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Charles B. Lindahl and William L. Jolly

May, 1964

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

May, 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.

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(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.

Introduction

The purpose of this investigation was to study some reactions in which diphosphorus tetrachloride acts as a base. The molecule was expected to have a Lewis-base strength similar to that of phosphorus trichloride, but to react difunctionally as other tetrasubstituted diphosphines do. Thus in the following paragraph we review some pertinent Lewis-base reactions of both phosphorus trichloride and tetrasubstituted diphosphines.

Phosphorus trichloride can displace all four molecules of carbon monoxide in $Ni(CO)_4$ to form $Ni(PCl_3)_4$,[2,3] but no displacement compounds

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

(3) W. C. Smith, Inorg. Syntheses, 6, 201 (1960).

form in the cases of $Mo(CO)_6$ and $Cr(CO)_6$ at temperatures up to 150°.[2] Substituted diphosphines have been found to react with various metal carbonyls to form the compounds $P_2(CF_3)_4[Ni(CO)_3]_2$,[4] $P_2(CH_3)_4[Ni(CO)_3]_2$,[5,6]

(4) A. B. Burg, and W. Mahler, J. Am. Chem. Soc., 80, 2334 (1959).

(5) L. A. Ross, Ph.D. Thesis, Indiana University, 1962.

(6) R. G. Hayter, Inorg. Chem., 3, 711 (1964).

$[P_2(CH_3)_4Ni(CO)_2]_x$,[5] $P_2(C_6H_5)_4[Ni(CO)_3]_2$,[6,7] $[NiP(C_6H_5)_2(CO)_2]_2$,[6] and

(7) W. Schweckendiek, German Patent 1,072,244, Dec. 31, 1959; Chem. Abstracts, 55, P12355g (1961).

$P_2(C_6H_5)_4[Fe(CO)_4]_2$.[7] Holmes[8] has shown that previous reports of adducts

(8) R. R. Holmes, J. Inorg. Nucl. Chem., 12, 266 (1960).

between PCl_3 and BCl_3[9] and BF_3[10] are erroneous, and that actually no

(9) A. Stieber, Comptes Rend. Acad. Sci. Paris, 195, 610 (1932).

(10) P. Baumgarten, and W. Bruns, Ber., 80, 517 (1947).

complexes form. Garrett and Urry[11] reported that B_2Cl_4 and PCl_3 form

(11) A. G. Garrett, and G. Urry, Inorg. Chem., 2, 400 (1963).

the adduct $B_2Cl_4 \cdot 2\ PCl_3$. Wiberg and Shuster[12] reported the adduct $PCl_3 \cdot BBr_3$

(12) E. Wiberg and K. Shuster, Z. anorg. Chem., 213, 94 (1933).

to be a white solid, melting at 42°. Holmes[8] showed that this adduct, on standing at room temperature, decomposes to BCl_3 and PBr_3, which do not form an adduct.

Experimental

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.

Reagents. - We prepared diphosphorus tetrachloride by using Sandoval and Moser's discharge method[13] in which white phosphorus reacts with

(13) A. A. Sandoval and H. C. Moser, Inorg. Chem., 2, 27 (1963).

PCl_3. Our yield varied, but was generally about 2 grams in runs of 6 to 10 hr. Diphosphorus tetrachloride was identified by its melting point of -28°[14] and its mass spectrum. The identification was confirmed by

(14) Besson and Fournier[15] originally reported -28° which was confirmed by Stock, Brandt, and Fischer,[16] Ross,[5] and Sandoval.[17] Finch[18] reported -34° to -35°.

(15) A. Besson and L. Fournier, Compt. Rend. Acad. Sci. Paris, 150, 102 (1910).

(16) A. Stock, A. Brandt, and H. Fischer, Ber., 58, 643 (1925).

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

(18) A. Finch, Can. J. Chem., 37, 1793 (1959).

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 (1.066 mmole) 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.), 39.8% (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

$$P_2Cl_4 \rightarrow PCl_3 + \frac{1}{x}(PCl)_x$$

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[19] using an immersible

(19) For experimental details, the reader is referred to University of California Radiation Laboratory Report UCRL - 11189, "Chemistry of Diphosphorus Tetrachloride", January, 1964.

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 $\log P_{mm} = 9.969 - 2958/T$. 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[5] (4 mm. at 0° and 10 mm. at 28°), Stock, Brandt, and Fischer[16] (5 mm. at 0°), and Besson and Fournier[15] (P_2Cl_4 distilled at 180° or 20 mm. at 95° to 96°) and agree with Sandoval[17] (about 1 mm. at 25°).

