To account for the results it was necessary to assume that the surfaces of group I-B metals which were chemically prepared have paramagnetic properties not possessed by the usual bulk metal.[10] Potassium azide melts were found to decompose with a considerably lower activation energy on surfaces of iron, cobalt, or nickel than on surfaces of copper or gold. This was attributed to the vacancies in the d-band which are not present in group I-B metals.[4] However, according to Dowden[12] the lattice defects present in chemically-formed group I-B metals can reduce the gap between the top of the d-band and the Fermi level. In massive group I-B metals the defects anneal out to a very low concentration, but when chemically formed they can be maintained by impurities and occlusions. Later, experimental evidence for these theories was given by Uhara and co-workers,[13–15] who studied the decomposition of diazonium chloride and other reactions on copper as catalyst. The catalytic activity was increased when copper was cold worked and returned during annealing to the original activity at about the same temperature where the strain energy was released. This happened with 99.96% pure copper at temperatures around 350°, but at 430° with copper containing a few tenths of a per cent of impurities. Chemically-produced copper showed even higher catalytic activity than cold worked copper. This was attributed to an enhanced defect structure which is also thermally more stable. Copper prepared by low current density electrolysis of copper sulfate solutions was catalytically like massive copper. When prepared at high current densities catalytically active copper was obtained. This was probably due to the occlusions and lattice distortions which are usually found in metals obtained by high current density electrolysis.[16,17]

The metals formed within the potassium azide melts can be expected to possess distorted structures. This was indicated by the diffuseness of their X-ray patterns, which may be due to both small grain size and lattice distortions. With group I-B metals this may lead to decreased energetic requirements for the formation of holes in the d-band by thermal activation which may explain the lower activation energies for potassium azide melt decomposition on surfaces of reaction-formed copper and gold.

Acknowledgment.—The author wishes to thank Dr. S. B. Newman, National Bureau of Standards, for the electron microscopic pictures and Mr. A. J. Coleman, Basic Research Laboratory, for mass spectrometric analysis of gas samples.

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Contribution from the Department of Chemistry,
The University of Texas, Austin, Texas 78712

The Iodides of Phosphorus. I. Lewis Basicity and Structure[1]

By A. H. COWLEY and S. T. COHEN

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The Lewis base behavior of PI_3 and P_2I_4 has been investigated by testing their reactivity toward the boron halides. Consistent with the order of Lewis acidity $BF_3 < BCl_3 < BBr_3 < BI_3$ it was found that neither of the phosphorus iodides reacted with BF_3 or BCl_3, but that both reacted with BBr_3 and BI_3. No reaction was observed with SO_2. The complexes isolated were $PI_3 \cdot BBr_3$, $P_2I_4 \cdot 2BBr_3$, and $PI_3 \cdot BI_3$. The isolation of $P_2I_4 \cdot 2BBr_3$ confirms the earlier work of Tarible. The structures of the complexes were investigated by infrared spectral measurements. The infrared spectra of PI_3 and P_2I_4 were also determined. The conformation of P_2I_4 in solution is probably *gauche.*

Introduction

There is comparatively little information in the literature concerning the simple chemistry of the phosphorus iodides, PI_3 and P_2I_4. This is remarkable when it is realized that these compounds have been known since the middle of the nineteenth century.[2] We have examined various aspects of the chemistry of these halides, such as their Lewis basicity, structures in solution, and some metathetical reactions. In this paper we discuss their reactivity toward the boron halides and sulfur dioxide and also their structures in carbon disulfide solution. Previous work[3,4] has shown that the donor behavior of a phosphorus trihalide depends on the electronegativity of the halogen substituents. Thus, PCl_3[5] and PBr_3[5] form 1:1 adducts with the Lewis acid BBr_3, while PF_3 appears to have no donor properties if only σ bonding is considered.[6] It was therefore of interest to test the basicity of PI_3

[1] Presented in part at the 20th Southwest Regional American Chemical Society Meeting, Shreveport, La., Dec. 1964.

[2] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y., 1928, Vol. 8, pp. 1038–1041.

[3] D. S. Payne, *Quart. Rev.* (London), **15**, 173 (1961).

[4] R. R. Holmes, *J. Chem. Educ.*, **40**, 125 (1963).

[5] R. R. Holmes, *J. Inorg. Nucl. Chem.*, **12**, 266 (1960).

