CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AND THE INORGANIC MATERIALS RESEARCH DIVISION OF THE LAWRENCE RADIATION LABORATORY, BERKELEY, CALIFORNIA

The Reactions of Diphosphorus Tetrachloride with Nickel Carbonyl and Boron Tribromide

BY CHARLES B. LINDAHL[1] AND WILLIAM L. JOLLY

Received May 28, 1964

Diphosphorus tetrachloride displaces carbon monoxide from nickel carbonyl at 0°. With large excesses of P_2Cl_4, the P_2Cl_4 reacts as a monofunctional base to form $Ni(CO)_2(P_2Cl_4)_2$ and probably $Ni(CO)(P_2Cl_4)_3$ and $Ni(P_2Cl_4)_4$. With large excesses of nickel carbonyl, the P_2Cl_4 reacts as a difunctional base to form $(CO)_3NiP_2Cl_4Ni(CO)_3$. With intermediate ratios of P_2Cl_4 to $Ni(CO)_4$, polymeric compounds containing both mono- and difunctional P_2Cl_4 groups are formed. In reactions with nickel carbonyl, P_2Cl_4 is a stronger base than PCl_3. Diphosphorus tetrachloride decomposes in the presence of boron tribromide at 0° to form a phosphorus trihalide and a phosphorus subhalide, $(PX)_x$. Halogen exchange occurs as completely as possible; with a sufficient excess of BBr_3, the adduct $PBr_3 \cdot BBr_3$ forms.

Introduction

The purpose of this investigation was to study some reactions in which diphosphorus tetrachloride acts as a base. The reactions with nickel carbonyl and boron tribromide were chosen for study because of possible analogies to the reactions of these molecules with phosphorus trichloride[2-5] and to the reactions of nickel carbonyl with tetrasubstituted diphosphines.[6-9]

Experimental[10]

Apparatus and Experimental Methods.—Sealed glass tubes with break-seals were used as reaction vessels, and a standard glass vacuum apparatus lubricated with KEL-F 90 grease (3M Company) was used for the transfer of reagents. Evolved CO was transferred with a Toepler pump and measured in a gas buret.

P_2Cl_4.—We prepared diphosphorus tetrachloride by using Sandoval and Moser's discharge method[11] in which white phosphorus reacts with PCl_3. Our yield varied, but was generally about 2 g. in runs of 6–10 hr. Diphosphorus tetrachloride was identified by its melting point of −28°[12] and its mass spectrum. The identification was confirmed by molecular weight determinations (freezing point depression of benzene solutions) that gave values of 215 and 231 (calculated for P_2Cl_4, 204), and by allowing 217.3 mg. of P_2Cl_4 to react with chlorine to yield 440.3 mg. of PCl_5 (calculated, 444.0 mg.). Diphosphorus tetrachloride decomposes at room temperature to a yellow solid and PCl_3. At 0° it decomposes only very slowly. Two samples were kept at 0° for 420 days. In one sample of P_2Cl_4 (0.2367 g.), 7.3% (0.0913 mmole) of the P_2Cl_4 decomposed, giving PCl_3 (0.0925 mmole) and traces of orange solid. In the other sample of P_2Cl_4 (0.0314 g.), 40.0% (0.061 mmole) of the P_2Cl_4 decomposed, giving PCl_3 (0.070 mmole) and orange solid. Thus, at 0° P_2Cl_4 decomposes according to the equation

$$P_2Cl_4 \longrightarrow PCl_3 + (1/x)(PCl)_x$$

Because of this 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 using 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 $\log P_{\text{mm}} = 9.969 - 2958/T$. 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 e.u. 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 considered as only approximate. The data disagree markedly with the values of Ross[7] (4 mm. at 0° and 10 mm. at 28°), Stock, Brandt, and Fischer[14] (5 mm. at 0°), and Besson and Fournier[13] (P_2Cl_4 distilled at 180° or 20 mm. at 95–96°) and agree with Sandoval[15] (about 1 mm. at 25°).

