# The Mechanism of the Chlorophosphonation of Hydrocarbons by Phosphorus Trichloride and Oxygen[1a]

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The chlorophosphonation of hydrocarbons and the oxidation of phosphorus trichloride have been studied. All of the evidence supports the hypothesis that the chlorophosphonation reaction is a competing side reaction of the phosphorus trichloride oxidation. The reaction was found not to be spontaneous if sufficient purity of reagents was attained. A mechanism for both chlorophosphonation and phosphosphorus trichloride oxidation is proposed which satisfactorily explains all the observed phenomena.

Since its discovery,[2] the apparent spontaneous reaction of phosphorus trichloride, oxygen, and hydrocarbons to give alkylphosphonyl dichlorides and phosphorus oxychloride has received much attention as a preparative method for alkylphosphonyl dichlorides.

$$2PCl_3 + O_2 + RH \longrightarrow RPOCl_2 + POCl_3 + HCl$$

There has been a considerable amount of work done to determine the experimental limitations of the reaction. With the exception of the work of Mayo,[3] very little attention has been paid to its exact mechanism, or to the mechanism of the competing oxidation of phosphorus trichloride.

$$2PCl_3 + O_2 \longrightarrow 2POCl_3$$

The present work is an investigation of both of these reactions through kinetic and product studies.

## Experimental Section

**Apparatus.**—The kinetics of oxygen uptake in the reaction were studied in the previously described apparatus.[4]

The runs for product analysis were carried out by connecting a jacketed reaction flask to a large reservoir in which the oxygen pressure could be adjusted to the desired value. A Dry Ice condenser was placed above the reaction vessel to prevent loss of materials by evaporation.

Water, thermostated to within ±0.05°, was continuously circulated through the thermostating jackets. All runs were carried out using 10 ml of solvent, hydrocarbon, or solvent–hydrocarbon mixture. The reaction appeared to be diffusion controlled if the concentration of phosphorus trichloride was greater than approximately 0.1 *M*, as was evidenced by the fact that initial portions of more concentrated runs gave apparent zero-order kinetics.

**Analysis.**—The relative amounts of phosphorus oxychloride and alkylphosphonyl dichloride present in the reaction mixture were determined by comparing the areas under the peaks corresponding to their respective phosphorus–oxygen stretch frequencies from infrared spectra of the mixture. From a spectrum of a known mixture it was found that the extinction coefficient of phosphorus oxychloride was approximately 1.04 times that for the phosphonyl dichloride. Since only the relative amounts were desired, no attempt was made to obtain the actual concentration. The spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer.

From the results of ref 2, it appears possible that from 10 to 20% of the $PCl_3$ in the preparative runs may have reacted in a side reaction to form an ester, $ROPOCl_2$. The P–O peak for this should occur about half way between that for the phosphorus oxychloride and for the phosphoryl dichloride[5] and could easily have been obscured by them. To the extent that this occurred, the absolute yields reported for the phosphonyl dichloride would be decreased. The over-all conclusions reported should not be affected, however, since they are based on the final $RPOCl_2/POCl_3$ ratio.

The reaction mixture from the direct reaction of *t*-butyl hydroperoxide and $PCl_3$ in the absence of oxygen was analyzed for alkyl chlorides by gas chromatography. Their presence was confirmed by absolute retention time and by the chromatogram of an enriched sample over both a silicone and a Carbowax column. There was no indication that detectable amounts of these were formed when the hydroperoxide was used in catalytic amounts.

**Reagents.**—The carbon tetrachloride employed was Baker Analyzed grade, further purified as described by Fieser.[6] It was stored under a dry nitrogen atmosphere in an all-glass container containing Drierite and silica gel to remove traces of water and hydroperoxides. The container was constructed in such a way that it could be flushed with dry nitrogen as portions were being withdrawn. All transferring of carbon tetrachloride was accomplished with hypodermic syringes.

The phosphorus trichloride used was Baker Analyzed reagent grade. It was purified by refluxing for 2.5 hr over raw linseed oil under a dry nitrogen atmosphere. After refluxing, it was distilled under nitrogen through a 36-in. glass packed column. Storage was under a nitrogen atmosphere in vessels similar to those used for carbon $CCl_4$. All transfers were made with glass pipets.

The fact that an initiator was removed by this process, rather than an inhibitor being produced, is demonstrated by the clean first-order dependence of the rate on AIBN initiator concentration. The apparent rate constants so obtained extrapolate to zero for zero AIBN concentration (Figure 1). There is also no apparent inhibition period in these AIBN-catalyzed reactions.

The *t*-butyl hydroperoxide used was from K and K Laboratories. It was distilled through a glass column at reduced pressure and stored in an all glass container at 0°. This was diluted to 0.1 *M* with carbon tetrachloride for a stock solution.

The AIBN employed was also from K and K Laboratories. It was further purified by recrystallization from benzene. A 0.25 *M* stock solution was made up in chlorobenzene.

The 2,3-dimethylbutane used in kinetic runs was from Matheson and was further purified by distillation under dry nitrogen and stored under a positive pressure of nitrogen over Drierite and silica gel in a sealed vessel. Withdrawals were accomplished through a fluorocarbon-coated rubber septum with a hypodermic needle.

The cyclohexane used in the preparative runs was Eastman White Label grade used without further purification.

The iodine employed was from Eimer and Amend, used without further purification.

The nitrogen, under which the reagents were stored, was passed through a train consisting of a copper, cupric ammonium solution, a sulfuric acid solution, and a drying tower.

The oxygen employed was U.S.P. grade, which was passed through a Drierite-packed column before using to remove traces of moisture.

**Cyclohexylphosphonyl Dichloride.**—Cyclohexylphosphonyl dichloride, for comparison with the reaction products, was pre-

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(1) (a) Taken from a thesis presented by R. L. F. in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Emory University, Aug 1961. Presented in part by C. E. B. at the 138th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1960. (b) To whom inqueries should be addressed: Department of Chemistry, Louisiana State University in New Orleans, New Orleans, La. 70122.

(2) (a) J. O. Clayton and W. L. Jensen, *J. Am. Chem. Soc.*, **70**, 3880 (1948); (b) L. F. Sobrovskii, Yu. M. Zinov'ev, and M. A. Englin, *Dokl. Akad. Nauk SSSR*, **67**, 293 (1949); (c) R. Graf, *Chem. Ber.*, **85**, 9 (1952).

(3) F. R. Mayo, L. J. Durham, and K. G. Griggs, *J. Am. Chem. Soc.*, **85**, 3156 (1963).

(4) M. B. Floyd and C. E. Boozer, *ibid.*, **85**, 984 (1963).

(5) C. E. Griffin, *Chem. Ind.* (London), 1058 (1960).

(6) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1955, p 283.

