off under high vacuum, collected in a trap cooled with liquid air, and then redistilled. 1,3-Difluorotetramethyldisilazane (9.70 g, 0.057 mole), bp 118° (692 mm) was obtained, yield 47.5%. The compound is hydrolytically unstable. *Anal.* Calcd for $F(CH_3)_2SiNHSi(CH_3)_2F$: C, 28.40; H, 7.69; N, 8.28; Si, 33.4; F, 22.49. Found: C, 28.62; H, 7.86; N, 8.21; Si, 30.0; F, 22.32.

Preparation of 1,1,3,3-Tetrachlorodimethyldisilazane.—Hexamethyldisilazane (20.00 g, 0.12 mole) was mixed with 90.0 g (0.6 mole) of methyltrichlorosilane and a catalytic amount (~200 mg) of anhydrous aluminum chloride was added. The mixture was refluxed for 2 hr and immediately distilled under high vacuum. The fractions were collected by cooling with liquid air. There was obtained 19.0 g (0.78 mole) of 1,1,3,3-tetrachlorodimethyldisilazane, bp 42° (0.1 mm), yield 65%. *Anal.* Calcd for $Cl_2(CH_3)SiNHSiCl_2(CH_3)$: C, 9.83; H, 2.92; N, 5.76; Cl, 58.43; Si, 23.04. Found: C, 10.12; H, 3.11; N, 5.70; Cl, 59.1; Si, 21.7. The compound is hydrolytically highly unstable.

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A Phosphorus-31 Nuclear Magnetic Resonance Study on the Phosphorus–Iodine System

BY ROBERT L. CARROLL AND RICHARD P. CARTER

A study of the reaction of white phosphorus and iodine was reported[1] in 1940; however, since that time there have been no further attempts to define this system. Wyllie, Ritchie, and Ludlam proposed a mechanism whereby P_2I_4 was obtained from its elements, *via* several iodide intermediates without breaking and re-forming the P–P bond. This mechanism has been extensively referred to as evidence for the existence of iodides other than the tetraiodide and triiodide, which have been isolated in their pure state.

The present report summarizes ^{31}P nuclear magnetic resonance and spectrophotometric eviden e that the formation of P_2I_4 from white phosphorus and iodine in the presence of greater than stoichiometric amounts of phosphorus does not take place as previously described.[1] We have shown that all of the P–P bonds are broken when the reaction is carried out in carbon disulfide or carbon tetrachloride at 25°. The initial reaction is rapid, proceeding directly to PI_3, which undergoes a slower reaction with the excess phosphorus to form P_2I_4.

Also, the phosphorus–iodine system is very labile, and evidence is presented for the existence of equilibria in solution.

Experimental Section

Reagents.—Diphosphorus tetraiodide and phosphorus triiodide were prepared in CS_2 from reagent grade iodine and white phosphorus, according to the method of Germann and Traxler.[2] The elemental phosphorus was purified by treatment with dilute

HNO_3 at 60°. Upon cooling, the solid was washed with distilled water, absolute methanol, and dry carbon tetrachloride. The CS_2 and CCl_4 solvents were reagent and spectroscopic grade chemicals, respectively. They were dried, distilled, and stored over P_2O_5. Spectroscopic grade cyclohexane was dried over P_2O_5 and used without additional purification. Normal precautions were observed to exclude air and moisture from all reactions.

[31]P **Nmr.**—The ^{31}P nmr spectra were obtained with a Varian high-resolution spectrometer operating at 24.288 Mc. Chemical shifts are reported in CS_2 and are relative to 85% H_3PO_4 as an external reference. For the kinetic measurements, a known quantity of iodine in CS_2 was added to a blackened, nitrogen-flushed nmr tube. The reaction was initiated by introducing a known amount of P_4 in CS_2 into the nmr tube. Solutions were transferred with syringes in order to avoid contamination by air and moisture. The nmr tube was then agitated before insertion into the probe.

Data for the kinetic experiments were obtained from the areas of the respective PI_3 and P_2I_4 peaks. Thus, each peak was traced on high-quality tracing paper and weighed. Three tracings were obtained on each peak, and the average weight was used. For a given run, all settings in the spectrometer were kept constant and precautions were taken to avoid saturation of the resonance signals. For some concentrations of the reactants, solids separated out of solution. The kinetic data used were obtained prior to the separation of solids.

The ^{31}P nmr chemical shift of P_2I_4 in CS_2 obtained on a sample of P_2I_4 (mp 124–126°) recrystallized from CS_2 was −108 ppm in contrast to the reported[3] value of −170 ppm. A similar value for the chemical shift of P_2I_4 in CS_2 at 25° was obtained in an independent investigation.[4] The earlier reported value is apparently in error, probably as a result of contamination by PI_3, for the PI_3 chemical shift in CS_2 is −178 ppm.

