activation (in benzene relative to water) of approximately 1.0 kcal./mole.

Equation 1 may be rearranged to the following form, which may be utilized to obtain the effective  $\sigma_R$  values for the +R substituents in various solvents from the shielding parameters listed in Tables II, IV, and V of this paper and Tables II–IX of ref. 6.

$$\vec{\sigma}_{\rm R} = (-0.0339)(\int_{\rm H}{}^{p-{\rm X}} - \int_{\rm H}{}^{m-{\rm X}}) \tag{4}$$

The solvent effects on  $\bar{\sigma}_R$  values obtained from eq. 4 may be taken to indicate the expected magnitudes of solvent effects on the reactivity effects of these sub-

stituents, but the precise quantative applicability of these substituent parameters is questionable.

In a subsequent paper linear relationships generated by plots of  $\int_{H}^{p-x} vs. \int_{H}^{p-x}$  for pairs of +R substituents (from the data of Tables II and IV) are considered in detail. The effect of solvent on the contribution of dipolar direct interaction forms is used as a model to obtain a generalized scale of solvent polarity; *i.e.*,  $\int_{H}^{p-x}$ values for +R substituents are utilized as measures of the ability of solvent to support charge separation in simple solute molecules. Applications to the effect of solvent on the rates of ion-forming reactions are made.

[CONTRIBUTION FROM STANFORD RESEARCH INSTITUTE, MENLO PARK, CALIF.]

# The Reaction of Alkanes with Phosphorus Trichloride and Oxygen<sup>1</sup>

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**Received October 9, 1962** 

The reaction of phosphorus trichloride and oxygen with alkanes to give alkylphosphonyl chlorides is a free radical chain reaction with chlorine atoms as one chain carrier. The mechanism of chain propagation has been deduced by studies of products of the reaction of cyclohexane. One experiment with cyclohexene and one with styrene are also reported. These studies have shown that phosphorus trichloride is 0.36 times as reactive as cyclohexane toward chlorine atoms, that phosphorus trichloride is half as reactive as oxygen toward cyclohexyl radicals, that  $C_6H_{11}PCl_9O$ . radicals decompose into  $C_6H_{11}POCl_9$  and Cl. 3.6 times as often as they decompose into POCl<sub>3</sub> and  $C_6H_{11}$ , and that cyclohexylphosphonyl chloride is one-third as reactive as cyclohexane toward chlorine atoms and in chlorophosphonation. At relatively high ratios of oxygen to phosphorus trichloride, cyclohexyl phosphodichloridate (found as cyclohexene in our analyses) is produced at the expense of cyclohexylphosphonyl chloride. Reactions of phosphorus trichloride toward free radicals and of other alkanes in chlorophosphonation are discussed.

#### 1. Introduction

A remarkable reaction of saturated hydrocarbons with phosphorus trichloride and oxygen was discovered independently some time ago by three groups of workers: by Clayton and Jensen<sup>2a</sup> in this country; by Soborovsky, Zinovyev, and Englin in the Soviet Union<sup>3a</sup>; and by Graf in Germany.<sup>4</sup> The latter was apparently the first to discover the reaction,<sup>4</sup> but the last to publish on it. Soborovsky and co-workers have extended the reaction to alkyl halides,<sup>1,3b</sup> ethers,<sup>3b</sup> and cyanides,<sup>3k</sup> to unsaturated compounds,<sup>3a,c,f,g,i,j</sup> and to chlorophosphines.<sup>3d,e,h,m</sup> The work on alkanes and phosphorus trichloride has recently been reviewed and extended by Isbell and Wadsworth.<sup>5</sup>

To a first approximation, saturated hydrocarbons give alkylphosphonyl chlorides by the over-all reaction  $^{3a,4}$ 

$$-H + 2PCl_3 + O_2 \longrightarrow R - POCl_2 + POCl_3 + HCl \quad (1)$$

This reaction is accompanied by a competing oxidation of phosphorus trichloride

(2) (a) J. O. Clayton and W. L. Jensen, J. Am. Chem. Soc., 70, 3880
(1948); (b) W. L. Jensen, Ph.D. Dissertation, Stanford University, 1948;
(c) W. L. Jensen and C. R. Noller, J. Am. Chem. Soc., 71, 2384 (1949).

(d) (a) L. Z. Soborovsky, Yu. M. Zinovyev, and M. A. Englin, Dokl. Akad. Nauk SSSR, 67, 293 (1949); (b) ibid., 73, 333 (1950); (c) Yu. M. Zinovyev, I. I. Muler, and L. Z. Soborovsky, J. Gen. Chem. USSR, 24, 391 (1954); (d) L. Z. Soborovsky and Yu. M. Zinovyev, ibid., 24, 527 (1954); (e) Yu. M. Zinovyev and L. Z. Soborovsky, ibid., 26, 3375 (1956); (f) L. Z. Soborovsky, Yu. M. Zinovyev, and L. I. Muler, Chem. Abstr., 51, 1825 (1957); (g) ibid., 54, 20844 (1960); (h) Yu. M. Zinovyev, V. N. Kulakova, and L. Z. Soborovsky, J. Gen. Chem., USSR, 28, 1600 (1958); (i) Yu. M. Zinovyev and L. Z. Soborovsky, Chem. Abstr., 54, 340 (1960); (j) L. Z. Soborovsky, Yu. M. Zinovyev, and T. G. Spiridonova, ibid., 54, 1270 (1960); (k) R. I. Bystrova, Yu. M. Zinovyev, and L. Z. Soborovsky, ibid., 54, 8604 (1960); (l) Yu. M. Zinovyev and L. Z. Soborovsky, ibid., 54, 10836 (1960); (m) ibid., 55, 1415 (1961).

(4) R. Graf, Chem. Ber., 85, 9 (1952).

R-

(5) A. F. Isbell and F. T. Wadsworth, J. Am. Chem. Soc., 78, 6042 (1956).

$$2PCl_3 + O_2 \longrightarrow 2POCl_3 \tag{2}$$

Since both reactions occur readily in the absence of light and added catalysts,<sup>2a,5</sup> and since both are susceptible to similar inhibitors,<sup>2b,5</sup> they must be closely related.<sup>6</sup> Reaction 1 has been pushed to about 60% of the theoretical yield with an excess either of phosphorus trichloride<sup>3a,4</sup> or of hydrocarbon.<sup>2a,5</sup> Cyclohexane has been most studied because it is one of the few alkanes to give a single, crystalline, monosubstitution product.<sup>2a,b,4</sup>

The most striking feature of the *chlorophosphonation* reaction (eq. 1) is its high rate at low temperatures. Isbell and Wadsworth<sup>5</sup> report that the reaction is "virtually instantaneous, the speed being governed only by the rate at which oxygen could be caused to dissolve in the reaction mixture." They found no significant change in products over the range  $-100^{\circ}$  to  $+100^{\circ}$  (vapor phase), and certainly none between  $-40^{\circ}$  and  $+70^{\circ}$ . Ethane reacted to  $-80^{\circ}$  without any induction period,<sup>4</sup> and again the rate depended on the oxygen supply. One object of the present work is to determine the mechanism by which alkanes are so easily involved in reaction 1. Another object is to determine why, in view of the competition between reactions 1 and 2, yields of phosphonyl chloride are insensitive to alkane-phosphorus trichloride feed ratios.<sup>5</sup>

The principal conclusions of this paper are summarized in sections 3, 4.1, and 5.

#### 2. Experimental and Details

2.1. Materials.—Phosphorus trichloride was reagent quality, obtained in 1-lb. bottles from J. T. Baker and from Mallinckrodt. Each lot of material was distilled in an atmosphere of nitrogen and stored in a glass-stoppered bottle. The material was occasionally redistilled to remove traces of hydrolysis and oxidation products. Cyclohexane, >99 mole %, was obtained from Phillips Chemical Co. Each lot was distilled before use. Melting points were 4-6.5°. Among the many lots of these reagents which we employed, there was no indication that their sources or histories were important.

<sup>(1)</sup> Preliminary accounts of this work were presented to the Division of Organic Chemistry at the 134th and 140th National Meetings of the American Chemical Society, Chicago, Ill., September 8, 1958, Abstracts, p. 6P, and September 5, 1961, Abstracts, p. 41Q, and to the Division of Petroleum Chemistry at the 137th National Meeting, Cleveland, Ohio, April 14, 1960, Abstracts, p. 17Q.

<sup>(6)</sup> F. R. Mayo, E. Acton, and K. Egger, unpublished work.

Cyclohexene and cyclohexanol were obtained from Matheson Coleman and Bell. The latter compound was distilled before use. Di-*n*-hexyl peroxide<sup>7</sup> was obtained from Professor H. S. Mosher. Dicyclohexyl peroxydicarbonate,<sup>8</sup> ( $C_6H_{11}O-CO_{2^-}$ )<sub>2</sub>, was prepared by Dr. L. Glover.