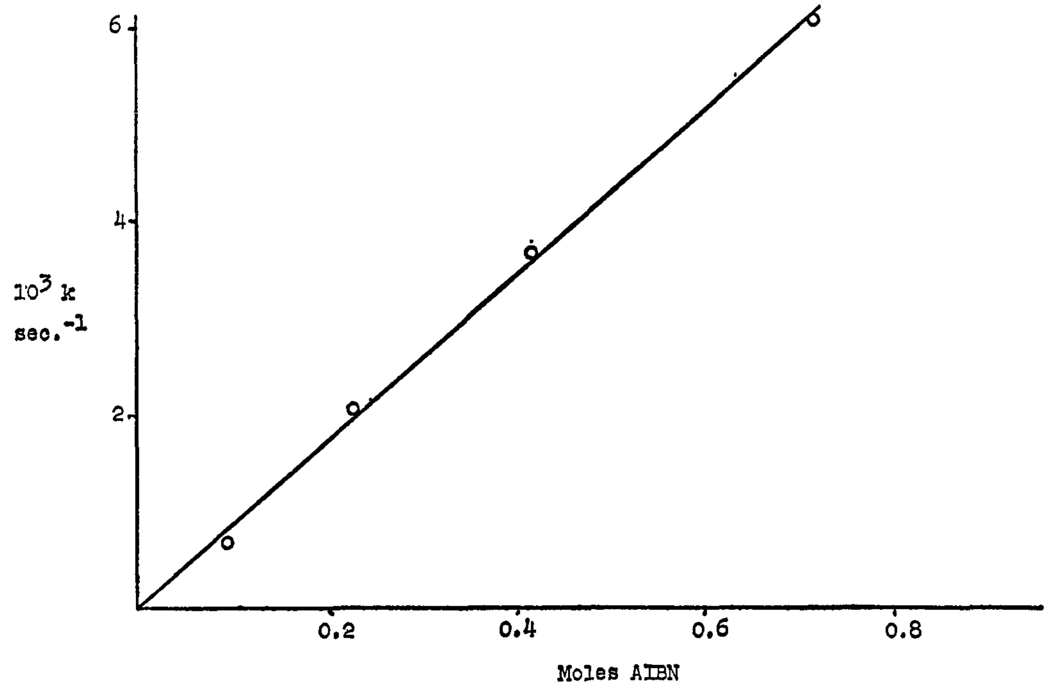

Figure 1.—Rate of $PCl_3$ oxidation *vs.* AIBN concentration; 5.1 × $10^{-2}$ *M* $PCl_3$ in 10 ml of $CCl_4$ at 45°.

pared by the method of Kinnear and Perren[7] [bp 105–108° (3 mm), lit. bp 90° (1 mm); dianilide mp 228–230°, lit. mp 229–230°].

**Treatment of Kinetic Data.**—Swinbourne's method[8] was applied to the kinetic data to determine the total amount of oxygen consumed in a reaction. This was then used with the usual logarithmic method for determining first-order rate constants.

Figure 2 presents a typical kinetic run for AIBN-catalyzed phosphorus trichloride oxidation. Figure 3 presents a similar plot for a hydroperoxide-catalyzed run.

**Cleaning of Glassware.**—All glassware used was first cleaned in a chromic acid bath. It was then rinsed well in the sequence water, ammonium hydroxide, water, and distilled water and dried in an oven at 130°.

## Results and Discussion

**Oxidation of Phosphorus Trichloride.**—In early experiments it was found that the rate of the phosphorus trichloride oxidation was very dependent on the purity of the solvent and reagents. In the presence of any slight impurities, the reaction was spontaneous and very rapid. The rates obtained from addition of successive aliquots of phosphorus trichloride to the same reaction mixture were slower for each sample, indicating either that an initiator was being used up or that a retarder was being formed. The first postulate was verified when the spontaneous initiation could be removed by rigorous purification of the reagents. Using the carefully purified reagents, 10-ml reaction mixtures containing 50% phosphorus trichloride in carbon tetrachloride did not take up a significant amount (~10% of theoretical) of oxygen in 2 hr. The addition of 0.1 μmole of *t*-butyl hydroperoxide gave sufficient initiation to cause the reaction to go to completion within 30 min. Azobisisobutyronitrile (AIBN) was also found to be an effective initiator at higher concentrations and higher temperatures.

The hydroperoxide-initiated reactions were very sensitive to impurities, and reproducible rates were difficult to obtain. The AIBN-initiated reactions were much less sensitive and more easily reproducible, but the AIBN solutions had to be freshly prepared. Old solutions of AIBN initiated the reaction much more effectively, apparently owing to hydroperoxide formation from the AIBN in contact with air.

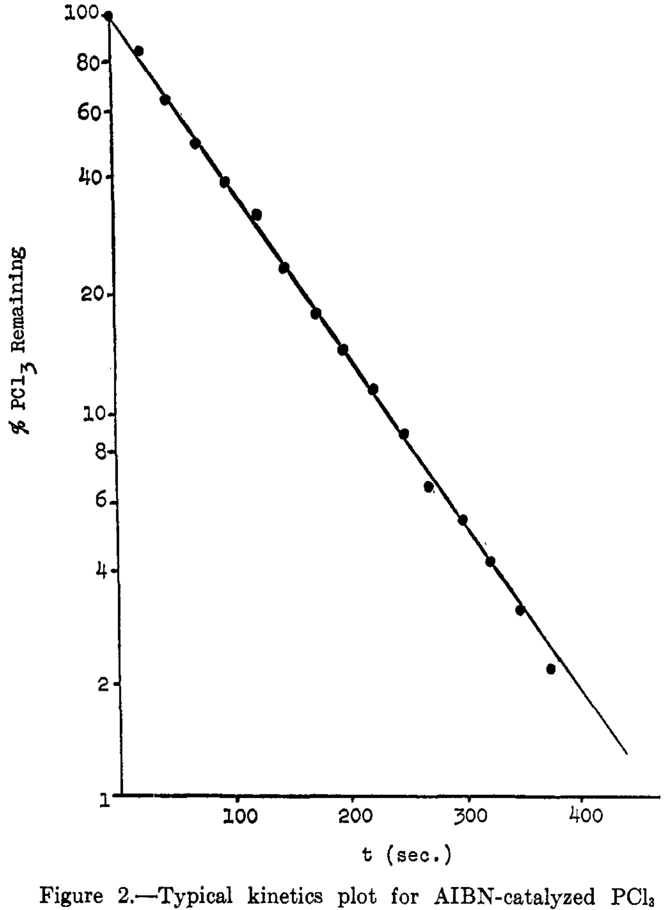

Figure 2.—Typical kinetics plot for AIBN-catalyzed $PCl_3$ oxidation; 2.27 × $10^{-3}$ *M* AIBN and 5.1 × $10^{-2}$ *M* $PCl_3$ in 10 ml of $CCl_4$ at 45°.

[7] A. M. Kinnear, and E. A. Perren, *J. Chem. Soc.*, 3437 (1952).

[8] E. S. Swinbourne, *ibid.*, 2371 (1960).

