Radical Reactions. I. Phosphorus Chloride Catalyzed Chlorination of Alkanes, Cycloalkanes, and Arylalkanes

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Phosphorus pentachloride and trichloride are highly effective catalysts for the radical type chlorination of alkanes, cycloalkanes, and arylalkanes. Reactions can be carried out conveniently at or above room temperature and in the dark. The reaction can be performed in chlorinated solvents of low polarity or in hydrocarbon solvents. Polar solvents, such as nitromethane, cause exclusive ionic chlorination to occur. The scope and mechanism of the novel, Lewis acid catalyzed radical chlorination reaction are discussed.

Because of their weak Lewis acidity, PCl_5 and PCl_3 are only infrequently used as Friedel–Crafts catalysts. Piazzi[3] found PCl_5 as a useful catalyst for cyclizations and Tada[4] reported its ability to promote the rearrangement of 1-chloro-1-nitrosocyclohexane. The PCl_5-catalyzed chlorination of aromatics tends to promote preferential chlorination of side chains over ring chlorination,[5] a result which is not expected for a Lewis acid catalyzed Friedel–Crafts chlorination. Wyman, *et al.*,[6] reported that PCl_5 itself serves as a chlorinating agent for alkanes and arylalkanes when the reactions are carried out at 100° and in the presence of benzoyl peroxide. Kimbrough[7] investigated the chlorination of several arylalkanes with PCl_5 at elevated temperatures. Kooyman[8] studied the chlorination of norbornane with PCl_5, initiated by uv light or peroxides. Fell and Kung[9] observed increased selectivity for chlorination of alkanes with molecular chlorine in the presence of phosphorus trichloride. All these reactions were considered to be typical radical chlorinations.[10]

In the course of our studies of electrophilic substitution reactions and in particular Friedel–Crafts catalyzed chlorinations, we observed repeatedly the irregular behavior of PCl_5-catalyzed chlorinations particularly the formation of substantial amounts of side chain chlorinated products in arylalkanes. We undertook now a detailed investigation of the phosphorus chloride catalyzed chlorination of alkanes, cycloalkanes, and arylalkanes to establish the scope and utility of these interesting and little studied reactions and also to clarify the mechanism of the reactions and particularly to distinguish conditions for homolytic or heterolytic chlorination.

Results and Discussion

Our investigations of the phosphorus chloride catalyzed chlorinations were carried out in the dark and at or slightly above room temperature, with radical reactions initiated by light or common radical initiators excluded. Liquid alkanes or arylalkanes were chlorinated either with no solvent used or with hydrocarbons dissolved in nonpolar solvents, such as CCl_4 or CH_2Cl_2. Arylalkanes are nearly exclusively chlorinated in the side chain. Adding a polar solvent (CH_3NO_2) to the chlorination mixtures in CCl_4 increases the amount of ring chlorination and by reaching 50% nitromethane, exclusive ring chlorination takes place. As is shown in Table I the PCl_5-catalyzed chlorinations of alkanes (carried out with chlorine under pressure in the dark at 25°) give good yields of haloalkanes (with the exception of the low yield in the case of methane). Since in blank reactions it was found that no chlorination occurred when PCl_5 was absent, or when the alkanes were kept in the presence of PCl_5 in the absence of chlorine under the same conditions, we have to assume that PCl_5 indeed acts as catalyst for the chlorinations. Phosphorus trichloride gave similar results to the PCl_5-catalyzed reactions. PCl_3, in the presence of chlorine of course, gives PCl_5. Thus in solvents of low polarity the equilibrium $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ must be assumed, explaining the similar results of chlorination observed using both PCl_5 and PCl_3. As all observed reactions gave similar results using either PCl_5 or PCl_3 (in the presence of chlorine) we are subsequently discussing these reactions only in case of PCl_5.

In considering the way in which PCl_5 would catalyze the chlorination of alkanes, first we needed to establish whether the reaction is radical or ionic in nature. This can be best done by determining the selectivity shown in the reactions and comparing them with the selectivities observed in typical radical chlorinations (for example the light-induced chlorination) and in recently observed cationic chlorinations.[11]