Spectrophotometric Measurements.—A Cary Model 14 spectrophotometer was used for all measurements. When pure recrystallized PI_3 is dissolved in cyclohexane, three absorption maxima in the ultraviolet region are apparent. These maxima are 374, 287, and 223 mμ. Moeller and Huheey[5] had assigned the 223-mμ maximum to P_2I_4. This assignment was made without considering the disproportionation of P_2I_4 to PI_3 and P_4 upon dissolution in cyclohexane. The existence of this equilibrium is supported by the fact that identical ultraviolet spectra are obtained on cyclohexane solutions of P_2I_4 and PI_3. Employing a value[6] of 1.54 × 10^3 for the molar absorptivity in cyclohexane at 374 mμ, values at 287 and 223 mμ are 7.34 × 10^3 and 1.45 × 10^4, respectively. The molar absorptivity calculated for solutions made by dissolving recrystallized P_2I_4 in the same solvent are, respectively, 7.13 × 10^8 and 1.49 × 10^4. These values were obtained soon after dissolution, thus minimizing interference by iodine. Also ^{31}P nmr results supporting the disproportionation of P_2I_4 are given in the next section of this paper.

Results and Discussion

Evidence for PI_3 as a Reaction Intermediate.—When white phosphorus and iodine react at 25°, PI_3 is the first stable compound that can be observed by ^{31}P nmr. When excess phosphorus is present, the PI_3 then reacts with the latter to form P_2I_4. This sequence of reactions, which can be represented by the equations

$$\tfrac{1}{2}P_4 + 3I_2 \longrightarrow 2PI_3 \tag{1}$$

$$2PI_3 + \tfrac{1}{4}P_4 \longrightarrow \tfrac{3}{2}P_2I_4 \tag{2}$$
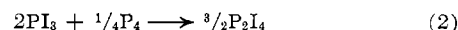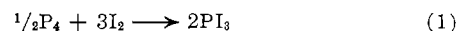
is represented graphically in Figure 1. The formation of PI_3 from the reaction of white phosphorus with iodine

(1) D. Wyllie, M. Ritchie, and E. B. Ludlam, *J. Chem. Soc.*, 583 (1940).

(2) F. E. E. Germann and R. N. Traxler, *J. Am. Chem. Soc.*, **49**, 307 (1927).

(3) H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **22**, 162 (1954).

(4) A. H. Cowley, private communication.

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

(6) V. C. Anselmo, F. M. Walters, and C. Sun, Abstracts of Papers, 151st National Meeting of the American Society, Pittsburgh, Pa., March 1966, Paper 53H.
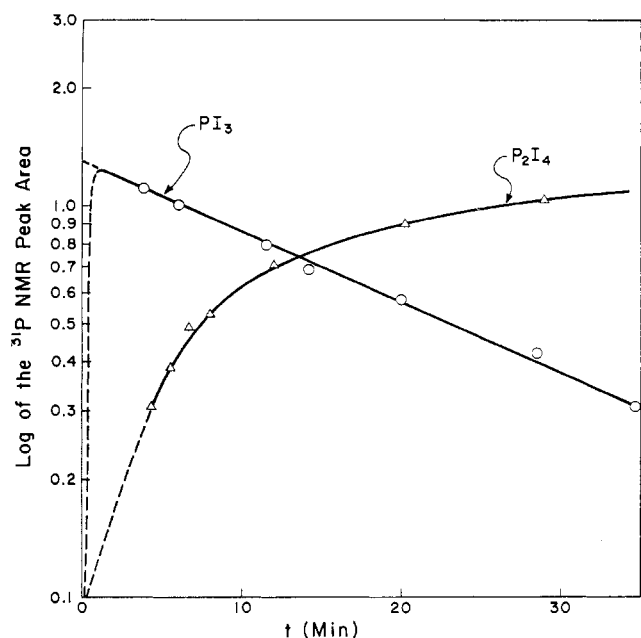
Figure 1.—The reaction of white phosphorus with iodine as a function of time followed by observing the ^{31}P nmr signals for PI_3 and P_2I_4.

(reaction 1) is, in most cases, essentially complete in CS_2 at 25° within approximately 1 min. The reaction of PI_3 with excess phosphorus is much slower and can be followed by conventional high-resolution nmr techniques.

However, the possibility that P_2I_4 is formed as an intermediate in reaction 1 cannot be completely eliminated. We have found that the reaction described by the equation

$$P_2I_4 + I_2 \longrightarrow 2PI_3 \qquad (3)$$
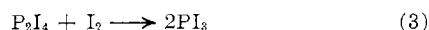
is very rapid, which would prevent any appreciable buildup of the P_2I_4 concentration in the presence of free iodine. In one such experiment when P_2I_4 was allowed to react at 25° with I_2 in CS_2 at concentrations of 0.190 and 0.295 M, respectively, the half-life was approximately 30 sec. The direct formation of P_2I_4 from white phosphorus and iodine, if such formation occurs, might be detectable at lower temperature by sufficiently sensitive analytical techniques, *e.g.*, high-resolution nmr utilizing computer-averaging techniques.