2.2. General Procedures.—In general these reagents were weighed out into a reaction flask of 2-4 times the required capacity. The gas was admitted to the flask via an inlet tube at the top and mixed with the liquid by vigorous stirring with a Fisher Vibro Mixer (45 mm. perforated plate); it was vented from the flask past a cold finger condenser containing powdered Dry Ice, which returned condensable materials to the reaction mixture. In reactions 103-125, oxygen or air was introduced through a small external tube sealed to the bottom of the reaction flask. The temperature was measured by a thermometer dipping into the splashing liquid.

This reaction flask was placed in a bath of ice and water, and the contents were stirred vigorously. When the liquid temperature approached that of the bath  $(1-2^\circ)$ , introduction of oxygen or air was begun. Reaction set in at once, as indicated by rapid rise in temperature. The rate was limited (in the absence of diluents and inhibitors) by the oxygen supply, usually so that the reaction temperature did not exceed 15°. When the phosphorus trichloride was exhausted, or nearly so, the temperature of the reaction mixture returned quickly to  $1-2^\circ$ . Stirring under oxygen was continued for 10-60 min. more. The reaction mixture was then weighed (no large weight changes were found, in agreement with eq. 1 and 2) and transferred to a Claisen distilling flask with a side arm like a Vigreux column and with thermometers to measure both liquid and vapor temperatures.

The bulk of the cyclohexane and phosphorus oxychloride was distilled at atmospheric pressure up to a residue temperature of about 150°. The residue was then transferred to a smaller flask and removal of cyclohexane and phosphorus trichloride was continued up to a vapor temperature of 50° at 20 mm. pressure. Cyclohexylphosphonyl chloride, easily separated from other materials, was collected up to 135° at 20 mm., or near 85° at 0.3 mm. It was usually colorless, with a melting point in the range  $35-39^{\circ}$  (m.p. after recrystallization from petroleum ether,  $39.5-40.5^{\circ}$ ). From reaction mixtures which initially contained more than four moles of phosphorus trichloride per mole of cyclohexane, a diphosphonyl chloride<sup>2b,4,5</sup> fraction was collected at about  $185^{\circ}$  at 0.3 mm. Usually, the whole distilling flask was finally heated sufficiently with a free flame (about  $250^{\circ}$ ) to drive over essentially all the volatile material in the residue and in the top of the flask.

The residue was weighed and analyzed for carbon and phosphorus. The diphosphonyl chloride fraction, if any, was also weighed and analyzed for both carbon and phosphorus. This ratio gave the proportions of  $C_6H_{11}POCl_2$  and  $C_6H_{10}(POCl_2)_2$  in this fraction (70–90%). Hydrolysis of this product on standing made chlorine analysis unreliable for assays.

Many reaction mixtures also contained some cyclohexylphosphodichloridate ( $C_6H_{11}OPOCl_2$ ). Most of this decomposed to cyclohexene during the distillations above and below. Cyclohexene was determined as follows. The cyclohexane-phosphorus oxychloride fractions were combined, extracted with water, dried, and distilled. The cyclohexane thus recovered was analyzed for cyclohexene, using the absorption band at 13.95  $\mu$  and a known standard (2% cyclohexene in cyclohexane). Because the cyclohexene was so dilute, many of these determinations may be in error by 10% or more. At high initial concentrations of phosphorus trichloride, recoveries of cyclohexane were small; evaporation losses were relatively high, and yields of cyclohexene were low. At high initial concentrations of cyclohexane, most of the latter was recovered, but proportions of cyclohexene were very low because little cyclohexane reacted. In normal experiments, no unidentified bands appeared in the infrared spectra of the cyclohexane fractions. The water washings were titrated and normally found to contain only a few tenths of 1% of the original trivalent phosphorus.

In order to correct for mechanical losses in transfers of material, products were weighed in the original vessel before transfer and in the next vessel after transfer, using the clean vessels as tares. In this way, nearly quantitative results could be calculated without rinsing vessels after transfer. The yields in Table I have been so corrected and are 5–10% higher than the actual experimental values. More than 90% of the cyclohexane was usually accounted for. In experiment 68 (Table I) 0.196 mole of cyclohexane was accounted for. The principal losses of C<sub>c</sub>-fragments are considered to be through evaporation of cyclohexane and cyclohexene and through solution of cyclohexale and cyclohexene and through solution of cyclohexale straction (sections 2.3 and 2.5).

(8) F. Strain, W. E. Bissinger, W. R. Dial, H. Rudoff, B. J. DeWitt, H. C. Stevens, and J. H. Langston, *ibid.*, 72, 1254 (1950). About one hundred reactions of cyclohexane, phosphorus trichloride, and oxygen were carried out. In many of these, only the yields of cyclohexylphosphonyl chloride were determined as a function of feed ratio, order of addition, oxygen supply, temperature, and solvent. In later experiments, analyses were introduced for diphosphonyl chloride, residue, and cyclohexene. Only the best of these early experiments are listed in Table I, but at least the yields of cyclohexylphosphonyl chloride have been amply checked.

2.3. Origin of Cyclohexene.—Sections 4.1 and 4.7 show how the formation of cyclohexene depends on a high ratio of  $O_2$ : PCl<sub>8</sub>. This section describes experiments 125 and 130 where this ratio was highest. Experiment 125 also shows that cyclohexene appears only on pyrolysis of cyclohexyl esters. In this experiment, 0.172 mole of cyclohexane was placed in the reaction vessel at 0° and stirred in the usual manner while saturated with oxygen introduced through the bottom of the vessel. Then, over about 0.5 hr., a mixture of 0.0503 mole of phosphorus trichloride and 0.331 mole of cyclohexane was added slowly through a capillary dipping below the level of the stirred liquid. The reaction mixture, 48.7 g., was then distilled at 10–20 mm. pressure, to give: (1) 44.5 g. of distillate obtained at residue temperatures below 30°, *free* from cyclohexene by infrared absorption; (2) 1.175 g. of distillate up to a residue temperature of 130°, with evidence of cyclohexene after dilution and infrared analysis; (3) 1.89 g. of cyclohexene from cyclohexine. Unfortunately, this clear-cut result was not available when the analytical method used in most of our experiments (section 2.2) was devised. The errors in that procedure are discussed in sections 2.4 and 2.5.

Experiment 130 was carried out similarly but with oxygen at 10 p.s.i. above atmospheric pressure; 10 ml. of cyclohexane was mixed with 13.7 g. (0.100 mole) of PCl<sub>3</sub>, and added during 67 min. from a dropping funnel under nitrogen pressure to 200 ml. (1.94 mole total) of cyclohexane. Stirring was continued for 28 min. more. During the entire 95 min., excess oxygen was introduced through a sintered glass disk below the level of the vigorously stirred liquid. Oxygen and hydrogen chloride (0.021 mole absorbed in water) escaped through a tube dipping into a deep column of mercury. Distillation at 25 mm. pressure, much as in the previous experiment, gave the results in Table I.

2.4. Reactions of Cyclohexanol with Phosphorus Trichloride and Phosphorus Oxychloride.—Our experiments with the title compounds were carried out with different objectives. At first we were concerned with the question, can cyclohexyl esters be intermediate in the formation of cyclohexylphosphonyl chloride? Later we were concerned with the formation of cyclohexene by pyrolysis of esters. In most of these experiments, cyclohexene and cyclohexylphosphonyl chloride were sought in suitable fractions from distillations. When water treatments were involved, losses of soluble phosphorus ester-acids could result in poor material balances. Details are therefore omitted.

The following experiments indicated, by the distillation criterion, that no cyclohexylphosphonyl chloride could be obtained via a cyclohexyl ester: (1) 0.10 mole each of cyclohexanol and PCl<sub>3</sub> reacted at 0°, then were treated with phosphorus oxychloride; (2) same, but with phosphorus chloride treatments reversed; (3) 0.1 mole each of cyclohexanol and PCl<sub>3</sub> in 0.18 mole of cyclohexane gave 0.036 mole of cyclohexane and 0.044 mole of cyclohexyl chloride; (4) 0.1 mole of cyclohexanol was added slowly to 0.12 mole of PCl<sub>3</sub> under nitrogen at 0° and the mixture was stirred for another 1.5 hr. Then 0.12 mole more of PCl<sub>3</sub> was added and the mixture was stirred with oxygen for 2 hr. more. Distillation at atmospheric pressure then gave 41%yield of cyclohexene as the only identifiable product.

We now consider the pyrolysis of cyclohexyl-phosphorus esters and its relation to our analytical method. Kosolapoff<sup>9</sup> states that secondary alcohols react with phosphorus oxychloride at or below room temperature to give ROPOCl<sub>2</sub> and RCl, with excess PCl<sub>3</sub> to yield ROPCl<sub>2</sub> and/or alkenes, and with a deficiency of PCl<sub>3</sub> to give  $(RO)_2PCl$ ,  $(RO)_2POH$ , and RCl. This section amplifies some of these conclusions.