In order to determine the relative selectivity of different hydrogen atoms of alkanes in the PCl_5-catalyzed chlorination we used a tenfold excess of alkane over chlorine (with the molar ratio Cl_2:PCl_5 = 10:1) and analyzed the resulting mixtures of isomers by means of glc. To avoid any side reactions, the mechanistics studies of chlorination were carried out at 25° with necessarily longer reaction times, although preparative chlorinations (to be reported separately) are more advantageously carried out at somewhat elevated temperatures. The results are summarized in Table II. *n*-Butane in CCl_4 as solvent gives a $RS_p{}^s$ value of 3.5 in good accordance with $RS_p{}^s = 3.9$ obtained for the light-induced chlorination in the gas phase at 35° by Fredericks and Tedder.[12] The PCl_5-catalyzed chlorination of isobutane gives an $RS_p{}^t$ value of 3.4 very similar to $RS_p{}^t = 3.5$ obtained for the photochlorination in CCl_4 by Hodnett and Juneja[13] and Russell.[14] When chlorobenzene is used as a solvent the chlorination is much more selective, a trend which is generally observed for chlorinations proceeding *via* a radical type mechanism.[14–16] For isobutane and butane the values are $RS_p{}^t = 7.3$ and $RS_p{}^s = 5.1$, respectively. 2,4-Dimethylpentane containing primary, secondary, and tertiary hydrogen atoms gives RS values very similar to those which are found for the photochlorination of the neat alkane at 25° or were reported by Russell[17] for the photochlorination in CCl_4 at 40°. In the PCl_5-catalyzed chlorination values of $RS_p{}^s = 2.2$ and $RS_p{}^t = 2.8$ respectively, were obtained.

In typical cationic chlorinations of alkanes,[11] not only C–H bond substitution (chlorination) but also C–C bond cleaving chlorination (chlorolysis) is observed. No such chlorolysis, however, is observed under radical conditions (only perchlorinated alkanes undergo pyrolytic chlorolysis at elevated temperatures). Since there is no indication of chlorolysis and the selectivities resemble those of radical chlorination, we can assume that the phosphorus chloride catalyzed chlorinations are indeed of radical nature. Phos-

Table I
PCl_5 Catalyzed Chlorination of Alkanes and Cycloalkanes in the Dark at 25° [a]

Hydrocarbon	Registry no.	Molar ratio Cl_2:PCl_5:alkane	Reaction time, hr	Reaction products[b] (%)
Methane	74-82-8	1:0.1:2	22	Methyl chloride[c] (1.0)
Methyl chloride	74-87-3	1:0.1:0.8	17	Dichloromethane (22.0) Chloroform (1.0)
Ethane	74-84-0	1:0.1:1	42	Ethyl chloride (21.3) 1,1-Dichloroethane (4.5) 1,2-Dichloroethane (1.8)
Propane	74-98-6	1:0.1:0.8	20	Isopropyl chloride (17.4) *n*-Propyl chloride (12.6)
Butane	106-97-8	1:0.1:1	28	1-Chlorobutane (5.4) 2-Chlorobutane (14.6) 1,2-Dichlorobutane (5.0) 1,3-Dichlorobutane (15.0)
2-Methylpropane (isobutane)	75-28-5	1:0.1:2	30	*tert*-Butyl chloride (8.0) 1-Butyl chloride (12.1)
2,2-Dimethylpropane (neopentane)	463-82-1	1:0.1:2	22	Neopentyl chloride (47.5) 1,1-Dichloro-2,2-Dimethylpropane (7.2)
Cyclopropane	75-19-4	1:0.1:2	30	Cyclopropyl chloride (5.0) 1,1-Dichlorocyclopropane (6.2) 1,3-Dichloropropane (11.8)
Cyclohexane	110-82-7	1:0.1:2	30	Cyclohexyl chloride (25.0)
Norbornane[d]	279-23-2	1:0.1:0.15	60	*exo*-2-Chloronorborane (12.0) *endo*-2-Chloronorborane (5.6) 7-Chloronorbornane (10.4)
Adamantane[e]	281-23-2	1:0.1:0.05	46	1-Chloroadamantane (40.0) 2-Chloroadamantane (14.4)
Adamantane[f]		1:0.1:0.05	17	1-Chloroadamantane (24.0) 2-Chloroadamantane (16.0)

[a] Without solvent. [b] Product analysis by glc or nmr spectroscopy, yield of the identifiable products based on the amount of alkane charged. [c] Analyzed by MS. [d] Reaction temperature 65°. [e] In CCl_4 at 60°. [f] In CH_2Cl_2 at 25°.

phorus chlorides also are excellent and highly selective catalysts for side-chain chlorination of arylalkanes. At 25° and in the dark they are capable of effecting almost exclusive side chlorination. For preparative purposes (to be reported separately) again somewhat elevated temperatures (50–60°), giving much faster reaction rates, are preferred.

