by Swarts who prepared the compound in small impure amounts by the electrolysis of aqueous solutions containing trifluoroacetate ion.¹⁴

Infrared transmission curves for several pressures of perfluorodimethyl peroxide are shown in Fig. 2. The mass spectrum contained a weak peak for the molecular ion of

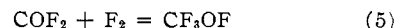
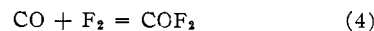
(14) F. Swarts, *Bull. Soc. Chim. Belg.*, **42**, 102 (1933).

mass number 170, as well as peaks for several other ions containing one and two oxygen atoms. The strongest peak by far resulted from the CF_3^+ ion.

A small sample of perfluorodimethyl peroxide was heated in the nickel vessel described above. By observing the change in pressure with temperature it was found that the sample started to decompose at about 225° and that the decomposition was complete when the temperature reached 325°. One product of the decomposition was carbonyl fluoride. The others were not identified.

In the course of this research perfluorodimethyl peroxide was produced by two methods in addition to that described above. In one of these a mixture of two volumes of fluorine with one of carbon dioxide was heated to 325° and then cooled. The resulting mixture contained about 10% by volume of CF_2OOCF_2 . In the other method, carbon monoxide and fluorine were passed through a reactor³ containing a catalyst composed of copper ribbon coated with fluorides of silver. Various reaction conditions were tried, and the best yield, about 60% of the theoretical, was obtained with a volume ratio of two of CO to three of F_2 , at a temperature of about 180°. The contact time in this case was about one and one-half hour. With the reactor at room temperature, carbonyl fluoride was formed at once, and unreacted fluorine remained. When this mixture was allowed to stand in the reactor for 24 hours, much of the carbonyl fluoride was converted to perfluorodimethyl per-

oxide. In the absence of a catalyst the reaction was slow at temperatures below 240°. In various trials with a hot-tube reactor containing no catalyst, the best yield of perfluorodimethyl peroxide was about 20% of theoretical. This was obtained at about 300° with a flow ratio of two volumes of CO to three volumes of F_2 and a contact time of about 3 minutes. Yields of about 20% were obtained at reactor temperatures as high as 400°. Since this is above the temperature for the complete decomposition of perfluorodimethyl peroxide, it seems probable that the peroxide was formed from CF_2OF and COF_2 as the gases left the reactor and passed through tubing at about 300° and below. When the ratio, by volume, of CO to F_2 was less than 1, the product was nearly all carbonyl fluoride. When the ratio was greater than 2, the product was trifluoromethyl hypofluorite containing unreacted fluorine. Probably the perfluorodimethyl peroxide produced in this process resulted from the steps



Acknowledgment.—This work was supported in part by the Office of Naval Research.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE PHYSICAL RESEARCH DIVISION, CHEMICAL WARFARE LABORATORIES]

Hydrogen Bonding of Phosphoryl Compounds with Chloroform and Other Solvents. II

By MARVIN W. HANSON AND JAMES B. BOUCK

RECEIVED MARCH 1, 1957

The order of hydrogen bonding ability of eight tri-substituted phosphoryl compounds was found to be as follows: $[(\text{CH}_3)_2\text{N}]_3\text{PO} > (\text{C}_6\text{H}_5\text{O})_3\text{PO} > (\text{C}_2\text{H}_5\text{S})_3\text{PO} > (\text{C}_6\text{H}_5\text{S})_3\text{PO} > (p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_3\text{PO} > (m\text{-CH}_3\text{C}_6\text{H}_4\text{O})_3\text{PO} > (o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_3\text{PO} > [(\text{C}_2\text{H}_5)_2\text{N}]_3\text{PO}$. The order of hydrogen bonding strengths of the chlorinated acceptor solvents was verified to be $\text{CHCl}_3 > \text{CHCl}_2\text{CCl}_3 > \text{CHCl}_2\text{CHCl}_2 > \text{CH}_2\text{Cl}_2$.