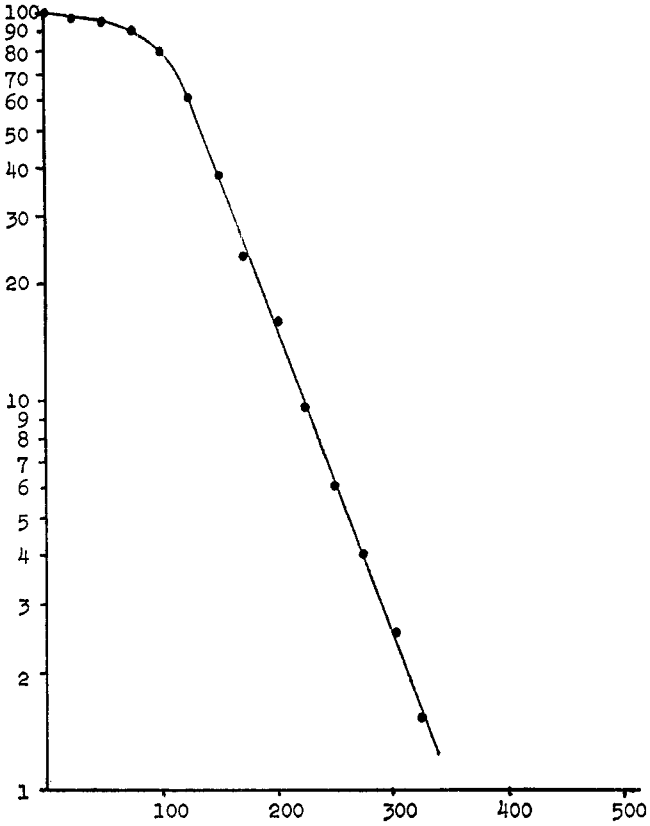

Figure 3.—Typical kinetics plot for *t*-butylhydroperoxide-catalyzed $PCl_3$ oxidation; $1 \times 10^{-4}$ *M* ROOH and $5.1 \times 10^{-2}$ *M* $PCl_3$ in 10 ml of $CCl_4$ at 25°.

The reactions were cleanly first order in phosphorus trichloride to >90% completion for dilute solutions (<0.1 *M*) (Figure 2). The first portion of the reaction in the more concentrated solutions gave apparent zero-order kinetics, owing to being limited by rate of diffusion of oxygen into solution. The later portion was cleanly first order for concentrations up to at least 50% $PCl_3$. The reactions were also first order in hydroperoxide concentration below hydroperoxide to $PCl_3$ ratio of $2.6 \times 10^{-3}$ and appeared to approach zero order above this concentration ratio (Figure 4). Induction periods were observed under these conditions which were inversely proportional to the hydroperoxide concentration over the concentration range studied (Figure 5).

Sulfur and iodine were found to be efficient inhibitors of both the hydroperoxide- and AIBN-catalyzed reactions. The iodine inhibition was studied in detail. Induction periods were obtained which were directly proportional to the iodine concentration as shown in Figure 6. The intercept for zero iodine concentration was the same as the normal induction period for the concentration of hydroperoxide used. From the inhibition periods, it was possible to deduce the kinetic chain length. With 0.051 mole of $PCl_3$ and $1 \times 10^{-4}$ mole of *t*-butyl hydroperoxide in 10 ml of carbon tetrachloride at 25°, the chain length was $7.1 \times 10^3$. The corresponding value for AIBN initiation at 45° was $4.5 \times 10^3$ with 0.0417 *M* AIBN and 0.102 *M* $PCl_3$. Extrapolation of an independent measure of the rate of initiation with AIBN in $CCl_4$[9] permits the calculation of a chain length of $4.4 \times 10^3$ under similar conditions. The initiation constants, obtained in the standard manner from inhibition periods, were $5.9 \times 10^{-4}$ sec$^{-1}$ for hydroperoxide at 25° and $5.3 \times 10^{-7}$ sec$^{-1}$ for AIBN at 45°. Extrapolation of the data from ref 9 to 45° yields a value of $5.4 \times 10^{-7}$ for the AIBN initiation constant.

The necessity of an initiator, the independence of the rate constants on $PCl_3$ concentration (Table I, column 5), and the direct dependence of the inhibition period on the inhibitor concentration (Figure 6) are taken as evidence that the autoxidation of $PCl_3$ is not spontaneous. The initiation process with hydroperoxides is obviously complicated; however, there is evidence for the following sequence, followed by reaction 1 of Chart I.

$$PCl_3 + ROOH \longrightarrow PCl_2OOR + HCl$$
$$PCl_2OOR \longrightarrow PCl_2O\cdot + RO\cdot$$

(The most important reactions for both phosphorus trichloride oxidation and chloro-

CHART I
CHLOROPHOSPHONATION

| | | |
|---|---|---|
| Initiation | $\text{initiator} \xrightarrow{k_i} 2RO\cdot$ | |
| | $RO\cdot + PCl_3 \xrightarrow{k_1} ROPCl_2 + Cl\cdot$ | (1) |
| Phosphorus trichloride oxidation | $Cl\cdot + PCl_4 \xrightarrow{k_2} \dot{P}Cl_4$ | (2) |
| | $\dot{P}Cl_4 + O_2 \xrightarrow{k_3} PCl_4OO\cdot$ | (3) |
| | $PCl_4OO\cdot + PCl_3 \xrightarrow{k_4} 2POCl_3 + Cl\cdot$ | (4) |
| Chlorophosphonation | $Cl\cdot + RH \xrightarrow{k_5} R\cdot + HCl$ | (5) |
| | $R\cdot + PCl_3 \xrightarrow{k_6} R\dot{P}Cl_3$ | (6) |
| | $R\dot{P}Cl_3 + O_2 \xrightarrow{k_7} RPCl_3OO\cdot$ | (7) |
| | $RPCl_3OO\cdot + PCl_3 \xrightarrow{k_8} RPOCl_3 + POCl_3 + Cl\cdot$ | (8) |
| Competing reactions | $R\cdot + O_2 \xrightarrow{k_9} ROO\cdot$ | (9) |
| | $ROO\cdot + PCl_3 \xrightarrow{k_{10}} RO\cdot + POCl_3$ | (10) |
| | $RO\cdot + RH \xrightarrow{k_{11}} ROH + R\cdot$ | (11) |
| Possible termination[a] | $\dot{P}Cl_4 + \dot{C}l \xrightarrow{k_{12}} PCl_3 + Cl_2$ | (12) |

[a] There are several other possible termination steps in the sequence.