[6] Various complexes are known which presumably involve π bonding, such as $Ni(PF_3)_4$, $PF_3 \cdot BH_3$, and $(PF_3)_2PtCl_2$. See ref. 3 and also R. W. Parry and T. C. Bissot, *J. Am. Chem. Soc.*, **78**, 1524 (1956).

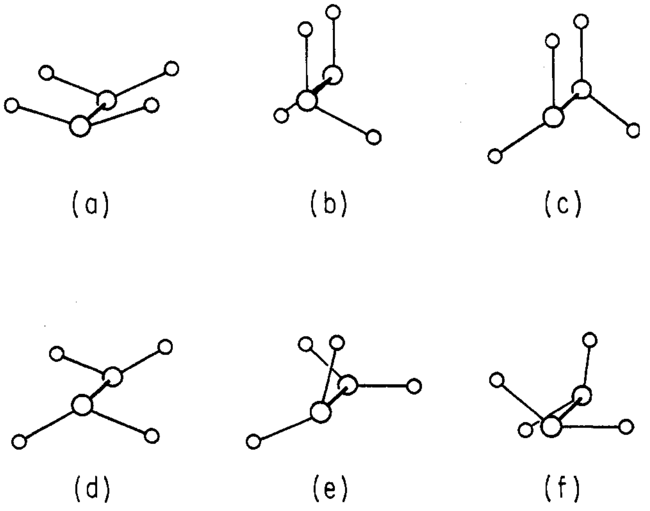

Figure 1.—Possible conformations for P_2I_4.

toward the boron halides, since the lower electronegativity of the iodine should render PI_3 the most basic of the phosphorus trihalides providing the steric effect of the iodine atoms is not too important. The adducts $PI_3 \cdot BI_3$[7] and $2PI_3 \cdot AlI_3$[8] were reported while our investigation was in progress.

The compound P_2I_4 should behave as a di-Lewis base since it has a lone pair of electrons on each phosphorus atom. In fact, an adduct of composition $P_2I_4 \cdot 2BBr_3$ was reported several years ago by Tarible.[9] However, since Baudler and Fricke[10] were unable to repeat this work it was apparent that the system was worthy of re-investigation.

It is possible to write six rotational isomers for P_2I_4 (Figure 1). It is reasonable to exclude the eclipsed form (a) on the basis of steric repulsion between the iodine atoms, and to a lesser extent the same applies to the semi-eclipsed forms (b) and (c); therefore the expected configuration is either the *trans* (d) or one of the spectroscopically indistinguishable *gauche* forms (e) and (f). It has been shown by X-ray crystallography[11] that P_2I_4 exists in the *trans* conformation in the solid state. We determined the infrared spectrum of P_2I_4 both in solution and in the solid state, to see if there is a change of configuration on going into solution.

Experimental

Materials.—The phosphorus iodides, PI_3 and P_2I_4, were prepared by a slight modification of the procedure of Germann and Traxler.[12] BF_3, BCl_3, BI_3, and SO_2 were obtained from commercial suppliers in research grade quality, and the BBr_3 was made according to the procedure of Gamble.[13] All solvents were dried and carefully fractionated prior to use.

Procedure.—The work involving BF_3, BCl_3, and SO_2 was done on a vacuum line of the usual design. The BBr_3 and BI_3 complexes were prepared by conventional techniques. All reactions were performed *in vacuo* or under a dry nitrogen atmosphere. Sample preparation, storage, etc., was done in a helium-filled drybox.

$PI_3 \cdot BBr_3$.—BBr_3 (9.64 g., 38.6 mmoles) in 100 ml. of CS_2 was added dropwise with stirring to 12.087 g. (29.4 mmoles) of PI_3 in 100 ml. of CS_2. A yellow precipitate was continuously formed during the addition. The reaction mixture was stirred for 1 hr. after the addition. After removing approximately half the CS_2 under reduced pressure the complex was isolated on a frit, vacuum dried, and transferred to a drybox. The melting point of the complex is 159–160°, but considerable darkening is observed from 100° upward. *Anal.*[14] Calcd. for $PI_3 \cdot BBr_3$: B, 1.63; Br, 36.21; I, 57.48; P, 4.68. Found: Br, 35.89; I, 57.51; P, 4.45. The complex can also be prepared in the absence of a solvent by shaking PI_3 with excess BBr_3 in a sealed tube for 48 hr.