Results

Reaction of P_2Cl_4 with $Ni(CO)_4$.—When P_2Cl_4 was allowed to react with $Ni(CO)_4$ at 0°, carbon monoxide was evolved. After a reaction period, usually of several days, the sample was frozen at −196°, and the carbon monoxide was measured. The sample was then allowed to warm, and unreacted P_2Cl_4 or $Ni(CO)_4$ was removed and measured to determine the reacting ratio. Table I lists the data for representative runs involving various initial ratios of reactants.[10]

With large excesses of $Ni(CO)_4$ (run 1), 2 mmoles of $Ni(CO)_4$ reacted with every mmole of P_2Cl_4, giving 2 mmoles of CO and a yellow solid product having a composition close to $P_2Cl_4[Ni(CO)_3]_2$. After the CO and excess $Ni(CO)_4$ had been removed, the compound was stable at −63° but evolved CO and $Ni(CO)_4$ slowly even at −45° and very rapidly at room temperature. The samples turned black during this gas evolution, suggesting the formation of metallic nickel or possibly nickel phosphides. In run 1 (in which the initial unreacted $Ni(CO)_4$, removed at −45°, indicated an empirical formula $P_2Cl_4Ni_{2.00}(CO)_{6.01}$) the sample

---

[1] Taken from a thesis presented by C. B. Lindahl for partial satisfaction of the requirements of the Ph.D. degree, University of California, Berkeley, 1964.

[2] J. W. Irvine, Jr., and G. Wilkinson, *Science*, **113**, 742 (1951).

[3] W. C. Smith, *Inorg. Syn.*, **6**, 201 (1960).

[4] E. Wiberg and K. Shuster, *Z. anorg. allgem. Chem.*, **213**, 94 (1933).

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

[6] A. B. Burg and W. Mahler, *J. Am. Chem. Soc.*, **80**, 2334 (1958).

[7] L. A. Ross, Ph.D. Thesis, Indiana University, 1962.

[8] R. G. Hayter, *Inorg. Chem.*, **3**, 711 (1964).

[9] W. Schweckendiek, German Patent 1,072,244 (Dec. 31, 1959); *Chem. Abstr.*, **55**, P12,355*g* (1961).

[10] For complete experimental details, the reader is referred to University of California Radiation Laboratory Report UCRL-11189, "Chemistry of Diphosphorus Tetrachloride," Jan., 1964.

[11] A. A. Sandoval and H. C. Moser, *Inorg. Chem.*, **2**, 27 (1963).

[12] Besson and Fournier[13] originally reported −28°, which was confirmed by Stock, Brandt, and Fischer,[14] Ross,[7] and Sandoval.[15] Finch[16] reported −34 to −35°.

[13] A. Besson and L. Fournier, *Compt. rend.*, **150**, 102 (1910).

[14] A. Stock, A. Brandt, and H. Fischer, *Ber.*, **58**, 643 (1925).

[15] A. A. Sandoval, Ph.D. Thesis, Kansas State University, 1963; see also *Dissertation Abstr.*, **24**, 1422 (1963).

[16] A. Finch, *Can. J. Chem.*, **37**, 1793 (1959).

TABLE I

REACTIONS OF P_2Cl_4 WITH $Ni(CO)_4$

Run	Initial ratio $\frac{\text{mmoles } Ni(CO)_4}{\text{mmoles } P_2Cl_4}$	$\frac{\text{CO evolved,}}{P_2Cl_4 \text{ reacted}}$ mmoles	$\frac{\text{CO evolved,}}{Ni(CO)_4 \text{ reacted}}$ mmoles	Final press., atm.	Run time, hr.
1	12.5	1.99	0.995	0.15	21
2	1.02	1.86	1.84	...	619
3	0.89	1.83	1.99	0.96	3953
4	0.24	0.96	2.04	1.8	288
5	0.13	...	3.36	0.71	3644

was warmed to 0° for 21 hr., yielding a residue with a ratio $CO:P_2Cl_4 = 5.12$. Four hours after warming this material to room temperature, the $CO:P_2Cl_4$ ratio had fallen to 2.43; another 20 hr. at room temperature lowered the ratio to 2.00, and at the end of 1 week the ratio was 0.60. In another run with 1 atm. of CO pressure, there was no change in color in 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 were allowed to react (runs 2 and 3), a yellow solid of approximate empirical formula $P_2Cl_4 \cdot Ni(CO)_2$ formed. After standing for long periods of time at 0° or room temperature, this material evolved CO and small amounts of PCl_3.

With large excesses of P_2Cl_4 (runs 4 and 5), each mmole of $Ni(CO)_4$ reacted initially with 2 mmoles of P_2Cl_4 to form a brownish yellow solid of approximate composition $Ni(CO)_2(P_2Cl_4)_2$. When long reaction times were provided, and when the CO pressures were sufficiently low, the product continued to react slowly with P_2Cl_4. After removal of the initial evolved CO in three other runs, the reaction products were exposed to excess P_2Cl_4 for an additional 6 to 17 weeks. The final ratios of the total CO evolved per $Ni(CO)_4$ were 3.63, 3.65, and 4.02. Apparently all four molecules of CO can be displaced from $Ni(CO)_4$.