TABLE I
EFFECT OF VARIABLES ON THE RATES OF THE HYDROPEROXIDE-CATALYZED REACTION OF $PCl_3$ WITH OXYGEN IN $CCl_4$ AT 25°[a]

| Initiator concn ($\times 10^5$), moles/l. | $p_{O_2}$,[b] mm | $(p_{O_2})^{1/2}$ | $k_{obsd} \times 10^3$ sec$^{-1}$ | $k_p/k_t$[c] |
|---|---|---|---|---|
| 2.5 | 635 | 25.2 | 2.15 | $2.89 \times 10^3$ |
| 5.0 | 635 | 25.2 | 4.46 | $3.00 \times 10^3$ |
| 7.5 | 635 | 25.2 | 6.50 | $2.91 \times 10^3$ |
| 10.0 | 635 | 25.2 | 8.57 | $2.88 \times 10^3$ |
| | | | Av | $2.92 \times 10^3$ |
| 10[d] | 635 | 25.2 | 7.90 | $2.66 \times 10^3$ |
| 10 | 552 | 23.5 | 7.35 | $2.65 \times 10^3$ |
| 10 | 388 | 19.7 | 6.30 | $2.71 \times 10^3$ |
| | | | Av | $2.67 \times 10^3$ |

[a] $5.1 \times 10^{-4}$ mole of $PCl_3$ in 10 ml of $CCl_4$. [b] Corrected for solvent vapor pressure. [c] Obtained from eq 16 using the experimentally determined $k_i$ ($5.9 \times 10^{-4}$ sec$^{-1}$) and partial pressure of oxygen expressed in millimeters. [d] In these runs $5 \times 10^{-8}$ mole of $I_2$ was added to allow pressure equilibrium before the reaction started.

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(9) G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Am. Chem. Soc.*, **77**, 3244 (1955).

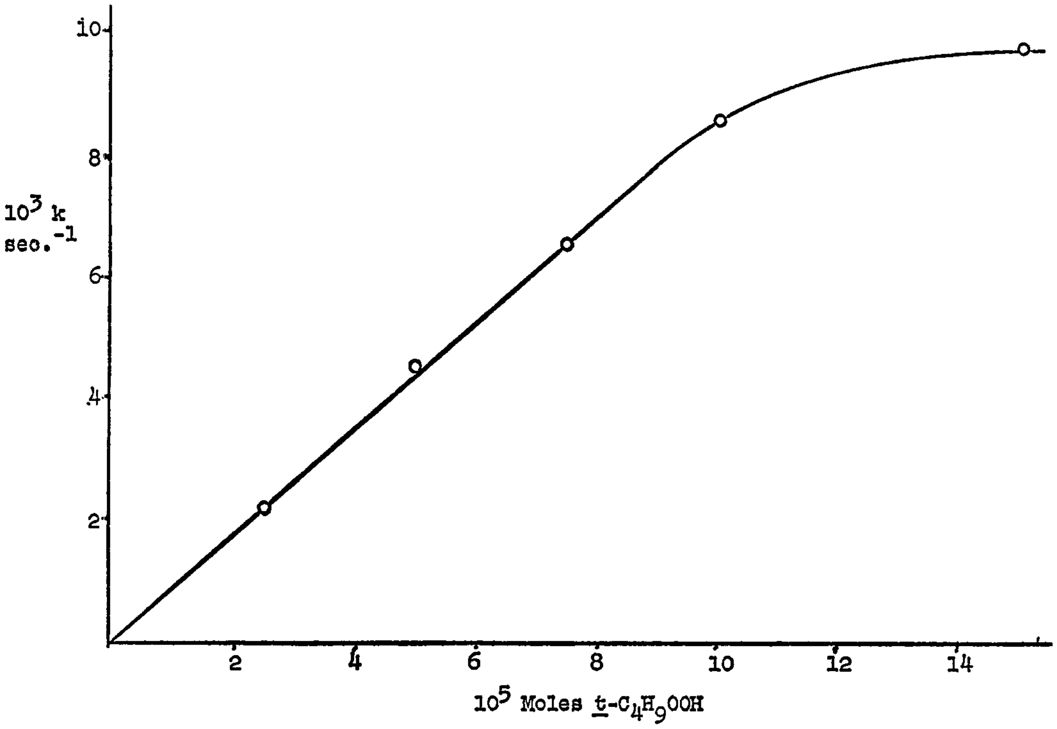

**Figure 4.**—Rate of $PCl_3$ oxidation *vs.* hydroperoxide concentration; 5.1 × $10^{-2}$ *M* $PCl_3$ in 10 ml of $CCl_4$ at 25°.

phosphonation are listed in Chart I. Other reactions in the text are numbered sequentially above 12.) Evidence for step 1 comes from the fact that phosphite esters are produced in the direct reaction of di-*t*-butylperoxide and $PCl_3$.

The reaction of $PCl_3$ (0.01 mole) and *t*-butyl hydroperoxide (0.005 mole) in $CCl_4$ (10 ml) in the absence of oxygen gave $POCl_3$ (~70% of $PCl_3$ by infrared analysis), phosphorus esters (~20% of $PCl_3$), and *t*-butyl chloride[10] [~50% of hydroperoxide by vapor phase chromatography (vpc)]. The reaction of $PCl_3$ (0.01 mole) with di-*t*-butylperoxide (0.01 mole) at 125° in a sealed tube gave very little $POCl_3$ (~10% of $PCl_3$). Phosphite esters were identified by the P–O–C band in the infrared spectrum of the reaction mixture. The volatile products were mostly acetone and *t*-butylchloride (~61% and 28% of the initial peroxide by vpc).

That the reaction $RO\cdot + PCl_3 \rightarrow POCl_3 + R\cdot$ is unlikely is evidenced by the very small amounts of $POCl_3$ formed in the reaction. The esters could not have been formed *via* the alcohol since it is known that *t*-butyl alcohol reacts with $PCl_3$ to give only the alkyl chloride.[10]

The addition of pentavalent phosphorus halides to the hydroperoxide-catalyzed reaction ($PCl_5$, $POCl_3$, $RPOCl_2$, etc.) eliminated the induction period and accelerated the rates. These reactions were first order in added phosphorus oxychloride, but were also subject to the leveling off effect (Figure 7). Essentially the same results were found for added $PCl_5$ and $RPOCl_2$.

Pentavalent phosphorus halides react with hydroperoxides about 100 times as fast as do trivalent phosphorus halides;[11] therefore, as phosphorus oxychloride is formed in the reaction it would be expected to replace $PCl_3$ in the initiation sequence. The $PCl_2O\cdot$

$$POCl_3 + ROOH \longrightarrow POCl_2OOR + HCl \qquad (13)$$

$$POCl_2OOR \longrightarrow POCl_2O\cdot + RO\cdot \qquad (14)$$

and $POClO_2\cdot$ radicals may start more chains by reacting analogous to step 1. The $POCl_3$ initiation sequence would account for the apparent induction periods with hydroperoxide catalysis (Figure 5) and is in accord with the rate dependence on $POCl_3$ (Figure 6). The leveling off effect of the rate dependence, both on hydroperoxide concentration (Figure 4) and on $POCl_3$ concentration (Figure 7), is probably due to a change in the rate-determining step from step 13 to step 14.