$P_2I_4 \cdot 2BBr_3$.—BBr_3 (7.344 g., 29.4 mmoles) in 50 ml. of CS_2 was added dropwise with stirring to 6.221 g. (10.9 mmoles) of P_2I_4 in 150 ml. of CS_2, resulting in the formation of a yellow precipitate. The complex was isolated by a similar procedure to that described for $PI_3 \cdot BBr_3$, m.p. 134–136° dec. *Anal.* Calcd. for $P_2I_4 \cdot 2BBr_3$: B, 2.03; Br, 44.78; I, 47.40; P, 5.79. Found: Br, 44.60; I, 47.82; P, 5.80. The complex can also be prepared in a sealed tube by shaking P_2I_4 with excess BBr_3 for 48 hr.

$PI_3 \cdot BI_3$.—BI_3 (4.350 g., 11.1 mmoles) in 100 ml. of CS_2 was added dropwise with stirring to 3.710 g. (9.01 mmoles) of PI_3 in 100 ml. of CS_2, resulting in the formation of a yellow-brown precipitate. The complex was isolated by a similar procedure to that described for $PI_3 \cdot BBr_3$. The complex does not melt below 250°. However, decomposition is observed below this temperature. *Anal.* Calcd. for $PI_3 \cdot BI_3$: B, 1.35; I, 94.80; P, 3.85. Found: I, 94.59; P, 3.80. The complex can also be prepared by adding CS_2 to a stoichiometric mixture of PI_3 and BI_3.

$P_2I_4 + BI_3$.—Reaction of BI_3 with P_2I_4 in a 2:1 mole ratio in CS_2 solution yields a precipitate of similar appearance to $PI_3 \cdot BI_3$ (slightly more orange). The material did not melt below 250°. However, decomposition is observed below this temperature. The infrared spectrum of the product was very similar to that of $PI_3 \cdot BI_3$. However, we were unable to obtain analyses that corresponded to a distinct complex (see Results and Discussion).

$PI_3 + BCl_3$ and $P_2I_4 + BCl_3$.—No association or chemical reaction was observed down to −70° as evidenced by the quantitative recovery of BCl_3. No reaction was detected in a sealed tube maintained at room temperature for over 1 year.

$PI_3 + BF_3$ and $P_2I_4 + BF_3$.—No association or chemical reaction was observed down to −120° as evidenced by the quantitative recovery of BF_3.

$PI_3 + SO_2$ and $P_2I_4 + SO_2$.—No association or chemical reaction was observed down to −70° as evidenced by the quantitative recovery of SO_2. No reaction was detected in a sealed tube at room temperature.

Infrared and N.m.r. Spectra.—The infrared spectra were measured on a Beckman I.R. 7 spectrophotometer equipped with NaCl and CsI optics. The solution spectra were run in a CsI solution cell of 0.2 mm. path length. The B^{11} n.m.r. spectra were recorded on a Varian V-4300 B spectrometer operating at 19.3 Mc.

X-Ray Diffraction Data.—Powder patterns were recorded photographically using a 114.6-mm. diameter Philips rotating sample camera with nickel-filtered Cu $K\alpha$ radiation. Intensities were visually estimated. Hydrolysis of the samples was prevented by sealing them in Lindemann glass capillaries under a nitrogen atmosphere.

Results and Discussion

The complexes isolated in the present study were $PI_3 \cdot BBr_3$, $PI_3 \cdot BI_3$, and $P_2I_4 \cdot 2BBr_3$. The crystalline individuality of these adducts was established by determining their X-ray diffraction patterns and compar-

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[14] All analyses were performed by A. Bernhardt, Mikroanalytisches Laboratorium im Max-Planck-Institut für Kohlenforschung, Mülheim, Ruhr, Germany.