Comparing the relative rates of α chlorination of toluene, ethylbenzene, and cumene shows that the change of the α hydrogen from a primary in toluene to a secondary in ethylbenzene increases its reactivity 3.3 times ($k_{EB}/k_T = 2.2$), whereas the change from a secondary hydrogen in ethylbenzene to a tertiary in cumene increases its reactivity 4.5 times (thus to a higher degree). The values obtained in competitive chlorination of the neat aromatic hydrocarbons show some differences from the results of photochlorination of the same substrates at 40° reported by Russell.[16] The values reported by Russell for the chlorination in nitrobenzene, cyclohexane, or CCl_4 show relative reactivities of the different C–H bonds toward chlorine atoms and of toluene:ethylbenzene (α):cumene (α) = 1:3.9:8.5 independent of the solvent used. Considering that our results were obtained in chlorination of near substrates, the relative reactivities of toluene:ethylbenzene (α):cumene (α) = 1:3.3:14.7 seem to indicate that the use of PCl_5 as catalyst gives comparable selectivities with previous chlorinations. The explanation for some differences could be the increasing stability of the π complexes formed between PCl_5 and the arylalkyl hydrocarbons going from toluene to cumene, which could favor chlorine attack on the tertiary C–H bond of cumene more than expected on a simple statistical basis. On the other hand the reaction in neat aromatics should also result in the involvement of a more complexed chlorinating agent which is more selective, as was shown by Wiberg[18] and Walling.[19] In a study of the kinetic isotope effect for chlorination of toluene-d_1 k_H:k_D = 1.3 was found in CCl_4 as solvent, whereas for the undiluted aromatic hydrocarbon k_H/k_D is 2.1.[18,20] The relative amounts of α and β isomers formed in the PCl_5-catalyzed chlorination of ethylbenzene and cumene are 10.95:1 and 8.66:1, respectively, using no solvent. When the substrates are diluted with CCl_4 the chlorination becomes less selective with increasing dilution (see Table III). The same trend was found by Russell when he investigated the photochlorination of the same aromatics in nitrobenzene solvent.[16] Comparing the reactivity of the hydrogen atoms in the side chain of toluene with those of cyclohexane, usually used as a standard in the determination of substrate selectivities, the PCl_5-promoted chlorination gives a relative rate of $k_{cyclohexane}/k_{toluene}$ = 13.6 in the competitive chlorination which was carried out with a 1:1 mixture of the substrates, without using any solvent. From this result it can be seen that the hydrogen atoms in cyclohexane are 3.4 times more reactive than the hydrogen atoms in the side chain of toluene. Russell and Brown[15] reported a relative rate of 11.2 in favor of cyclohexane for the competitive photochlorination at 80°, very close to our result. However, when the results of the competitive chlorination of cyclohexane and toluene are compared with the rate ratio of chlorination of the neat substrates, one finds that cyclohexane reacts much slower than toluene (in 30 hr only 25% cyclohexyl chloride is formed, whereas 51% benzyl chloride is formed in 30 min). In order to clarify this seeming discrepancy we determined the rate of chlorination of cyclohexane in different aromatic solvents (1:1 mixtures of cyclohexane and aromatics were

Table II
Substrate and Positional Selectivity of the PCl_5-Catalyzed Chlorination of Alkanes and Arylalkanes in the Dark at 25° [a]

Hydrocarbon	Solvent	Reaction products (%)	Selectivity
Butane	$CCl_4(PCl_5)$	1- + 2-Chlorobutane	$\mathrm{RS_p}^s = 3.5$
	$C_6H_5Cl(PCl_5)$	1- + 2-Chlorobutane	$\mathrm{RS_p}^s = 5.1$
	Gas phase 35°	1- + 2-Chlorobutane	$\mathrm{RS_p}^s = 3.9$[13]
2-Methylpropane (isobutane)	$CCl_4(PCl_5)$	1- + 2-Chloro-2-methylpropane	$\mathrm{RS_p}^t = 3.4$
	$C_6H_5Cl(PCl_5)$	1- + 2-Chloro-2-methylpropane	$\mathrm{RS_p}^t = 7.3$
	CCl_4, $h\nu$, 24°	1- + 2-Chloro-2-methylpropane	$\mathrm{RS_p}^t = 3.5$[15]
	Neat, $h\nu$, −15°	1- + 2-Chloro-2-methylpropane	$\mathrm{RS_p}^t = 4.5$[16]
	C_6H_5Cl, $h\nu$, −15°	1- + 2-Chloro-2-methylpropane	$\mathrm{RS_p}^t = 29$[16]
2,4-Dimethylpentane	Neat (PCl_5)	1-Chloro-2,4-dimethylpentane (54.8)	$\mathrm{RS_p}^t = 2.8$
	Neat (PCl_5)	2-Chloro-2,4-dimethylpentane (25.3)	
		3-Chloro-2,4-dimethylpentane (20.0)	$\mathrm{RS_p}^s = 2.2$
	Neat, $h\nu$	1-Chloro-2,4-dimethylpentane (52.0)	$\mathrm{RS_p}^s = 2.6$
		2-Chloro-2,4-dimethylpentane (25.5)	
		3-Chloro-2,4-dimethylpentane (22.5)	$\mathrm{RS_p}^t = 2.9$
	CCl_4, $h\nu$, 40°	1-Chloro-2,4-dimethylpentane (55.1)	$\mathrm{RS_p}^t = 2.5$
		2-Chloro-2,4-dimethylpentane (22.9)	
		3-Chloro-2,4-dimethylpentane (22.0)	$\mathrm{RS_p}^s = 2.4$[17]
Cyclohexane:toluene (1:1)	Neat (PCl_5)	Cyclohexyl chloride Benzyl chloride	k_C/k_T[b] = 13.6
	$h\nu$, 80°	Cyclohexyl chloride Benzyl chloride	$k_C/k_T = 11.2$
Ethylbenzene:toluene (1:1)	Neat (PCl_5)	Benzyl chloride α-Chloroethylbenzene (91.6) β-Chloroethylbenzene (8.4)	$k_{EB_\alpha}/k_{T_\alpha} = 2.2$[c] $k_{EB_\alpha}/k_{EB_\beta} = 10.95$
Cumene:toluene (1:1)	Neat (PCl_5)	Benzyl chloride α-Chlorocumene (89.6) β-Chlorocumene (10.4)	$k_{C_\alpha}/k_{T_\alpha} = 4.9$[c] $k_{C_\alpha}/k_{C_\beta} = 8.66$

