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Charles B. Lindahl

(Ph. D. Thesis)

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ABSTRACT

PCl_3 in a Discharge

If a microwave discharge is established in a stream of PCl_3 vapor at 1 to 5 mm pressure, the emerging vapor contains metastable species of remarkably long lifetimes. These species react or disproportionate at cold surfaces to give PCl_5, PCl_3, and red and yellow-tan phosphorus-like subchlorides of phosphorus (e. g. P_5Cl). Part of the metastable species remains for at least 3 hr after the initial discharge reaction.

A plug of bronze wool placed past the PCl_3 discharge reacts to form $CuCl$. No PCl_5 or red or yellow-tan solids are formed in the subsequent cold traps, but small amounts of P_2Cl_4 are found.

The data are consistent with the assumption that the vapor leaving the PCl_3 discharge contains PCl_5 and one or more of the reduced species P, P_2, or PCl. The presence of the radical PCl_2 in any significant amount is not consistent with the data.

Some Reactions of P_2Cl_4

Diphosphorus tetrachloride, with a lone pair of electrons on each phosphorus, can react as a monofunctional or difunctional Lewis base.

Nickel carbonyl and P_2Cl_4 can react at $0°$ C to form a series of compounds whose relative amounts depend upon the relative ratios of the reactants and the CO pressure in the reaction vessel. A large excess of $Ni(CO)_4$ reacts with P_2Cl_4 to form the yellow-white solid $P_2Cl_4 \cdot 2Ni(CO)_3$. In the absence of CO pressure of at least 0.3 atm this material decomposes at $0°C$. With equal molar amounts of P_2Cl_4 and $Ni(CO)_4$, a yellow solid is formed having the approximate empirical formula $P_2Cl_4 \cdot Ni(CO)_2$. A polymeric structure $[P_2Cl_4 \cdot Ni(CO)_2]_x$ with terminal groups of P_2Cl_4 or $Ni(CO)_3$ is suggested for this

material. Large excesses of P_2Cl_4 react with $Ni(CO)_4$ to form a yellow-brown solid $(P_2Cl_4)_2 \cdot Ni(CO)_2$. If the CO pressure in the reaction vessel does not build up to $\geqslant 0.7$ atm by the evolution of CO in the formation of this compound, the compound continues to react slowly with P_2Cl_4 to yield compounds approaching the compositions $(P_2Cl_4)_3NiCO$ and $Ni(P_2Cl_4)_4$ until the CO pressure does reach 0.7 atm. Experiments with PCl_3, P_2Cl_4, and $Ni(CO)_4$ show that P_2Cl_4 can replace PCl_3 in $(PCl_3)_{4-x} \cdot Ni(CO)_x$ compounds and that in mixtures of PCl_3 and P_2Cl_4 with $Ni(CO)_4$ most of the reaction is due to P_2Cl_4. Thus, P_2Cl_4 is a better Lewis base than PCl_3; this is in agreement with an argument based upon the inductive effect.

Diphosphorus tetrachloride does not react, or reacts only extremely slowly, at $0°$ with $Fe(CO)_5$, $Cr(CO)_6$ or $Mo(CO)_6$.

With BBr_3 at $0°$, P_2Cl_4 reacts to yield PBr_3, BCl_3, the mixed chloro-bromo-trihalides of phosphorus and boron, and phosphorus subhalides. Boron trichloride and BF_3 do not react with P_2Cl_4 at $0°$, which is in agreement with the known Lewis acid trend $BBr_3 > BCl_3 > BF_3$.

Diphosphorus tetrachloride reacts with B_2H_6 causing decomposition producing H_2, BCl_3, $BHCl_2$, and yellow-orange solids indicative of phosphorus subhalides or subhydrides.

Because P_2Cl_4 has vacant low-energy d orbitals on each phosphorus, it is also a potential Lewis acid. No reaction was observed between P_2Cl_4 and C_2H_4, C_2H_2, or C_3F_6 at $0°$ or at room temperature. However, reaction between P_2Cl_4 and trimethylamine at temperatures of $0°$ and $-78°C$ produces large quantities of yellow-orange nonvolatile solids. The apparent products of reaction are $PCl_3 \cdot N(CH_3)_3$ and phosphorus.

Thus, P_2Cl_4 undergoes reaction both as a Lewis acid and as a Lewis base. However, all reactions except the reaction with $Ni(CO)_4$ involve rupture of the phosphorus-phosphorus bond in P_2Cl_4.

I. INTRODUCTION

A compound containing phosphorus-phosphorus bonds was prepared as long ago as 1813, when--in one of the early experiments with the newly-discovered element iodine--Gay Lussac[1] fused phosphorus with iodine to form what was later determined to be P_2I_4. However, relatively little effort has been made to study this or other compounds containing phosphorus-phosphorus bonds, and little is known of the reactions they undergo. Huheey has reviewed the preparation, characterization, and known reactions of compounds containing phosphorus-phosphorus bonds.[2,3,4]

Phosphorus-phosphorus bonds are present in the various forms of elemental phosphorus, the lower hydrides, oxyacids, organic diphosphine chalcogenides ($S_2P_2R_4$ and $O_2P_2R_4$), organic cyclophosphines (the cyclic tetramer, P_4R_4, and perhaps others) and in compounds containing two tri-coordinated phosphorus atoms with the formula P_2R_4 where R can be organic, H, I, or Cl. Ross[5] has summarized and briefly discussed the known compounds of P_2R_4.

Diphosphine, P_2H_4 (as substituents of which all of the organic P_2R_4 compounds are named) is a by-product in the preparation of phosphine. Diphosphine is unstable and decomposes to yield phosphine and solid lower hydrides of phosphorus.

Diphosphorus tetraiodide, P_2I_4, which is thermodynamically stable with respect to phosphorus triiodide and white phosphorus at normal temperatures, can be easily prepared from the elements (see for example, Moeller and Huheey[4]).

The only other known P_2R_4 compound which contains no organic groups is diphosphorus tetrachloride, P_2Cl_4.

Diphosphorus tetrachloride was first prepared by Besson and Fournier in 1910 by passing PCl_3 and H_2 through a silent electric discharge.[6] They describe it as a colorless, oily liquid with a freezing point of -28°. They report that it decomposes at room temperature to a yellow solid of composition P_7Cl_2 and PCl_3 and that it fumes in air. In 1925 Stock, Brandt, and Fischer[7] prepared about 40 mg of P_2Cl_4, (mp -28°) by using a zinc arc in liquid PCl_3. Gutmann in 1955 reported

the passage of PCl_3 and H_2 through a discharge to yield red phosphorus and uninvestigated liquid products.[8] In 1959 Finch reported the production of 200 mg of P_2Cl_4 per day by passing PCl_3 through a mercury-electrode apparatus.[9] Molecular weights of 191 and 194 (calculated for P_2Cl_4, 204) were determined by vapor-tension depression of CCl_4. Finch, however, reported a melting point of -34° to -35°. Finch also mentioned the decomposition of P_2Cl_4 at room temperature in vacuum.

Thus, at the initiation of our research, P_2Cl_4 was a laboratory curiosity known to be unstable, reactive, and prepared in only very small quantities. We started our research seeking to improve the yield of P_2Cl_4 by studying reactions of PCl_3 in a discharge. Our goal was synthesis of enough P_2Cl_4 to begin to study some of its chemistry including reactions of P_2Cl_4 as a monofunctional or difunctional Lewis base, and possibly as a Lewis acid, as well as reactions of the phosphorus-phosphorus bond. During the course of our research, Sandoval and Moser[10,11] reported methods for preparing gram quantities of P_2Cl_4. Later, another preparation of P_2Cl_4 was reported by Ross.[5] These methods are discussed in Sec. III.

II. PCl_3 IN ELECTRIC DISCHARGES

Electric discharges can sometimes be used to synthesize compounds of unusual structure or to synthesize compounds that are thermodynamically unstable with respect to their starting materials. The use of discharges in synthetic inorganic chemistry has recently been reviewed by Jolly[12] and Massey.[13]

Because the best reported yield of P_2Cl_4 at the initiation of this research was 200 mg/day, our initial research involved the attempted preparation of large amounts of P_2Cl_4 from PCl_3 by electric-discharge techniques.

A. Microwave-Discharge Experiments with PCl_3

Initial studies of PCl_3 in a discharge were carried out using a microwave discharge. A microwave discharge was chosen both because it is an "electrodeless" discharge with no possibility of contamination by metal electrodes and because it was successfully used in the preparation of Ge_2Cl_6[14,15] from $GeCl_4$ and B_2Cl_4[16] from BCl_3. The apparatus is shown in Fig. 1. A Raytheon QK60 magnetron tube producing 10-cm microwaves was coupled to the cylindrical resonance cavity. The power supply was run at 1100 V and 110 mA corresponding to 120 W. The QK60 is rated to operate at 50 W. The excess power put through the tube did not seem to damage it but did more than double its energy output. Because the heat generated in the cavity was intense enough to melt holes in quartz tubing, the cavity and reaction tubes were at all times cooled by an air blast.

If a microwave discharge is established in a stream of PCl_3 vapor at 1 to 5 mm pressure, the emerging vapor contains metastable species of remarkably long lifetime. If this vapor is allowed to pass through a series of four traps cooled to -22°, -45°, -63°, and -196°, successively, then PCl_5--identified by its sublimation point and by elemental analyses-- condenses in the -22° trap, a red material is formed in the -45° trap, a yellow-tan material is formed in the -45° and -63° traps, and PCl_3 condenses in the -63° and -196° traps. The red and yellow-tan materials are nonvolatile at room temperature, amorphous to x rays,
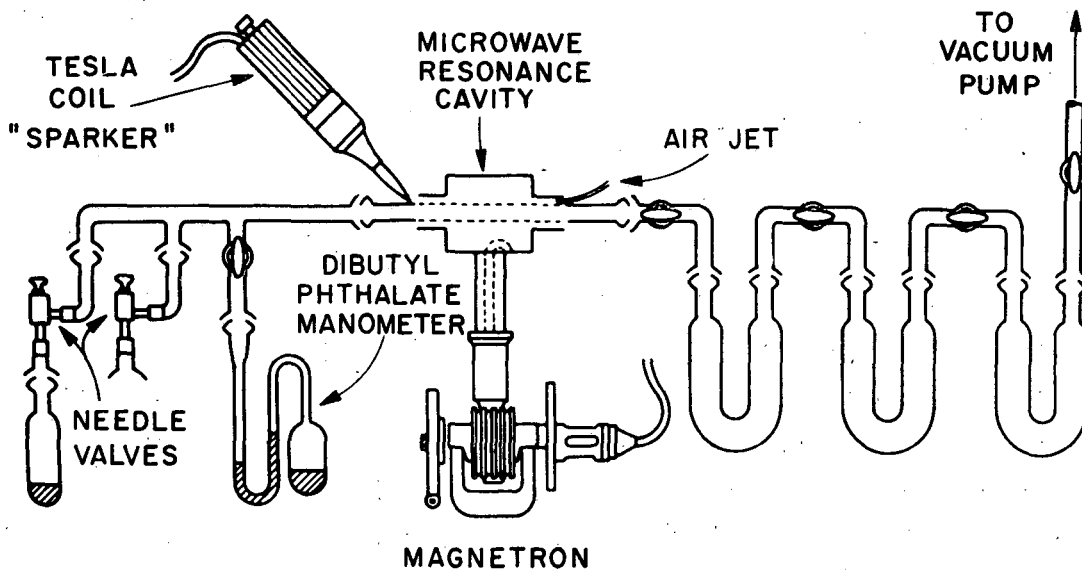
Fig. 1. Microwave-discharge apparatus.

MU-22279-A

frequently pyrophoric, and contain variable amounts of phosphorus and chlorine; the P:Cl ratio of the red material varies from 5.5:1 to ∞:1, and the yellow-tan material varies from 2.2:1 to 5.0:1. Table I lists elemental analyses of several of these products from different runs.

Table I. Analyses of nonvolatile solids.

Cold Bath	-11	-22	-22 & -45	-45	-63 & -196	-196
Color	Red	Red	Yellow-tan and red	Red (reacted with PCl_5)	Yellow-tan	Yellow-tan
Ratio P/Cl	7.62	5.43	3.48	2.19	4.96	2.47 3.45 3.97

In some other runs the red materials that had condensed in the trap at -22° reacted with PCl_5 as the PCl_5 was sublimed away. Other red materials showed no test for chloride. The red materials have a higher P/Cl ratio than the yellow-tan materials, but the ratios cover large ranges.

The results of a series of runs with PCl_3 in a microwave discharge are shown in Table II.

In general, the higher the pressure of flow rate in the system the lower the percent of PCl_3 destroyed. In these runs from 1.2 to 71.5% of the PCl_3 passed was destroyed. Table II also shows that most of the chlorine from the destroyed PCl_3 ended up in PCl_5.

If a mixture of PCl_5 and the red and yellow materials is exposed at room temperature to a stream of vapor emerging from the discharge, the red and yellow materials disappear, but the PCl_5 remains. After long standing, the red and yellow materials react with PCl_5 to form PCl_3.

If the vapor emerging from the discharge is allowed to fill an evacuated bulb to a pressure of several mm, red and yellow materials and PCl_5 can be condensed by cooling part of the bulb with liquid nitrogen 3 hours after closing off the bulb. After 15 hr only PCl_3 can be condensed. Thus, the metastable species have a long lifetime before they back react to re-form PCl_3. The mass spectrum of the

Table II. PCl_3 in a microwave discharge.