Three attempts were made to reverse the reaction of P_2Cl_4 with $Ni(CO)_2(P_2Cl_4)_2$ by the application of CO pressures of up to 2.5 atm. for several days. The experimental errors in determining the CO absorbed were so great, however, that we can only say that, in these samples with about 3.6 CO replaced per $Ni(CO)_4$, less than 0.3 mmole of CO was absorbed per mmole of Ni.

Reactions of P_2Cl_4 and PCl_3 with $Ni(CO)_4$.—Table II lists the results of our experiments at 0° on mixtures of PCl_3, P_2Cl_4, and $Ni(CO)_4$ with ratios of both $PCl_3:Ni(CO)_4$ and $P_2Cl_4:Ni(CO)_4$ of at least 2.3. In all cases most of the reaction was due to P_2Cl_4. In two cases, slightly more than 100% recovery was achieved, a result attributable to some decomposition of P_2Cl_4. In another run excess P_2Cl_4 was allowed to react with a sample formed by reaction of 4.97 mmoles of PCl_3 and 1.28 mmoles of $Ni(CO)_4$. The solid reacted with 4.55 mmoles of P_2Cl_4, replacing 4.73 mmoles of PCl_3.

TABLE II

REACTIONS OF PCl_3 AND P_2Cl_4 WITH $Ni(CO)_4$ AT 0°

$\frac{\text{CO evolved}}{Ni(CO)_4}$	Final press., atm.	P_2Cl_4 reacted, mmoles	PCl_3 reacted, mmoles	CO evolved, mmoles
2.09	0.64	1.58	(−0.23)[a]	1.63
1.99	1.22	2.77	0.21	3.20
2.57	0.69	1.09	(−0.14)[a]	1.36
2.11	0.63	1.82	0.32	1.22

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

Reaction of P_2Cl_4 with Boron Trihalides.—Boron trifluoride was not absorbed by P_2Cl_4 at 0° or room temperature. When an excess of BCl_3 was placed in a sealed tube with P_2Cl_4 at 0°, the starting materials were recovered unchanged after 2 months.

When boron tribromide was mixed with P_2Cl_4 at 0° or room temperature, a reaction occurred producing a yellow-orange nonvolatile solid, boron trichloride, and, in runs with $BBr_3:P_2Cl_4$ ratios greater than 1.42, a white volatile solid. Quantitative results were obtained in thirteen runs with $BBr_3:P_2Cl_4$ ratios of from 0.38 to 36. Representative results from five runs are presented in Table III.

The second column of Table III gives the mgrams of nonvolatile orange solid formed per mmole of P_2Cl_4; the values lie between the formula weights for PCl, 66.4, and PBr, 110.9. The third column of Table III gives the mgrams of solid (per mmole of P_2Cl_4) stopped by a −45° trap in a fractional condensation of the volatile products. The values lie between or near the molecular weights of $PBBr_6$, 521.2, and $PBBr_4Cl_2$, 432.3. In addition, the white solids were analyzed by precipitation of silver halide, Volhard determination of total halogen, and treatment of the solid with chlorine followed by measurement of the liberated bromine and BrCl. Twenty-one determinations gave values for x (in $PBBr_{6-x}Cl_x$) of 0–1.67, with the majority of the results in the range 0–0.5. On standing, these chlorine-containing samples continued slow halogen exchange until only stable $PBBr_6$ (identical with the known adduct of PBr_3 and BBr_3[5,17]) remained. Solids containing chlorine had melting points depressed as much as 10–20° from the 61–62° melting point of pure $PBBr_6$ and usually melted over a range of several degrees. The fourth column of Table III gives the mgrams of material (per mmole of BBr_3) which passed a −78° trap in a fractional condensation of the volatile products in runs with excess P_2Cl_4. The results, in agreement with the molecular weight of BCl_3, 117.2, and confirmed by infrared spectra which showed BCl_3 to be the principal component, indicated almost complete conversion of BBr_3 to BCl_3 in the presence of excess P_2Cl_4. With excess BBr_3, infrared spectra showed

---

(17) J. Tarible, *Compt. rend.*, **116**, 1521 (1893).