TABLE I

X-RAY DIFFRACTION DATA FOR THE PHOSPHORUS IODIDES AND THEIR BORON HALIDE ADDUCTS

PI_3		P_2I_4		$PI_3\cdot BBr_3$		$P_2I_4\cdot 2BBr_3$		$PI_3\cdot BI_3$		$P_2I_4 + BI_3$	
d, Å.	I/I_0[a]	*d*, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0
4.72	w	4.51	s	3.56	m	5.47	w	3.58	s	4.31	w
3.68	s	4.19	w	3.09	vs	4.23	w	3.40	m	3.87	s
3.55	w	3.77	s	2.99	s	3.52	m	3.31	m	3.47	s
3.19	vs	3.48	w	2.81	vs	3.25	s	3.25	m	3.31	s
2.56	m	3.24	vs	2.69	w	3.19	s	3.11	vs	3.20	w
2.34	w	2.97	w	2.08	w	2.97	vs	2.85	w	3.12	w
2.05	m	2.64	w	1.98	w	2.84	w	2.75	w	2.98	vs
2.02	m	2.59	w	1.91	w	2.65	w	2.56	w	2.85	w
1.96	vw	2.44	m	1.82	w	2.07	w	2.42	vw	2.69	vw
1.91	vw	2.30	m	1.76	w	1.91	w	2.17	w	2.63	vw
1.84	vw	2.26	m	1.69	w	1.81	w	2.12	m	2.32	vw
1.79	m	2.20	m			1.74	w	2.00	w	2.24	vw
1.72	m	2.03	w			1.68	w	1.91	w	2.14	w
		1.96	m			1.64	w	1.88	w	2.08	w
		1.88	w					1.80	w	2.02	w
		1.86	w					1.78	w	1.89	m
		1.81	w							1.86	w
										1.83	w

[a] I/I_0 = relative intensity; vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

TABLE II

INFRARED ABSORPTION FREQUENCIES OF BX_3 COMPLEXES

$PI_3\cdot BBr_3$ Frequency (cm.$^{-1}$), tentative assignment	
(a) Nujol Mull	
315 m[a] 331 s	P–I str.
361 w	B–Br sym. str.?
390 s	P–B str.?
443 w	
597 m	
647 s	B–Br asym. str. (B^{11})
682 m	B–Br asym. str. (B^{10})
(b) Solution (CS_2)	
305 w 327 s	P–I str.
381 m[b]	B–Br sym. str.?
807 s	B–Br asym. str. (B^{11})
843 m	B–Br asym. str. (B^{10})

$P_2I_4\cdot 2BBr_3$ Frequency (cm.$^{-1}$), tentative assignment	
(a) Nujol Mull	
302 m 335 s 347 sh	P–I str.
360 w	B–Br sym. str.?
397 s 412 sh	P–B str.?
443 m	
463 vw	
598 m	
648 s	B–Br asym. str. (B^{11})
681 m	B–Br asym. str. (B^{10})
(b) Solution (CS_2)	
305 vw 327 s	P–I str.
381 m[b]	B–Br sym. str.?
807 s	B–Br asym. str. (B^{11})
843 m	B–Br asym. str. (B^{10})

$PI_3\cdot BI_3$ Frequency (cm.$^{-1}$), tentative assignment	
(a) Nujol Mull	
287 m	B–I sym. str.?
304 s 329 m	P–I str.
384 s	P–B str.?
423 w	
564 s	B–I asym. str. (B^{11})
590 m 598 sh	B–I asym. str. (B^{10})
(b) Solution (CS_2)	
327 m	P–I str.
690 m	B–I asym. str. (B^{11})
724 w	B–I asym. str. (B^{10})

$P_2I_4 + BI_3$ Frequency (cm.$^{-1}$), tentative assignment	
(a) Nujol Mull	
286 w	B–I sym. str.?
307 s 329 m	P–I str.
383 s	P–B str.?
425 w	
563 m	B–I asym. str. (B^{11})
592 w	B–I asym. str. (B^{10})
(b) Solution (CS_2)	
327 m	P–I str.

[a] m, medium intensity; w, weak intensity; s, strong intensity; sh, shoulder. All of these intensities are relative. [b] This frequency was observed in CCl_4 solution.

ing them with those of the parent iodides (Table I). That no reaction was observed between the phosphorus iodides and BCl_3 or BF_3 is consistent with the order of Lewis acidity $BF_3 < BCl_3 < BBr_3 < BI_3$.[15] In terms of Lewis basicity PI_3 seems to be comparable to PBr_3 in that the relatively strong acceptor BBr_3 is necessary for complexation.[5] The isolation of a complex of composition $P_2I_4\cdot 2BBr_3$ confirms the earlier observation of Tarible.[9] In the case of the reaction of P_2I_4 with BI_3 we were unable to obtain analytical results that corresponded to the complex $P_2I_4\cdot 2BI_3$. The infrared spectrum of the reaction product was very similar to that of $PI_3\cdot BI_3$ (Table II). It is therefore possible that P_2I_4 disproportionates into PI_3 and a polymeric lower iodide $(PI)_n$,[16] both of which could undergo reaction with BI_3

$$P_2I_4 \longrightarrow PI_3 + (1/n)(PI)_n$$

(Disproportionation of this kind has been suggested by Moeller and Huheey[17] in connection with the reaction of P_2I_4 with alcohols, phenols, and amines.) However, there is no evidence for $PI_3\cdot BI_3$ in the X-ray powder pattern of the $P_2I_4 + BI_3$ reaction product.