Pressure (mm Hg)	Flow rate $\left(\dfrac{mmole}{PCl_3/min}\right)$	PCl_3 destroyed (%)	PCl_3 destroyed (mmole)	PCl_5 found (mmole)	P in PCl_5 (%)	Cl in PCl_5 (%)
4	6.33	3.45	15.80	8.27	52.3	87.2
3	3.13	1.22	4.59	2.55	55.6	92.5[a]
2	4.88	3 to 4	-	1.68	-	-[b]
2	2.05	18.1	73.32	>2.50	>35.1	>56.8
1	0.56	71.5	98.4	-	-	-
1	0.21	64.3	68.21	40.8	59.8	99.7
4 to 8	0.19	15.7	8.16	4.54	55.6	92.6
1/2	0.11	61.1	50.8	-	-	-
3	2.43	28.5	49.8	28.0	56.2	93.7
1	1.32	19.1	23.2	-	-	-

[a] Vapors from discharge first passed through 60 cm of stainless steel tubing.

[b] Bronze wool placed past -22° cold trap.

vapor in the bulb (as determined with a Consolidated 21-103a spectrometer), both before and after condensation of red and yellow materials and PCl_5, was found to be the same as that for pure PCl_3.

B. Microwave-Discharge Experiments with PCl_3 and H_2

If H_2 is mixed with the PCl_3 entering the discharge in ratios of $P_{H_2}/P_{PCl_3} > 1$, red phosphorus is deposited throughout the line beyond the discharge; the thickness of the deposit decreases with increasing distance from the discharge. Hydrogen chloride forms, but no PCl_5 forms. In our experiments with a ratio of $P_{H_2}/P_{PCl_3} < 1$, PCl_5 and the red and yellow solids were found along with HCl. No P_2Cl_4 was observed in any of these runs. Preparations of P_2Cl_4 from PCl_3 and H_2 in discharges have been reported since this part of our work was completed by Sandoval and Moser[11] and Ross.[5] These will be discussed with the other preparations of P_2Cl_4.

C. Microwave-Discharge Experiments with PCl_3 and Bronze Wool

A plug of bronze wool placed past the PCl_3 discharge reacts to form CuCl, identified by its x-ray powder pattern. No PCl_5 or red or yellow solids are formed in subsequent cold traps, but small amounts of P_2Cl_4 were produced in yields ranging from 0 to 77% based on the 0.07 to 0.63% PCl_3 reacted. These results are listed in Table III and show that the plug of bronze wool greatly changes the products of the reaction. In two cases the bronze wool was analyzed for chloride and was found to agree quite well with the gain in weight of the bronze wool, if one considers the experimental error in the weighings (18.6 mg Cl vs 20.6 mg, and 9.2 mg Cl vs 10.7).

D. Miscellaneous Microwave-Discharge Experiments

In an effort to understand the function of the bronze wool in the microwave experiments, we ran several other microwave experiments. These included three runs made with glass wool, one with aluminum wool, one with iron wire and one with steel wool. In the glass wool runs much PCl_5 and red and yellow solids were observed. In one run the PCl_5 plugged the glass wool and prevented further flow. In the other

Table III. PCl_3 + bronze wool in a microwave discharge.

P_2Cl_4 Produced (mmoles)	Converted (%)	Yield (%)	PCl_3 destroyed (%)	PCl_3 destroyed (mmoles)	PCl_3 flow rate (mmoles/min)	Gain in wt. of bronze wool (g)
0.2336	0.37	77	0.49	0.608	1.71	0.0377
0.0368	0.07	24	0.28	0.313	1.26	-
0.1629	0.07	28	0.25	1.16	4.03	0.0206
0.0746	0.10	17	0.60	0.58	1.89	0.0351
0.1698	0.11	47	0.23	0.73	0.91	0.0107
0.0255	0.03	48	0.07	0.11	0.35	-
0.0108	0.07	15	0.46	0.16	0.68 ⎫	0.0125
0.0034	0.02	34	0.63	0.20	0.70 ⎭	

two runs, 44.2 and 73.5% of the PCl_3 passed was destroyed. In the aluminum wool run 13.9% of the PCl_3 was destroyed, and in the iron wire run 38.3% of the PCl_3 was destroyed. Red and yellow solids and PCl_5 were observed in each case. There may not be a valid comparison to be made between the iron wire and aluminum wool and the bronze wool because the iron and aluminum were in much coarser strands. Coarse strands would have less area available for contact with the reactive species, and this could have accounted for the large amounts of PCl_3 destroyed. In the steel wool run only 1.64% of the PCl_3 was destroyed. Yellow solids were visible, but no PCl_5 was seen. The steel wool had definitely reacted. After exposing the wire to the atmosphere, we analyzed a powder pattern and found $FeCl_2 \cdot 4H_2O$.

E. Discussion of Microwave-Discharge Experiments

The data are consistent with the assumption that the vapor leaving the PCl_3 discharge contains PCl_5 and one or more of the reduced species, P, P_2, or PCl. Upon condensation, the reduced species immediately disproportionates or reacts with PCl_3 to form a red phosphorus-like subchloride of phosphorus (e. g. P_5Cl). We know the radical PCl_2 cannot be present in a significant amount because 71.5% of the PCl_3 can be decomposed in the over-all reaction. From the following equations it is clear that if the initial discharge products were PCl_2 and PCl_5, it would be impossible to decompose more than 57% of the PCl_3.

$$PCl_3 \longrightarrow \underbrace{[0.67PCl_2]}_{} + 0.33PCl_5$$
$$\downarrow$$
$$0.046P_5Cl + 0.43PCl_3$$
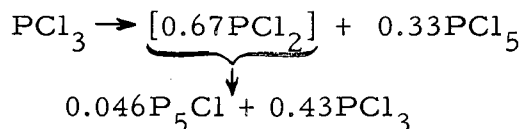
However, if the initial discharge products were PCl and PCl_5, it would be possible to decompose as much as 86% of the PCl_3.

$$PCl_3 \longrightarrow \underbrace{[0.5PCl]}_{} + 0.5PCl_5$$
$$\downarrow$$
$$0.07P_5Cl + 0.14PCl_3$$
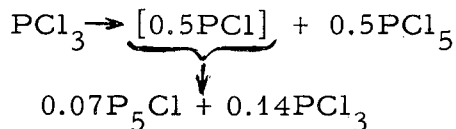
Also, if the initial discharge products were PCl_5 and either P or P_2, it is conceivable that 100% of the PCl_3 might be decomposed.

$$PCl_3 \longrightarrow \underbrace{[0.4P]} + 0.6PCl_5$$
$$+ \downarrow 0.029PCl_3$$
$$0.086P_5Cl$$
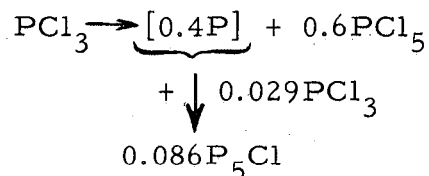
The bronze wool is an efficient catalyst in the back-reaction forming PCl_3 (up to 71.5% PCl_3 decomposition without bronze and up to only 0.6% with bronze). This is not just a function of a large surface area, as glass wool has no apparent effect. In addition, the bronze reduces any remaining PCl_5 to PCl_3 and catalyzes the reaction of the reduced species with PCl_3 to form P_2Cl_4.

Using a microwave discharge, we have been successfully able to prepare small amounts of P_2Cl_4. However, the amounts were extremely small and have been formed only when bronze wool was present. As a result, it was decided that a discharge system using bronze-wool electrodes should be tried.

F. Discharge Experiments Using Bronze-Wool Electrodes with PCl_3

Numerous variations of the apparatus described by Wartik[17] (in which B_2Cl_4 is prepared by passing BCl_3 through a 60-cycle discharge between bronze-wool plugs) were tried in an attempt to find an efficient process for the reaction

$$2PCl_3 + 2Cu \xrightarrow{\text{discharge}} P_2Cl_4 + 2CuCl.$$
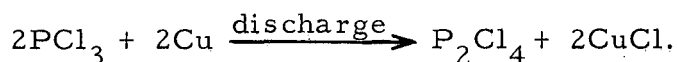
G. Low-Pressure Flow Experiments

One series of flow experiments with PCl_3 pressures of 1 to 3 mm is listed in Table IV. These runs were made with the reaction tube shown in Fig. 2. The electrodes were connected to a 115 to 15 000 V luminous tube transformer (Gardner Neon and Ignition Transformers Inc., Oakland, California) regulated by an autotransformer. Phosphorus trichloride vapor was passed through the tube and through a series of

Table IV. PCl_3 in an ac bronze-wool glow discharge.

P_2Cl_4 (g)	P_2Cl_4 (mmoles)	Conv (%)	Yield (%)	Destroyed (%)	Flow rate (mole/min)	Time (min)	mA
0.0229	0.11	0.20	-	-	-	-	-
0.0451	0.22	0.41	4.0	10.4	0.87	125	-
0.0556	0.27	0.44	1.8	24.1	1.03	120	44
0.0558	0.27	0.42	1.5	27.2	2.04	65	38
0.0422	0.21	0.73	5.2	13.9	1.60	36	23
0.0517	0.25	1.12	11.6	9.6	1.89	24	11
0.0420	0.21	0.33	14.0	2.3	0.87	162	4
0.2375	1.17	0.11	11.4	0.95	2.91	752	10[a]
0.0252	0.12	0.53	3.5	12.7	0.77	60	16[b]
0.0090	0.04	0.30	2.9	10.4	0.49	60	15[b]
0.0244	0.12	0.60	9.7	6.2	0.66	60	15[b]
0.0137	0.07	0.40	6.8	5.9	0.55	60	14[b]
0.0106	0.05	0.42	8.0	5.2	0.62	60	13[b]
0.0059	0.03	0.17	3.2	5.5	0.56	60	13[b]
0.0053	0.03	0.24	3.7	7.6	0.50	43	13[b]
-	-	-	-	4.9	0.63	134	13[b]

[a]Bigger reaction vessel with more bronze wool.

[b]Series of reactions run in same vessel without changing wool.

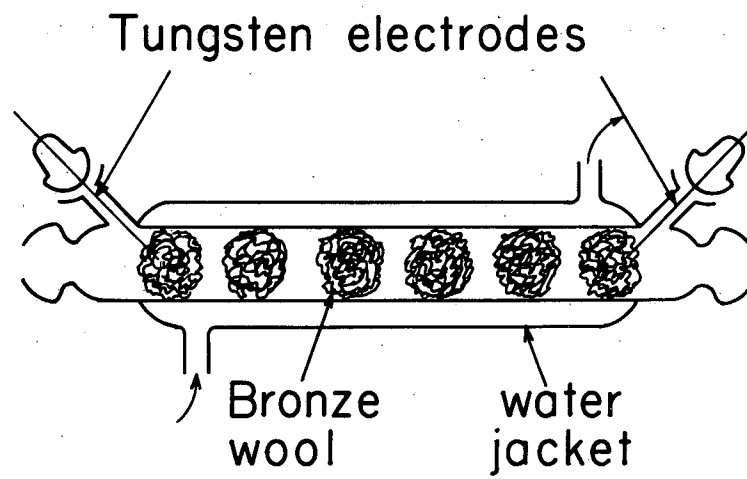Tungsten electrodes

Bronze wool

water jacket

FIG.2. BRONZE WOOL DISCHARGE TUBE.

MU-27900

Fig. 2.   Bronze-wool discharge tube.

cold traps. A -45° cold trap condensed P_2Cl_4; -78° and -196° cold traps condensed the unreacted PCl_3. The results show a higher percentage yield with lower current flows, which indicates less decomposition, but in all cases the yield is still low compared to other methods. A decreasing conversion of PCl_3 with increasing length of run is also observed. The amounts of P_2Cl_4 produced in several of the runs are about the same. These results suggest that only part of the bronze wool can react with PCl_3. After the surface is coated, little further reaction occurs. Therefore, only a very limited amount of P_2Cl_4 can be made in each run. The small amounts of P_2Cl_4 produced, as well as tedious cleaning and setting up of runs, make this method undesirable.

H. High-Pressure Static Runs

Several experiments were carried out by using bronze wool and PCl_3 in static systems, which were held at 0° in order to maintain a PCl_3 pressure of 35 mm. Table V lists a series of four experiments carried out in a round-bottom flask identical with that shown in Fig. 3, except that bronze wool was wrapped around each electrode. The yield of 75 mg of P_2Cl_4 (0.37 mmoles) in 18 min was encouraging, but the longer runs did not give good results. Again, apparently the CuCl coating which forms on the relatively small amount of bronze wool reduces its reactivity. In six other static runs at 0° made with a series of large bronze-wool plugs, three produced no P_2Cl_4 and three others produced only 6.2 mg, 7.3 mg, and 10.0 mg.

Table V. PCl_3 and bronze wool in static runs at 0°.