Table I lists several experiments carried out at 25° at different phosphorus and iodine concentrations. In all experimental runs, the phosphorus concentration was in excess of the stoichiometric amount necessary for the formation of P_2I_4. All experiments, except run 8, were carried out in the absence of light and in dry CS_2. The reaction mixtures appeared homogeneous for the period in which kinetic measurements were made. For most concentrations employed, orange crystals of P_2I_4 began separating out of solution near the end of the reaction. A plot of the logarithm of the area of the ^{31}P nmr peak for PI_3 *vs.* time at the concentrations employed was always linear, indicating that the reaction is first order or pseudo first order. In all cases the reaction was followed for at least 2 half-lives with a mini-

TABLE I

KINETIC DATA FOR THE REACTION OF PHOSPHORUS TRIIODIDE WITH WHITE PHOSPHORUS IN CARBON DISULFIDE

Run no.	$[I_2],^a$ M	$[P_4],^a$ M	k, min^{-1}
1	0.479	1.106	3.50×10^{-2}
2	0.571	0.961	3.27×10^{-2}
3	0.488	1.032	3.38×10^{-2}
4	0.321	0.997	3.10×10^{-2}
5	0.374	1.943	3.39×10^{-2}
6	0.341	2.024	3.13×10^{-2}
7	0.412	1.850	3.18×10^{-2}
8^b	0.523	1.038	2.72×10^{-1}

^{a} Initial concentration. ^{b} Reaction run in presence of light.

mum of eight experimental points. The "k" used in this paper is defined as $(-d[PI_3]/dt)/[PI_3]$, where concentrations are in moles per liter and the time unit is minutes. The disappearance of PI_3 at these concentrations appears to be independent of the P_4 concentration. This is evident from runs 2 and 5, where the phosphorus concentrations are 0.961 and 1.943 M, respectively. The observed first-order rate constants are, respectively, 3.27×10^{-2} and 3.39×10^{-2} min^{-1}. Other runs in Table I illustrate the zero-order dependence upon the P_4 concentration.

Also, to test if the reaction is light sensitive, run 8 was carried out in the presence of light at approximately the same concentration as run 3. The observed first-order rate constant is 2.72×10^{-1} min^{-1}, compared with 3.38×10^{-2} min^{-1} (run 3) which was obtained in a blackened tube. The reaction of PI_3 with P_4 is probably a chain reaction. A feasible initiation step could be the dissociation of the PI_3 into PI_2 and I. Since all experiments were carried out with a large excess of phosphorus, this mechanism cannot be properly evaluated at this time.

With repeated sweeping over about 750 ppm, no species were detected except PI_3, P_4, and P_2I_4 at the resolution and temperatures available. Also, no attempt was made to follow the reaction by observing changes in the ^{31}P nmr signal of the P_4 molecule. This is due, in part, to the large excess of phosphorus employed.

Employing the ultraviolet absorption maximum at 374 mμ we have established that the reaction sequence in CCl_4 is identical with that in CS_2. This is apparent from the increase and the subsequent decay of the absorption at this wavelength. For example, using a solution with initial P_4 and I_2 concentrations of 2.1×10^{-3} and 4.4×10^{-4} M, respectively, the absorption at 374 mμ passed through a maximum after about 1 hr.

The investigation of Wyllie, Ritchie, and Ludlam[1] was conducted in carbon tetrachloride. In their work, they apparently overlooked the possibility that PI_3 could be formed directly from its elements. Their rate data were obtained by visually observing the decrease in iodine color. However, in addition to the inherent errors in this method, there is the complication of interference by the PI_3 color. Also, the concentrations were calculated assuming that the reaction proceeded directly to P_2I_4. They found that the rate of disappearance of the iodine actually went through a

minimum. This observation probably is due to the formation of the colored intermediate (PI_3). Hence, it would appear that the reactions actually studied were (1) and (2), principally the former. Our rate data in CS_2, as well as the qualitative data in CCl_4, would support this conclusion. For the latter, the rate of disappearance of the iodine reported by Wyllie[1] was of the same order as that calculated from the rate of formation of PI_3 in CCl_4 at 25° measured spectrophotometrically.

Evidence for Equilibria in Solution.— An investigation by spectrophotometric and ^{31}P nmr methods on concentrated and dilute solutions of PI_3 and P_2I_4 has shown that rapid equilibria do exist A detailed study of these equilibria is complicated by the formation of poorly characterized insoluble material. Moreover, these solutions are unstable with respect to the formation of colloidal dispersions.