The dependence on AIBN concentration was similar to that for hydroperoxide, but these reactions did not

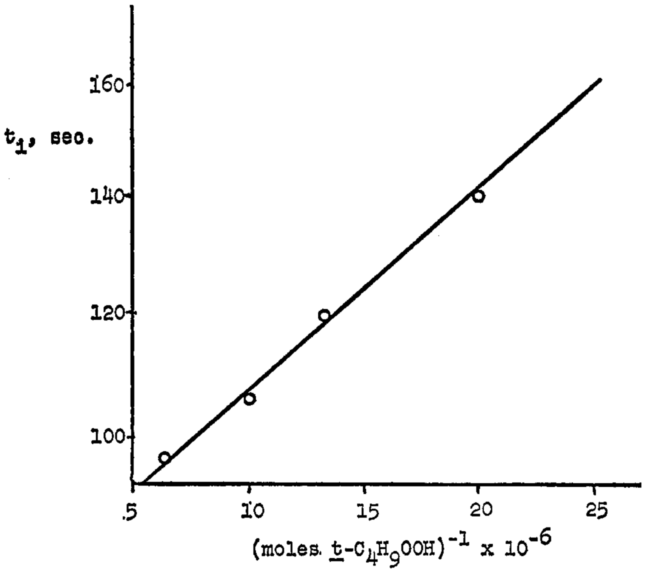

Figure 5.—Variation of induction period in $PCl_3$ oxidation with inverse hydroperoxide concentration; 5.1 × $10^{-2}$ *M* $PCl_3$ in 10 ml of $CCl_4$ at 25°.

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[10] Presumably arising from *t*-butyl alcohol since phosphorus trichloride quantitatively converts *t*-butyl alcohol to the chloride: C. R. Noller, "Textbook of Organic Chemistry," 2nd ed, W. B. Saunders Co., Philadelphia, Pa., 1958, p 70.

[11] B. Gehauf, *et al.*, *Anal. Chem.*, **29**, 278 (1957).

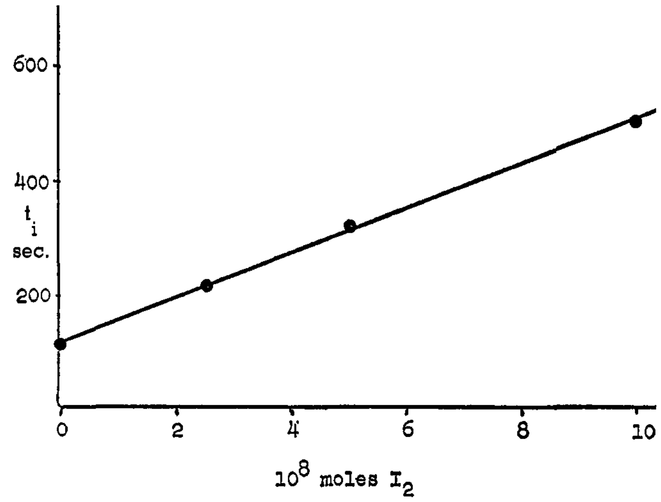

Figure 6.— Dependence of induction periods in $PCl_3$ oxidation on iodine concentration; $5.1 \times 10^{-2}$ *M* $PCl_3$ and $1 \times 10^{-4}$ *M* $t\text{-}C_4H_9OOH$ in 10 ml of $CCl_4$ at 25°.

exhibit the induction periods or the leveling off effect on increasing concentration over the concentration range studied (Figure 1). Added pentavalent phosphorous compounds had no apparent effect on the AIBN-catalyzed reaction.

When AIBN is used, the initiation process may be depicted as is shown in the following sequence.

$$\text{AIBN} \longrightarrow 2\text{R}\cdot + N_2$$

$$\text{R}\cdot + O_2 \longrightarrow \text{ROO}\cdot$$

$$\text{ROO}\cdot + PCl_3 \longrightarrow \text{RO}\cdot + POCl_3$$

The RO· may then enter into step 1 to produce a chlorine radical. The alternative attack of the alkyl radical directly on $PCl_3$ would be a competing route leading to the same results as indicated by the proposed chlorophosphonation sequence in eq 6–8. Either sequence accounts for the absence of induction periods and the lack of dependence on $POCl_3$ concentration in AIBN-initiated reactions. The third of the above reactions is probably the mode of formation of the $POCl_3$ in the oxygen-free reaction of hydroperoxides and $PCl_3$. The peroxy radical would come from an induced decomposition[12] of the hydroperoxide in the more concentrated solution used for product analysis.

The dependence on oxygen pressure was tested. It was found that the rate of the reaction varied approximately with the square root of the oxygen pressure with hydroperoxide initiator (Table I). The dependence changed to the approximately first power of the oxygen pressure with AIBN initiation (Table II). (The actual observed order over the range studied was 0.85. This is probably not a significant deviation from unity.)

The apparent over-all activation energy for the hydroperoxide initiated oxidation of $PCl_3$, obtained from the variation of rate with temperature, was about 0.23 kcal/mole. This was derived from the data in Table III, making use of eq 16 to compensate for the difference in partial pressure of oxygen at the two temperatures.

TABLE II

EFFECT OF VARIABLES ON THE RATES OF AIBN-CATALYZED REACTIONS OF $PCl_3$ WITH $O_2$ AT 45°[a]

| (AIBN) × $10^2$ moles/l. | Solvent | $p_{O_2}$,[b] mm | $k_{obsd} \times 10^3$ sec$^{-1}$ | $k_p/k_t$[c] |
|---|---|---|---|---|
| 0.96 | $CCl_4$ | 464 | 0.67 | $1.41 \times 10^2$[d] |
| 2.27 | $CCl_4$ | 464 | 2.07 | $1.85 \times 10^2$ |
| 4.17 | $CCl_4$ | 464 | 3.70 | $1.80 \times 10^2$ |
| 7.15 | $CCl_4$ | 464 | 6.10 | $1.73 \times 10^2$ |
| | | | Av | $1.79 \times 10^2$ |
| 4.17 | Benzene | 520 | 2.32 | $1.01 \times 10^2$ |
| 7.15 | Benzene | 520 | 4.10 | $1.04 \times 10^2$ |
| 8.35 | Benzene | 520 | 4.75 | $1.03 \times 10^2$ |
| | | | Av | $1.03 \times 10^2$ |
| 5.00 | $CCl_4$ | 462 | 4.29 | $1.75 \times 10^2$ |
| 5.00 | $CCl_4$ | 301 | 2.93 | $1.83 \times 10^2$ |
| 5.00 | $CCl_4$ | 130 | 1.45 | $2.10 \times 10^2$ |
| | | | Av | $1.89 \times 10^2$ |

[a] $1.02 \times 10^{-3}$ mole of $PCl_3$ in 10 ml of solution. [b] Corrected for solvent vapor pressure. [c] Obtained from eq 15 using the experimentally determined $k_1$ ($5.3 \times 10^{-7}$ sec$^{-1}$) and the partial pressure of oxygen expressed in millimeters. [d] Not included in average.