Phosphorus trichloride (Mallinckrodt) was purified by fractional condensation in traps at -45, -78, and -196°. The -78° fraction had a 0° vapor tension of 36 mm. (literature,[11] 36.1 mm.). Nickel carbonyl (K and K Laboratories, Jamaica, New York) was purified by a similar fractional condensation. The -78° fraction had a 0° vapor tension of 135 mm. (literature,[5] 133 mm.). Iron carbonyl (K and K) was fractionally condensed in traps at -22, -45, and -196°. The -45° fraction was retained. Chromium hexacarbonyl (K and K) and molybdenum hexacarbonyl (Climax Molybdenum Company, New York) were used without purification. Boron trifluoride (Matheson) was purified by passing the gas 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,[8] 298 mm.). Boron trichloride (Matheson) was condensed in traps at -78°, -112°, and -196°. The -112° fraction had a 0° vapor tension of 480 mm. (literature,[11] 477 mm.). Boron tribromide (American Potash and Chemical) was condensed in traps at -45, -78, and -196°. The -78° fraction had a 0° vapor tension of 19 mm. (literature,[8] 19 mm.). Diborane was prepared[20] from reaction of potassium borohydride with sulfuric

(20) H. G. Weiss and I. Shapiro, J. Am. Chem. Soc., 81, 6167 (1959).

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,[21] 225 mm.).

(21) A. B. Burg, J. Am. Chem. Soc., 74, 1340 (1952).

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 a series of reactions involving various initial ratios of reactants.

With excesses of $Ni(CO)_4$ (runs 2 to 6), nearly 2 mmole of $Ni(CO)_4$ reacted with every mmole of P_2Cl_4, giving 2 mmole of CO and a solid product having a composition close to $P_2Cl_4[Ni(CO)_3]_2$. This material was yellow at 0° and yellowish white at -63°. The excess $Ni(CO)_4$ could be slowly removed at -63° leaving a product stable at -63°. After the CO and excess $Ni(CO)_4$ had been removed, the compound evolved CO and $Ni(CO)_4$ slowly even at -45° and very rapidly at room temperature. The samples turned black during these latter reactions, suggesting the formation of metallic nickel. We could not determine how much metallic nickel had formed, but we were able to follow the CO/P_2Cl_4 ratio for the residue. Thus in run 3, the unreacted $Ni(CO)_4$ was removed during a 3-hr. period at -45°, the data indicating a product of composition $P_2Cl_4Ni_{2.02}(CO)_{6.09}$. During 42 more hours at -45°, the sample darkened, and further evolution of CO and $Ni(CO)_4$ indicated a ratio CO/P_2Cl_4 = 4.77 for the residue. In run 2 (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 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

Table I.

Reactions of P_2Cl_4 with $Ni(CO)_4$.

Run	$Ni(CO)_4$ in / P_2Cl_4 in	CO evolved / P_2Cl_4 reacted	CO evolved / $Ni(CO)_4$ reacted	$Ni(CO)_4$ reacted / P_2Cl_4 reacted	Final press (atm)	Rxn time (hr)	Average sum of P_2Cl_4 and Ni 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	1.344	1.011	—	619	13.87
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	—

fallen to 2.43; another twenty hours at room temperature lowered the ratio to 2.00, and at the end of one week the ratio was 0.60. The data of run 1 indicate that, even when the evolved CO is not removed, the $P_2Cl_4[Ni(CO)_3]_2$ decomposes during extremely long storage periods at 0°. Negligible amounts of nickel metal formed in this run. 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 minutes at room temperature.

When roughly equal amounts of $Ni(CO)_4$ and P_2Cl_4 were allowed to react (runs 7 to 9), 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 10-18), 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 slowly reacted further with P_2Cl_4. After removal of the evolved CO in runs 12, 14 and 16, the reaction products were kept in the presence of the excess P_2Cl_4 for additional long periods of time (2700, 2900 and 1000 hrs, respectively). The final ratios of the total CO evolved per $Ni(CO)_4$ were, respectively, 3.65, 3.63 and 4.02. Apparently all four molecules of CO can be displaced from $Ni(CO)_4$.

Several 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 2.5 atm. for several days. The experimental errors in determining the CO absorbed were so great, however, that we can only say that less than 0.3 mmole of CO was

absorbed per mmole of $Ni(CO)_2(P_2Cl_4)_2$ in these experiments.