For the nmr study on solutions of P_2I_4, a fresh sample was prepared and slowly crystallized from a CS_2 solution containing 14% excess white phosphorus. The material was washed with cold CS_2 and recrystallized again from CS_2. A ^{31}P nmr spectrum was obtained on a 0.31 M solution, and the initial spectrum taken within 5 min showed the presence of small amounts of PI_3 and P_4 in the phosphorus atom ratio of 2:1. The phosphorus atom ratios obtained from this experiment are consistent with the equation

$$\tfrac{3}{2}P_2I_4 \rightleftharpoons 2PI_3 + \tfrac{1}{4}P_4 \qquad (4)$$
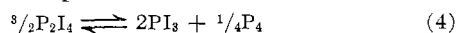
After approximately 0.5 hr, traces of insoluble red material began to separate from the previously clear orange solution. Identical results were obtained on a once recrystallized sample.

Additional evidence in support of the above equilibrium (eq 4) was obtained from spectrophotometric measurements. We have found that when P_2I_4 was dissolved in cyclohexane or carbon tetrachloride, the characteristic spectrum of PI_3 was observed. As has been shown in the Experimental Section PI_3 has three characteristic maxima in the ultraviolet region in cyclohexane, while no spectrum was observed for P_2I_4. Upon standing, these dilute solutions decomposed into iodine and a phosphorus-containing colloid. The only absorption exhibited in the ultraviolet region can be attributed to iodine. Also, there was a noticeable increase in the over-all absorption, as one would expect for the presence of colloidal material.

Additional evidence for the tendency of P_2I_4 to undergo disproportionation has been observed[7] in the reaction of AlI_3 and P_2I_4. The adduct $2PI_3 \cdot AlI_3$ and polymeric materials containing iodine, aluminum, and phosphorus were found in addition to the adduct $P_2I_4 \cdot AlI_3$. Polymeric materials were also observed by Moeller and Huheey[5] in connection with their investigation of the reaction of P_2I_4 with alcohols, phenol, and amines.

When pure PI_3 was dissolved in dry cyclohexane in a nitrogen atmosphere, the ultraviolet spectrum exhibited three absorption maxima, *i.e.*, 374, 287, and 223 mμ. Upon standing, this solution gave the char-

(7) M. Baudler and G. Wetter, *Z. Anorg. Allgem. Chem.*, **329**, 3 (1964).

acteristic iodine color, as evident from absorption at 520 mμ. The increased absorption at 520 mμ was accompanied by a concurrent decrease in the absorption of the three maxima attributed to PI_3. The possibility of the I_2 resulting from oxidation by oxygen must be considered in any interpretation of the above observations. However, similar results were obtained on solutions which were rigorously protected from oxygen with helium and scrubbed with the latter in order to expel any dissolved oxygen. In spite of these precautions, it is still possible that the system contained small amounts of residual oxygen.

Excluding the possibility of oxidation by oxygen, the following equilibrium could account for the iodine produced in this system.

$$2PI_3 \rightleftharpoons P_2I_4 + I_2 \qquad (5)$$

Confirmation of eq 5 is difficult since ^{31}P nmr measurements indicate that the equilibrium greatly favors PI_3, and also the existence of P_2I_4 was not established by spectroscopic methods. In addition, the decomposition of PI_3 in dilute solutions is rapid, particularly when exposed to ultraviolet or visible light. A possibility does exist that PI_3 and/or P_2I_4 are in equilibrium with P_4 and I_2 which would result in the catalytic conversion[8] of the white phosphorus into red phosphorus. The latter would be free to react with the iodine in solution to form phosphorus–iodine polymers. Polymeric material may also result from polymerization of other intermediates not observed by the techniques employed in this study.

The reaction of PI_3 with glacial acetic acid at 80° followed by ^{31}P nmr offers additional support for eq 5 since the main products of the reaction are P_2I_4 and H_3PO_4. These results are consistent with the initial reaction of PI_3 with CH_3CO_2H to give H_3PO_3 which is oxidized by I_2 to H_3PO_4. The removal of the I_2 results in a driving force for the buildup of P_2I_4. The catalytic decomposition by diethyl ether of PI_3 to P_2I_4 and I_2 has been reported by Feshchenko and Kirsanov.[9] They reported that, at 20°, 71% conversion occurs in 7 hr. Catalysis by dioxane was also reported, but to a lesser extent.

(8) T. W. DeWitt and S. Skolnik, *J. Am. Chem. Soc.*, **68**, 2305 (1946).
(9) N. G. Feshchenko and A. V. Kirsanov, *Zh. Obshch. Khim.*, **30**, 3041 (1960).

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Preparation and Reactions of Potassium Nitrobenzenide

BY GLEN A. RUSSELL AND ALAN G. BEMIS[1]

The reaction of deficient quantities of sodium with nitrobenzene in solvents such as tetrahydrofuran yields