TABLE III

TEMPERATURE DEPENDENCE OF HYDROPEROXIDE-CATALYZED REACTIONS[a]

| Initiator concn (× $10^5$), moles/l. | 25° $p_{O_2}$, mm | 25° $(p_{O_2})^{1/2}$ | 25° $k_{obsd} \times 10^3$ sec$^{-1}$ | 40° $p_{O_2}$, mm | 40° $(p_{O_2})^{1/2}$ | 40° $k_{obsd} \times 10^3$ sec$^{-1}$ |
|---|---|---|---|---|---|---|
| 2.0 | 635 | 25.2 | 2.00 | 515 | 22.7 | 2.61 |
| 5.0 | 635 | 25.2 | 4.46 | 515 | 22.7 | 5.77 |
| 7.5 | 635 | 25.2 | 6.50 | 515 | 22.7 | 8.57 |

[a] $5.1 \times 10^{-4}$ mole of $PCl_3$ in 10 ml of $CCl_4$.

The proposed propagation sequence, steps 2–4, employing chlorine as the chain carrier, is based on the solvent effect on the chlorophosphonation yield and the similarity of the chlorophosphonation isomer distribution[13] to that of free-radical chlorination,[14] This is in agreement with the conclusions of Mayo.[3] The inhibition by iodine and sulfur is consistent with a chlorine radical chain carrier.[15]

The termination step is the most difficult to determine. There is some spectroscopic evidence that traces of chlorine are formed during the reaction. Also, vapors above the reaction mixture give a positive starch–iodine test. Neither of these are conclusive, however. Equation 12 represents one of many possible termination steps. The first-order dependence on initiator concentration generally implies a unimolecular termination step;[16] however, in some such instances a bimolecular termination has been postulated.[17]

A complete kinetic equation could not be derived from the postulated reaction mechanism owing to lack of knowledge of the exact termination step. However, the empirical kinetic equations are, for AIBN catalysis, eq 15 or, for hydroperoxide catalysis, eq 16.

$$\text{rate} = \frac{-dPCl_3}{dt} = k_{obsd}\,(\text{AIBN})(PCl_3)(O_2) \qquad (15)$$

$$\text{rate} = \frac{-dPCl_3}{dt} = k_{obsd}\,(\text{ROOH})(POCl_3)(O_2)^{1/2} \qquad (16)$$

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[12] F. H. Seubold, Jr., F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **73**, 18 (1951).

[13] G. Geiseler, F. Asinger, and M. Fedtke, *Chem. Ber.*, **93**, 765 (1960).

[14] C. Walling and M. F. Mayahi, *J. Am. Chem. Soc.*, **81**, 1485 (1959).

[15] N. N. Semenov, "Some Problems in Chemical Reactivity and Kinetics," Princeton University Press, Princeton, N. J., 1958, p 191.

[16] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., 2nd ed, New York, N. Y., 1961, p 241.

[17] M. Bodenstein and H. Plaut, *Z. Physik. Chem.* (Frankfurt), **110**, 339 (1924).

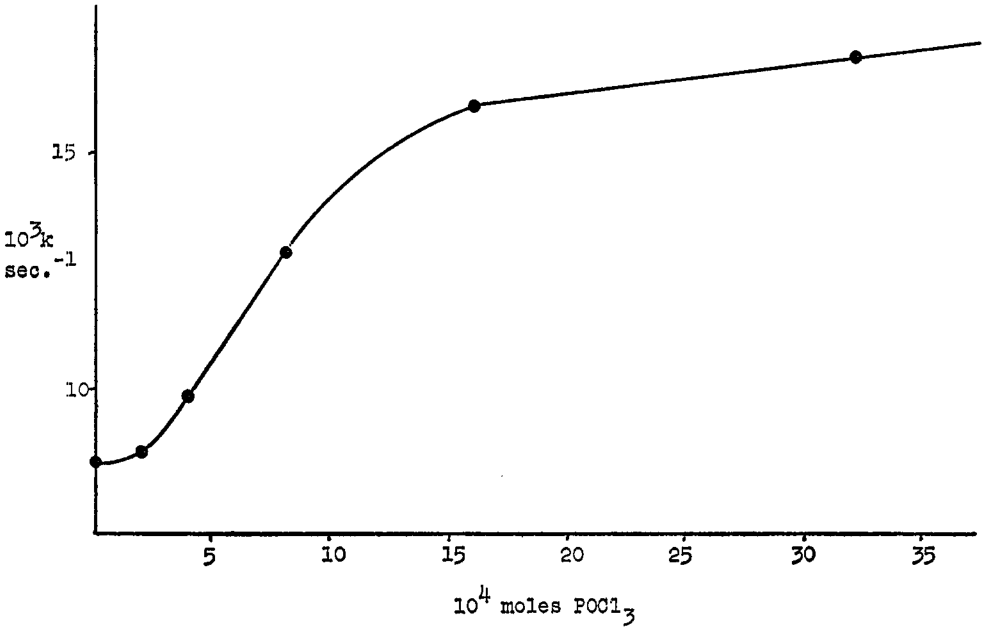

Figure 7.—Variation of rate of $PCl_3$ oxidation with initial phosphorus oxychloride concentration; $10.2 \times 10^{-2}$ *M* $PCl_3$ and $1 \times 10^{-4}$ *M* hydroperoxide in 10 ml of $CCl_4$ at 25°.

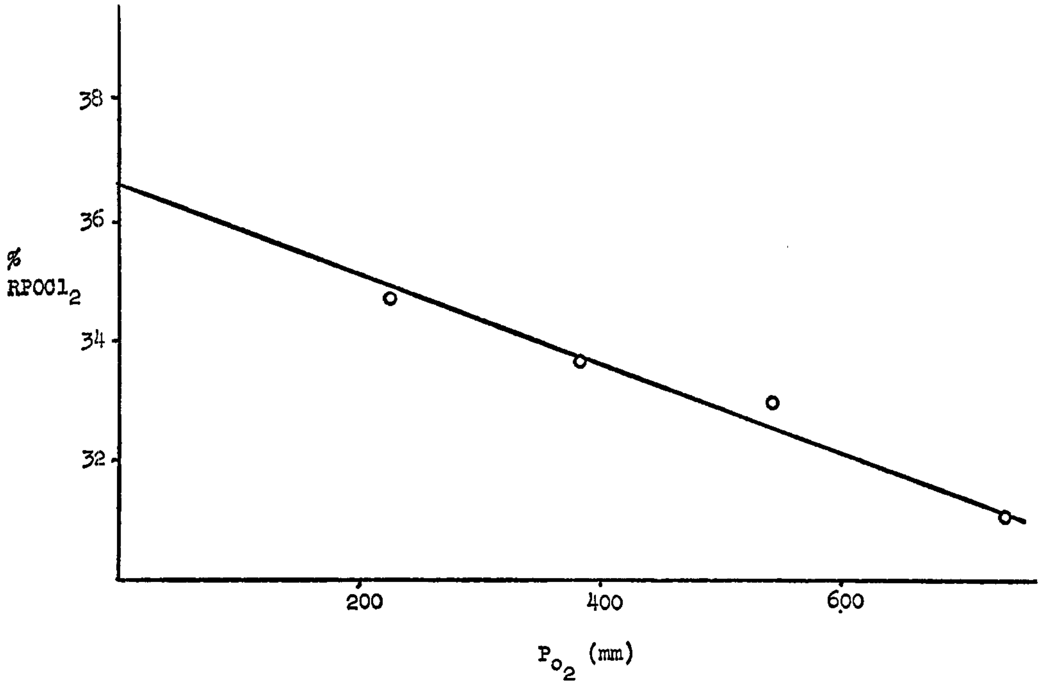

Figure 8.—Dependence of yield of $RPOCl_2$ on oxygen pressure; 1.02 *M* $PCl_3$ in 10 ml of cyclohexane at 25°; initiated by 1 μmole of hydroperoxide.