Reactions of P_2Cl_4 and PCl_3 with $Ni(CO)_4$. - Table II lists the results of our 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 $P_2Cl_4/Ni(CO)_4$ ratios from 2.3 to 7.1 and with $PCl_3/Ni(CO)_4$ ratios from 2.6 to 13.5. 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 than 100% recovery of PCl_3 was achieved, a result attributable to some decomposition of P_2Cl_4.

In another run, 4.553 mmoles of P_2Cl_4 was allowed to react with a sample formed by reaction of 4.970 mmoles of PCl_3 and 1.284 mmoles of $Ni(CO)_4$. 4.729 mmoles of PCl_3 was recovered.

Reaction with Diborane. - When B_2H_6 was exposed to P_2Cl_4 at 0°, a slow increase in pressure due primarily to evolution of H_2 continued 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.

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 two months.

When boron tribromide was mixed with P_2Cl_4 at 0° or room temperature, a reaction occured producing a yellow-orange non-volatile solid, boron trichloride, and, with a sufficient excess of BBr_3, a white volatile solid. Quantitative data are presented in Table III. Only those runs with BBr_3/P_2Cl_4 ratios greater than 1.421 involved the formation of white volatile solids.

Table II.

Reactions of PCl_3 and P_2Cl_4 with $Ni(CO)_4$ at 0°.

$\frac{CO \text{ evolved}}{Ni(CO)_4}$	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.

Table III.

Products of the Reaction of BBr_3 with P_2Cl_4

$\frac{BBr_3}{P_2Cl_4}$	$\frac{\text{mg PX}}{\text{mmole } P_2Cl_4}$	$\frac{\text{mg } PBX_6}{\text{mmole } P_2Cl_4}$	$\frac{\text{mg } BCl_3}{\text{mmole } BBr_3}$
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	
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

The white solids had the composition $PBCl_xBr_{6-x}$, where x varied from zero to about two. The solids exchanged halogen with large excesses of BBr_3 until only stable $PBBr_6$ remained which was identical with the known adduct of PBr_3 and BBr_3.[8,22] Solids containing chlorine had melting

(22) J. Tarible, Comptes Rend. Acad. Sci., Paris, 116, 1521 (1893).

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. Analysis of the solid was accomplished by precipitation of silver halide, Volhard analyses for total halogen, and treatment of the solid with chlorine followed by measurement of the liberated bromine and BrCl. In eleven silver halide 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 from 0 to 1.67, with nine of the results between 0 and 0.5. Five determinations of halogen by the Volhard method, and six determinations of bromine by treatment with chlorine confirmed the values of x in these samples to be in the range 0 to 1.5.

The second column of Table III gives the mg. of nonvolatile orange solid formed per mmole of P_2Cl_4; except for two high values, all the values lie between the formula weights for PCl, 66.4, and PBr, 110.9. Because the PBX_6 sublimes slowly, it is quite likely that the high values of 118.2 and 157.5 are due to traces of PBX_6 left with the nonvolatile solid. The third column of Table III gives the mg. of solid (per mmole of P_2Cl_4) stopped in a -45° trap in a fractional condensation of the volatile products. Most of the values lie between the molecular weights

of $PBBr_6$, 521.2, and $PBBr_4Cl_2$, 432.3. The fourth column of Table III gives the mg. of material (per mmole of BBr_3) which passed a -78° trap in a fractional condensation of the volatile products. All but the last two values are in fair agreement with the molecular weight of BCl_3, 117.2. In the last two runs, the reaction yielded large amounts of PCl_3, traces of which could have passed the -78° trap. Infrared spectra indicated that the principal component of all samples was BCl_3.

Reactions having an excess of BBr_3 yielded $BBrCl_2$ and BBr_2Cl. Those having an excess of P_2Cl_4 yielded PCl_2Br and $PClBr_2$.

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, 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 average sum of the P_2Cl_4 groups and Ni atoms per molecule may be calculated from the function $(\underline{a} + \underline{b})/(\underline{a} - \underline{ab} + \underline{b})$, where $\underline{a}$ = CO evolved/P_2Cl_4 reacted and $\underline{b}$ = CO evolved/$Ni(CO)_4$ reacted.[23] This function has been tabulated in the last

(23) This formula is based on the assumption that there are no ring structures formed.

column of Table I. It will be noted that the function has values fairly close to three, corresponding to $P_2Cl_4[Ni(CO)_3]_2$ or $Ni(CO)_2(P_2Cl_4)_2$, in runs involving large excesses of either reagent. High values are obtained for runs 7, 8 and 9, in which there was no large excess of either reagent.