Time of run (min)	PCl_3 destroyed (mmole)	P_2Cl_4 made (mmole)	Yield (%)
18	5.10	0.3705	9.84
53	3.64	0	0
123	11.21	0.0932	1.11
44	9.83	0.1477	2.00

0.060-in. tungsten
electrodes
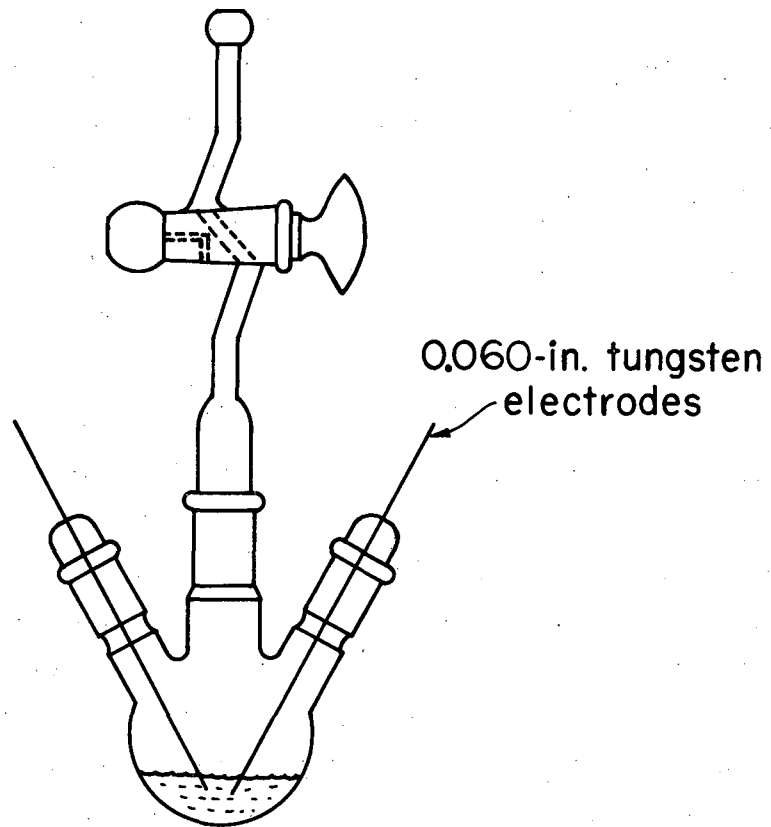
MU-30946

Fig. 3. Reaction vessel for P_2Cl_4 preparation.

J. Conclusions to Section II

Both microwave and alternating-current discharge methods have been used to prepare small quantities of P_2Cl_4. However, during the course of these studies, Sandoval and Moser[10] reported the preparation of gram quantities of P_2Cl_4. Since our methods were clearly not as productive as theirs, we terminated our studies of new preparative methods and adopted theirs to prepare the quantities of P_2Cl_4 needed for the study of some of its reactions.

III.   PREPARATION OF P_2Cl_4

Since the start of our research, two other groups have reported the preparation of P_2Cl_4.

Sandoval and Moser first reported the preparation of 4 to 5 g of P_2Cl_4 in a 7-hr reaction period.[10]   Their reaction vessel, shown in Fig. 3, was a 100-ml three-neck round-bottom flask.   The discharge was maintained between two molybdenum electrodes above the surface of liquid PCl_3, which contained white phosphorus in solution or red phosphorus in suspension.   In later reports, Sandoval and Moser report a yield of 1.5 g of P_2Cl_4 after a 3-hr period using PCl_3- P (white), and a yield of 0 to 0.40 g after 7-hr periods using PCl_3- P (red).[11,18] One preparation with PCl_3- P (red) gave a yield of 4 to 5 g of P_2Cl_4 in an 8-hr period.   They also report preparation of P_2Cl_4 in quantities as high as 7.0 g in a 2-hr period using a PCl_3/H_2 mole ratio of two at a total pressure of 19 mm.

Ross[5] has reported the preparation of 300 to 400 mg of P_2Cl_4 in a 2-day reaction period during which PCl_3 vapor was repeatedly and automatically passed through a copper-wool discharge tube.   Using a vapor-phase reaction of PCl_3 and H_2 in a low-pressure glow discharge, he reported a reproducible yield of 400 to 500 mg in a 3.5- to 4-hr run using 25 cc of liquid PCl_3.

The method of Sandoval and Moser using white phosphorus in PCl_3 was the most satisfactory for the preparation of P_2Cl_4.   Our brief attempts to prepare P_2Cl_4 with their H_2- PCl_3 discharge method were unsuccessful, apparently because we did not achieve the careful control of PCl_3 and H_2 pressures which are necessary to prepare P_2Cl_4. Therefore, this method was abandoned in favor of the white phosphorus in PCl_3 reaction.

The results of our preparations of P_2Cl_4 using their white phosphorus method are given in Table VI.

A total of 37 preparative runs have been made over a two-year period.   In the initial 15 runs, no data were collected on the amount of PCl_3 used, and in only 6 (reported in Table VI) of these runs was the

Table VI. Preparations of P_2Cl_4.

PCl_3 (mmoles)	PCl_3 reacted (mmoles)	P_2Cl_4 (g)	P_2Cl_4 (mmoles)	Conv (%)	Yield (%)	PCl_3 destroyed (%)	Rxn time (min)
a		0.5251	2.577				338
a		1.6209	7.953				670
a		1.6007	7.854				558
a		0.4972	2.440				672
a		0.17	0.83				114
a		5.02	24.6				997
204.7	52.35	6.291	30.87	20.1	78.6	25.6	900
252.5	18.06	1.7109	8.40	4.43	62.0	7.15	1510[c]
137.0	13.69	0.34	1.67	1.82	18.2	9.99	1009[d]
104.0	14.93	1.3461	6.61	8.47	59.0	14.4	731
87.60	9.10	0.8887	4.36	6.64	63.9	10.4	288
103.7	17.33	2.1614	10.61	13.6	81.6	16.7	534
86.58	39.32	0	0	0	0	45.4	589[e]
104.2	23.52	2.72	13.35	17.1	75.7	22.6	462
94.15	25.56	3.290	16.14	22.9	84.3	27.1	531
68.37	18.49	a	b	b	b	27.0	376
49.73	10.41	1.3845	6.79	18.2	87.0	20.9	420
80.61	7.87	0.3788	1.86	3.07	31.5	9.76	441
97.28	21.99	2.8389	13.93	19.1	84.5	22.6	555
111.6	15.88	2.1633	10.62	12.7	89.2	14.2	467
98.59	17.91	2.3459	11.51	15.6	85.7	18.2	398
34.95	5.75	0.4202	2.06	7.87	47.8	16.5	353
28.98	6.12	a	b	b	b	21.1	412
22.86	a	0.4297	2.11	b	b	b	411
92.11	19.00	2.4588	12.07	17.5	84.6	20.6	458
73.11	17.62	1.7596	8.63	15.7	65.3	24.1	442
155.0	7.28	0.8333	4.09	3.52	74.9	4.70	458
137.6	8.08	1.1221	5.51	5.33	90.8	5.87	468

[a] Not measured.   [c] Reaction vessel solids used without fresh P_4.   [e] Unusual discharge.
[b] Not calculable.   [d] Electrodes broken.

amount of P_2Cl_4 measured. In the remaining 22 runs (listed in chronological order) data were collected on both PCl_3 consumed and P_2Cl_4 produced.

The preparative technique developed in the early runs and employed throughout consisted of dropping a 2 to 5 g lump of white phosphorus into water in the bottom of the 3-neck flask. Next, the electrodes (sealed through 19/38 sleeve joints) and the adapter with stopcock were placed in the three necks using KEL-F 90 grease (Minnesota Mining and Manufacturing Company, 3M, St. Paul, Minnesota). The flask was then evacuated, and the water distilled out at room temperature. The white phosphorus was next melted under vacuum to eliminate any volatile impurities. Phosphorus trichloride (Mallinckrodt Chemical Works, St. Louis, Missouri), purified by fractional condensation through successive -45°, -78°, and -196° cold traps with the -78° fraction retained, was then distilled into the flask. After the flask was removed from the vacuum line, immersed in a 0° bath up to the necks and connected to a luminous tube transformer, 6 000 to 15 000 V were applied. After the reaction the P_2Cl_4, PCl_3, and solid products were separated by fractional condensation. The vapors were passed through successive -22°, -45°, and -78° and -196° traps. In approximately an hour the -22° trap contained P_2Cl_4 and traces of white phosphorus. The -45° trap contained some P_2Cl_4 and part of the PCl_3. The majority of the PCl_3 was in the -78° trap. The -22° and -45° traps were recombined and passed through 0° (white phosphorus), -45° (P_2Cl_4) and -196° (remaining PCl_3) baths. This separation technique was convenient and necessary because P_2Cl_4 passed a -22° bath only very slowly and some PCl_3 condensed in the -45° bath when passed at the pressures necessary to pass 100 mmoles an hour. The initial -22° trap also cooled the vapor so that almost no P_2Cl_4 was entrained in the PCl_3 sufficiently to pass a -45° bath.

Only minor modifications have been made in the method of Sandoval and Moser. We substituted tungsten electrodes for molybdenum. Our early electrodes were 0.040 in. in diameter, and disintegrated in the discharge area in 10 or 12 hours. In later runs, 0.060-in. electrodes,

which disintegrated at a much slower rate, were employed. In our runs the white phosphorus was not distilled in, but was dropped into water. We substituted KEL-F 90 grease for KEL-F wax. Sandoval and Moser stated that their electrodes were 2 mm above the surface of the liquid. In most of our runs the electrodes extended into the solution. Actually, in runs carried out at temperatures as high as $0°$, there is little difference because the voltages applied do not break down the liquid but only the gas. As a result, all the discharge occurs in the gas phase.

The yields of the 22 measured runs were from 0 to 6.3 g (0 to 30.9 mmoles) of P_2Cl_4. The results were somewhat erratic, but some general conclusions can be drawn. In most of the runs, the conversion of PCl_3 to P_2Cl_4 was 10 to 20% and the yield based on PCl_3 reacted was 75 to 90%. A few preparations gave lower results for the reasons indicated in Table VI, and a few gave lower results for no apparent reasons. The yield based on reacted PCl_3 is surprisingly high. An 80% yield would correspond to the reaction

$$5PCl_3 + P_{4(excess)} \rightarrow 3P_2Cl_4 + 3P_xCl$$
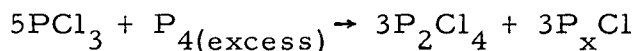
The reaction of 10 to 20 % of the PCl_3 in the vessel, apparently quite independent of the total amount of PCl_3, is also excellent for such an efficient discharge reaction.

Nothing can be said about the reaction with excess PCl_3 because, to make a maximum amount of P_2Cl_4, white phosphorus was purposely kept in excess in all of the runs.

Little can be said about the importance of reaction duration because most of the reactions were run for a 6 to 10 hr period as a matter of convenience. Among the times of our reactions no great difference can be noted, but the longer runs appear to produce more P_2Cl_4 with no increase in phosphorus subchlorides.

The method is entirely satisfactory for preparing 1 to 3 g of P_2Cl_4. It requires only relatively common glassware in addition to a high-voltage transformer. The technique is quite simple and requires minimal control. Thus, the method is a good preparation for gram quantities of P_2Cl_4.

A. Discussion of All Methods of P_2Cl_4 Preparation

The preparations of P_2Cl_4 can be classified into three types depending upon the reducing agent in the discharge. There are discharge preparations using PCl_3 with either H_2, metals, or elemental phosphorus.

The preparation of P_2Cl_4 with H_2 and PCl_3 was the first preparation of P_2Cl_4 by Besson and Fournier[6] and was also employed by Sandoval and Moser[11,12,18] and Ross.[5] This method gives the best reported yield (7 g in 2 hr) but also is apparently the most sensitive to relative amounts of reagents. One must achieve a delicate balance of the ratio of H_2 to PCl_3. With a deficiency of H_2 the reaction
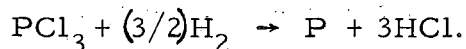
$$(5x-1)PCl_3 \rightarrow (3x-1)PCl_5 + 2P_xCl$$
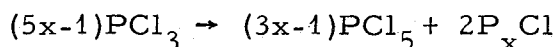
occurs, while with an excess of H_2 the reaction is

$$PCl_3 + (3/2)H_2 \rightarrow P + 3HCl.$$

Thus, the absence of P_2Cl_4 in the discharge reaction of H_2 and PCl_3 in the work of Gutmann,[8] in the early work of Sandoval and Moser,[10] and in our work can be explained by the difficulty in controlling the relative amounts of PCl_3 and H_2. While the best yields of P_2Cl_4 have resulted from careful adjustment of flow rates of H_2 and PCl_3, this adjustment is difficult and this method frequently leads to no yield at all.

The reduction of PCl_3 in a discharge by zinc, mercury, or copper wool has led only to small yields, probably because the limited surface area of the metal becomes covered with reaction products.

The preparation of P_2Cl_4 from PCl_3 and white phosphorus is much more consistent both in the work of Sandoval and Moser[10,11,18] and in our work. As a result, this method is presently the easiest and most reliable way to prepare a few grams of P_2Cl_4.

IV. PROPERTIES OF P_2Cl_4

The properties of P_2Cl_4 reported by the several investigators are in fairly good agreement.

A. Melting Point

The melting point of -28° reported by Besson and Fournier[6] has been confirmed by Stock, Brandt, and Fischer (-28°),[7] Sandoval (-28±1°)[18] and Ross (-28°).[5] Using the Stock falling plunger method, we also measured a melting point of -28°. Finch has reported that P_2Cl_4 melts sharply between -34° and -35°.[9] Because of the agreement of five other investigators, it is probable that Finch's observation was in error due to impure materials, lack of temperature equilibrium, or an inaccurate thermometer.

B. Vapor Pressures

Measurements of vapor pressures of P_2Cl_4 have been in less agreement. Besson and Fournier[6] distilled P_2Cl_4 at 180° but said it distilled with less decomposition at 20 mm at 95° to 96°. Stock, Brandt, and Fischer[7] reported a 0° vapor pressure of 5 mm. Ross[5] reported 4 mm at 0° and 10 mm at 28°. Garrett and Urry describe purification of P_2Cl_4 by distillation through -23°, -45°, and -196° traps.[19] The process was repeated with the -45° fraction until the material in that fraction exhibited a vapor tension of 5 mm at 0°. However, in their only reported experiment they stated their P_2Cl_4 contained a small amount of PCl_3. In his thesis, Garrett[20] mentions only the vapor pressure of the sample of P_2Cl_4 containing a small amount of PCl_3 which was used in the experiment reported by Garrett and Urry.[19] He reported the vapor pressure of the mixture at 0° to be 7.2 mm and referred to 5.0 mm as the literature vapor pressure of P_2Cl_4. Sandoval[18] reported about 1 mm at 25°. The various results are inconsistent due to PCl_3 contamination and decomposition of P_2Cl_4. Finch wrote, "Lack of volatility at low temperatures, and the rate of decomposition at room temperature, precluded vapor-pressure measurements."[9]

Using an immersible mercury tensiometer, we have measured the vapor pressure of P_2Cl_4 at several temperatures. Because of the decomposition of P_2Cl_4 above 0°, the pressures are difficult to determine accurately. After each series of readings the tensiometer was cooled to 0° to determine if any decomposition had occurred. A slow reaction of P_2Cl_4 with mercury also limits the accuracy of the results. The results of our measurements of the pressure of P_2Cl_4 are listed in Table VII.