As noted by Holmes[5] the possibility of halogen exchange exists in complexes of the type $PX_3\cdot BY_3$ where the halogen atoms differ on the phosphorus and boron atoms. We undertook an infrared spectroscopic study

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(15) The order of Lewis acidity $BF_3 < BCl_3 < BBr_3$ was first established by H. C. Brown and R. R. Holmes, *J. Am. Chem. Soc.*, **78**, 2173 (1956). The order $BF_3 < BCl_3 < BBr_3 < BI_3$ was established by D. Cook, *Can. J. Chem.*, **41**, 522 (1963).

(16) This is the formula for cyclic structures and very long chains where $n \rightarrow \infty$. For shorter chains the formula would be P_nI_{n+2}. The authors wish to thank one of the referees for pointing this out.

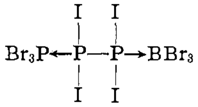
(17) T. Moeller and J. E. Huheey, *J. Inorg. Nucl. Chem.*, **24**, 315 (1962).

of the boron halide complexes both to investigate the halogen-exchange question and also to provide additional structural information. The frequencies observed in the 250–1000 cm.$^{-1}$ range are shown in Table II along with some tentative assignments.

In general the configurations of the phosphorus iodides are not expected to change appreciably upon complexation, hence the vibrational frequencies of the free and combined phosphorus iodides should be similar. By contrast complexation of the boron halide involves a change in configuration from trigonal planar to approximately tetrahedral. This change of configuration, with consequent changes in the force constants, is expected to introduce significant changes in the vibrational frequencies of the BX_3 group. Bands in the 300–350 cm.$^{-1}$ region in both the solid phase and solution spectra have been assigned to P–I stretching on the basis that PI_3 and P_2I_4 absorb in this region (*vide infra*). Recent spectroscopic studies of amine–boron halide complexes[18] have shown that the boron–halogen asymmetric stretching frequency is lowered when the BX_3 group is bonded to a donor atom. In the solid phase spectra of the BBr_3 complexes a reasonable choice for the B–Br asymmetric stretch would be the bands at 647–648 and 681 cm.$^{-1}$ since their intensities correspond to the B^{11}/B^{10} isotopic ratio. (In the complex $(CH_3)_3N \cdot BBr_3$ the B–Br asymmetric stretch occurred at 677 and 706 cm.$^{-1}$.) Analogous bands at 564 and 590 cm.$^{-1}$ in the solid phase BI_3 complex could be assigned to B^{11}–I and B^{10}–I asymmetric stretching. In CS_2 solution bands appear at 807 and 844 cm.$^{-1}$ in the BBr_3 complexes. Since these frequencies are very close to those reported for pure BBr_3 in CS_2 solution[19] this would suggest that the complexes are undergoing dissociation in solution. Additional evidence for this suggestion is our observation that the B^{11} n.m.r. spectra of both the BBr_3 complexes (in CS_2 solution) consist of broad, weak singlets at -36.8 p.p.m., a chemical shift close to that found for BBr_3 in CH_2Cl_2 solution.[20] Bands corresponding to pure BI_3 were also observed in the infrared spectrum of $PI_3 \cdot BI_3$ in CS_2 solution, hence it appears that this complex also undergoes dissociation in solution. In contrast to the B–X asymmetric stretch, the B–X symmetric stretch seems to increase in frequency upon complexation of the BX_3 group.[18] The extent to which the frequency is increased, together with the low infrared intensity of the mode, introduces some uncertainty about its assignment. One possibility is to assign the 360–361 cm.$^{-1}$ band to B–Br symmetric stretch and the 287 cm.$^{-1}$ band to B–I symmetric stretch. However, it is equally plausible to assign bands at 443 cm.$^{-1}$ (BBr_3 complexes) and 423 cm.$^{-1}$ (BI_3 complex) to these modes.