[a] Analysis by glc after 10% of the hydrocarbons were chlorinated. [b] Represents overall cyclohexane:toluene rate ratio (substrate selectivity) without statistical correction for positions. [c] Relative rates of α-chlorination were obtained by nmr spectroscopy; relative selectivities α/β were obtained by glc analysis of the chlorination products of neat ethylbenzene and cumene.

Table III
PCl_5-Catalyzed Chlorination of Alkylaromatics in the Dark at 25° [a]

Hydrocarbon	Registry no.	Solvent	% side-chain chlorination	% ring chlorination
Toluene (T)	108-88-3	Neat	97.3	2.7 (o/p = 1.65)
		CCl_4 (T:CCl_4 = 1:10)[b]	>99	Traces
		$C_6H_5NO_2$ (T:NB = 1:5)[b]	0	100 (o/p = 1.36)
		CH_3NO_2 (T:NM = 1:5)[b]	0	100 (o/p = 1.32)
		Neat + 10% *m*-DNB	90	10
		Neat + 20% *m*-DNB	2	98
Ethylbenzene (E)	100-41-4	Neat	98 α/β = 10.95	2
		CCl_4 (E:CCl_4 = 1:5)[b]	100 α/β = 7.24	0
		CCl_4 (E:CCl_4 = 1:10)[b]	100 α/β = 5.08	0
Cumene (C)	98-82-8	Neat	98 α/β = 8.66	2
		CCl_4 (C:CCl_4 = 1:5)[b]	100 α/β = 5.21	0
		CCl_4 (C:CCl_4 = 1:10)[b]	100 α/β = 4.27	0
o-Xylene	95-47-6	Neat	93.4	6.6
m-Xylene[d]	108-38-3	Neat	35	65
p-Xylene	106-42-3	Neat	95	5
Mesitylene[d]	108-67-8	Neat	0	100

[a] Reactions were carried out with a 10:1 mol ratio of aromatics:PCl_5. Chlorine gas was continuously introduced into the solutions. Chlorination products were analyzed by glc. [b] Molar ratios. [c] *m*-Dinitrobenzene. [d] Ring chlorination occurs also without PCl_5.

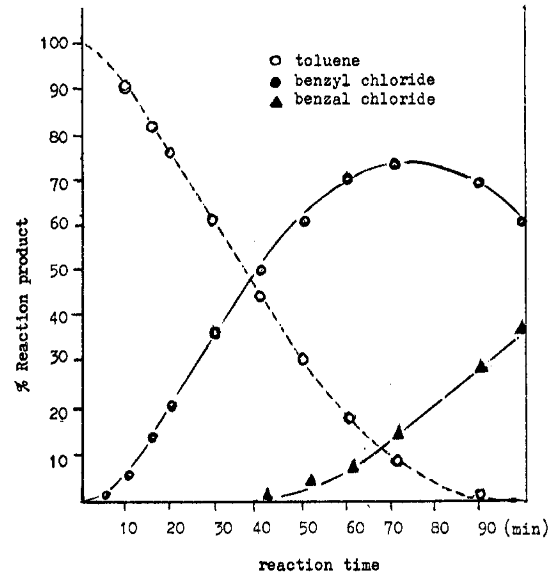


Figure 1. PCl_5 catalyzed chlorination of toluene in the dark at 25°.