Table VII. Vapor pressures of P_2Cl_4.

T(°C)	76.3	65.7	52.8	47.8	43.2	38.4	33.6	25.3
Exp. (mm)	30.7	17.5	8.2	5.5	4.4	2.8	2.1	1.1
Calc. (mm)	31.9	17.4	7.8	5.6	4.2	3.0	2.1	1.1
Deviation (%)	3.9	0.57	4.9	1.8	4.5	7.1	0	0

Figure 4 shows a plot of log P_{mm} against $1/T$. For comparison the data of other investigators are also plotted. The equation of the best straight line is

$$\log P_{mm} = 9.969 - \frac{2958}{T} .$$

Pressures calculated by use of this equation are listed in Table VII. The calculated boiling point is 144°. The $\Delta H°$ of vaporization is calculated to be 13.5 kcal/mole and the $\Delta S°$ to be 32.4 cal/deg-mole.

Because of the decomposition of P_2Cl_4 and the reaction of P_2Cl_4 with mercury, these values should be treated as only approximate. They do show that the 0° vapor pressure is much less than 1 mm and agree with the pressure of about 1 mm at 25° reported by Sandoval.[18]

C. Decomposition

The decomposition of P_2Cl_4 in vacuo has been reported by several investigators. Besson and Fournier[6] reported P_2Cl_4 decomposes at room temperature to give PCl_3 and a solid of composition P_7Cl_2. Finch reported P_2Cl_4 to decompose at room temperature at a rate which precluded vapor-pressure measurements.[9] Sandoval reported
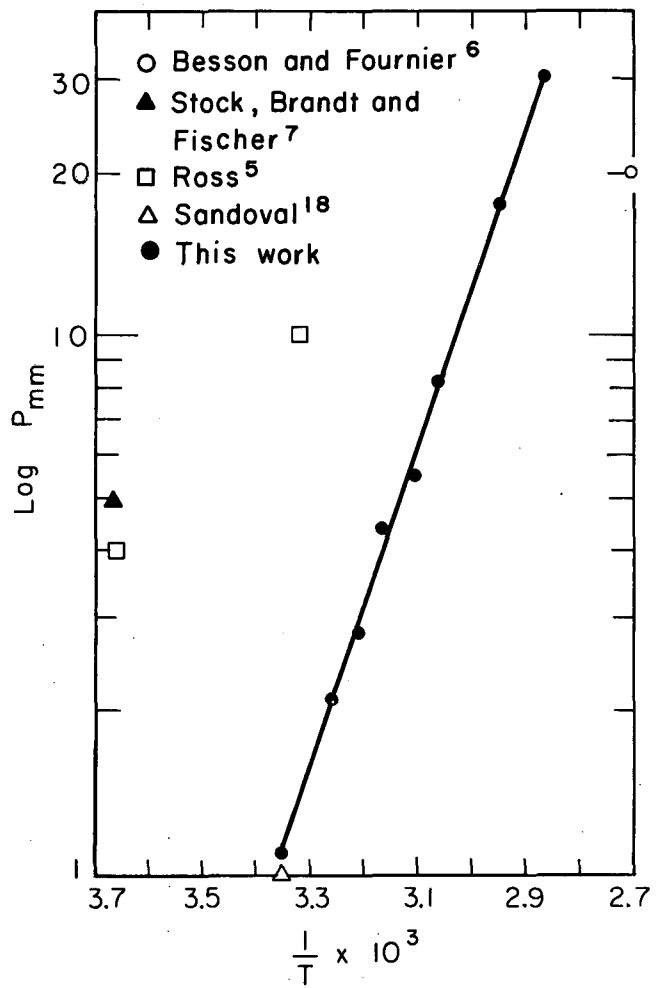
Fig. 4. Vapor pressure of P_2Cl_4.

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P_2Cl_4 decomposed at ambient temperature in darkness to yield PCl_3 and white phosphorus.[18] At higher temperature and in the presence of light, he reported it decomposed to give red phosphorus and PCl_3. He also mentioned that the purity of the sample affected the rate of decomposition; minute amounts of air appear to increase the rate of decomposition.

We have also observed the decomposition of P_2Cl_4. At room temperature, P_2Cl_4 assumed a yellow color in a few days. Later distillation of P_2Cl_4 gave small quantities of PCl_3 and left traces of a nonvolatile yellow solid. Even samples stored at -78° in tubes with stopcocks, acquired a yellow color. This could be due to trace impurities.

Two samples of P_2Cl_4 were distilled into tubes, sealed off, and placed in a 0° bath for long periods of time. One sample of 0.2367 g (1.1614 mmoles) P_2Cl_4 at 0° for 419 days evolved 0.0127 g (0.0925 mmoles) PCl_3 because of decomposition of 0.0186 g (0.0912 mmoles) P_2Cl_4. Another sample of 0.0314 g (0.1541 mmoles) P_2Cl_4 at 0° for 423 days evolved 0.0096 g (0.070 mmoles) PCl_3 because of decomposition of 0.0125 g (0.0614 mmoles) P_2Cl_4. The first sample had decomposition of 7.3% while the second sample had 39.8% decomposition. These two results are certainly not in good agreement. Since the first sample contained about eight times as much P_2Cl_4 making the percent error in the weighings and separations by fractional condensation much less, and since trace impurities seem to speed decomposition, the observation of 7.3% in 419 days is probably more valid. In any case, P_2Cl_4 decomposes only quite slowly at 0°.

D. Thermodynamic Observations

Sandoval has used appearance potentials from mass spectrometric studies to make thermochemical calculations of the heat of formation of P_2Cl_4 and P-P bond energy.[18,21] In these calculations the heats of formation of $PCl_{3(g)}$, $Cl_{(g)}$, $P_{(g)}$ and $P_{2(g)}$ were taken as -73.22, 29.01, 75.18 and 33.82 kcal/mole, respectively. He also assumed the energy of dissociation of PCl_3 to PCl_2 and Cl, $D(PCl_2-Cl)$, to be

equal to the average energy necessary to break a P-Cl bond in PCl_3, $D(PCl_2-Cl) = E(P-Cl) = 78$ kcal/mole. From these studies he calculates $\Delta H_f[P_2Cl_{4(g)}] = -111.5$ and -100.5. The average of -106 kcal/mole was used in his bond-energy calculation. By recalculating his data with $\Delta H^\circ_{298}[PCl_{3(g)}] = -66.6,$[22] making $E(P-Cl) = 76$ kcal, we obtain values of -88 and -99 kcal/mole. He also calculates bond energies for the P-P bond of 52 and 63 kcal/mole. By recalculating these using $E(P-Cl) = 76$, we get 50 and 61 kcal/mole. He also reports $\Delta H_f[P_2Cl_{4(g)}]$ from bond energies $= -96$ kcal. This is equivalent to $\Delta H^\circ = 0$ for the reaction

$$3P_2Cl_{4(g)} \rightarrow 4PCl_{3(g)} + \frac{1}{2}P_{4(g)}.$$
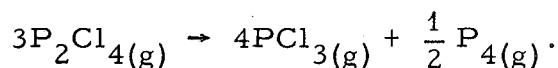
Recalculation gives $\Delta H^\circ_{298}[P_2Cl_{4(g)}] = -88.8$ kcal.

Because of the decomposition of P_2Cl_4 at $0°$, it is probable that the reaction

$$3P_2Cl_{4(\ell)} \rightarrow 4PCl_{3(g)} + \frac{1}{2}P_{4(g)}$$
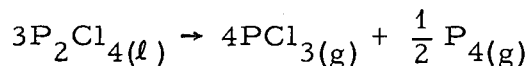
has $\Delta F° \leq 0$. It is not definite only because some $(PCl)_x$ is formed (about which we have no thermodynamic data) instead of PCl_3 and white phosphorus. This would place an upper limit on the stability of P_2Cl_4 of $\Delta H^\circ_{298}[P_2Cl_{4(g)}] = -89$ kcal because the positive $\Delta S°$ of the above reaction is more than compensated for by the positive $\Delta F°$ of vaporization of $P_2Cl_{4(\ell)} \rightarrow P_2Cl_{4(g)}$. Since even the recalculated average of Sandoval's measurements is thermodynamically improbable, any further discussion is unwarranted. This is not unwise in any case because he was looking for P-P bond-energy differences--which could only be a few kilocalories--by using a method in which each measurement was only reproducible to ± 0.2 or 0.3 eV. The best values for a P-P bond are the thermochemical bond energy of 46.8 kcal/mole reported by Gunn[23] for P_2H_4, and of 47.5 calculated by Dainton[24] for P-P in P_4. Estimates[25] of "strain" energy raise the bond energy to 51 to 55 kcal for P-P in P_4. The experiments of Sandoval give no indication that the P-P bond energy in P_2Cl_4 is significantly different from these values.

E. Mass Spectrum

The mass spectrum of P_2Cl_4 was recorded with a Consolidated Model 21-103A mass spectrometer.   The results are shown in Table VIII.   Peaks corresponding to a trace of CCl_4 are omitted. Peaks marked with a question mark are probably attributable to small impurities.   Ions found agree with those reported by Sandoval.[18,11] The parent peaks are found in the ratio predicted from chlorine distribution, and the spectrum contains all expected fragmentation products.

F.   Other Spectra

Sandoval[18,11] reported that the NMR spectrum of P_2Cl_4 exhibits a single absorption peak which appeared at -3770 ± 1 cps from the peak that corresponds to phosphorus in 85% H_3PO_3.   The chemical shift was calculated to be -155 ppm.

We have observed that the spectrum of P_2Cl_4 in the infrared region from 2 to 25 μ consists of a single broad peak centered at about 19.8 μ (505 cm^{-1}).   These spectra were recorded using 8-cm gas cells and NaCl and KBr 137 Infracords (Perkin-Elmer Corporation).   The infrared peak could not be distinguished from PCl_3.

G. Molecular-Weight Determination

Finch[9] reported that molecular-weight determinations of P_2Cl_4 by depression of the vapor tension of CCl_4 give values of 191 and 194 for different samples (calculated for P_2Cl_4, 204).   We obtained values of 215 and 231 for the molecular weight of P_2Cl_4 by depression of the freezing point of benzene.   Actually, the mass spectrum of P_2Cl_4 gives a much better confirmation of P_2Cl_4, as well as a determination of its purity.

H.   Reactions of P_2Cl_4

In addition to the decomposition of P_2Cl_4 in vacuo reported earlier, qualitative observations on the reaction with air have been reported. Besson and Fournier[6] and Finch[9] reported P_2Cl_4 to fume in air. Sandoval[18] reported copious white fumes when air reacted with P_2Cl_4.

Table VIII. Mass spectrum of P_2Cl_4.

m/e	Relative intensities	Ion	m/e	Relative intensities	Ion
31	28.3	P^+	134	1.39	$P_2Cl_2^+$
35	21.8	Cl^+	136	3.63	$P_2Cl_2^+ + PCl_3^+$
36	13.4	HCl^+	138	3.32	PCl_3^+
37	7.31	Cl^+	140	1.51	PCl_3^+
38	4.13	HCl^+	142	1.03	PCl_3^+
62	13.8	P_2^+	144	1.25	?[a]
66	32.2	PCl^+	167	11.5	$P_2Cl_3^+$
68	10.5	PCl^+	169	11.1	$P_2Cl_3^+$
97	8.99	P_2Cl^+	171	3.59	$P_2Cl_3^+$
99	2.15	P_2Cl^+	173	0.40	$P_2Cl_3^+$
101	100.00	PCl_2^+	179	1.12	?
103	64.2	PCl_2^+	183	1.58	?
105	11.8	PCl_2^+	185	1.68	?
107	2.30	?	202	10.3	$P_2Cl_4^+$
109	3.04	?	204	13.3	$P_2Cl_4^+$
111	1.32	?	206	6.41	$P_2Cl_4^+$
124	2.91	P_4^+	208	1.38	$P_2Cl_4^+$
132	2.15	$P_2Cl_2^+$			

[a]Peaks marked ? are probably attributable to small impurities.

We have also observed P_2Cl_4 to fume when exposed to air. Since PCl_3 fumes when exposed to air to form $POCl_3$ (among other products), this same type of oxidation is likely for P_2Cl_4.

Sandoval reports the hydrolysis of P_2Cl_4 at 0° to yield H_3PO_2 and H_3PO_3 as well as yellow solids.[18]

The only other report on P_2Cl_4 concerns its reactions with B_2Cl_4[19,20] which will be discussed in a later section--and with $B_2[N(CH_3)_2]_4$.[20] Garrett[20] reported that a small unmeasured amount of P_2Cl_4 was allowed to react with excess $B_2[N(CH_3)_2]_4$ at 0°. As in the reaction with PCl_3 a white, flocculent precipitate started to form. After two minutes a bright yellow band appeared and the entire reaction mixture turned yellow and then yellow orange. No further work was done on this reaction or characterization of the reaction between PCl_3 and $B_2[N(CH_3)_2]_4$.