The strong bands at 390 and 397 cm.$^{-1}$ in the solid-state spectra of the BBr_3 complexes would admit the possibility of halogen exchange since the symmetric and asymmetric P–Br stretching modes of PBr_3 appear at 390 cm.$^{-1}$.[21] However, $PI_3 \cdot BI_3$ also exhibits a strong band of similar appearance at 384 cm.$^{-1}$, and since there is no question of halogen exchange in this case we are inclined to assign the bands in the range 384–397 cm.$^{-1}$ to P–B stretching. Widely different values have been quoted for this vibration. The values assigned to $F_3P \cdot BH_3$[22] and the ring stretching vibrations of trimeric and tetrameric phosphinoborines[23] fell in the range 500–700 cm.$^{-1}$, while those of some complexes of cyclic phosphites with various boron acceptors[24] occurred in the 750–870 cm.$^{-1}$ range. Bands in the 1400–1500 cm.$^{-1}$ region have been assigned to P=B double bond stretching.[25] Apparently the P–B stretching frequency is a sensitive criterion of the strength of the P–B bond. The relatively low frequencies that we have assigned to this mode would be in accord with the low Lewis basicity of the phosphorus iodides and the possibility that additional P–B bond weakening could arise from the steric effects of the bromine and iodine atoms.

The complexes $PI_3 \cdot BBr_3$ and $PI_3 \cdot BI_3$ are expected to have ethane-type structures. On the basis of the similarity of the infrared spectra of $PI_3 \cdot BBr_3$ and $P_2I_4 \cdot 2BBr_3$, it is tentatively suggested that the structure of the complex $P_2I_4 \cdot 2BBr_3$ is



$$\begin{array}{ccccc} & I & & I & \\ & | & & | & \\ Br_3P \leftarrow & P & — & P & \rightarrow BBr_3 \\ & | & & | & \\ & I & & I & \end{array}$$

Of the twelve nondegenerate modes expected for the P_2I_4 molecule four might be described as P–I stretching (ν_1, ν_2, symmetric P–I stretch; ν_8, ν_9, asymmetric P–I stretch). If the molecule has a *trans* (C_{2h}) configuration (Figure 1) only two P–I stretching modes [$\nu_1(A_u)$ and $\nu_9(B_u)$] are infrared-active. On the other hand, all four P–I stretching modes [$\nu_1(A)$, $\nu_2(A)$, $\nu_8(B)$, and $\nu_9(B)$] are infrared-active if the configuration is *gauche* (C_2). The observation that Nujol mulls of P_2I_4 exhibit two infrared frequencies in the P–I stretching region (Table III, Figure 2) is in com-

TABLE III

INFRARED ABSORPTION FREQUENCIES OF THE PHOSPHORUS IODIDES

PI_3		P_2I_4	
Frequency (cm.$^{-1}$)	assignment	Frequency (cm.$^{-1}$)	assignment
(a) Nujol Mull		(a) Nujol Mull	
294–328 s^{a,b}	$\nu_1(A_1) + \nu_3(E)$ P–I str.	300 s	$\nu_1(A_u)$ P–I sym. str.
(b) Solution (CS_2)		329 s	$\nu_9(B_u)$ P–I asym. str.
305 w	$\nu_1(A_1)$ P–I sym. str.	(b) Solution (CS_2)	
327 s	$\nu_3(E)$ P–I asym. str.	313 m	P–I sym. str.
		328 s 332 s	$\nu_8(B) + \nu_9(B)$ P–I asym. str.
		355 w	P–I sym. str.

^{a} s, strong intensity; m, medium intensity; w, weak intensity. All of these intensities are relative. ^{b} Broad, featureless absorption.

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[23] A. C. Chapman, *Trans. Faraday Soc.*, **59**, 806 (1963).

[24] C. W. Heitsch and J. G. Verkade, *Inorg. Chem.*, **1**, 863 (1962).