In a pair of experiments carried out with phosphorus oxychloride, cyclohexanol (0.328 mole) was added slowly during 2.5 hr. to 0.405 mole of phosphorus oxychloride, stirred in an ice bath. One portion of this reaction mixture was distilled at reduced pressure, first at 12 mm., finally at 0.5 mm., to a final vapor temperature of 31°, a residue temperature of 125°, where evolution of hydrogen chloride began. The distillate was extracted with ice water, dried, and redistilled to give 87% yield of cyclohexene. Another 3% of the cyclohexanol appeared in the distillation residue which must have consisted mostly of phosphoric acids. Only 10% of the cyclohexanol was unaccounted for. Another portion of the same reaction mixture was distilled as described in section 2.2, starting at atmospheric pressure. This experiment gave 48% cyclohexene, 3% of cyclo-

<sup>(7)</sup> F. Welch, H. R. Williams, and H. S. Mosher, J. Am. Chem. Soc., 77, 551 (1955).

<sup>(9)</sup> G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 180, 211.



Fig. 1.—Conversions of cyclohexane and phosphorus trichloride to cyclohexylphosphonyl chloride in their reaction with oxygen near 0°.

hexyl groups in the residue, 13% cyclohexyl chloride, and 36% of cyclohexanol unaccounted for, probably lost as ester-acid in washing of the first distillate. Cyclohexyl phosphodich! ridate was also prepared from cyclohexanol, phosphorus oxychloride, and 2,6-lutidine.<sup>10</sup> Distillation of 0.015 mole of this ester with 20 ml. of cyclohexane at atmospheric pressure from a 200° bath gave 44% yield of cyclohexene, in fair agreement with the experiment next above.

These experiments indicate that removal of most of the phosphorus oxychloride at low pressure before the cyclohexyl ester is pyrolyzed leads to the best recovery of cyclohexene, approaching 90%. Preliminary distillation at atmospheric pressure, as in our usual analytical methods, results in formation of some cyclohexyl chloride and losses of cyclohexyl residues as high as 40%. These losses apparently occur through the solubility in water (after hydrolysis) of compounds such as  $C_6H_{11}OPOCl_2$ . However, section 2.5 suggests that losses in typical chlorophosphonation experiments are less serious.

A similar pair of experiments was carried out with phosphorus trichloride. Although very little trivalent phosphorus survived our chlorophosphonations, these experiments support our conclusions with phosphorus oxychloride. One-tenth mole of cyclohexanol was added slowly with stirring to 0.12 mole of PCl<sub>3</sub> under nitrogen at 0° and stirring was continued for 1.5 hr. This product was distilled, first at 21 mm., finally at 0.8 mm., up to a residue temperature of 212°. We obtained, per mole of cyclohexanol, 0.22 mole of cyclohexene, at least 0.52 mole of (presumably) C<sub>6</sub>H<sub>11</sub>OPCl<sub>2</sub>, and 0.03 mole each of cyclohexanol and cyclohexyl chloride, 0.02 mole of cyclohexyl groups in the distillation residue. The stated 0.52 mole of Cyclohexyl groups in the distillation residue. The stated 0.52 mole of cyclohexyl nuclei unaccounted for must have been lost as ester-acid in the washing. In a comparison experiment, distillation was started at atmospheric pressure and completed at reduced pressure as described in section 2.2. Here, the total recovery of cyclohexene after two distillations was only 53%; 3% of the cyclohexanol was found in the distillation.

2.5. Effects of Added Cyclohexylphosphonyl Chloride, Phosphorus Oxychloride, Water, and Cyclohexanol.—We confirmed previous reports that neither cyclohexylphosphonyl chloride<sup>5</sup> nor phosphorus oxychloride, <sup>30, 5</sup> added initially, affect significantly the course of the chlorophosphonation reaction. These tests were carried out with phosphonyl chloride, cyclohexane, and phosphorus trichloride in the mole ratio 0.23:2:1 (some increase in residue at expense of phosphonyl chloride) and with phosphorus oxychloride, cyclohexane, and phosphorus trichloride, cyclohexane, and phosphorus trichloride in the mole ratio 0.23:2:1 (some increase in residue at expense of phosphonyl chloride) and with phosphorus oxychloride, cyclohexane, and phosphorus trichloride in the mole ratios 1:2:1 and 1:10:1. Comparison of experiments 59 and 68 in Table I shows the

Comparison of experiments 59 and 68 in Table I shows the effect of added water on the chlorophosphonation reaction. The decreases in yields of phosphonyl chloride corresponded to about one-third of the number of moles of water added. Thus traces of water should have no important effect. The data indicate also that the yield of cyclohexene was halved by addition of water, but these yields of cyclohexene are small and unreliable.

Addition of cyclohexanol increases the yield of cyclohexene and decreases the yield of phosphonyl chloride. Comparison of experiment 59 with 63 and of experiment 71 with 75 (to allow for different oxygen flow rates) shows that addition of 4% of cyclohexanol on the initial phosphorus trichloride, either before or

(10) H. A. C. Montgomery and J. H. Turnbull, J. Chem. Soc., 1963 (1958).

after oxidation, increases the yield of cyclohexene by very nearly the amount of cyclohexanol added, through esterification and The effects of cyclohexanol on the yields of cracking of the ester. cyclohexylphosphonyl chloride in the same experiments are less When the cyclohexanol was added after rapid absorption simple. of oxygen was complete (with stirring in oxygen for another halfhour at 2°, expt. 75), esterification took place with both POCla and RPOCl<sub>2</sub>; the resulting decrease in yield of the latter corresponded to about 64% of the cyclohexanol added. When the cyclohexanol was added initially (expt. 63) the decrease in yield of phosphonyl chloride was greater (100-105%) of the cyclohexanol added) because of the retarding properties of the alcohol: titration here showed that 0.0108 mole, 8.5%, of the original phosphorus trichloride was still in the trivalent form, even though the fast reaction was over within 0.5 hr. and an additional 3 hr. had been allowed for reaction

Experiment 62 (not in Table I) brings out the retarding effect of higher proportions of cyclohexanol. This experiment was carried out like expt. 59 but with 0.0141 mole of cyclohexanol (11 mole % on the PCl<sub>3</sub>). When oxygen was supplied, the reaction temperature rose abruptly, but only from 2 to  $6.5^{\circ}$  within 3 min., returned to  $2^{\circ}$  in 10 min. more, and remained there for 4 hr. This experiment yielded about 3.5 g. of unidentified highboiling material and distillation residue. From the distillate, 0.003 mole of cyclohexylphosphonic acid was isolated after hydrolysis and 0.0054 mole of cyclohexene was found; 0.0753 mole of trivalent phosphorus, 59%, was found by titration. These experiments indicate that substantial proportions of cyclohexanol or its ester or minor proportions of their oxidation or degradation products retard both chlorophosphonation and the oxidation of phosphorus trichloride. However, in only a few and unusual experiments in Table I are the yields of cyclohexene high enough that cyclohexyl esters might have caused trouble in the chlorophosphonation reaction.

2.6. Cyclohexene.—Alkenes react with phosphorus trichloride and oxygen to produce  $\beta$ -chloroalkylphosphonyl chlorides.<sup>38,1,g</sup> One chlorophosphonation of cyclohexene was carried out with a mixture of 0.20 mole of cyclohexane, 0.050 mole of cyclohexene, and 0.126 mole of phosphorus trichloride. From the weights of the phosphonyl chlorides and residues obtained and the composition of recovered hydrocarbons (17.4 mole % cyclohexene) it was estimated that 12.5% of the alkane and 26% of the alkene were converted to phosphonyl chlorides. Thus cyclohexene is about 2.3 times as reactive as cyclohexane in the competitive reaction. However, section 2.3 establishes that cyclohexene is formed only on distillation of the reaction mixture, and so no correction is necessary for reaction of cyclohexene. 2.7. Reactions of Phosphorus Trichloride with Alkoxy

2.7. Reactions of Phosphorus Trichloride with Alkoxy Radicals.—The reactions of alkoxy radicals with phosphorus trichloride were examined under two sets of conditions. These experiments indicate that alkoxy radicals may abstract organic hydrogen to give alcohols and their esters but that they do not react directly with phosphorus trichloride to give phosphonyl chlorides (although they may give other products).

In the first approach, di-*n*-hexyl peroxide, phosphorus trichloride, and cyclohexane, in molar proportions of 1:4:1 and of 1:4:10, were heated in a steam bath for 48 hr. in sealed evacuated tubes. Phosphonyl chlorides or phosphonic acids were the only products sought. The first experiment gave no evidence of such products. The second experiment also gave no evidence of phosphonyl chloride, but hydrolysis of the distillation residue gave 0.044 mole of cyclohexylphosphonic acid (identified by m.p. and m.m.p. with known compound) per initial mole of di*n*-hexyl peroxide. Formation of this product must be due to liberated or dissolved oxygen in the reaction mixture.