We have used the reaction of P_2Cl_4 with Cl_2 to give PCl_5 as one means of identifying P_2Cl_4. We found that 0.2173 g (1.066 mmoles) of P_2Cl_4 reacts with excess chlorine to give 440.3 mg (2.114 mmoles) PCl_5 (calculated for 1.066 mmoles P_2Cl_4, 444.0 mg). Thus, the reaction is quantitative.

V. P_2Cl_4 AS A LEWIS BASE

A. Introduction

Diphosphorus tetrachloride, with a lone pair of electrons on each phosphorus atom, is a potential Lewis base. We have investigated the reactivities of P_2Cl_4 with the compounds $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, BBr_3, BCl_3, BF_3 and B_2H_6 in order to compare the acid-base reactions of P_2Cl_4 with those of PCl_3 and to determine whether P_2Cl_4 can act as either a monofunctional or a difunctional base.

Phosphorus trichloride[26,27] can displace all four molecules of carbon monoxide in nickel carbonyl to give $Ni(PCl_3)_4$. The literature also contains three reports on reactions of $Ni(CO)_4$ with organic diphosphines. Burg and Mahler[28] report the reaction of $P_2(CF_3)_4$ with $Ni(CO)_4$ to yield $P_2(CF_3)_4 \cdot [Ni(CO)_3]_2$. Ross[5] reports the preparation of $P_2(CH_3)_4 \cdot [Ni(CO)_3]_2$ in the presence of an excess of $Ni(CO)_4$ over $P_2(CH_3)_4$, and the preparation of $[P_2(CH_3)_4 \cdot Ni(CO)_2]_x$ with equal amounts of reagents or an excess of $P_2(CH_3)_4$. The preparation of $P_2(C_6H_5)_4 \cdot [Ni(CO)_3]_2$ from $P_2(C_6H_5)_4$ and $Ni(CO)_4$ is reported in a German patent by Schweckendiek.[29] Using $Fe(CO)_5$ and $P_2(C_6H_5)_4$ Schweckendiek[29] reports that $Fe(CO)_5$ and $P_2(C_6H_5)_4$ yield $P_2(C_6H_5)_4 \cdot [Fe(CO)_4]_2$ after several hours at 170° to 180°. Irvine and Wilkinson[26] report no replacement compounds of PCl_3 with molybdenum and chromium hexacarbonyls at temperatures up to 150°.

Holmes[30] has shown that the previous reports of adducts between PCl_3 and BCl_3[31] and BF_3[32] are erroneous and that no complexes actually form. Garrett and Urry[19,20] report that B_2Cl_4 and PCl_3 form the adduct $B_2Cl_4 \cdot 2PCl_3$. Their results and conclusions on the reaction of B_2Cl_4 and P_2Cl_4 will be discussed.

Wiberg and Shuster[33] report the adduct between PCl_3 and BBr_3 to be a white solid with a melting point of 42°. Holmes found that if he allowed the adduct to stand at room temperature, it decomposed to BCl_3 and PBr_3, which do not form an adduct.[30]

B. Experimental

1. Apparatus and Experimental Methods

All transfers were carried out in the absence of air and moisture in a standard glass vacuum apparatus. Stopcocks and ground-glass joints were lubricated with KEL-F 90 grease (3M Company). Reactions were carried out in sealed glass tubes which were opened by means of break seals. Evolved carbon monoxide was transferred by a Toepler pump and measured in a gas buret. Amounts of diborane and BF_3 were determined by PVT measurements. All other reagents were weighed in tubes with stopcocks.

2. Reagents

We prepared diphosphorus tetrachloride by using Sandoval and Moser's discharge method[11] in which white phosphorus reacts with PCl_3. Our yields varied from 0 to 6 g in several runs, but were generally about 2 g in runs of 6 to 10 hr. Diphosphorus tetrachloride was identified by its melting point of $-28°$[34] and its mass spectrum (parent peaks in the ratio expected according to chlorine isotopes and its cracking pattern). The identification was confirmed by molecular-weight determinations (freezing-point depression of benzene) that gave values of 215 and 231 (calculated for P_2Cl_4, 204), and by allowing 217.3 mg P_2Cl_4 (1.066 mmoles) to react with chlorine to yield 440.3 mg PCl_5 (calculated for 1.066 mmoles P_2Cl_4, 444.0 mg PCl_5). Diphosphorus tetrachloride decomposes at room temperature to a yellow solid and PCl_3. At $0°$ it decomposes only very slowly. Two runs were kept at $0°$ for a long period of time. In one sample of 0.2367 g P_2Cl_4 after 419 days, 7.3% (0.0913 mmoles) of the P_2Cl_4 had decomposed giving PCl_3 (0.0925 mmoles) and traces of orange solid. In the other sample of 0.0314 g (0.1541 mmoles) P_2Cl_4 39.8% (0.061 mmoles) of the P_2Cl_4 decomposed giving PCl_3 (0.070 mmoles) and orange solid in 423 days. Thus, at $0°$ P_2Cl_4 decomposes according to the equation

$$P_2Cl_4 \rightarrow PCl_3 + \frac{1}{x}(P_xCl).$$
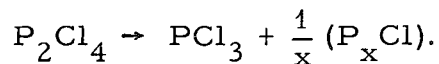
Because of the instability of P_2Cl_4, reactions were carried out at $0°$ or for short periods of time at room temperature.

The vapor pressure of P_2Cl_4 was measured by use of an immersible mercury tensiometer at eight temperatures between 25° and 76°. The vapor pressure may be calculated, with an average deviation of ±2.9%, from the equation

$$\log P_{mm} = 9.969 - \frac{2958}{T} .$$

The data yield an extrapolated boiling point of 144°, a heat of vaporization of 13.5 kcal/mole, and a Trouton constant of 32.4 eu. Because of decomposition of P_2Cl_4, reaction of P_2Cl_4 with the mercury, and the unusually high value calculated for the Trouton constant, these vapor-pressure results should be treated as only approximate. The data disagree markedly with the values of Ross[5] (4 mm at 0° and 10 mm at 28°), Stock, Brandt, and Fischer[7] (5 mm at 0°), and Besson and Fournier[6] (P_2Cl_4 distilled at 180° or 20 mm at 95° to 96°) and agree with Sandoval[18] (about 1 mm at 25°).

Phosphorus trichloride (Mallinckrodt) was purified by fractional condensation through traps at -45°, -78°, and -196°. The -78° fraction had a 0° vapor tension of 36 mm (literature, 35.3 mm). Nickel carbonyl (K and K Laboratories, Jamaica, New York) was passed through -45°, -78°, and -196° traps. The -78° fraction had a 0° vapor tension of 135 mm (literature, 134 mm). Iron carbonyl (K and K) was passed through -22°, -45°, -196° traps. The -45° fraction was retained. Chromium hexacarbonyl (K and K) and molybdenum hexacarbonyl (Climax Molybdenum Company, New York) were used without further purification. Boron trifluoride (Matheson) was purified by passing through a -160° trap into one at -196°. The purified BF_3 was tensiometrically homogeneous and had a CS_2 slush vapor tension of 307 mm (literature, 309 mm). Boron trichloride (Matheson) was passed through -78°, -112°, and -196° traps. The -112° fraction had a 0° vapor tension of 480 mm. Boron tribromide (American Potash and Chemical) was passed through -45°, -78°, and -196° traps. The -78° fraction had a 0° vapor tension of 19 mm (literature, 19 mm). Diborane was

prepared[35] from reaction of potassium borohydride with sulfuric acid and was purified by passage through a -112° trap to a -196° trap. The purified sample had a CS_2 slush vapor tension of 218 mm (literature, 225 mm).

C. Results

1. Reaction of P_2Cl_4 with $Ni(CO)_4$

When P_2Cl_4 is allowed to react with $Ni(CO)_4$ at 0°, carbon monoxide is readily evolved. After a reaction period, usually of several days, the sample was frozen at -196° and the carbon monoxide measured. The sample was then allowed to warm, and unreacted P_2Cl_4 or $Ni(CO)_4$ was removed to determine the ratio of reactants. Table IX. lists a series of reactions using varying ratios of reactants.

With a large excess of $Ni(CO)_4$ (runs 2 to 6), 1 mmole of P_2Cl_4 reacts with 2 mmole of $Ni(CO)_4$ giving 2 mmole of CO and a product of empirical formula $P_2Cl_4 \cdot [Ni(CO)_3]_2$. This material is a yellow solid when in the presence of excess $Ni(CO)_4$ at 0°, and is yellowish white at -63° after the CO and excess $Ni(CO)_4$ are removed. The excess $Ni(CO)_4$ can be slowly removed at -63° leaving a product stable at -63°. When the CO and excess $Ni(CO)_4$ are removed, the compound evolves CO and $Ni(CO)_4$ slowly even at -45° and very rapidly at room temperature. For example in run 3, after removing the unreacted $Ni(CO)_4$ after 3 hr at -45°, it was found that apparently 2.02 mmole of $Ni(CO)_4$ had reacted per millimole P_2Cl_4. After 42 more hours at -45°, further evolution of small amounts of CO and $Ni(CO)_4$ indicated an empirical composition of $P_2Cl_4 \cdot [Ni(CO)_3]_{1.59}$ for the residue. Run 2 [in which the initial removal of unreacted $Ni(CO)_4$ at -45° gave an apparent ratio of 2.00 $Ni(CO)_4$ reacted per P_2Cl_4] was warmed to 0° for 21 hr, thereby evolving small amounts of CO and $Ni(CO)_4$ and yielding a residue of empirical composition $P_2Cl_4 \cdot [Ni(CO)_3]_{1.71}$. The warming of this to room temperature caused it to evolve large amounts of CO and turn black rapidly indicating the presence of large amounts of metallic nickel. Within 4 hr the ratio of constituents had fallen from 5.12 per P_2Cl_4 [corresponding to 1.78 $Ni(CO)_4$ reacted per P_2Cl_4] to 2.43 CO per

Table IX. Initial reactions of P_2Cl_4 with $Ni(CO)_4$.

Run	$\dfrac{Ni(CO)_4 \text{ in}}{P_2Cl_4 \text{ in}}$	$\dfrac{CO \text{ evolved}}{P_2Cl_4 \text{ reacted}}$	$\dfrac{CO \text{ evolved}}{Ni(CO)_4 \text{ reacted}}$	$\dfrac{Ni(CO)_4 \text{ reacted}}{P_2Cl_4 \text{ reacted}}$	Final press (atm)	Rxn time (hr)	Average sum of P_2Cl_4 and $Ni(CO)_x$ units per molecule
1	29.183	2.805	>1.536	—	0.33	3165	—
2	12.475	1.986	0.995	1.996	0.15	21	2.99
3	4.968	1.991	0.987	2.017	0.6	92	2.94
4	4.908	1.885	1.223	1.541	1.35	234	3.87
5	3.685	1.963	1.036	1.895	1.95	16	3.11
6	3.170	1.957	1.196	1.636	0.7	17	3.88
7	1.015	1.865	1.844	1.011	—	619	13.8
8	0.8886	1.833	1.989	0.922	0.96	3953	21.7
9	0.8879	1.775	1.874	0.947	2.06	593	11.3
10	0.4930	1.549	1.956	0.792	1.78	336	7.37
11	0.3859	1.219	1.981	0.615	0.65	456	4.08
12	0.3530	—	2.243	—	0.59	693	—
13	0.2388	0.956	2.044	0.468	1.8	288	2.87
14	0.2140	—	2.098	—	0.77	138	—
15	0.1927	0.698	2.042	0.342	0.32	161	2.08
16	0.1927	—	2.159	—	0.74	353	—
17	0.1777	1.313	2.29	0.573	0.23	569	6.04
18	0.1323	—	3.36	—	0.71	3644	—

P_2Cl_4. Another 20 hr lowered it to 2.00 CO per P_2Cl_4 [corresponding to the empirical formula $P_2Cl_4 \cdot Ni(CO)_2$]. Carbon monoxide continued to be slowly evolved. At the end of 1 week the ratio was 0.60 CO per P_2Cl_4 in the sample. In run 5, qualitative observations were made to determine the effect of CO pressure on decomposition. With 1 atm of CO pressure, no change in color was seen over a 16-hr period at 0°; the edges of the material turned gray in 30 min, at room temperature.

When roughly equal amounts of $Ni(CO)_4$ and P_2Cl_4 are allowed to react (runs 7 to 9), a yellow solid of approximate empirical formula $P_2Cl_4 \cdot Ni(CO)_2$ forms. After standing for long periods of time at 0° or room temperature, this material evolves CO and small amounts of PCl_3.

With a large excess of P_2Cl_4 (runs 10, 11, 13 to 15), 1 mmole of $Ni(CO)_4$ reacts initially with 2 mmole of P_2Cl_4 with evolution of 2 mmole of CO. A brownish yellow solid of approximate composition $Ni(CO)_2(P_2Cl_4)_2$ remains. At sufficiently low CO pressures (runs 12, and 16 to 18), or when the CO is removed, the product can slowly react further with P_2Cl_4. The results of a series of runs where the carbon monoxide was removed with an excess of P_2Cl_4 present are listed in Table X. Carbon monoxide approaching all four molecules per $Ni(CO)_4$ can be replaced with P_2Cl_4 molecules.

In some cases, the initial reactions were stopped before completion. In two runs with a large excess of $Ni(CO)_4$ stopped after 15.5 and 26 min, 1.91 and 1.90 CO/P_2Cl_4 had been evolved. In four runs with 4 to 8 $P_2Cl_4/Ni(CO)_4$ stopped after 14, 31, 928, and 973 min, 0.27, 0.41, 1.33 and 1.39 $CO/Ni(CO)_4$, respectively, had been evolved. Thus, reactions with excess $Ni(CO)_4$ are more rapid than reactions with excess P_2Cl_4.