From the work of Kosolapoff and McCullough¹ and Halpern, *et al.*,² it has been found that the propensity of the phosphoryl compound to form hydrogen bonds with chloroform is dependent upon the groups substituted on the phosphorus atom. Halpern² studied other acceptor solvents and found the order of bonding strength to be $\text{CHCl}_3 > \text{CHCl}_2\text{-CCl}_3 > \text{CHCl}_2\text{CHCl}_2 > n\text{-C}_7\text{H}_{16}$ (none).

An additional study has been carried out in order to extend the knowledge of the effect of substituent groups upon the hydrogen bonding of the phosphoryl group with an acceptor solvent. The association of eight tri-substituted phosphoryl compounds with chloroform, *sym*-tetrachloroethane, pentachloroethane and dichloromethane has been investigated in the present work.

The order of hydrogen bonding strength of the solvents was found to be: $\text{CHCl}_3 > \text{CHCl}_2\text{-CCl}_3 > \text{CHCl}_2\text{-CHCl}_2 > \text{CH}_2\text{Cl}_2$ which substantiates the work of Halpern.² The order of hydrogen bonding strength of the phosphoryl compounds was found to be: $[(\text{CH}_3)_2\text{N}]_3\text{PO} > (\text{C}_6\text{H}_5\text{O})_3\text{PO} > (\text{C}_2\text{H}_5\text{S})_3\text{PO} > (\text{C}_6\text{H}_5\text{S})_3\text{PO} > (p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_3\text{PO} > (m\text{-CH}_3\text{C}_6\text{H}_4\text{O})_3\text{PO} > (o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_3\text{PO} > [(\text{C}_2\text{H}_5)_2\text{N}]_3\text{PO}$.

Equipment.—Perkin-Elmer, Model 21 Spectrometers equipped with calcium fluoride and sodium chloride prisms

(1) G. M. Kosolapoff and J. F. McCullough, *THIS JOURNAL*, **73**, 5392 (1951).

(2) E. Halpern, J. Bouck, H. Finegold and J. Goldenson, *ibid.*, **77**, 4472 (1955).

were used to study the C-H absorption bands of the solvents and the phosphoryl absorption bands of the phosphorus compounds, respectively. The instruments were calibrated using the known frequencies of water vapor, carbon dioxide and polystyrene. The instrument equipped with the sodium chloride prism was set for minimum deviation at 10 μ . Over the wave length region studied, the true position of the absorption bands could be determined within 2-3 cm^{-1} by reference to a calibration curve prepared by observing the known frequencies of water vapor, carbon dioxide and polystyrene. The relative frequency shifts of the phosphoryl bands could be observed by superimposing the spectral records of the samples under study.

Reagents.—The phosphoryl compounds were either obtained commercially or prepared in this Laboratory. The commercial samples were either fractionally distilled or recrystallized until the boiling point or melting point corresponded with the accepted literature value. The hexamethylphosphoramide contained less than 5% $[(\text{C}_2\text{H}_5)_2\text{N}]_3\text{P}(\text{O})\text{Cl}$ but decomposed in attempts at further purification. The chloroform was purified as described previously.² The carbon tetrachloride was Eastman Kodak

TABLE I
ORDER OF HYDROGEN BONDING

Phosphoryl compound	CHCl_3	$\frac{\Delta A/A_0}{A_0} \times 100$		CH_2Cl_2
		$\text{CHCl}_2\text{-CCl}_3$	CHCl_2	
$[(\text{CH}_3)_2\text{N}]_3\text{PO}$	350	100	77	50
$(\text{C}_6\text{H}_5\text{O})_3\text{PO}$	200	100	77	12
$(\text{C}_2\text{H}_5\text{S})_2\text{PO}$	180	90	31	0
$(\text{C}_6\text{H}_5\text{S})_3\text{PO}$	120	90	54	0
$(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_3\text{PO}$	120	90	38	0
$(m\text{-CH}_3\text{C}_6\text{H}_4\text{O})_3\text{PO}$	120	40	31	0
$(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_3\text{PO}$	100	40	23	0
$[(\text{C}_2\text{H}_5)_2\text{N}]_3\text{PO}$	100	0	-15	-37