In the second approach, 6.05 mmoles of dicyclohexyl peroxydicarbonate (section 2.1) and 34.4 mmoles of phosphorus trichloride were heated in a sealed evacuated tube for 17 hr. at 65°. The product was transferred quantitatively with ether and distilled. Although the distilling flask was heated to 145°, all distillate appeared below 43° at 18 mm. and therefore contained little or no cyclohexylphosphonous dichloride (C<sub>6</sub>H<sub>11</sub>PCl<sub>2</sub>, b.p. 93° at 12 mm.).<sup>11</sup> After washing inorganic phosphorus compounds out of the distillate with water, the water-insoluble material contained at least 2.1 mmoles of cyclohexene by infrared analysis. The distillation residue weighed 0.57 g. and analyzed for 33.3% C, 4.88% H, and 8.94% P. 2.8. Solubility of Oxygen in Phosphorus Trichloride.—To

2.8. Solubility of Oxygen in Phosphorus Trichloride.—To determine the plausibility of formation of a phosphorus trichloride-oxygen complex,<sup>3b,4</sup> advantage was taken of the inhibiting effect of iodine on the reaction of oxygen with phosphorus trichloride to measure the solubility of oxygen in the latter. A flask fitted with a thermometer, a Teflon-covered magnetic stirrer, and a gas inlet was charged with 21.3 mg. of iodine and 39.3 g. of freshly-distilled phosphorus trichloride. The solution was degassed on a vacuum line and connected to a gas buret filled with dry oxygen at 27°. Uptake of gas was followed over

(11) T. Weil, B. Preji, and H. Erlenmeyer, Helv. Chim. Acta, 36, 1314 (1953).

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# TABLE I REACTIONS OF CYCLOHEXANE AND PHOSPHORUS TRICHLORIDE WITH OXYGEN (MOSTLY<sup>k,1</sup> NEAR $(0^{\circ})$ )

							Reaction pr	oducts, moles-			
					C6H11POCl2 and				Tota	al C	
Expt.	Ini	itial reactants,	moles	Oxygen,°	C6H10-		idue ——		. 100	Caled.	$k_{4}/k_{11}$
no.	PC13	$C_{6}H_{12}$	$PCl_3/C_6H_{12}$	ml./min.	$(POCl_2)_2^p$	C6	Р	$C_6H_{10}$	Found	eq. 18	eq. 21
31	1.003	0.0500	20.06	30	0.0226 $0.0140^{a,p}$	0.0110	0.0220		0.0476	0.0500	
81	$0.550^b$	.0549	10.02	41	.0243	.0022	.0038	0.00002 <sup>m</sup>	.0278	$.0285^{b}$	(1.8)
<b>6</b> 0	1.250	. 1274	9.81	65	.0704	.0142	.0293	.00015	. 1140	. 1274	(1.2)
64	0.503	. 1025	4.91	15	.0292	.0025	.0050	.00006	.0768	.0955	(2.6)
7	252	131	1.92	465	.0158	.0094°			.0583°	0737	
8	250	125	2.00	42	0486	0076			0562	0725	
58	251	250	1 004	33	0679	0039	0075	0.0006	0724	0836	0.66
50	1957	250	0.503	51	0400	0035	0073	0000	0444	0451	41
71	1954	.250	502	102	0402	.0000	0045	.0009	0497	.0451	.41
71	1204	. 200	. 502	200	.0402	.0020	.0040	.0010	.0437	.0400	.37
50	. 1250	.250	. 500	320 f	.0400	.0034	.0055	.0000	.0445	.0449	. 58
54'	. 1250	.250	. 500	<b>.</b>	.0360	.0030	• • • •	.0023	.0413	.0449	,
53"	. 1250	.250	< .500%	Fast	.0362	.0042		.0036	. 0440	<i>v</i>	
68 <sup>n</sup>	.1250	.250	. 500	27	.0361	.0038	.0065	.0004	.0403	<i>*</i>	۸
63'	. 1267	.250	. 507	37	.0347	.0030	. 0055	. 0063	.0440	1	•
75'	. 1250	.250	. 500	125	.0374	.0030	.0060	.0065	. 0469	2	3
$84^{\prime\prime}$	. 233	. 460	. 506	27	.0691	.0050	.0097	.0021	.0762	k	k
67	.0504	. 499	. 1010	19A°	.0185	.0006 <sup>a</sup>		. 0003	$.0194^{d}$	.0191	0.4
57	.0507	. 500	. 1014	22A	.0184	.0003ª		None	$.0187^{d}$	.0192	
18	.0500	. 500	. 1000	49A	.0180	.0019		None	.0199	.0190	
56	.0502	. 500	. 1004	59	.0176	.0004°		0.0007	.0187°	.0190	0.9
69	.0500	. 499	. 1002	79	.0161	.0020*		.0008	.0189°	.0190	.8
17	.0501	. 500	. 1002	Verv fast	.0152	.0011		.0013	.0176	.0190	45
				(4  min.)							
125	0503	. 503	< .1000	182	.0094	.0064	0.0060	.0092	.0210	0	ø
130	100	1.94	< .05159	Moderate	.0045	.0067	.0212	.023	.0340	g	g
115	0684	3 39	0202	$2.7(5)^{\circ}$	0249	0010	0008	None	0259	0262	
100	0663	2 21	0202	2 54	0215	0026	0025	None	0241	0252	••
110	.0005	2 20	0200	2.64	0210	0020	0020	0.00047	0267	0252	(1.0)
110	0666	0.02	.0200	261	0201	.0091	0000	0007	.0207	.0208	(1.9)
110	.0000	0.04	.0199	30A 61	.0213	.0020	0020	0007	.0240	0202	1.1
112	.0078	0.00 0.00#	.0200	70	.0200	.0020	.0035	.0020	.0207	.0257	1.5
61	.0768	3.625	.0212	12	. 0230	.0025	.0043	.0046	.0301	.0297	0.89
113	.0727	3.28	< .0221*	255	.0089	.0044	.0118	.0108	.0241	e.	0.57
65°	.0290	1.391	. 0209	12	.0071	(.32	2 g.)	.0022	• • • •	• •	
				Reaction mix	ctures made	up to 250 r	nl. with C	Cl <sub>4</sub>			
104	0.0524	0.100	0.524	390	0.0093	0.0054	0.0077	• • • •			
103	.0527	. 100	. 527	331	.0092	.0032	. 0068	None	0.0124	0.0193	
105	.0524	. 100	.524	917	.0082	.0035	.0071	0.0013	.0130	0.0187	1.0
107	.0525	. 100	Small <sup>n</sup>	2.5A°	.0109	.0027	.0050	.0008	.0144	n	n
106	.0525	. 100	$Small^n$	<b>3</b> 60	.0025	.0053	.0077	.0018	.0096	n	n
			R	leaction mixt	ures made uț	o to 250 ml	. with ben	zene			
116	0.0494	0.500	0.099	3.8A	0.0125	0.00195	0.0014				
119	0.0504	0.504	0.100	185	0.0064	0.0018	0.0011			• • • •	
-										~	

<sup>a</sup> Based on weight of high-boiling fraction and analysis of the corresponding fraction in expt. 60: 9.96 mole % of  $C_8H_{11}POCI_2$  and 90.04 mole % of  $C_8H_{10}(POCI_2)_2$ . <sup>b</sup> Carried only to 51% reaction of PCI<sub>5</sub>; *cf.* section 4.4. <sup>c,d.e</sup> Based on weight of residue and 25.0% C found in residue in 58° or 26.6% C found in residue in expt. 18' or 36.5% C found in residue in expt. 17.<sup>e</sup> <sup>-1</sup> Reaction carried out rapidly in a falling film by adding reactants slowly through an inclined Vigreux column at 0° during 3.5 hr. The product drained into a Claisen flask. Oxygen was supplied fast enough through the side arm of this flask to maintain some emission of oxygen from the top of the column. <sup>e</sup> PCl<sub>5</sub>, mixed with a minor portion of the  $C_8H_{12}$ , was added slowly to the remainder of the  $C_6H_{12}$  through the bottom of the reactor vessel, during 69 min. in expt. 53 and during 43 min. in expt. 113, and as described in section 2.5 for expt. 125 and 130 (at superatmospheric pressure). <sup>h</sup> 0.0125 mole of H<sub>2</sub>O added to initial reaction mixture; 1.8% of initial trivalent P found after reaction (3.0 hr.); 0.196 mole of  $C_6H_{12}$  was recovered, 94.5% being accounted for. <sup>i,j</sup> 0.0051 mole<sup>i</sup> or 0.0050 mole<sup>j</sup> of cyclohexanol added to reaction mixture before<sup>i</sup> or after<sup>j</sup> oxidation. In expt. 63,<sup>i</sup> 8.5% of the initial trivalent P was found after reaction (3.6 hr.); expt. 71 is most comparable to 75<sup>j</sup> in oxygen supply. <sup>k</sup> Carried out at the lowest temperature possible without too much solidification of reaction mixture, starting at  $-68^\circ$ , ending at  $-28^\circ$ . <sup>i</sup> Reaction temperature 57-58° in warm water bath. <sup>m</sup> Mass spectrographic analysis indicated 0.09%  $C_6H_{10}$  in recovered  $C_6H_{12}$ ; infrared indicated none. <sup>n</sup> Cyclohexane and PCl<sub>3</sub> in CCl<sub>4</sub> added slowly to 50 ml. of Cl<sub>4</sub>. <sup>o</sup> A and (5) indicate that oxygen was supplied as dry air or as a 5% mixture with nitrogen at gas flows 5 or 20 times those indicated. <sup>p</sup> Indicates moles of  $C_8H_{10}(POCl_2)_2$  formed.

a 5-hr. period so that allowance could be made for any slow reaction.