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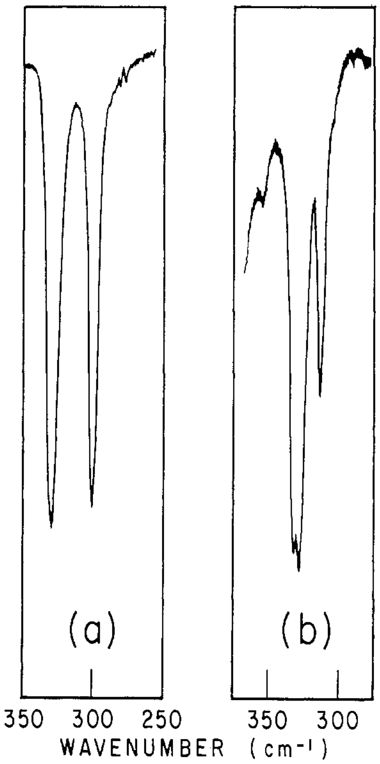

Figure 2.—Infrared spectrum of P_2I_4: (a) Nujol mull; (b) saturated CS_2 solution.

plete agreement with the X-ray crystallographic result[11] that this molecule has the *trans* configuration in the solid state. Four infrared frequencies were observed in CS_2 solutions of P_2I_4. The two strong bands are probably the asymmetric P–I stretching modes, $\nu_8(B)$ and $\nu_9(B)$, and the lower intensity bands can be assigned to the P–I symmetric stretching modes $\nu_1(A)$ and $\nu_2(A)$. Another possibility is that the band at 355 cm.$^{-1}$ is a combination, overtone, or impurity peak since it is less intense and somewhat higher in frequency than other P–I stretching modes. If this is so then one must also consider the possibility of a *cis* (C_{2v}) configuration for which three infrared-active P–I stretching frequencies are predicted [$\nu_2(A_1)$, $\nu_8(B_2)$, and $\nu_9(B_1)$]. However, this configuration is rather unlikely on steric grounds, hence we tend to favor the *gauche* conformation for P_2I_4 in solution, although it is important to realize that the above data could also correspond to an average over a number of configurations.

In accordance with its C_{3v} configuration,[26] PI_3 exhibits two infrared-active P–I stretches in CS_2 solution (Table III). The strong 327 cm.$^{-1}$ band is assigned to asymmetric P–I stretching [$\nu_3(E)$] and the weak 305 cm.$^{-1}$ band to symmetric P–I stretching [$\nu_1(A_1)$]. This is in excellent agreement with the 325 and 303 cm.$^{-1}$ bands reported for the Raman spectrum of PI_3 in CS_2 solution.[27]

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Contribution from the Department of Chemistry,
University of Florida, Gainesville, Florida

The Reactions of Dialkylchlorophosphines with Gaseous Chloramine and Ammonia

By HARRY H. SISLER and STEPHEN E. FRAZIER

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The reactions of a mixture of chloramine and excess ammonia with compounds of the general formula R_2PCl where R = CH_3, C_2H_5, and *n*-C_4H_9 were carried out in dry benzene. The compounds of the formula $[R_2P(NH_2)_2]Cl$ were obtained in each case. Along with these compounds the compounds $[(C_2H_5)_2P(NH_2)NP(NH_2)(C_2H_5)_2]Cl$ and $[(C_4H_9)_2PN]_3$ were obtained in the appropriate instances. Pyrolysis of the $[R_2P(NH_2)_2]Cl$ was shown to yield phosphonitrilic materials of the general formulas $(R_2PN)_3$ and $(R_2PN)_4$. Pyrolysis of $[(C_2H_5)_2P(NH_2)NP(NH_2)(C_2H_5)_2]Cl$ was shown to yield a 4:1 mixture of $[(C_2H_5)_2PN]_4$ and $[(C_2H_5)_2PN]_3$.

In an earlier communication[1] from this laboratory it was reported that the reaction of diphenylchlorophosphine with a gaseous mixture of ammonia and chloramine produces $[(C_6H_5)_2PN]_3$ in about 12% yield and an intermediate $[(C_6H_5)_2P(NH_2)N{=}P(NH_2)(C_6H_5)_2]Cl$ in about 50% yield based on the diphenylchlorophosphine used. A reaction sequence was proposed and is generalized in the following steps.

$$R_2PCl + 2NH_3 \longrightarrow R_2PNH_2 + NH_4Cl \quad (1)$$

$$R_2PNH_2 + NH_2Cl \longrightarrow [R_2P(NH_2)_2]Cl \quad (2)$$

$$2[R_2P(NH_2)_2]Cl \longrightarrow [R_2P(NH_2)N{=}P(NH_2)R_2]Cl + NH_4Cl \quad (3)$$

$$[R_2P(NH_2)_2]Cl + [R_2P(NH_2)N{=}P(NH_2)R_2]Cl \longrightarrow [R_2PN]_3 + NH_4Cl \quad (4)$$

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