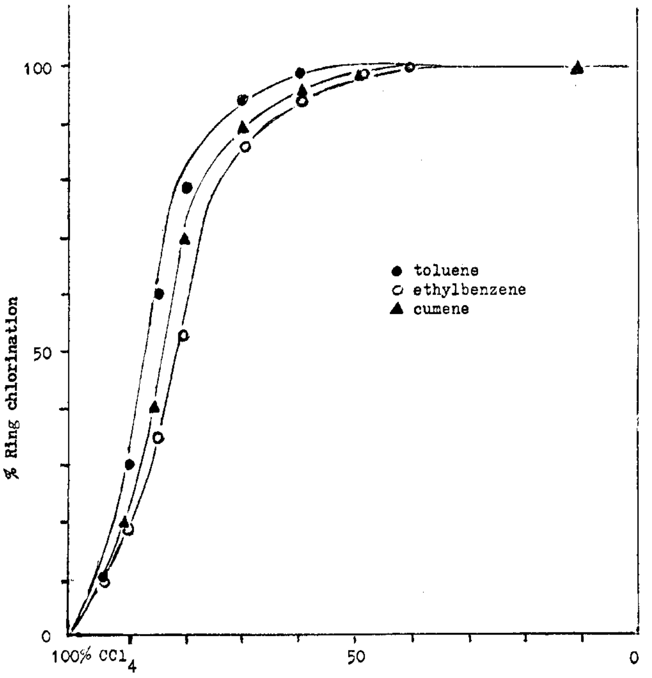


Figure 2. Dependence of the substitution in the PCl_5 catalyzed chlorination of arylalkanes with varying amount of apolar (CCl_4) and polar (CH_3NO_2) solvent.

used). Data showed that the amount of cyclohexyl chloride is substantially enhanced when an alkylated aromatic is used as solvent. Benzene itself gives an increase of the rate of chlorination which is substantially further enhanced when using (in sequence) *tert*-butylbenzene, toluene, ethylbenzene, and cumene. During the chlorination the amount of added alkylaromatics remains nearly constant at about 80% (with 20% dichlorinated product formed) of the introduced amount, whereas cyclohexane is continuously used up as its chlorination proceeds.

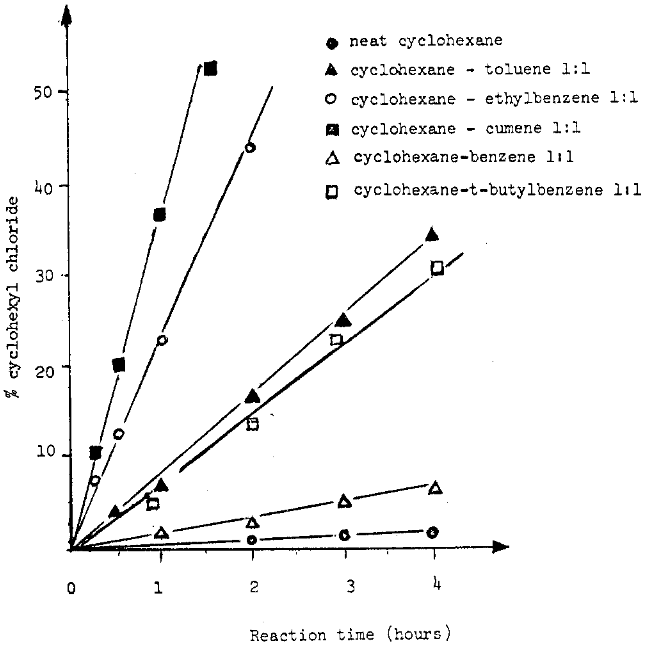


Figure 3. Chlorination of cyclohexane. Influence of aromatic solvents on the reaction rate (ratio cyclohexane: PCl_5 = 10:1).

The observation that cyclohexane is more reactive in competitive experiments than toluene, but reacts more slowly in individual noncompetitive runs, may be, however, misleading.[21] The rate of a radical chain reaction depends on the composite rate constant, including termination as well propagation rate constants, whereas competitive experiments only evaluate the latter. In the absence of independent information concerning the termination reaction comparison between the noncompetitive experiments may be invalid, as the propagation rate in neat cyclohexane may be slow. Till further data are obtained, we are consequently not attempting any conclusions.