$k_{obsd}$ is the directly observed pseudo-first-order rate constant.

Two possible explanations for the change in dependence on oxygen pressure on changing the initiator are a possible change due to the oxygen involvement in the initiation in the AIBN-catalyzed reaction or the possibility that the autocatalytic role of the $POCl_3$ in the hydroperoxide-initiated reaction might affect the apparent order of oxygen dependence.

The ratio of propagation to termination rates may be obtained from the apparent rate constants by relationships 17 for AIBN catalysis and 18 for ROOH catalysis. (*a* is the initiator efficiency. Equation 18 is for reactions with no initial $POCl_3$ added.)

$$k_p/k_t = \frac{k_{obsd}}{2ak_i(\mathrm{AIBN})(\mathrm{O_2})} \tag{17}$$

$$k_p/k_t = \frac{k_{obsd}}{2ak_i(\mathrm{ROOH})(\mathrm{O_2})^{1/2}} \tag{18}$$

These values are presented in Table I and II, assuming that *a* equals unity.

**Chlorophosphonation.**—The chlorophosphonation reaction is considered to be a competing side reaction to the oxidation of phosphorus trichloride. The kinetic scheme of the reaction would, therefore, be expected to be essentially the same as that for the phosphorus trichloride oxidation, with the appropriate modifications to allow for the side reactions.

In preliminary kinetic studies involving added 2,3-dimethylbutane, the rate of reaction in the presence of the hydrocarbon appeared to be approximately first order in hydrocarbon concentration. Reproducible results were very difficult to obtain, however. After the intensive studies on hydroperoxide-catalyzed $PCl_3$ oxidation, it was assumed that the small deviation from zero order in hydrocarbon concentration was caused by failure to remove all hydroperoxides from the hydrocarbon (*i.e.*, if peroxide-free hydrocarbons could be obtained, the reaction should be zero order in hydrocarbon). Evidence supporting this assumption was obtained from the observation that the rates depended roughly on the time of exposure of the hydrocarbon to oxygen before adding the phosphorus trichloride. From a comparison of the hydrocarbon-initiated rates with the hydroperoxide rates, it was estimated that 1 part of hydroperoxide in $10^4$ to $10^5$ parts of hydrocarbon was sufficient to cause the observed rates.

For product studies, cyclohexane was chosen as the hydrocarbon substrate since it would yield only a single product. In preparative runs, using excess cyclohexane as the solvent, limiting yields of cyclohexylphosphonyl dichloride were near those reported by Mayo.[3] Three factors, oxygen pressure, solvent effects, and temperature, have been found to have a definite influence on the yield of the chlorophosphonation reaction.

The production of alkylphosphonyl dichloride may be visualized as arising from the following sequence of steps. The first is an attack by a chlorine radical on the hydrocarbon (reaction 5). Evidence for this step is drawn from the similarity of the chlorophosphonation isomer distribution to that for free-radical chlorination[12,13] and the solvent and temperature dependence of the yield (Tables IV and V). In both cases, decreasing the selectivity of the chlorine radical leads to increased attack on the hydrocarbon relative to $PCl_3$, *i.e.*, reaction with the less reactive substrate of the two. To the extent that alcohol is formed in reaction 11, one of the competing reactions, hydrocarbon radicals are diverted from the chlorophosphonation sequence into the formation of by-products (possibly esters[3]). The effect of this would be to make the decrease in selectivity of the propagating radicals with increasing temperature greater than is implied by the data in Table V.

TABLE IV

EFFECT OF VARIOUS SOLVENTS ON THE CYCLOHEXANE CHLOROPHOSPHONATION YIELD[a]

| Solvent | Mole fraction | % $RPOCl_2$[b] |
|---|---|---|
| Cyclohexane | 1.0 | 31.0 |
| Carbon tetrachloride | 0.219 | 31.0 |
| | 0.425 | 28.8 |
| | 0.626 | 27.7 |
| | 0.817 | 25.6 |
| Chlorobenzene[c] | 0.175 | 29.1 |
| | 0.365 | 24.9 |
| | 0.518 | 23.3 |
| | 0.842 | 16.0 |
| | 0.906 | 15.4 |
| α-Chloronaphthalene | 0.075 | 28.1 |
| | 0.154 | 23.3 |
| | 0.323 | 21.4 |
| | 0.521 | 17.8 |
| | 0.740 | 15.1 |

[a] 0.2 ml of $PCl_3$ and 2 μmoles of *t*-butyl hydroperoxide in 10 ml of total solution. [b] Based on initial $PCl_3$. [c] 0.6 ml of $PCl_3$ in 6 ml of total solution.

TABLE V

VARIATION OF CHLOROPHOSPHONATION YIELD WITH TEMPERATURE[a]

| Temp, °C | % $RPOCl_2$[b] |
|---|---|
| 25 | 31.0 |
| 45 | 31.8 |
| 60 | 32.5 |

[a] $2.04 \times 10^{-3}$ mole of $PCl_3$ in cyclohexane. Initiated by $2 \times 10^{-7}$ mole of *t*-butyl hydroperoxide. [b] Based on original $PCl_3$.

The effect of solvent composition for the addition of several inert solvents is shown in Table IV. The presence of significant amounts of any solvent other than the hydrocarbon gave a decrease in the yield of cyclohexylphosphonyl dichloride. This decrease was more pronounced in those solvents capable of forming a "π complex" with radicals. The effect increased in the order carbon tetrachloride, chlorobenzene, and α-chloronaphthalene. This is in qualitative agreement with Russell's data for the solvent effect on the reactivity of chlorine radicals.[18] Since the chlorophosphonation yield is essentially independent of hydrocarbon concentration above a hydrocarbon to phosphorus trichloride ratio of approximately 10,[3] the effect must be almost entirely a solvent effect rather than a concentration effect in the range studied.

If chlorophosphonation is in competition with the oxidation of phosphorus trichloride, chlorophosphonation yield should be proportional to the reciprocal of the absolute temperature. This is consistent with the data in Table V. Extrapolation of the data to an infinite temperature ($1/T = 0$), although unjustified, would give an approximate maximum yield of 50% for the chlorophosphonation reaction. This limit is imposed by eq 8.