In Figure 1 we have plotted the CO evolved/$Ni(CO)_4$ reacted against the final CO pressure for all our runs involving an excess of P_2Cl_4. The numbers near the points correspond to the hours of reaction time. Presumably if any of the runs had been terminated after a reaction time shorter than that indicated, the point would have fallen somewhere on the line joining the indicated point and the origin. It will be noted that 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 0.77 atm. Whenever the final pressure of carbon monoxide was greater than 0.77 atm., the CO evolved/$Ni(CO)_4$ reacted was, within experimental error, equal to two. Although we were unable to obtain good evidence for the reversibility of any of these reactions, we believe that the equilibrium pressure of CO over a mixture containing P_2Cl_4, $Ni(CO)_2(P_2Cl_4)_2$ groups, and $Ni(CO)(P_2Cl_4)_3$ groups is approximately 0.77 atm., and we write

$$Ni(CO)_2(P_2Cl_4)_2 + P_2Cl_4 = Ni(CO)(P_2Cl_4)_3 + CO \quad K \approx 0.77$$

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.

<u>Reactions of P_2Cl_4 and PCl_3 with $Ni(CO)_4$</u>. - The data indicate that P_2Cl_4 is a stronger Lewis base than PCl_3 in reactions with Ni(0). This result might have been predicted from a consideration of the inductive effect.

Phosphorus trichloride has three electron-withdrawing chlorine atoms per phosphorus atom, whereas P_2Cl_4 has only two chlorine atoms per phosphorus atom.

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

$$5\ BBr_3 + P_2Cl_4 \rightarrow 4\ BBr_2Cl + PBBr_6 + \frac{1}{x}(PBr)_x$$

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

$$BBr_3 + 3\ P_2Cl_4 \rightarrow BCl_3 + 3\ PCl_2Br + \frac{3}{x}(PCl)_x$$

We initially studied this reaction with the hope of making $P_2Cl_4 \cdot 2\ BBr_3$; 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.

Acknowledgement. - This work was supported in part by the U.S. Atomic Energy Commission.

Figure Caption

Figure 1. Data for reactions of $Ni(CO)_4$ with excess P_2Cl_4.

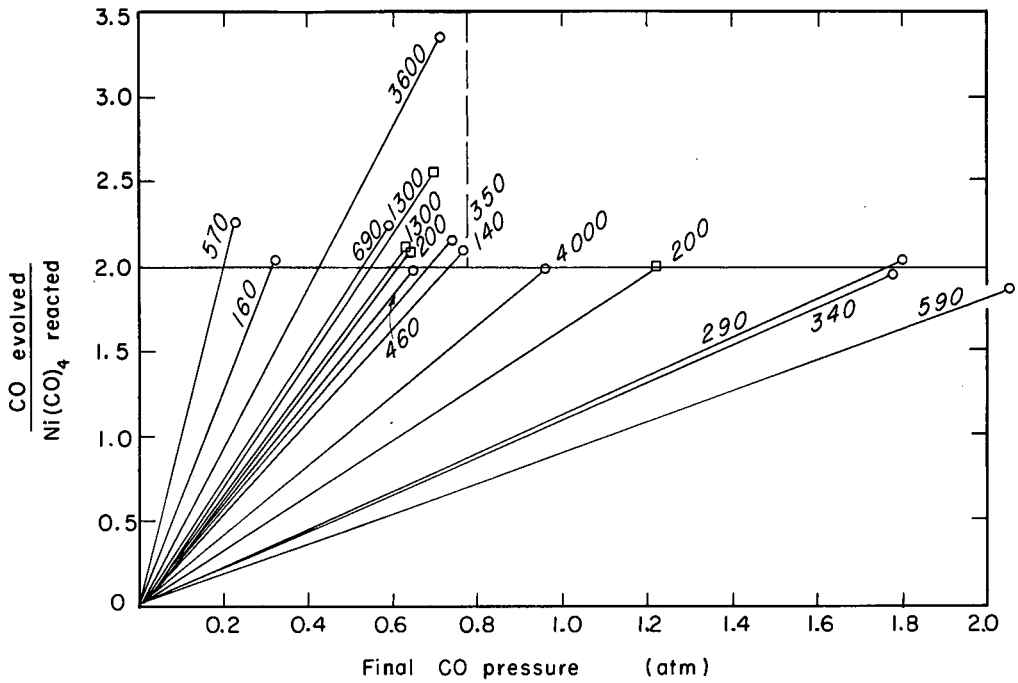
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
CO evolved / Ni(CO)4 reacted
Final CO pressure (atm)
3600
1300
690
300
200
350
140
510
160
460
4000
200
290
340
590
MU-33362

Fig. 1.