The rate of reaction of $(P_2Cl_4)_2 \cdot Ni(CO)_2$ with P_2Cl_4, as seen in Table X, is much slower than the initial reactions.

In an attempt to reverse the reaction of P_2Cl_4 with $(P_2Cl_4)_2 \cdot Ni(CO)_2$ higher pressures of CO were used. Three runs each with about 3.6 CO replaced per $Ni(CO)_4$ were exposed to CO pressures of about 2.5 atm. In two of the runs of only a few days duration, very little or no CO was

Table X. Carbon monoxide evolution with $\dfrac{P_2Cl_4}{Ni(CO)_4} > 1$.

$\dfrac{\text{Initial}}{Ni(CO)_4}$ CO evolved	Hours at 0°	$\dfrac{\text{Final}}{Ni(CO)_4}$ CO evolved	$\dfrac{P_2Cl_4 \text{ available}}{Ni(CO)_4}$
0.27	3.5	1.10	6.03
1.036	1100	2.14	1.83[a]
2.089	1900	2.90	2.07
0.405	3100	3.57	3.25
2.098	2900	3.63	4.67
2.243	2700	3.65	2.83
2.159	1000	4.02	5.19

[a]Original sample had excess $Ni(CO)_4$. Excess P_2Cl_4 was added only after initial CO had been removed.

absorbed. In one run with 2.54 atm. CO. pressure with the reaction vessel at 0° for 625 hr, a maximum of 0.3 CO per $Ni(CO)_x$ could have been absorbed. However, this result could be caused by experimental error due to slight leakage or inaccuracies of adding a total of 20 CO samples. A reaction of 0.3 CO per $Ni(CO)_x$ would correspond to reaction of only 3×10^{-4} mmoles CO per hour which was about the rate of evolution of CO of this sample when the reaction was terminated.

2. Reaction of P_2Cl_4 and PCl_3 with $Ni(CO)_4$

To compare the relative Lewis base strengths of PCl_3 and P_2Cl_4, we studied some reactions of PCl_3 with $Ni(CO)_4$, reactions of a mixture of PCl_3 and P_2Cl_4 with $Ni(CO)_4$, and P_2Cl_4 with the product of PCl_3 and $Ni(CO)_4$. Both reported preparations of $Ni(PCl_3)_4$ were done by refluxing excess PCl_3 and $Ni(CO)_4$ at 76°, the boiling point of PCl_3.[26, 27] Our results of the reactions of PCl_3 and $Ni(CO)_4$ at 0° and room temperature are shown in Table XI.

Table XII lists the results of four experiments on mixtures of PCl_3, P_2Cl_4, and $Ni(CO)_4$ at 0°. In each case there were excesses of P_2Cl_4 and PCl_3 with from 2.3 to 7.1 $P_2Cl_4/Ni(CO)_4$ and from 2.6 to 13.5 $PCl_3/Ni(CO)_4$. The first two samples were allowed to react about 200 hr and the last two about 1300 hr. In all cases most of the reaction was due to P_2Cl_4. In two cases, slightly more PCl_3 was recovered than put in apparently due to some decomposition of P_2Cl_4.

In one run, excess P_2Cl_4 was allowed to react with a sample formed by reaction of 0.6826 g (4.970 mmole) PCl_3 and 0.2192 g (1.284 mmole) $Ni(CO)_4$. The solid product containing 3.87 $PCl_3/Ni(CO)_x$ reacted with 0.9278 g (4.553 mmoles) P_2Cl_4 to give 0.6495 g (4.729 mmole) PCl_3 and a product with 3.55 $P_2Cl_4/Ni(CO)_x$.

3. Reaction with Diborane

When B_2H_6 is exposed to P_2Cl_4 at 0° a slow increase in pressure due primarily to evolution of H_2 continues over a long period of time. This experiment was terminated after 17 days of continuous H_2 evolution. Boron trichloride and $BHCl_2$ (identified by their infrared spectra) were also evolved.

Table XI. Reactions of PCl_3 and $Ni(CO)_4$

$\dfrac{Ni(CO)_4}{PCl_3}$	$\dfrac{CO}{Ni(CO)_4}$	$\dfrac{CO}{PCl_3}$	Pressure (atm)	Time (hr)
2.786	—	0.741	2.52	170
2.586	$\geqslant 3.63^a$	2.17	2.56	6600
2.514	$\geqslant 2.82^a$	0.999	1.94	6600
1.906	—	0.710	2.19	170
0.125	2.38	—	2.59	460
0.078	2.38	—	1.91	4700
0.064	0.60	—	0.29	1300^b

[a]We did not include decomposition due to $Ni(CO)_4$ or to the complex during removal of excess $Ni(CO)_4$.

[b]At 0°. All other runs at room temperature.

Table XII. PCl_3 and P_2Cl_4 with $Ni(CO)_4$ at 0°.

$\dfrac{CO\ evolved}{Ni(CO)_4}$	Pressure (atm)	P_2Cl_4 reacted (mmole)	PCl_3 reacted (mmole)	CO evolved (mmole)
2.089	0.64	1.575	$(-0.234)^a$	1.626
1.992	1.22	2.766	0.206	3.197
2.568	0.69	1.092	$(-0.142)^a$	1.361
2.115	0.63	1.824	0.322	1.223

[a]More PCl_3 was recovered than put in reaction vessel.

4. Reaction with Boron Trihalides

No boron trifluoride or boron trichloride is absorbed by P_2Cl_4 at 0° or room temperature. When an excess of BCl_3 is placed in a sealed tube with P_2Cl_4 at 0°, the reactants can be recovered unchanged even after two months.

When boron tribromide is allowed to react with P_2Cl_4 at 0° or room temperature, a reaction occurs producing yellow-orange non-volatile solids, boron trichloride, and, with a sufficient excess of BBr_3, a white volatile solid. Table XIII lists several reactions with ratios of BBr_3 to P_2Cl_4 greater than two, and Table XIV lists several reactions with BBr_3 to P_2Cl_4 ratios less than two. All runs with ratios of BBr_3 to P_2Cl_4 of 1.63 and higher produced the white volatile solid, while all runs of 1.42 and lower produced only products liquid at room temperature.

The white solids produced are $PBCl_xBr_{6-x}$, where x varies from zero to about two. The solids evolve BCl_3 and mixed chloro-bromo-boron trihalides (and presumably mixed chloro-bromo-phosphorus trihalides) until only stable $PBBr_6$ remains which is identical with the adduct of PBr_3 with BBr_3.[30,36] Solids containing some chlorine often melted over a range of several degrees. Some of the solids started melting as low as 41° and others started melting only at 54°. Small amounts of chlorine had depressed the melting points of our samples from the value of 61-62° reported for pure $PBBr_6$.[30,36]

Analysis of the solid was accomplished by precipitation of silver halide, Volhard analyses for total halogen, and treatment of the solid with chlorine with measurement of the bromine and BrCl liberated. In 11 silver nitrate determinations, the ratio of mg AgX to mg sample varied from 2.16 to 2.35 (calculated for $PBBr_6$, 2.161; $PBBr_5Cl$, 2.270; $PBBr_4Cl_2$, 2.400) giving x in $PBCl_xBr_{6-x}$ values of from 0 to 1.67 with nine of the results between 0 and 0.5. Five determinations of mg sample per mmole halogen by the Volhard method, and six determinations of % Br_2 in sample by treatment with chlorine confirmed the values of x in these samples to be in the range 0 to 1.5.

Table XIII. $\dfrac{BBr_3}{P_2Cl_4} > 2.$

$\dfrac{BBr_3}{P_2Cl_4}$	$\dfrac{mg \text{ nonvolatile}}{mmole \text{ } P_2Cl_4}$	$\dfrac{-45° \text{ } mg}{mmole \text{ } P_2Cl_4}$
35.90	94.1	523.5
5.793	157.5	483.0
4.596	95.5	597.8
3.472	85.5	552.0
3.349	69.3	484.4
3.109	118.2	501.2
2.100	95.8	434.5

Table XIV. $\dfrac{BBr_3}{P_2Cl_4} < 2.$

$\dfrac{BBr_3}{P_2Cl_4}$	$\dfrac{mg \text{ nonvolatile}}{mmole \text{ } P_2Cl_4}$	material not trapped at $-78°$ $\dfrac{mg}{mmole \text{ } BBr_3}$
1.6288	103.6	109.2
1.421	70.6	116.7
1.334	80.7	110.1
1.299	96.3	105.6
0.5258	101.2	152.1
0.3838	61.3	167.4

Table XIII lists mg solid per mmole P_2Cl_4 stopped in the $-45°$ trap in fractional condensation of the products of the reaction between P_2Cl_4 and BBr_3. The data are in reasonable agreement with the molecular weights of $PBBr_6$, 521.2, $PBBr_5Cl$, 476.8 and $PBBr_4Cl_2$, 432.3. Tables XIII and XIV list mg nonvolatile orange solid per mmole P_2Cl_4; these data are in quite good agreement with the molecular weights of mixtures of PCl, 66.4, and PBr, 110.9. Since the PBX_6 solids sublime only slowly, it is quite likely that the two high results of 118 and 157 are due to traces of PBX_6 left with the nonvolatile solid. Table XIV lists the mg material per mmole BBr_3 which passes a $-78°$ bath when there is a deficiency of BBr_3. Infrared spectra indicate all materials are BCl_3 with small amounts of other BX_3 present. These data are in agreement with the molecular weight of BCl_3 except for the last two entries. In these runs, the reactants included a very large excess of P_2Cl_4, which yielded large quantities of PCl_3, traces of which could have passed a $-78°$ bath.

The exchange of chlorine and bromine atoms by the phosphorus and boron compounds complicates analysis of the products. With an excess of BBr_3, halogen exchange occurs giving $BBrCl_2$ and BBr_2Cl in an equilibrium mixture. With an excess of P_2Cl_4, halogen exchange again occurs giving mixed chloro-bromo-phosphorus trihalides.

D. Discussion of Results

1. Reaction with $Ni(CO)_4$

Diphosphorus tetrachloride can form a series of compounds with $Ni(CO)_4$ depending upon relative concentration of the reactants and upon the pressure of carbon monoxide. This series includes $P_2Cl_4 \cdot 2Ni(CO)_3$, $[P_2Cl_4 \cdot Ni(CO)_2]_x$, $(P_2Cl_4)_2Ni(CO)_2$ and probably $(P_2Cl_4)_3NiCO$ and $Ni(P_2Cl_4)_4$ as well as intermediate polymeric compounds. We propose in all cases that the lone pair of electrons on a phosphorus atom has replaced a CO molecule on nickel yielding a phosphorus-nickel dative bond. Thus, a P_2Cl_4 molecule can replace either 1 or 2 CO molecules, and 1 to 4 CO molecules on each nickel atom can be replaced by 1 to 4 P atoms. With a large excess of either reagent, one molecule of the deficient reagent reacts with two molecules of the reagent in excess.

The results could be explained by assuming that in all cases a transient intermediate of composition $P_2Cl_4 \cdot Ni(CO)_3$ had formed. In the presence of excess $Ni(CO)_4$, the reaction

$$Ni(CO)_4 + P_2Cl_4 \cdot Ni(CO)_3 \rightarrow (CO)_3Ni \cdot P_2Cl_4 \cdot Ni(CO)_3 + CO$$
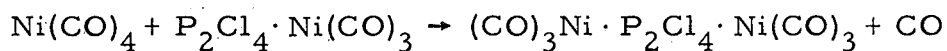
took place. In the presence of excess P_2Cl_4, the reaction

$$P_2Cl_4 + P_2Cl_4 \cdot Ni(CO)_3 \rightarrow P_2Cl_4 \cdot Ni(CO)_2 \cdot P_2Cl_4 + CO$$
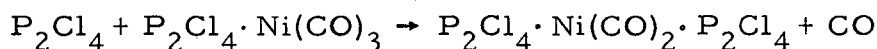
took place. When there was neither a large excess of P_2Cl_4 nor of $Ni(CO)_4$, the concentration of the intermediate was relatively large and some polymerization took place. Probably a complex mixture of products containing species such as $P_2Cl_4 \cdot Ni(CO)_2 \cdot P_2Cl_4 \cdot Ni(CO)_3$, $(CO)_3Ni \cdot P_2Cl_4 \cdot Ni(CO)_2 \cdot P_2Cl_4 \cdot Ni(CO)_3$, etc., were formed. With equal amounts of reagents, the products tend toward the empirical formula $Ni(CO)_2 \cdot P_2Cl_4$. The difference between CO molecules reacted per $Ni(CO)_4$, or per P_2Cl_4, and two can give some indication of the average sum of P_2Cl_4 and $Ni(CO)_x$ groups in each chain if we assume no ring formation occurs. With an unbranched chain we find two terminal groups [either $Ni(CO)_3$ or P_2Cl_4] per chain of alternating P_2Cl_4 and $Ni(CO)_2$ repeating units. Thus, the average sum of P_2Cl_4 and $Ni(CO)_x$ molecules in each chain can be counted by determining the percentage of P_2Cl_4 and $Ni(CO)_x$ groups which are terminal. (Even if the chain were branched, this calculation would hold. Terminal groups caused by branching are not counted and do not need to be considered, since for each such terminal group--which has only evolved or replaced one CO--there is one extra CO displaced per $Ni(CO)_2$ at that branch.)