The alkyl radical produced in eq 5 may lead to the chlorophosphonation product by a direct attack on a phosphorus trichloride molecule, followed by oxidation of the adduct (reactions 6–8). Equation 8 imposes a 50% maximum theoretical yield on the reaction. In the presence of oxygen, a competition (reaction 9) for the alkyl radical would occur. This is analogous to the alkyl radical reaction in the AIBN initiation sequence. The peroxy radical reactions would also be analogous (eq 10 and 1). Evidence for such a competition is found in the effect of oxygen pressure on the chlorophosphonation yield. On varying the oxygen pressure, it was found that the yield of alkylphosphonyldichloride decreased in direct proportion to oxygen pressure (Figure 8). Extrapolation of Figure 8 to an oxygen pressure of zero gives an apparent maximum yield of 36.5%. This is in good agreement with Mayo's maximum yield of 36% with large excesses of solvent and under conditions where the rate of reaction was controlled by the ratio of phosphorus trichloride to oxygen.[3] The rate of diffusion of oxygen into solution would serve to compound this effect.

In the presence of hydrocarbon an additional reaction could occur (reaction 11). The alcohol so produced would appear in the products as either an alkyl chloride or an ester.[3] Reactions 3 and 11 also account for the observation of Mayo[3] that the yield of esters increases on increasing the oxygen pressure.

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(18) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987 (1958).

It is seen that in no case does the entrance of hydrocarbon break the kinetic chain.

The over-all chlorophosphonation scheme is summarized in Chart I.

## Conclusions

The chlorophosphonation reaction and the oxidation of phosphorous trichloride have been studied in detail. Chlorophosphonation seems to be a competing side reaction in the phosphorous trichloride oxidation. The chlorophosphonation mechanism (Chart I) presented is in essential agreement with that postulated by Mayo.[3]

The kinetic study of the phosphorus trichloride oxidation revealed that this reaction was not spontaneous if sufficient reagent purity was obtained. Apparently the spontaneous nature of the chlorophonation reaction arises from the presence of trace amounts of an initiator (probably hydroperoxides) in the hydrocarbon. Owing to the extreme sensitivity of the phosphorus trichloride oxidation to hydroperoxides, it should be possible to use the rate of phosphorus trichloride oxidation as an analytical method for measuring low concentrations of hydroperoxides.

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# Phosphonic Acids and Esters. XV. Preparation and Proton Magnetic Resonance Spectra of the Diethyl α- and β-Chlorovinylphosphonates[1,2]

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The oxidative chlorophosphonation of vinyl chloride has been shown to lead to the formation of dichloroethylphosphonic dichlorides which can be converted by esterification to a mixture of diethyl β,β-dichloroethylphosphonate (**1b**) and diethyl α,β-dichloroethylphosphonate (**2b**). The former ester is the major component of the reaction mixture. In contrast to the results of Soborovskii, it was found that treatment of the mixture of esters with triethylamine leads to rapid dehydrochlorination of **2b** with the formation of diethyl α-chlorovinylphosphonate (**5**); **1b** undergoes a relatively slow dehydrochlorination to yield isomeric *trans*-β-chlorovinylphosphonate (*trans*-**3**). The *trans* ester can also be formed by photolysis of *trans*-1-chloro-2-iodoethylene in the presence of triethyl phosphite; a small amount of *cis*-**3** is also isolated in this reaction. The structures and stereochemistry of the vinylphosphonates (*cis*- and *trans*-**3**, **5**) were established by proton magnetic resonance spectroscopy. Each of these compounds yielded a first-order ABX spectrum and unequivocal assignments of $P^{31}$–$H^1$ and $H^1$–$H^1$ coupling constants (*gem, cis,* and *trans*) have been made.

As part of an extensive study of the oxidative chlorophosphonation of olefins,[4] Soborovskii, *et al.*,[5] have shown that a mixture of isomeric phosphonic dichlorides results from reactions with unsymmetrical olefins. For example, **1a** (30–35%) and **2** (65–70%) are reported to be formed by the reaction of vinyl chloride, phosphorus trichloride, and oxygen.[5] Since

$$\underset{\mathbf{1}}{CHCl_2CH_2P(O)X_2} \qquad \underset{\mathbf{2}}{CH_2ClCHClP(O)X_2}$$

$$\mathbf{a},\ X = Cl;\ \mathbf{b},\ X = OC_2H_5$$

**1a** and **2a** were inseparable, evidence for their existence was provided by an esterification–dehydrohalogenation sequence. The mixture of esters **1b** and **2b** formed from **1a** and **2a** was also inseparable, but reaction with triethylamine indicated the presence of two materials. The β,β-dichloro ester (**1b**) was reported to undergo dehydrohalogenation to yield diethyl β-chlorovinylphosphonate (**3**) while the α,β isomer (**2b**)

$$\underset{\mathbf{3}}{CHCl{=}CHP(O)(OC_2H_5)_2}$$

was reported to be unreactive. The latter isomer did, however, undergo dehalogenation on reaction with zinc to yield diethyl vinylphosphonate (**4**). The failure of **2b** to undergo dehydrohalogenation with triethylamine was surprising, particularly in view of the later report by Medved and Kabachnik[6] that the reaction of **2a** with ethanol and triethylamine in ether led to the formation of a dehydrohalogenated product, diethyl α-chlorovinylphosphonate (**5**). This observation

$$\underset{\mathbf{5}}{CH_2{=}CClP(O)(OC_2H_5)_2}$$

indicated that **5** should also have been formed in the reaction of the mixture of **1b** and **2b** with triethylamine.

In order to clarify this point and to obtain samples of **3** and **5** for use in Diels–Alder and proton magnetic resonance (pmr) studies, the oxidative chlorophosphonation of vinyl chloride has been reinvestigated. Following the procedure of Soborovskii,[5] equal volumes of vinyl chloride and oxygen were passed through phosphorus trichloride until reaction ceased. Distillation gave a phosphonic dichloride fraction with physical constants comparable with those reported[5] for the mixture of **1a** and **2a**; no separation of the mixture could be achieved by distillation. The pmr spectrum of this provided little structural information. Complex second-order multiplets centered at $\tau = 3.6$, 5.3, 5.7, and 6.1 ppm were observed; elements

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(2) Part XIV: R. H. Churi and C. E. Griffin, *J. Am. Chem. Soc.*, **88**, 1824 (1966).

(3) National Science Foundation Cooperative Graduate Fellow, 1961–1964.

(4) For a summary of these studies, see G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," The Macmillan Co., New York, N. Y., 1964, pp 172, 173.

(5) L. Z. Soborovskii, Y. M. Zinov'ev, and L. I. Muler, *J. Gen. Chem. USSR*, **29**, 3907 (1959).

(6) T. Y. Medved and M. I. Kabachnik, *Izv. Akad. Nauk SSSR., Otdel. Khim. Nauk*, 270 (1961); *Chem. Abstr.*, **55**, 20922 (1961).