A total of 120.7 ml. of oxygen (corrected to  $0^{\circ}$  and 760 mm. and extrapolated to zero time) was absorbed in the evacuated flask in a  $0^{\circ}$  bath, where the vapor pressure of phosphorus trichloride is 39 mm.<sup>12</sup>; 116.2 ml. was required to supply 720 mm. of oxygen

(12) "International Critical Tables," Vol. 3, p. 213.

to the 122.6 ml. of vapor phase. The remaining 4.5 ml., 2.0  $\times$  10<sup>-4</sup> mole, dissolved in the 0.286 mole of phosphorus trichloride, a mole fraction of 0.00070, at a total pressure of 760 mm.

The phosphorus trichloride was apparently saturated with oxygen within a minute after filling the flask with gas. The apparent volume of oxygen reacting in 5 hr. was 0.9 ml.

#### 3. Results

This section summarizes our most important experimental results and refers to our other results. Our basic experimental data are listed in Table I and are correlated in Fig. 1 and 2. These data are presented in terms of initial ratios of phosphorus trichloride to cyclohexane. Nearly all our reactions proceeded to exhaustion of the phosphorus trichloride, and so each initial ratio decreased steadily to zero.



Fig. 2.—Distribution of reacted cyclohexane as a function of initial mole ratio of phosphorus trichloride to cyclohexane.

Figure 1 shows the conversions of both phosphorus trichloride and cyclohexane to cyclohexylphosphonyl chloride as functions of the initial proportions of reactants. At high initial ratios of phosphorus trichloride a maximum of 57% of the cyclohexane can be converted to cyclohexylphosphonyl chloride. Figures 1 and 2 show that the further substitution of cyclohexylphosphonyl chloride and the formation of nonvolatile residues account for the maximum and for the decreasing vields of known products at the highest proportions of phosphorus trichloride. Under these conditions, nearly all the phosphorus trichloride is oxidized to phosphorus oxychloride. The residues in such experiments tended to be soft and orange to yellow, to give phosphine odors on strong heating, and to contain about two phosphorus atoms per cyclohexane residue, e.g., around 30%C, 25% P.

With high initial proportions of cyclohexane, 36-37% of the phosphorus trichloride can be converted to cyclohexylphosphonyl chloride. This limit is maintained to very high cyclohexane feeds when the oxygen supply is restricted (Fig. 1) but passes through a maximum with an ample supply of oxygen. Figure 2 shows that cyclohexene is produced at high cyclohexane feeds, more when sufficient oxygen was supplied. The increase in yield of cyclohexene with high oxygen supplies approximates the decrease in yield of cyclohexylphosphonyl chloride. Since no cyclohexene is actually present in the reaction mixtures, but is formed by pyrolysis of cyclohexyl esters during our analyses (sections 2.3 and 2.4), reaction of cyclohexene with phosphorus trichloride and oxygen (section 2.6) need not be considered further. The residues found during analysis of experiments at high cyclohexane feeds were black and brittle. They contained about equal molar proportions of phosphorus and cyclohexane residues, e.g., 35% C, 15-20% P. They are apparently associ-ated with pyrolysis of phosphoric esters and the formation of cyclohexylphosphonic acid and its anhydrides.





The effect of oxygen supply at low ratios of phosphorus trichloride to cyclohexane is really due to the more favorable ratio of oxygen to phosphorus trichloride and was not detected when the concentration of phosphorus trichloride was high. Thus, expt. 7 and 8 in Table I gave the same yield of phosphonyl chloride whether the oxygen supply permitted completion of reaction in 35 min. or in 5.5 hr. Figures 1 and 2 show only how the phosphorus trichloride: oxygen ratio has been decreased by adding cyclohexane. The phosphorus trichloride:oxygen ratio during reaction can be decreased further, with formation of C<sub>6</sub>H<sub>11</sub>O- $\mathrm{POCl}_2$  (found as cyclohexene) at the expense of  $\mathrm{C}_6\mathrm{H}_{11}\text{-}$ POCL, by adding diluted phosphorus trichloride slowly to cyclohexane saturated with oxygen (section 2.3, expt. 113 and 125 at atmospheric pressure), and still further by the use of oxygen at 10 p.s.i.g. (expt. 130), or by diluting the reaction mixture with carbon tetrachloride (expt. 103-105) or benzene (expt. 119), or by a combination of methods (expt. 106). By these procedures, conversions of phosphorus trichloride to phosphonyl chloride have been decreased from 36% to as low as 5%, and conversions to cyclohexyl phosphodichloridate to as high as 23% (expt. 130). The dilution of phosphorus trichloride by an inert solvent is counteracted by simultaneous dilution of oxygen with nitrogen (expt. 107).

Another way of obtaining a high concentration of oxygen was to introduce the reaction mixture dropwise into a cooled condenser in a stream of oxygen so that most of the reaction occurred in a falling film (expt. 54). The results were much the same as in expt. 53, where phosphorus trichloride was added slowly to cyclohexane saturated with oxygen.

The effects of phosphorus trichloride:oxygen ratio are treated quantitatively in section 4.7.

Material balances on cyclohexane have ranged up to 95% and the principal losses have been accounted for. The analyses for cyclohexene are most susceptible to error. This alkene arises from cyclohexanol through pyrolysis of its esters and the difficulties and errors are considered in sections 2.3 and 2.4.

We have confirmed previous conclusions that added phosphorus oxychloride and phosphonyl chloride have no significant effects on the chlorophosphonation reaction (section 2.5).

# 4. Discussion

4.1. Mechanism of Chlorophosphonation.—The oxidation of phosphorus trichloride and the chlorophosphonation of alkanes are competing reactions which are inhibited by similar materials.<sup>2b,5,6</sup> Since the products of these competing reactions have been correlated on the basis of competition of phosphorus trichloride and cyclohexane for a common chain carrier (section 4.4), the reactions must be very similar. For our present purposes, the reaction of phosphorus trichloride with oxygen is self-initiating and this same step apparently starts the reaction with cyclohexane.13 Efforts have been made with only limited success to determine the rate and mechanism of the spontaneous initiation and to correlate over-all rates of oxidation of phosphorus trichloride alone and in carbon tetrachloride.6 The present paper establishes the important features of the mechanism of chlorophosphonation of cyclohexane by using products and *relative* rates of reactions. Since the reaction chains are obviously long, the mechanisms of the initiation and termination steps and the over-all rates can be neglected.

Several considerations point to chlorine atoms as the chain carriers which permit rapid attack of alkanes at low temperatures.  $(\overline{1})$  Chlorine atoms have the necessary reactivity, and no sufficiently reactive substitute is apparent. (2) Isomer distributions in the chlorination<sup>14</sup> and chlorophosphonation,<sup>3b</sup> compared in Table II, show that the agent attacking the alkane in the chlorophosphonation is the same as in the chlorination, namely, a chlorine atom.<sup>15,16</sup> (3) Alkenes react to give  $\beta$ -chloroalkylphosphonyl chlorides,<sup>3a,c,f,g,i</sup> without evolution of hydrogen chloride. (4) A P-Cl bond is apparently essential for the reaction. Methyl-,<sup>3d</sup> ethyl-,<sup>3d</sup> and phenyldichlorophosphines<sup>3e</sup> and alkyldichlorophosphites<sup>3h</sup> react like phosphorus trichloride, but phosphorous esters, (RO)<sub>3</sub>P, are rather inert toward oxygen.17

TABLE II

COMPARISON OF POSITIONS TAKEN BY ENTERING SUBSTITUENTS IN 1-CHLOROBUTANE

	Positions taken					
	1, %	2, %	3, %	4, %		
Chlorination in bulk, 34°14	6.6	23.5	51.5	18.4		
68°14	7.8	23.5	49.2	19.5		
Chlorophosphonation at 20-70°3b	9.5	20.5	54.0	18.0		

All of our observations on the chlorophosphonation reaction are consistent with the chain mechanism described by reactions 3-14 in Fig. 3. We present two important quantitative tests of this general scheme. At low oxygen concentrations, reaction 11 and its successors (12, 13, 14) can be neglected. The principal products of the reaction are then determined by the competition between cyclohexane (reaction 3) and phosphorus trichloride (reaction 8) for chlorine atoms. The ratio  $k_8/k_3$  is shown to be about 0.36 over a wide range of reaction mixtures (section 4.4). However, with certain reasonable assumptions (section 4.2), experiments at high oxygen concentrations lead to the same result. When the phosphorus trichloride: cyclohexane ratio is less than about 0.5, then reactions 8-10become unimportant and the products of the reaction are determined by the competition of phosphorus trichloride (reaction 4) and oxygen (reaction 11) for cyclo-hexyl radicals. The ratio  $k_4/k_{11}$  is shown to be about 0.5 (section 4.7).