In addition to the selectivity studies we also investigated the time dependence of the chlorination by introducing a constant stream of chlorine through a mixture of toluene and PCl_5 (10:1) in the dark, at 25°, and determining the reaction products by nmr and glc. As is seen from Figure 1 the chlorination of toluene is very selective and benzyl chloride free from benzal chloride is formed up to about 50% conversion, whereafter further chlorination increasingly gives benzal chloride.

The use of polar solvents changes the course of the PCl_5-catalyzed chlorination drastically, as was shown in the case of toluene. In nitrobenzene or nitromethane solution only ring-substituted isomers were obtained. Since Russell[16] found in the case of the photochlorination of toluene in nitrobenzene as solvent no such change and alkylbenzenes gave only side-chain chlorinated products, the change from radical-type side-chain chlorination in CCl_4 to ionic-type ring chlorination in nitrobenzene or nitromethane solutions in the presence of PCl_5 must be due to a basic change in the catalytic behavior of this weak Lewis acid when changing the solvent polarity. Figure 2 shows the result of chlorination of toluene, ethylbenzene, and cumene, compounds whose reactivities toward atomic chlorine differ only slightly in dependence of the solvent polarity by changing the relative amounts of CCl_4 and nitromethane in this mixed solvent system. A continuous change from radical to ionic chlorination is observed. With an increasing dielectric constant of the solvent system and a ratio of CCl_4:CH_3NO_2 = 40:60 v/v or less, only ring chlorination is observed.

We also studied the relative rate of the PCl_5-catalyzed chlorination of benzene and toluene in nitromethane using the competitive method. The obtained values for the substrate selectivity k_T/k_B = 62.5 (25°) and the isomer distribution o:m:p = 56.9:0.1:43.0% show that PCl_5 is a relatively weak Friedel–Crafts catalyst for electrophilic aromatic ring

Table IV
PCl_5-Catalyzed Chlorination of Arylalkanes in the Dark at 25° [a]

Hydrocarbon	Solvent	Reaction time, min	Reaction products [b] (%)
Toluene	Neat	30	Benzyl chloride (51.0)
			Chlorotoluenes (1.0)
	Nitromethane	30	*o*-Chlorotoluene (45.5)
			m-Chlorotoluene (<0.5)
			p-Chlorotoluene (34.0)
Ethylbenzene	Neat	30	α-Chloroethylbenzene (49.0)
			β-Chloroethylbenzene (1.7)
			o-, *m*-, *p*-Chloroethylbenzene (1.0)
	Nitromethane	30	*o*-Chloroethylbenzene (36.9)
			m-Chloroethylbenzene < (0.5)
			p-Chloroethylbenzene (37.6)
Cumene	Neat	30	α-Chlorocumene (54.6)
			β-Chlorocumene (1.4)
			o-, *m*-, *p*-Chlorocumenes (1.2)
	Nitromethane	30	*o*-Chlorocumene (32.5)
			m-Chlorocumene < (0.5)
			p-Chlorocumene (47.6)
tert-Butylbenzene	Neat	30	β-Chloro-*tert*-butylbenzene (4.0)
	Nitromethane	30	*o*-Chloro-*tert*-butylbenzene (6.2)
			m-Chloro-*tert*-butylbenzene (<0.5)
			p-Chloro-*tert*-butylbenzene (32.4)
o-Xylene	Neat	30	α-Chloro-*o*-xylene (42.0)
			3-, 4-Chloro-*o*-xylene (2.6)
	Nitromethane	30	3-Chloro-*o*-xylene (19.6)
			4-Chloro-*o*-xylene (50.0)
m-Xylene	Neat	30	α-Chloro-*o*-xylene (16.6)
			2-Chloro-*m*-xylene (15.5)
			3-Chloro-*m*-xylene (50.5)
	Nitromethane	30	2-Chloro-*m*-xylene (12.3)
			3-Chloro-*m*-xylene (62.1)
p-Xylene	Neat	30	α-Chloro-*p*-xylene (22.0)
			α, α′-Dichloro-*p*-xylene (56.0)
			2-Chloro-*p*-xylene (4.5)
Mesitylene	Neat	30	2-Chloromesitylene (59.0)
			2, 4-Dichloromesitylene (41.0)

[a] Chlorine was continuously introduced into the system. [b] Yield based on hydrocarbons, determined by glc and pmr.

chlorination. In contrast to this result the $FeCl_3$-catalyzed chlorination, a much stronger Lewis acid, gives the values k_T/k_B = 13.5 and o:m:p = 67.8:2.3:29.9%.[22] However, in comparison the uncatalyzed chlorination with molecular chlorine in nitromethane gave k_T/k_B = 1100 and o:m:p = 35.1:0.1:64.8%, a result very similar to that obtained by Stock.[23] These results show that PCl_5 in nitromethane has a considerable catalytic effect for the ring chlorination of benzene and toluene. Table IV summarizes the results of the chlorination of alkylbenzenes.

m-Xylene and mesitylene, aromatics with a much higher basicity than toluene, are chlorinated to a high degree on the ring even when no solvent is used. Since nearly the same ratio of ring-chlorinated products is obtained without using PCl_5 and also the isomer distribution remains constant, we have to assume that the uncatalyzed chlorination by molecular chlorine is becoming the dominant reaction with increasing basicity of the aromatics. PCl_5 is increasingly strongly complexed by the π-aromatic systems and thus deactivated in its effect to coordinate with chlorine.