The average sum of P_2Cl_4 and $Ni(CO)_x$ groups in a chain can be expressed by the equation:

Average sum of P_2Cl_4 and Ni(CO)$_x$ per chain =

$$\frac{2\left[1 + \dfrac{Ni(CO)_4}{P_2Cl_4}\right]}{2 - \dfrac{CO}{P_2Cl_4} + \dfrac{Ni(CO)_4}{P_2Cl_4}\left[2 - \dfrac{CO}{Ni(CO)_4}\right]}.$$

In cases where $Ni(CO)_4$ is equal to P_2Cl_4 this reduces to:

Average sum of P_2Cl_4 and Ni(CO)$_x$ per chain =

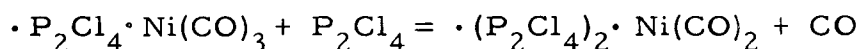$$\frac{2}{2 - \dfrac{CO}{P_2Cl_4 \text{ or } Ni(CO)_4}}.$$

Numbers calculated from this equation are listed in Table VIII. This gives the expected value of three for the products formed with a large excess of either reagent $P_2Cl_4 \cdot 2Ni(CO)_3$ or $Ni(CO)_2(P_2Cl_4)_2$. Higher values indicating polymer formation are found where there is no large excess of either reagent. These values reach a peak when equal amounts of reagents were employed.

We feel that these numbers are only very approximate but do give some indication of the average sum of P_2Cl_4 and Ni(CO)$_x$ groups in each polymer formed. We feel in these cases there was significantly less CO evolved than 2CO per P_2Cl_4 or $Ni(CO)_4$, which would be required by a cyclic or infinite chain system.
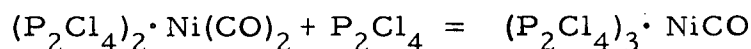
Ross[5] suggested either a trimer or a polymer for the reaction of equal amounts of $P_2(CH_3)_4$ with $Ni(CO)_4$ to give $[P_2(CH_3)_4 \cdot Ni(CO)_2]_x$. With his data on three runs, we calculate average sums of $P_2(CH_3)_4$ and Ni(CO)$_x$ groups in each chain of 10.3, 10.0, and 9.8 molecules.

The use of the intermediate $P_2Cl_4 \cdot Ni(CO)_3$ easily explains the products; it also makes the first step in the reaction identical regardless of which reagent is in excess. Thus, it is difficult to explain how with excess P_2Cl_4 we find at least a few hours required to evolve 1 CO per $Ni(CO)_4$, and, with excess $Ni(CO)_4$, only a few minutes required to evolve 1.9 CO per P_2Cl_4. The intermediate is a good device to explain the products, but the reactions are probably more complex.
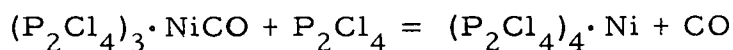
If the CO pressure in the original reaction vessel is much less than 1 atm, further reaction occurs in some cases. With a large excess of $Ni(CO)_4$, no further reaction with P_2Cl_4 can occur because both phosphorus atoms are coordinated. Thus, decomposition of $Ni(CO)_4$ or the product occurs, as was observed in run 1 where a metallic nickel coating was observed 20 hr after the reaction started. More CO than could have been replaced by P atoms was also found. In run 2 with a CO pressure of 0.15 atoms, some black nickel coating was also observed. With a large excess of P_2Cl_4 and low CO pressure, a slow reaction causing replacement of more than 2 molecules of CO per $Ni(CO)_4$ occurs. The results of several of the runs, listed in Tables IX and XII, in which there was an excess of P_2Cl_4, are plotted in Fig. 5. In five of the runs where pressures were higher than 0.95 atm, the reaction was terminated at 2.0 $CO/Ni(CO)_4$. However, in other runs, slow reaction continued until the pressure built up to 0.59 to 0.77 atm or the runs were terminated. These results are in agreement with the following equilibria:

$$\cdot P_2Cl_4 \cdot Ni(CO)_3 + P_2Cl_4 = \cdot (P_2Cl_4)_2 \cdot Ni(CO)_2 + CO$$

$$K_{eq} \approx P_{CO} \geqslant 2 \text{ atm}$$

$$(P_2Cl_4)_2 \cdot Ni(CO)_2 + P_2Cl_4 = (P_2Cl_4)_3 \cdot NiCO$$

$$K_{eq} \approx P_{CO} \approx 0.7 \text{ atm}$$

$$(P_2Cl_4)_3 \cdot NiCO + P_2Cl_4 = (P_2Cl_4)_4 \cdot Ni + CO$$

$$K_{eq} \approx P_{CO} \geqslant 0.7 \text{ atm}.$$

In these equilibria $\cdot$ stands for a possible bond or bonds to other nickel atoms.

The reactions of compounds with two or more $P_2Cl_4/Ni(CO)_4$ with P_2Cl_4 are slow. The results are only approximate but do show a definite pressure dependence. The three experiments attempting to reach these apparent equilibria by the reaction of the products with excess CO were unsuccessful due to the slowness of the reaction or the failure to react.
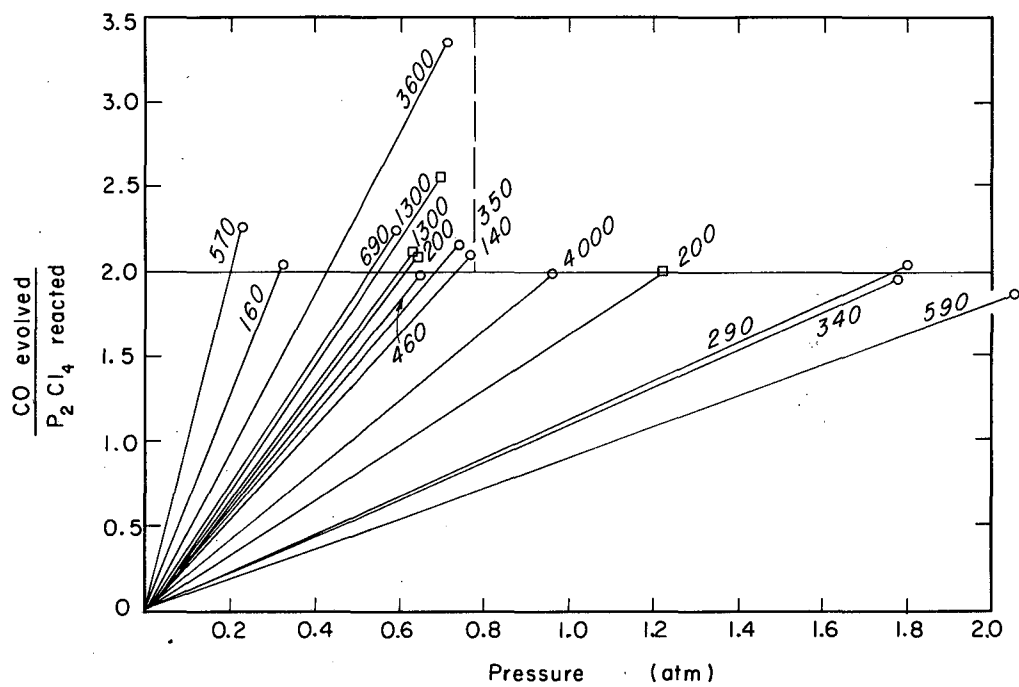
Fig. 5. Reactions of $Ni(CO)_4$ with excess P_2Cl_4.

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2. $Ni(CO)_4 - PCl_3 - P_2Cl_4$ Reactions

In the runs with both PCl_3 and P_2Cl_4 with $Ni(CO)_4$, P_2Cl_4 is shown to be the better Lewis base. In the four runs in which both reagents were mixed with $Ni(CO)_4$, shown in Table XII, most of the reaction was due to P_2Cl_4. In the run where the $Ni(PCl_3)_4$ product was allowed to react with P_2Cl_4, the P_2Cl_4 replaced the PCl_3. At $0°$, excess PCl_3 replaced only 0.6 CO per $Ni(CO)_4$ in 1300 hr, again indicating P_2Cl_4 is a better Lewis base than PCl_3. Comparison of the room temperature reaction of PCl_3 with $0°$ reactions of P_2Cl_4 is difficult because of differences caused both by the temperature and by the high CO pressures built up in the $PCl_3 - Ni(CO)_4$ cases.

The stronger Lewis base strength of P_2Cl_4 relative to PCl_3 is predictable from consideration of an inductive argument. Phosphorus trichloride has three electron-withdrawing chlorine atoms per phosphorus, while P_2Cl_4 has only two chlorine atoms per phosphorus. Thus, the lone pair on each phosphorus atom would be more available for dative bonding in P_2Cl_4 than in PCl_3.

3. Other Carbonyls

With $Mo(CO)_6$, $Cr(CO)_4$, or $Fe(CO)_3$ at $0°$, we find P_2Cl_4 reacts only extremely slowly or not at all. This is not surprising because of the negative results with PCl_3 and $Mo(CO)_6$ and $Cr(CO)_4$ at temperatures up to $150°$, and because of the temperature of $170°$ to $180°$ required for reaction of $Fe(CO)_5$ with $P_2(C_6H_5)_4$. Such high temperatures would rapidly decompose P_2Cl_4.

4. Reaction with B_2Cl_4

Garrett and Urry[19, 20] report a qualitative experiment where an unmeasured sample of P_2Cl_4 containing PCl_3 was mixed with B_2Cl_4 at $-23°$, which immediately precipitated $B_2Cl_4 \cdot 2PCl_3$. After 0.5 hr, both B_2Cl_4 and P_2Cl_4 were recovered. In a further reaction period of 24 hr at $0°$, some orange solids formed. Unreacted B_2Cl_4 and P_2Cl_4 were recovered along with $B_2Cl_4 \cdot 2PCl_3$. Garrett and Urry concluded that no complex is formed with P_2Cl_4.

We feel that their result indicates that B_2Cl_4 does react with P_2Cl_4 and causes rupture of the P-P bond. In view of the stability of P_2Cl_4 at 0° (only 7.3% and 29.8% decomposition in 14 months) and the failure of P_2Cl_4 to react with BCl_3 in a 2-month period at 0°, it seems unlikely that the apparent rupture of the P-P bond could be due to decomposition of P_2Cl_4. Thus, P_2Cl_4 seems to react with B_2Cl_4 to form an unstable complex that decomposes with rupture of the P-P bond according to the overall equation:

$$2P_2Cl_4 + B_2Cl_4 \rightarrow B_2Cl_4 \cdot 2PCl_3 + \frac{2}{x}(P_xCl) .$$
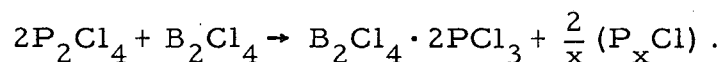
If P_2Cl_4 is a stronger Lewis base than PCl_3, as predicted by an inductive effect and as demonstrated with $Ni(CO)_4$, we would expect it to react with B_2Cl_4 in the absence of a steric effect. The possible failure of P_2Cl_4 to react in 0.5 hr with B_2Cl_4 at -23° is reasonable because P_2Cl_4 reacts only very slowly with BBr_3 at -23°. Obviously, quantitative experiments need to be made to study the reaction of B_2Cl_4 with P_2Cl_4.
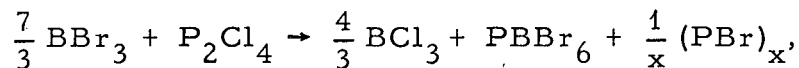
5. Reaction with Diborane

Evidently P_2Cl_4 reacts with B_2H_6 causing slow decomposition and rupture of the P-P bond rather than any recognizable complex formation.

6. Reaction with Boron Trihalides

Boron trifluoride and boron trichloride are not strong enough Lewis acids to form adducts or react with P_2Cl_4. With boron tri-bromide, rupture of the P-P bond in P_2Cl_4 occurs. This could be due to halogen exchange causing decomposition without adduct formation, to formation of an adduct which gives a mechanism for halogen exchange and decomposition, to formation of an unstable adduct which decomposes followed by halogen exchange, or to rupture due to both unstable adduct formation and halogen exchange.

Possible overall reaction limits are with a large excess of BBr_3:

$$\frac{7}{3} BBr_3 + P_2Cl_4 \rightarrow \frac{4}{3} BCl_3 + PBBr_6 + \frac{1}{x} (PBr)_x,$$

and with a large excess of P_2Cl_4

$$BBr_3 + 3P_2Cl_4 \rightarrow BCl_3 + 3PCl_3Br + \frac{3}{x} (PCl)_x.$$
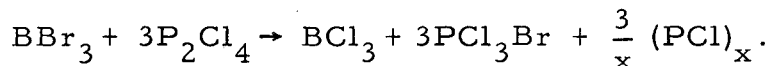
Excesses of BBr_3 over P_2Cl_4 greater than 7:3 result in mixed boron chloro-bromo-trihalides. With ratios of BBr_3 to P_2Cl_4 of greater than 4:3, some white PBX_6 solid would be expected. With less than 4:3 all chlorine could go into BCl_3 which forms no adduct with PBr_3 or PCl_3. In all runs with 1.63 or greater BBr_3 per P_2Cl_4, white solids were observed. In all runs with 1.33 or less BBr_3 per P_2Cl_4, no solids were observed. In the run with 1.42 BBr_3 per P_2Cl_4, no solid was observed, probably because any traces of solid present were dissolved in the excess liquids. These results are in agreement with all possible chlorine forming B-Cl bonds, while the bromine is incorporated in P-Br bonds.

Experiments carried out with PBr_3 and P_2Cl_4, and HBr and P_2Cl_4, as well as a discharge reaction with PBr_3 and white phosphorus, failed to produce any P_2Br_4. Phosphorus tribromide reacting with P_2Cl_4 gave PCl_3 and orange solids. Hydrogen bromide reacting with P_2Cl_4 yielded HCl and orange solids. In both of these cases, halogen exchange and decomposition occurred with little probability of adduct formation.