To account for our results, we have introduced reaction 7 as a competitor for reaction 6. We assume that  $C_6H_{11}PCl_3O_2$  reacts with  $PCl_3$  to give  $POCl_3$  and  $C_6H_{11}PCl_3O$ . The latter may then eject either a chlorine atom (main reaction 6) or a cyclohexyl

R. L. Flurry, Jr., Dissertation Abstr., 22, 3852 (1962).
(14) C. Walling and M. F. Mayahi, J. Am. Chem. Soc., 81, 1485 (1959).
(15) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 452.

(16) G. Geiseler, F. Asinger, and M. Fedtke, Chem. Ber., 93, 765 (1960). (17) Q. E. Thompson, J. Am. Chem. Soc., 83, 845 (1961).

radical (side reaction 7). From considerations in section 4.3, we have taken  $k_6/k_7$  as 3.5 and this value is the basis for most other calculations in this paper.

In carrying out the calculations above, some complications are encountered. Phosphorus trichloride may be oxidized by three routes, two of which can be essentially eliminated (section 4.2). With low concentrations of cyclohexane, the cyclohexylphosphonyl chloride may be substituted further, the monosubstitution product being one-third as reactive as cyclohexane toward chlorine atoms (section 4.6).

The first accounts of this work<sup>1</sup> proposed that an alkoxy radical reacts with phosphorus trichloride to give alkylphosphonyl chloride and a chlorine atom. This proposal was abandoned when no direct evidence for this step could be obtained (section 2.7) and when oxygen concentrations were found to be important in determining products.

The Oxidation of Phosphorus Trichloride.---4.2. Reactions 8, 9, and 10 are proposed for the mechanism of oxidation of phosphorus trichloride alone,<sup>6</sup> with chlorine atoms as chain carriers. Apparently other radicals can also catalyze oxidation of phosphorus trichloride. Section 4.3 explains why reaction 7 is re-quired. The sequence 4, 5, 7 is then analogous to 8, 9, 10, with an alkyl radical replacing a chlorine atom, but the sequence 4, 5, 7 cannot repeat itself frequently with cyclohexane because of competition from reaction 6. It may be more important with some other hydrocarbons (section 5).

Reactions 11, 12, and 14 provide another possible route for the oxidation of phosphorus trichloride. Here, a peroxide radical oxidizes phosphorus trichloride in a chain reaction. Walling and co-workers have supplied precedents for reaction 14 in the reaction of cumyloxy radicals with triethyl phosphite,<sup>18a</sup> of *t*-butoxy radicals with triphenylphosphine<sup>18b</sup> and of mercaptan radicals with phosphines and phosphites.<sup>18b</sup> More recently, Buckler has proposed a sequence closely analogous to 11, 12, 14 for the oxidation of trialkyl-phosphines.<sup>19</sup> The latter sequence may be important in accounting for low yields in the chlorophosphonation of toluene and related hydrocarbons (section 5). Whether reaction 13 excludes or accompanies reaction 14 with cyclohexane is neither clear nor important for our discussion. Table I shows that the maximum conversion of  $0.39 \pm 0.01$  mole of cyclohexane per mole of phosphorus trichloride is obtained as readily with fast oxygen supplies (expt. 61 and 112 where 10-15%of the reacting cyclohexane appeared as cyclohexene) as with limited oxygen supplies (expt. 67, 110, and 115 where only 0-3% of the reacting cyclohexane appeared as cyclohexene). Hence, within experimental error, the relative rates of consumption of phosphorus trichloride and cyclohexane must be about the same in reactions 11-14 as in reactions 3-7. Either the sequence 11-13 leads to this ratio, or else reaction 14 provides the necessary compensation. Reaction 14 can never be a major reaction with cyclohexane because it would require high concentrations of both oxygen (reaction 11) and phosphorus trichloride, which are incompatible.

4.3. Evaluation of  $k_6/k_7$ .—In order to cons der the competition between cyclohexane and phosphorus trichloride for chlorine atoms, it is simpler to keep the oxygen concentration low and thus to minimize reaction 11. Under these conditions, reactions 3-6 and 8-10 lead to the relation

<sup>(13)</sup> C. E. Boozer and R. L. Flurry, Jr., paper presented before the Division of Organic Chemistry at the 138th National Meeting of the American Chemical Society, New York, N. Y., September 15, 1960, Abstracts, p. 82P, report that an initiator is required in very dilute solutions of phosphorus trichloride in an alkane. Our statements are consistent. Cf. also

<sup>(18) (</sup>a) C. Walling and R. Rabinowitz, ibid., 81, 1243 (1959); (b) C. Walling, O. H. Basedow and E. S. Savas, ibid., 82, 2181 (1960) (19) S. A. Buckler, ibid., 84, 3093 (1962).

$$\frac{-\mathrm{d}[\mathrm{PCl}_{3}]}{-\mathrm{d}[\mathrm{C}_{6}\mathrm{H}_{12}]} = \frac{2k_{3}[\mathrm{PCl}_{3}]}{k_{3}[\mathrm{C}_{6}\mathrm{H}_{12}]} + 2$$
(15)

of which the integrated form is

$$\log \frac{[C_{6}H_{12}]_{0}}{[C_{6}H_{12}]} = \frac{1}{\frac{2k_{8}}{k_{3}} - 1} \log \left[ \frac{\left(\frac{2k_{8}}{k_{3}} - 1\right) \frac{[PCl_{3}]_{0}}{[C_{6}H_{12}]_{0}} + 2}{\left(\frac{2k_{8}}{k_{3}} - 1\right) \frac{[PCl_{3}]}{[C_{6}H_{12}]} + 2} \right]$$
(16)

Zero subscripts indicate initial concentrations. Since the final concentration of phosphorus trichloride in most experiments in Table I is zero, the denominator in the log term on the right side of equation 16 is usually 2.

Inspection of the data in Table I suggests why no usable or constant ratio,  $k_8/k_3$ , was obtained. Equation 15 states that every time reaction 8 occurs, two molecules of phosphorus trichloride are oxidized, and that every time reaction 3 occurs, two molecules of phosphorus trichloride and one molecule of cyclohexane are consumed. Therefore, from feeds high enough in cyclohexane, 50% of the phosphorus trichloride should be converted to phosphonyl chloride. However, Table I and Fig. 1, and the discussion below, indicate that the limit is only about 36%, even when by-products are negligible. Reaction 7 is proposed to account for this limit.

To evaluate  $k_6/k_7$ , we have made the following plausible assumptions: (1) Cyclohexane itself reacts only via reactions 3 or 13. (2) Cyclohexanol and cyclohexyl esters formed appear as cyclohexene or in the distillation residue (justified largely by section 2.4). (3) The relative consumptions of phosphorus trichloride and cyclohexane in the side reactions (11–14) are the same as in the main reaction (3–7). This latter assumption is based on limiting conversions of phosphorus trichloride to phosphonyl chloride at high and low concentrations of oxygen (section 4.2). It is unnecessary if we consider only low oxygen experiments.

From these assumptions and the limiting conversions discussed in section 4.2 (0.39 mole of total C<sub>6</sub> in Table I per phosphorus trichloride reacting), 78% of the C<sub>6</sub>H<sub>11</sub>PCl<sub>3</sub>O<sub>2</sub> radicals must react with phosphorus trichloride by reaction 6, 22% by reaction 7, and  $k_6/k_7 = 3.5$ . Thus at least 2.6 moles (1/0.39) of phosphorus trichloride are consumed per phosphorus trichloride reacting, either in the sequence 3–7 or (to a fair approximation) in the sequence 11–14.

Equation 1 therefore becomes

$$\begin{array}{r} C_6H_{12} + 2.6PCl_3 + 1.3O_2 \longrightarrow C_6H_{11}POCl_2 + \\ 1.6POCl_3 + HCl & (3 + 4 + 5 + 6 + 7) \end{array}$$

and 15 and 16 become

$$\frac{-d[PCl_3]}{-d[C_6H_{12}]} = \frac{2k_8[PCl_3]}{k_3[C_6H_{12}]} + 2.6$$
(17)

$$\log \frac{[C_{6}H_{12}]_{0}}{[C_{6}H_{12}]} = \frac{1}{\frac{2k_{8}}{k_{3}} - 1} \log \left[ \frac{\left(\frac{2k_{8}}{k_{3}} - 1\right) \frac{[PCl_{3}]_{0}}{[C_{6}H_{12}]_{0}} + 2.6}{\left(\frac{2k_{8}}{k_{3}} - 1\right) \frac{[PCl_{3}]}{[C_{6}H_{12}]} + 2.6} \right]$$
(18)