As a consequence of the drastic change in the nature of the chlorination of aromatic hydrocarbons by changing the solvent polarity, we also attempted the chlorination of aliphatic hydrocarbons in nitromethane solution, in order to see if any ionic type of chlorination can be achieved. Due to the generally limited solubility of the lower alkanes in this polar solvent and to exclude the possibility of any gas-phase chlorination we used 2,4-dimethylpentane, cyclohexane, and norbornane as substrates. However, in all three cases after 24 hr reaction time the yields of chlorinated products were less than 1% (molar ratio alkane: Cl_2:PCl_5 = 1:1:0.1, 25°)

The phosphorus chlorides under the reaction conditions used seem not to cause any isomerization of chlorinated products (added pure chloroalkanes, cycloalkanes, or arylalkanes could be recovered unchanged from the reaction mixtures). Product and isomer composition data are thus not affected by secondary isomerization.

Mechanism and Conclusions

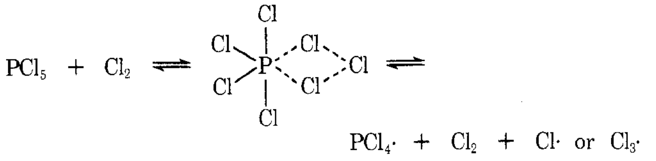
One of us wrote 10 years ago on the catalytic activity of PCl_5 in chlorination: "It must be noted, however, that as a chlorination catalyst the action of PCl_5 is not clear, because it is known to promote side chain chlorination of alkylbenzenes preferentially over ring chlorination, a reaction generally characteristic of free radical conditions."[5]

Product composition and selectivity data obtained in the present study indicate that the phosphorous chloride catalyzed chlorinations of arylalkanes, cycloalkanes, and alkenes are radical and not ionic type reactions.

To further prove the radical nature of the reactions, in control experiments we carried out chlorination of toluene and ethylbenzene at 25° in the dark with PCl_5 catalyst (*i.e.*, under conditions giving predominant α substitution) under experimental conditions where we continuously saturated the reaction mixtures with oxygen. Under these reaction conditions no or only limited side-chain chlorination was observed, thus showing that oxygen was able to inhibit the radical reactions.

In our studies we also investigated the effect of glass reaction vessels used in the reactions. When carrying out the experiments in Teflon reaction vessels, excluding contact with glass, little change in the product compositions was observed. This contrasts sharply with observations in our subsequently to be reported studies on bromination reactions, which were found quite sensitive to the effect of glass, causing more ionic type of aromatic ring bromination to occur. The less polarizable chlorine shows no such effects and results obtained in the usual glass apparatus were found to be reproducible.

The ability of phosphorus chlorides to act as catalysts for radical chlorination is considered to be a consequence of their ability to coordinate with Lewis acids and subsequently lead to homolysis of the weak end chlorine–chlorine bond. Downs and Jonson[24,25] showed that phosphorus pentachloride exchanges readily with radioactive chlorine and the exchange reaction always effects only the equatorial chlorine atoms. To account for this exchange reaction an intermediate complex of covalent phosphorus pentachloride (known to be of trigonal bipyramidal structure, as contrasted with the predominantly ionic PCl_4^+ PCl_6^- present in polar solvents or as the crystalline solid[26]) must be assumed, in which the chlorine–chlorine bond is weakened due to the coordination of chlorine to PCl_5 acting as an electron acceptor. The complex can account for chlorine exchanging exceedingly readily with phosphorus pentachloride, but it is also conceivable that cleavage takes place giving $PCl_4\cdot + Cl_2 + Cl\cdot$ ($PCl_6\cdot$ is not known and a heptaatomic radical probably would not be stable).