TABLE III

PRODUCTS OF THE REACTION OF BBr_3 WITH P_2Cl_4

Initial ratio BBr_3:P_2Cl_4	mg. of nonvol. prod. / mmole of P_2Cl_4	mg. of white solid / mmole of P_2Cl_4	mg. of vol. at −78° / mmole of BBr_3
35.9	94	524	*a*
3.35	69	484	*a*
2.10	96	435	*a*
1.42	71	0	117
1.30	96	0	106

[a] Inseparable mixed boron trihalides.

the presence of the four possible BCl_xBr_{3-x} compounds which are rapidly formed in any BCl_3–BBr_3 mixture.

Discussion

Reaction of P_2Cl_4 with $Ni(CO)_4$.—It appears that either one or both phosphorus atoms of P_2Cl_4 can act as donors to nickel and that one to four CO molecules can be displaced from nickel carbonyl by the phosphorus atoms of P_2Cl_4. Thus in the presence of a large excess of $Ni(CO)_4$, the binuclear complex $(CO)_3NiP_2Cl_4Ni(CO)_3$ forms; in the presence of a large excess of P_2Cl_4, mononuclear complexes such as $(CO)_2Ni(P_2Cl_4)_2$, $(CO)Ni(P_2Cl_4)_3$, and $Ni(P_2Cl_4)_4$ form. When there is no large excess of either reactant, we believe that polymeric materials, in which nickel atoms are bridged by P_2Cl_4 molecules, are formed. For all of these compounds, or mixtures of compounds, the approximate average sum of the P_2Cl_4 groups and Ni atoms per molecule may be calculated from the function $(a + b)/(a - ab + b)$, where a = CO evolved/P_2Cl_4 reacted and b = CO evolved/$Ni(CO)_4$ reacted.[18] In runs with a large excess of either reagent, the function has values fairly close to 3 (*e.g.*, 3.0 in run 1 and 2.9 in run 4 of Table I), corresponding to $P_2Cl_4Ni(CO_3)_2$ or $Ni(CO)_2(P_2Cl_4)_2$. Values of 14 and 22 are obtained for runs 2 and 3, suggesting the formation of polymeric materials when there was no large excess of either reagent.

In fifteen runs involving an excess of P_2Cl_4, the only runs in which significantly more than two molecules of CO per $Ni(CO)_4$ were displaced by P_2Cl_4 molecules were those runs of long duration in which the final pressure of carbon monoxide was less than about 0.8 atm. Whenever the final pressure of carbon monoxide was greater than 0.8 atm., the CO evolved/$Ni(CO)_4$ reacted was, within experimental error, equal to 2. This result suggests that an equilibrium is achieved in mixtures containing CO, P_2Cl_4, $Ni(CO)_2(P_2Cl_4)_2$ groups, and $Ni(CO)(P_2Cl_4)_3$. Although three experiments in which we attempted to reach this equilibrium by reaction with excess CO were inconclusive (possibly due to slowness of the reaction), we write

$$Ni(CO)_2(P_2Cl_4)_2 + P_2Cl_4 = Ni(CO)(P_2Cl_4)_3 + CO \qquad K \approx 0.8$$

It should be made clear, however, that some of the coordinated P_2Cl_4 molecules in this equation may form bridges to other nickel atoms.

Reactions of P_2Cl_4 and PCl_3 with $Ni(CO)_4$.—The data indicate that P_2Cl_4 is a stronger Lewis base than PCl_3 in reactions with Ni(0), as might have been predicted from a consideration of the inductive effect.

Reaction of P_2Cl_4 with Boron Trihalides.—The reaction of P_2Cl_4 with BBr_3 involves both the quantitative disproportionation of the P_2Cl_4 to PCl_3 and $(PCl)_x$ and the quantitative conversion, as far as possible, of PCl_3 and $(PCl)_x$ to PBr_3 and $(PBr)_x$ and of BBr_3 to BCl_3. The disproportionation and halogen-exchange reactions cannot be separated, however. In the presence of a large excess of BBr_3, the net reaction is

$$5BBr_3 + P_2Cl_4 \longrightarrow 4BBr_2Cl + PBBr_6 + (1/x)(PBr)_x$$

In the presence of a large excess of P_2Cl_4, the reaction is

$$BBr_3 + 3P_2Cl_4 \longrightarrow BCl_3 + 3PCl_2Br + (3/x)(PCl)_x$$

We initially studied this reaction with the hope of making $P_2Cl_4 \cdot 2BBr_3$; indeed, this adduct may be an intermediate in the complicated reaction observed. In this regard it is interesting to note that the weaker acids BF_3 and BCl_3 neither react with P_2Cl_4 nor accelerate its decomposition.

Acknowledgment.—This work was supported in part by the U. S. Atomic Energy Commission.

---

[18] This formula is based on the assumption that there are no ring structures formed.