4.4. Evaluation of  $k_8/k_3$ .—Section 4.3 shows that the products of reaction at high cyclohexane feeds become independent of the PCl<sub>3</sub>/C<sub>6</sub>H<sub>12</sub> ratio. Such experiments are therefore unsuitable for the determination of  $k_8/k_3$ , and we shall now consider experiments at high phosphorus trichloride feeds. Here the low yields of cyclohexene show that reactions 11–14 are largely eliminated by the high concentration of phosphorus trichloride. On the other hand, the reaction is complicated by formation of mixed diphosphonyl chlorides of cyclohexane. Experiment 81, carried out to 51% reaction (49% remaining) of the phosphorus tri-

chloride, proved to contain 49.3% of the original cyclo-Thus, by a fortunate choice of feed ratios, hexane. the phosphorus trichloride cyclohexane ratio varied only from an initial 10.02 to a final 9.96, and the proportion of disubstitution product was low in comparison with an experiment (60) carried to complete reaction of phosphorus trichloride. The differential equation (17) can therefore be applied. For consistency, we shall employ the assumptions in sections 4.3 and assume that the residues contain mono- and diphosphonyl chlorides and phosphonic anhydrides in the proportions indicated by carbon and phosphorus analyses. When the phosphorus trichloride reacting is corrected for that which appears in disubstitution products,  $k_8/k_3$  is found to be 0.36 by the relation

$$\frac{-\mathrm{d}[\mathrm{PCl}_3]}{-\mathrm{d}[\mathrm{C}_6\mathrm{H}_{10}]} = \frac{0.2800 - 2.6(0.0013 + 0.0016)}{0.0278}$$

 $2 \times 9.99 k_8/k_3 + 2.6$ 

4.5. Test of Equation 18,  $k_6/k_7$  and  $k_8/k_3$ .—In the next-to-last column of Table I, we have calculated how much cyclohexane should have reacted according to eq. 18 (which takes  $k_6/k_7 = 3.5$ ) using the assumptions in section 4.3 and the value  $k_8/k_3 = 0.36$ , derived just above. At an initial  $PCl_3/C_6H_{12}$  ratio of 0.02, the agreement is within experimental error because  $k_6/k_7$  was based solely on such experiments (which are insensitive to  $k_8/k_3$ ). Table I shows that the integrated eq. 18 (which ignores diphosphonyl chlorides) applies well in the incomplete expt. 81 where the proportion of diphosphonyl chloride is low, but that eq. 18 applies poorly in other experiments with an initial excess of phosphorus trichloride when significant proportions of diphosphonyl chlorides are formed. Indeed, eq. 18 predicts that for  $k_8/k_3 = 0.36$ , cyclohexane as well as phosphorus trichloride will be completely exhausted when the initial  $PCl_3/C_6H_{12}$  ratio exceeds 9.28. That the cyclohexane is not exhausted in such experiments is due to its partial protection by its phosphonyl chloride (cf. section 4.6).

Experiments at intermediate initial  $PCl_3/C_6H_{12}$  ratios, 0.50 and 0.10, show agreement within experimental error among the calculated and observed extents of reaction of cyclohexane. Thus, over a 500-fold change in initial  $PCl_3/C_6H_{12}$ , from 0.02 to 10, except for complications due to disubstitution, eq. 18 correlates the competition of the two reactants for a common intermediate, a chlorine atom (or something very closely resembling it in reactivity).

4.6. Substitution of Cyclohexylphosphonyl Chloride.—The previous section indicated that cyclohexylphosphonyl chloride partially protects cyclohexane from substitution. We shall now evaluate K, the relative reactivity of cyclohexylphosphonyl chloride as compared to cyclohexane, toward chlorine atoms. The equation

$$\frac{-d[C_{6}H_{11}POCl_{2}]}{-d[C_{6}H_{12}]} = \frac{k_{3}K[C_{6}H_{11}POCl_{2}] - k_{3}[C_{6}H_{12}]}{k_{3}[C_{6}H_{12}]} = \frac{K[C_{6}H_{12}]}{[C_{6}H_{12}]} - 1 \quad (19)$$

follows from the fact that phosphonyl chloride is being produced steadily by reaction 3.

The integrated form is

$$\log \frac{[C_{6}H_{12}]_{0}}{[C_{6}H_{12}]} = \frac{1}{K-1} \log \frac{\frac{(K-1)[C_{6}H_{11}POCl_{2}]_{0}}{[C_{6}H_{12}]_{0}} - 1}{\frac{[C_{6}H_{12}]_{0}}{[C_{6}H_{12}]} - 1}$$
(20)

The numerator in the log term on the right is simply -1 when  $[C_6H_{11}POCl_2]_0 = 0$ . To apply this equation, we assume that the residue consists of mono- and disubstitution products in the proportions indicated

by their  $C_6/P$  ratios. Equation 20 was solved for K for expt. 31, 81, 60, and 64 in Table I, yielding the respective values 0.36, 0.28, 0.32, and 0.33. Thus cyclohexylphosphonyl chloride is very close to onethird as reactive as cyclohexane toward chlorine atoms.

4.7. Evaluation of  $k_4/k_{11}$ .—On the assumption that 78% of the reactions of cyclohexyl radicals with phosphorus trichloride produce cyclohexylphosphonyl chloride (section 4.3) and that all the reactions of cyclohexyl radicals with oxygen lead by our analytical methods to cyclohexene (sections 2.3, 2.4) we obtain the relation

$$d[C_6H_{11}POCl_2]/d[C_6H_{10}] = 0.78k_4[PCl_3]/k_{11}[O_2] \quad (21)$$

To determine  $k_4/k_{11}$  for any experiment, we use the total moles of phosphonyl chloride (including diphosphonylchloride, if any) and cyclohexene produced, as recorded in Table I, the average number of moles of phosphorus trichloride present (half the initial quantity since the compound is eventually exhausted, except in expt. 81) and the number of moles of oxygen which would be present in a saturated reaction mixture. This quantity is taken as the total of the oxygen which would dissolve in the individual reactants at 760 mm. total pressure for each solution, neglecting any effect of temperature on this solubility. The mole fractions of oxygen in the saturated solutions were taken as 0.00070 in phosphorus trichloride at  $0^{\circ}$  (section 2.8), 0.00143 in cyclohexane at  $25^{\circ}$  (estimated),  $^{20}$  and 0.00115mole fraction in carbon tetrachloride at  $25^{\circ}$ .<sup>20</sup> When air was the source of oxygen, 21% of these values was taken.

Calculated values of  $k_4/k_{11}$  are listed in the last column of Table I. Values are omitted only when cyclohexene was not produced or not determined, when phosphorus trichloride was added slowly to the reaction mixture, or when cyclohexanol was added initially. Values of  $k_4/k_{11}$  range from 0.4 to 2.6, but four out of the five highest values (in parentheses) are obviously associated with experiments with large amounts or proportions of phosphorus trichloride and/or restricted supplies of oxygen, so that the solutions were not saturated with oxygen. All but one (which is unaccounted for) of the remaining twelve experiments give values of  $k_4/k_{11}$  in the range 0.37 to 1.1. They apply to experiments with  $PCl_3/C_6H_{12}$  ratios from 0.02 to 1.00, to two experiments with air instead of oxygen, and to one diluted with 15 volumes of carbon tetrachloride (105). In view of the uncertainties in some determinations of cyclohexene (up to 30%), the difficulties in keeping solutions saturated with oxygen, and the approximations in the solubilities and calculations, this agreement is considered satisfactory. From consideration of oxygen saturation, low values of  $k_4/k_{11}$  are preferred, and the probable value is between 0.4 and 0.6.

That the highest apparent values of  $k_4/k_{11}$  are only 5-6 times the preferred values indicates that the oxygen supply may be depleted below the saturation value, but never below about 15% of the value (on the average). Possibly at low oxygen concentrations, chain initiation and consumption of oxygen slow down until a necessary oxygen concentration can be maintained. Reaction 4 ordinarily outruns reaction 11 because the concentration of phosphorus trichloride is so much greater than the concentration of oxygen.

4.8. Reversibility of Reaction 4: Reaction of Styrene with  $PCl_3 + O_2$ .—Since free radicals react so readily with oxygen, the value of the ratio  $k_4/k_{11} \simeq$ 0.5 indicates an extremely high rate of reaction of cyclohexyl radicals with phosphorus trichloride.

(20) J. H. Hildebrand and R. L. Scott, "Solubility of Non-Electrolytes," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 243.

To account for the exceptionally fast reaction of phosphorus trichloride with free radicals in the presence of oxygen, we propose that reaction 4 is very fast but readily reversible and is completed only when the  $RPCl_3$  radical reacts further:  $R + PCl_3 \rightleftharpoons RPCl_3$ . In our cyclohexane experiments, oxygen was available to react rapidly and irreversibly with RPCl<sub>3</sub> (reaction 5). In our styrene experiments the only reaction available to RPCl<sub>3</sub> in the absence of oxygen, except for decomposition, was the relatively slow reaction with styrene monomer. Qualitative support for this conclusion was obtained from two experiments with 3-4 moles of styrene per mole of phosphorus trichloride, with a generous supply of oxygen at  $0^{\circ}$  in one experiment, and with ABN at 50° and moderate precautions to exclude air in the other. These experiments prove that much more phosphorus (as well as oxygen) was incorporated in the polymer in the presence of oxygen; they suggest that phosphorus trichloride can compete with oxygen for styrene radicals, even though oxygen is at least 10<sup>7</sup> times as reactive as styrene monomer toward such radicals.<sup>21</sup>

The quantitative interpretation of these styrene experiments is beset with so many difficulties that experimental details and calculations are omitted, but the difficulties deserve mention. Moderate precautions to exclude oxygen from styrene-PCl3 mixtures were inadequate and our best product contained more oxygen than phosphorus, averaging (C<sub>8</sub>H<sub>8</sub>)<sub>27</sub>P<sub>1.96</sub>Cl<sub>3.63</sub>O<sub>5.12</sub>. Apparently rigid exclusion of oxygen is necessary at all times between mixing the reactants and analyzing the products.<sup>22</sup> The reaction with oxygen was carried to the end of the fast reaction at 0°. This product apparently contained peroxides and polymerized spontaneously at room temperature. Since reactions 7 and 14 are probably facile for styrene derivatives (section 5), we expected nearly all the phosphorus to be bound to carbon in this reaction product, averaging  $(C_8H_{7.1})_{2.76}P_{1.43}Cl_{3.05}O_{4.11}$ . However, hydrolysis experiments to establish this crucial point have been inconclusive.