In Garrett and Urry's experiment with B_2Cl_4, decomposition occurred with possible adduct formation and no possibility of halogen exchange. We were unable to study another interesting experiment in which halogen exchange would be impossible--P_2Br_4 and BBr_3--because of our inability to prepare P_2Br_4. Thus, in the reaction of P_2Cl_4 with BBr_3, which caused the rupture of the P-P bond, there exists the possibility of rupture due to either unstable adduct formation or halogen exchange or both.

The fact that BCl_3 and BF_3 do not form an adduct or react with P_2Cl_4, whereas BBr_3 and B_2Cl_4 do react, is in agreement with the known Lewis acid trends $BF_3 < BCl_3 < BBr_3$ and $BCl_3 < B_2Cl_4$.

VI. P_2Cl_4 AS A LEWIS ACID

Because of the vacant low-energy d-orbitals on phosphorus, P_2Cl_4 is a potential Lewis acid. Holmes[37] has reported that the reaction of phosphorus trichloride with the donor molecule trimethylamine gives a solid $Cl_3P \cdot N(CH_3)_3$. Burg[38] has reported that the addition of $P_2(CF_3)_4$ to ethylene at room temperature gives the product $(CF_3)_2PCH_2CH_2P(CF_3)_2$. Burg and Street[39] have very recently reported that this bis-phosphine reacts with nickel carbonyl to form a volatile heterocyclonickel dicarbonyl.

Burg[38] has also reported that the reaction of C_2H_4 with $P_2(CH_3)_4$ at 200° to 300° gives $(CH_3)_2PCH_2CH_2P(CH_3)_2$.

We have studied the reactivity of P_2Cl_4 with C_2H_4, C_2H_2, C_3F_6, and $N(CH_3)_3$ to see if P_2Cl_4 undergoes reaction as a Lewis acid with these compounds.

Ethylene was purified by passage through a -160° trap into one at -196°. The -196° fraction had a CS_2 slush vapor tension of 455 mm (literature, 453 mm). Ethylene at about 0.5 atm was exposed to P_2Cl_4. No ethylene was absorbed by P_2Cl_4 at temperatures of -78°, -45°, 0° and room temperature.

Acetylene was purified by passage through cold traps of -112°, -160° and -196°. The -196° fraction had a CS_2 slush vapor tension of 66.5 mm (literature, 67 mm). Acetylene at about 0.5 atm was exposed to P_2Cl_4. No acetylene was absorbed by P_2Cl_4 at 0° or room temperature, and the acetylene was quantitatively recovered after the experiments.

Perfluoropropylene, C_3F_6, (Peninsular Chemresearch, Gainesville, Florida) was used without further purification. In a sealed-tube reaction of 21 days at 0°, no reaction was observed, and the reactants were recovered unchanged except for traces of P_2Cl_4 which had decomposed.

Trimethylamine, generated by thermal decomposition of the hydrochloride, was purified by passage through baths of -95°, -112°, and -196°. The -112° fraction had a 0° vapor tension of 679 mm (literature, 680 mm).

Trimethylamine reacts with P_2Cl_4 at $0°$ or $-78°$ in sealed tubes to produce orange solids. Separation of the products by frantional condensation with traps of $-78°$ and $-196°$ gives the results listed in Table XV. In the absence of a thorough study of the reaction, we tentatively suggest the main reaction to be

$$P_2Cl_4 + \frac{4}{3} N(CH_3)_3 \rightarrow \frac{4}{3} PCl_3 \cdot N(CH_3)_3 + \frac{2}{3} P .$$
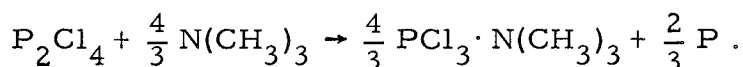
In all cases, unreacted $N(CH_3)_3$ was recovered in the $-196°$ trap. The infrared spectrum of the material in the $-78°$ trap was identical with $N(CH_3)_3$ although $N(CH_3)_3$ easily passes a $-78°$ trap. The spectrum also showed absorption in the P-Cl region. Therefore, it is likely that the material in the $-78°$ trap was $PCl_3 \cdot N(CH_3)_3$. Table XV lists mmoles $N(CH_3)_3$ reacted per mmole P_2Cl_4. In three runs this ratio was approximately 4:3. In one of the other cases, agreement would not be expected due to a deficiency of $N(CH_3)_3$ in the reaction vessel. In the other case, a large quantity of PCl_3 complicated separation. The molecular weight of 196.4 calculated for $PCl_3 \cdot N(CH_3)_3$ is in fairly good agreement with the results calculated by dividing the weight (in mg) of material which does not pass a $-78°$ trap by either 4/3 times mmoles P_2Cl_4 or by mmoles of $N(CH_3)_3$ reacted. Again the results of the run with added PCl_3 were not meaningful. In all cases the $-78°$ trap held less than the expected amount of $PCl_3 \cdot N(CH_3)_3$ according to the above equation. The listing of mg nonvolatile solid per 2/3 mmole P_2Cl_4 is consistently higher than predicted by the above equation. These two facts suggest that the reaction either leaves some chlorine in the nonvolatile phosphorus solid, or some other nonvolatile decomposition products are present in small amounts.

More work needs to be done to confirm the exact course of the reaction between P_2Cl_4 and $N(CH_3)_3$, but the reaction does definitely involve rupture of the P-P bond in P_2Cl_4 and production of the adduct $PCl_3 \cdot N(CH_3)_3$ at temperatures as low as $-78°$.

Table XV. P_2Cl_4 and $N(CH_3)_3$.

$\dfrac{N(CH_3)_3 \text{ in}}{P_2Cl_4 \text{ in}}$	$\dfrac{N(CH_3)_3 \text{ reacted}}{P_2Cl_4}$	$\dfrac{\text{mg nonvolatile}}{\frac{2}{3}\text{ mmole } P_2Cl_4}$	$\dfrac{\text{mg } -78°}{\frac{4}{3}\text{ mmole } P_2Cl_4}$	$\dfrac{\text{mg } -78°}{\text{mmole } N(CH_3)_3 \text{ reacted}}$
2.964	1.369	69.1	179	174
2.497	1.417	60.6	185	175
1.611	1.312	42.1	190	193
1.462	0.839	63.3	158	252[a]
1.155	1.125	83.4	—	179

[a]Reaction carried out in large excess of PCl_3.

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APPENDICES

A. Complete List of All P_2Cl_4 - $Ni(CO)_4$ Reactions

Run	Initial $\dfrac{Ni(CO)_4}{P_2Cl_4}$	$\dfrac{CO \text{ evolved}}{P_2Cl_4 \text{ reacted}}$	$\dfrac{CO \text{ evolved}}{Ni(CO)_4 \text{ reacted}}$	$\dfrac{Ni(CO)_4 \text{ reacted}}{P_2Cl_4 \text{ reacted}}$	Pressure (atm)	Hours at 0°	Average sum of $P_2Cl_4 + Ni(CO)_4$ per molecule	Listed in Table
8/16 #2	29.183	2.805	>1.536	—	0.33	3165	—	IX
11/29 #3	22.967	1.917	—	—	—	768	—	—
6/20 #2	.15.62	1.906	—	—	—	0.25	—	Text
11/29 #2	14.962	1.980	—	—	1.19	768	—	—
5/13 #3	12.475	1.986	0.995	1.996	0.15	21	2.99	IX
6/3 #1	9.156	1.896	—	—	—	0.43	—	Text
11/29 #1	7.097	1.945	—	—	—	1488	—	—
5/13 #4	4.968	1.991	0.987	2.017	0.6	92	2.94	IX
8/16 #1	4.908	1.885	1.223	1.541	1.35	234	3.87	IX
10/18 #2	4.636	1.89	—	—	2.06	168	—	—
10/18 #1	3.797	2.020	—	—	3.37	27	—	—
7/3 #1	3.685	1.963	1.036	1.895	1.95	16	3.11	IX
5/13 #1	3.170	1.957	1.196	1.636	—	17	3.88	IX
1/25 #1	2.617	1.800	—	—	2.45	1224	—	—
1/25 #2	1.015	1.865	1.844	1.011	—	619	13.8	IX
3/21 #1	0.8886	1.833	1.989	0.922	0.96	3953	21.7	IX
1/25 #3	0.8879	1.775	1.874	0.947	2.06	593	11.3	IX
2/26 #1	0.4930	1.549	1.956	0.792	1.78	336	7.37	IX
9/24 #2	0.4252	1.156	1.992	0.580	1.22	183	3.39	XII *
11/29 #4	0.3859	1.219	1.981	0.615	0.65	456	4.08	IX
7/17 #3	0.3530	—	2.243	—		693	—	IX
10/29 #3	0.3004	0.671	2.115	0.317	0.63	1341	2.01	XII *
5/22 #2	0.2684	—	1.393	—	0.15	16	—	Text
10/29 #2	0.2629	1.245	2.568	0.485	0.69	1315	4.24	XII *
2/26 #2	0.2388	0.956	2.044	0.468	1.8	288	2.87	IX
7/23 #1	0.2140	—	2.098	—	0.77	138	—	IX
7/1 #1	0.2092	—	0.405	—	0.069	0.50	—	Text
5/13 #5	0.1927	0.698	2.042	0.342	0.32	161	2.08	IX
7/3 #2	0.1927	—	2.159	—	0.74	353	—	IX
5/22 #1	0.1777	1.313	2.29	0.573	0.23	569	6.04	IX
6/20 #1	0.1658	—	0.270	—	—	0.25	—	Text
9/24 #1	0.1408	1.156	2.089	0.553	0.64	212	2.75	XII *
7/17 #2	0.1323	—	3.36	—	0.71	3644	—	IX
5/22 #3	0.1316	—	1.331	—	—	15	—	Text

* PCl_3 - P_2Cl_4 - $Ni(CO)_4$ runs

B. Attempts to Prepare Xenon Compounds

The interest of chemists and particularly synthetic inorganic chemists was greatly stimulated by the discovery of the first compounds of xenon. [40,41,42] With our experimental apparatus and interest in electric discharges, it was natural for us to attempt to prepare compounds of xenon. The subsequent discovery of XeO_3 by Templeton, Zalkin, Forrester, and Williamson[43] again stimulated our investigations after our initial unsuccessful experiments with xenon and oxygen, and we attempted to prepare xenon compounds by using oxygen, chlorine, and hexafluoroacetone.

1. Xenon-Oxygen Experiments

We conducted xenon-oxygen experiments by using both microwave and ozonizer-type discharges, as well as a combined experiment in which we used both an ozonizer-type discharge and ultraviolet light.

Xenon (Airco) was obtained in a bulb with a break seal and was purified by allowing it to pass a -160° trap into a -196° trap. Oxygen was obtained from the thermal decomposition of potassium permanganate.

In the experiments using the microwave discharge, both xenon and oxygen were passed through the discharge at a total pressure of 0.5 to 1.5 mm with oxygen in large excess. [44] The gas emerging from the discharge was passed through a -112° and two -196° baths. No materials were observed in the discharge zone, in the -112° trap, or in subsequent fractionation of the -196° trap materials in a -160° trap in the four runs made.

In an attempt to cause the xenon to react with higher energy species of oxygen, such as ozone, we set up a static ozonizer discharge. We constructed a quartz ozonizer tube having a gap of 6 mm with a total volume--including a storage area-- of 340 mm. By using only oxygen at 602-mm Hg, we converted 23.7% of the oxygen to ozone, proving the existence of quantities of O_3, as well as O_2 and other excited short-lived species, in our experimental setup. Two runs were made at a temperature of -78° by using the ozonizer and a 4-W germicidal lamp.   In

addition, four runs were made using the ozonizer and a 450-W Hanovia 679A ultraviolet lamp. Three of these runs were at -78° and one was at room temperature open to a cold zone at -78°. Runs were made using both forms of excitation simultaneously and by alternation of the uv source and the ozonizer. In all cases, no xenon was reacted and no products were obtained other than ozone. At no time did we have a suggestion of any product resembling XeO_3.

2. Xenon-Chlorine Experiments

Because of the relatively high electronegativity of chlorine, we attempted to react it with xenon. Two attempts were made. In one we used the ozonizer-type discharge with the Hanovia 679A lamp, and in the other we used the microwave apparatus. In the ozonizer experiment with the reaction vessel at -78°, the ultraviolet source was on about 1 hr and the ozonizer-type discharge was on 20 hr. After this time, both the chlorine and the xenon were recovered quantitatively. In the microwave experiment, the mixed gasses were repeatedly allowed to pass from one trap through the discharge zone to the other trap for a total of 5 hr. No new materials were observed and the reactants were recovered quantitatively.

3. Xenon-Hexafluoroacetone Experiments

Hexafluoroacetone decomposes photolytically[45,46] in the presence of ultraviolet light. The initial step produces CF_3 radicals, and the only products are C_2F_6 and CO. We attempted to initiate a reaction between these CF_3 radicals and Xenon in the ozonizer-type discharge. A series of three runs were made including both room temperature and -78° runs. In each case the ozonizer discharge and ultraviolet source were on for several hours. Each run produced carbon monoxide and small amounts of solids which condensed in a -112° trap. The mass spectral-cracking pattern of each sample was observed. In each case positive ions of many compounds of carbon, fluorine, and oxygen to masses of 285 to 300 were observed, but no xenon was present in the samples.

Thus, in all the cases we studied, we were unsuccessful in making compounds between xenon and either oxygen, chlorine, or triflouromethyl radicals by electrical-discharge techniques. Of course, these experiments in no way prove that the compounds cannot be formed. For example, XeO_3 has been made only by hydrolysis of xenon tetrafluoride. Our studies were not exhaustive; however, since no positive indication of reactions were obtained, the studies were terminated.

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