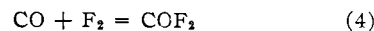


mass number 170, as well as peaks for several other ions containing one and two oxygen atoms. The strongest peak by far resulted from the CF_3^+ ion.

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



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

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

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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 ₂ Cl ₂
		CHCl ₂ -CCl ₃	CHCl ₂ -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

Spectro-Grade. The *sym*-tetrachloroethane, pentachloroethane and dichloromethane were distilled and the spectrum of each gave no evidence of impurities when compared with accepted spectra.

Experimental.—The experimental conditions and calculations were the same as those described by Halpern.² The relation $\Delta A/A_s \times 100$ in Table I was used to determine the relative hydrogen bonding strength of the phosphoryl compounds and the acceptor solvents. ΔA is the increase in integrated absorption intensity of the solvent C-H band due to hydrogen bonding and A_s is the integrated absorption intensity of the C-H band of the pure solvent. The integrated absorption intensities were determined by using a compensating polar planimeter.

Data and Discussion.—When a bond is formed between the hydrogen of one molecule and a donor atom of another molecule, there is a change in the original single bond by which the hydrogen is held. This change involves the stretching of the covalent bond by which the hydrogen is held to the rest of the molecule. Infrared spectroscopy offers a valuable means of studying this phenomenon because the relatively small mass of the hydrogen atom in comparison with the rest of the molecule makes the vibrational frequency of the hydrogen nearly independent of the rest of the molecule. When the hydrogen atom becomes involved in the formation of a hydrogen bond, there will be a change in the vibration frequency. In general, the shift of the absorption band is toward lower vibration frequencies. The amount of shift depends upon the activity of the hydrogen or upon the strength of the bond formed.

Another feature, which is the result of the bond formation, is the increase in the absorption intensity. An increase in absorption intensity indicates an increase in the ionic character of the binding upon forming a hydrogen bond. This necessarily involves an increase in the separation of the proton and the atom to which it was originally attached and therefore, an increase in the dipole moment of the bond. The governing factor for the absorption intensity is the ratio of the change in dipole moment to the change in bond distance.

Table I gives the values of $\Delta A/A_s \times 100$ and the order of hydrogen bonding strength of the solvents and phosphoryl compounds. Hydrogen bonding strength of the solvents decreases to the right and the hydrogen bonding strength of the phosphoryl compounds decreases from top to bottom.

Phosphoryl Absorption Band.—Daasch and Smith³ noted that as different groups were substituted on the phosphorus atom the position of the phosphoryl absorption band was shifted. This

(3) I. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

shift in the absorption frequency indicates the P-O bond distance is variable and the negative charge on the oxygen is variable as proposed by Bell⁴ and Halpern.²

For any given phosphoryl compound, there should be a shift in the position of the phosphoryl absorption band and an increase in the P-O bond distance, just as there is an increase in the C-H bond distance and shift of the band for the solvents, when hydrogen bonding takes place. This increase in bond distance should result in a shift of the absorption band to longer wave lengths. The data in Table II shows this to be true.

TABLE II
POSITION OF PHOSPHORYL ABSORPTION BANDS
Solvent and phosphoryl comp.
(wave length, μ)

Phosphoryl compd.	Solvent and phosphoryl comp. (wave length, μ)				
	CCl ₄	CHCl ₃	CHCl ₂ - CCl ₂	CHCl ₂ - CHCl ₂	CH ₂ Cl ₂
[(CH ₃) ₂ N] ₃ PO	8.26	8.32	8.32	8.30	8.28
(C ₆ H ₅ O) ₃ PO ^a	7.63	7.64	7.64	7.63	7.63
	7.71	7.72	7.72	7.71	7.71
(C ₂ H ₅ S) ₃ PO	8.33	8.34	8.34	8.34	8.33
(C ₆ H ₅ O) ₃ PO	8.19	8.22	8.22	8.20	8.19
(<i>p</i> -CH ₃ C ₆ H ₄ O) ₃ PO ^a	7.64	7.65	7.65	7.65	7.64
	7.73	7.77	7.76	7.74	7.73
(<i>m</i> -CH ₃ C ₆ H ₄ O) ₃ PO ^a	7.64	7.66	7.66	7.66	7.64
	7.73	7.73	7.73	7.73	7.73
(<i>o</i> -CH ₃ C ₆ H ₄ O) ₃ PO ^a	7.65	7.67	7.67	7.66	7.65
	7.72	7.76	7.75	7.72	7.72
[(C ₂ H ₅) ₂ N] ₃ PO	8.02	8.04	8.04	8.02	8.02

^a Doublet.

The greatest shift in absorption frequency, 13.5 cm.^{-1} , is shown by hexamethylphosphoramide, which forms the strongest hydrogen bond with the solvents. Dichloromethane, which exhibits hydrogen bonding only with hexamethylphosphoramide and triphenyl phosphate, causes no observable shift in the position of the phosphoryl band of the remaining compounds.

It is apparent from Table II that the amount of shift in the position of the phosphoryl band decreases with decreasing hydrogen bonding strength of the solvents. Therefore, when the spectrum of a phosphoryl compound in the presence of a solvent is obtained, the position of the phosphoryl absorption band is dependent upon the nature of the solvent as well as the kind of groups substituted on the phosphorus atom.

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(4) J. V. Bell, J. Heisler, H. Tannenbaum and J. Goldenson, *THIS JOURNAL*, **76**, 5185 (1954).