These considerations now account for the observations that alkenes react poorly with phosphorus trichloride alone<sup>22</sup> but readily with phosphorus trichloride and oxygen<sup>3a</sup> (section 2.6): the RPCl<sub>3</sub> radical has a fast reaction available in the latter case but not in the former.

Errede and Pearson<sup>23</sup> have shown that p-xylylene copolymerizes with phosphorus trichloride at low temperatures to give a copolymer approaching  $(-CH_2-C_6H_4 CH_2$ -PCl<sub>3</sub>-)<sub>n</sub>. This result also supports our view above that phosphorus trichloride reacts readily with radicals, even rather unreactive ones; but for this reactivity to be effective, the RPCl<sub>3</sub> radical should be offered a reagent approaching another free radical in reactivity, e.g., oxygen or p-xylylene.

#### 5. Conclusions

The exceptionally fast reaction of cyclohexane, phosphorus trichloride, and oxygen to give cyclohexylphosphonyl chloride is satisfactorily accounted for by the mechanism represented by reactions 3-14 in Fig. 3. The essential and novel features are: (1) the spontaneous but not yet elucidated chain initiation by phosphorus trichloride and oxygen,6 (2) the ability of chaincarrying chlorine atoms to attack cyclohexane readily, (3) the ability of phosphorus trichloride to scavenge cy-

(21) F. R. Mayo, J. Am. Chem. Soc., 80, 2465 (1958).
(22) M. S. Kharasch, E. V. Jensen, and W. H. Urry, *ibid.*, 67, 1864 (1945). Their 1-octene-PCls product was identified only by chlorine analysis. The reported chlorine content (41.1%) is closer to that of  $C_8H_{16}$ . POCl<sub>3</sub> (40.0%) than to that of  $C_8H_{16}PCl_3$  (42.6%)

(23) L. A. Errede and W. A. Pearson, ibid., 83, 954 (1961).

clohexyl radicals before they react with oxygen, and (4)the utilization of oxygen to oxidize trivalent phosphorus and regenerate chlorine atoms. By suitable adjustment of concentration of oxygen and phosphorus trichloride, the reaction has been diverted so that 68% of the cyclohexane reacting was converted to cyclohexyl esters (section 3). Graf<sup>4</sup> reported the formation of substantial proportions of EtOPOCl<sub>2</sub> as well as of EtPOCl<sub>2</sub> from the liquid phase reaction of ethane, phosphorus trichloride, and oxygen under superatmospheric pressure at 0 to 40°, but not at atmospheric pressure at  $-75^{\circ}$ . He ascribed the increasing yields of ester with increasing temperatures to the effect of temperature. However, the higher reaction temperatures were maintained by faster supplies of oxygen, and it now seems that he was observing an effect of oxygen concentration rather than of temperature.

The limiting conversion of phosphorus trichloride to cyclohexylphosphonyl chloride is about 36% over a wide range of feed ratios which contain excess cyclohexane. Here, reaction 2 is largely eliminated and the limit is apparently set by reaction 7.

Competition between reactions 6 and 7 now accounts for several puzzling results in the literature on the chlorophosphonation of hydrocarbons. When the alkyl group has considerable resonance stabilization, then the alkyl group is lost more easily than the chlorine atom and reaction 7 predominates. Thus the alkyl group acts as a catalyst for the oxidation of phosphorus trichloride and conceivably may react several times through the sequence 4, 5, 7, with little net change. When the alkyl group has little resonance stabilization, then the chlorine atom is released and reaction 6 predominates. Jensen and Noller<sup>2c</sup> report that toluene gave only 13% yield of benzylphosphonyl chloride; that ethylbenzene gave 11% of  $\beta$ -phenethylphosphonyl chloride and none of the  $\alpha$ -isomer; that diphenylmethane gave only 2% of substitution product, and that triphenylmethane did not react. Lesfauries and Rumpf<sup>24</sup> report that tetralin reacts to give only one product, apparently the  $\beta$ -phosphonyl chloride. All of these results suggest that benzyl radicals undergo reaction 7 readily and that secondary and tertiary benzyl radicals undergo reaction 7 exclusively, while  $\beta$ -tetralyl and  $\beta$ -phenethyl radicals favor reaction 6.

Those radical properties which favor reaction 7 should also favor reaction 14. Indeed, if benzyl radicals are relatively more reactive than alkyl radicals toward oxygen (section 4.8), then reaction 14 rather than reaction 7 may account for the low yields of benzylphosphonyl chlorides.

The present work suggests that phosphorus trichloride, and perhaps many other trivalent phosphorus compounds, may be excellent scavengers for free radicals, as good as oxygen or iodine, but that to take advantage of this reaction, a scavenger for  $RPX_3$  radicals is necessary.

Acknowledgment.—Prof. Cheves Walling and Prof. C. E. Boozer have contributed to useful discussions of this problem. Prof. Boozer was the first to suggest an effect of oxygen pressure in chlorophosphonation Dr. Dale VanSickle carried out the chlorophosphonations at superatmospheric pressure. Mrs. Niki Ferguson carried out experiment 84 at low temperature. Miss K. C. Crawford assisted with the styrene experiments.

(24) P. Lesfauries and P. Rumpf, Bull. soc. chim., 542 (1950).

[CONTRIBUTION FROM THE RESEARCH CENTER OF THE SPRAGUE ELECTRIC CO., NORTH ADAMS, MASS.]

# Displacement Reactions on Silicon. The Reaction of 2-Propanol with Chlorotriphenylsilane in Carbon Tetrachloride

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RECEIVED APRIL 25, 1963

The rates of reaction of 2-propanol with chlorotriphenylsilane have been measured in carbon tetrachloride at 24.8° with and without added benzyltriethylammonium chloride. The observations indicate that in the absence of the salt the reaction proceeds only through autocatalysis by associated HCl. This is further interpreted to support the concept of a pentavalent silicon intermediate. Apparent catalysis observed with the added salt is attributed to uncatalyzed attack by associated benzyltriethylammonium isopropoxide.

A number of basic questions with respect to the mechanism of nucleophilic displacements on organosilicon halides are still incompletely resolved. One of the questions is whether these reactions involve an intermediate with pentacovalent silicon or proceed by an SN2 mechanism with synchronous bond-making and bond-breaking. Another pertains to the kinds of catalysis that operate in these reactions.

Swain, Esteve, and Jones<sup>1</sup> studied the hydrolysis of triphenylsilyl fluoride in 50% aqueous acetone and proposed that an intermediate was involved. The pertinent considerations were that the fluoride reacts with hydroxide ion  $10^6$  times as fast as with water, that the reaction with water was retarded by *p*-methyl substituents but accelerated by both neutral salts and increasing polarity of medium, and that triphenylsilyl chloride is much more reactive than the fluoride. Hughes, however, suggested<sup>2</sup> that these observations are equally consistent with a modified SN2 mechanism in which bond-making influences are dominant.

(1) C. G. Swain, R. M. Esteve, Jr., and R. H. Jones, J. Am. Chem. Soc., 71, 965 (1949).

This latter position was supported by Allen, *et al.*,<sup>3,4</sup> after a detailed kinetic study of the reactions of several trisubstituted silyl chlorides with alcohols and water in a variety of solvents. The reactions were facilitated by increasing polarity of the medium, and in some, but not all, cases a high order with respect to the hydroxylic reagent was observed. When the concentration of the hydroxylic reagent was low, both autocatalysis and strong catalysis by added chloride salts were noted.

The aforementioned studies included measurements of the rates of hydrolysis of chlorotriphenylsilane in both nitromethane and dioxane at  $25.1^{\circ}$ . These determinations were complicated by the high reactivity of the substrate, the occurrence of autocatalysis, and a significant reverse reaction. The combination of these factors necessitated the measurement of initial rates by extrapolation to zero time.

Such extrapolations can introduce major uncertainties, particularly in cases where the instantaneous

<sup>(2)</sup> E. D. Hughes, Quart. Rev. (London), 5, 245 (1951).

<sup>(3)</sup> A. D. Allen, J. C. Charlton, C. Eaborn, and G. Modena, J. Chem. Soc., 3668 (1957).

<sup>(4)</sup> A. D. Allen and G. Modena, *ibid.*, 3671 (1957).