The formed $PCl_4\cdot$ and $Cl\cdot$ (or $Cl_3\cdot$) radicals subsequently can initiate typical free-radical chlorination reactions.

$$R{-}H + PCl_4\cdot \longrightarrow R\cdot + HCl + PCl_3$$

$$R{-}H + Cl\cdot \longrightarrow R\cdot + HCl$$

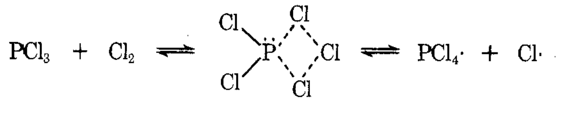
$$R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot\text{, etc.}$$

As the selectivity of the chlorination of alkanes, as expressed by RS_p^s values in the RH–CH_2–PCl_5 systems, is comparable to those in RH–CH_2 systems and Fell and Kung[9] report much higher values for RH–PCl_5 systems indicating a hydrogen-abstracting radical other than $Cl\cdot$, probably $PCl_4\cdot$, the contribution of the latter in the RH–CH_2–PCl_5 system must be limited.

Phosphorus pentachloride in low polarity media can always be considered to be in equilibrium with PCl_3.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

PCl_3 is a very weak Lewis acid, as well as a Lewis base. Its interaction with chlorine (using radio chlorine) is also known to involve addition only into the equatorial positions. This can be accounted for by interaction somewhat similar to that of PCl_5, when acting as a Lewis acid.



If acting as a Lewis base, then the interaction of the lone pair of electrons on phosphorus is with the back lobe of the antibonding chlorine–chlorine orbital (polarized through some $Cl_2 \cdots Cl_2$ association in the low polarity medium). Subsequent cleavage (homolytic) of the chlorine–chlorine bond gives $PCl_4\cdot$ and $Cl_3\cdot$ (or $Cl\cdot$ and Cl_2).

Esr studies of the $PCl_4\cdot$ radical showed that an unpaired electron is located in an equatorial position.[27]

The high efficiency of side-chain chlorination of arylalkanes could be further facilitated by π complexing of PCl_5 by the aromatic π system, as well as the formed chlorophosphorus and chlorine radicals. This effect is also demonstrated by the faciliatation of alkane chlorination observed in aromatic solvents.

The small amount of competing ionic chlorination observed in hydrocarbon or CCl_4 solution is due to heterolytic cleavage of the chlorine–phosphorus pentachloride complex. Using polar solvents, such as nitromethane or nitrobenzene, heterolytic cleavage is becoming predominant and the homolytic pathway can not further be observed.

Preparative aspects of the application of the phosphorus chloride (and related arsenic chloride) catalyzed chlorination reactions will be reported separately.

Experimental Section

Alkanes, cycloalkanes, and aromatic hydrocarbons used were of highest commercially available purity. PCl_5 high purity grade (MCB) was used without further purification. Nitromethane and carbon tetrachloride (spectrograde) were kept over molecular sieves (Linde A4).

General Procedure for the Chlorination of Alkanes and Cycloalkanes. PCl_5 (0.03 mol) was placed into a 50-ml monel pressure bomb cooled to −78° in a Dry Ice–acetone bath. Chlorine (0.3 mol) was condensed into the bomb and depending on the alkane used it was added either through a valve under pressure (methane, ethane) or condensed into the bomb at −78° (propane, *n*-butane, isobutane, neopentane, cyclopropane). Liquid alkanes were added neat and solid alkanes were dissolved in methylene chloride (0.01 mol in 10 ml of solvent) or used neat when chlorinations were carried out at temperatures above their melting point (norbornane). For the amounts of alkanes used see Table I. After the bombs were closed they were allowed to warm to room temperature and the reactions were carried out by mechanical shaking for the times shown in Table I.

Products were removed by connecting the outlet valve of the bomb through a water-cooled reflux condenser to a 50-ml two-necked round-bottom flask. The second neck was connected to a trap which was immersed into a Dry Ice–acetone bath. Both the round-bottom flask and the cold trap were charged with 10 ml of ether. By opening the valve the gaseous reaction products as well as unreacted chlorine and hydrocarbons were dissolved in ether. The ether solutions were washed several times with saturated aqueous sodium bisulfite solution. After opening the bomb liquid products were also dissolved in ether and washed in the same way. After drying, the ether solutions were analyzed by glc (after adding an internal standard). The gas chromatographic analyses of the reaction products were performed on a Perkin-Elmer Model 226 chromatograph equipped with an electronic integrator (Infotronics Model CRS-1) using an automatic readout system or on a Varian Associates Aerograph Model 1200 chromatograph. Coated stainless steel open tubular columns or packed columns (see data for individual alkanes) were used. For the quantitative determination of the product yields measured amounts of a known internal standard were added or products were determined relative to unreacted starting material.

Ethane: (A) stainless steel open tubular column, 150 ft × .01 in.; stationary phase, squalane; column temperature 60°; helium pressure 12 psi; retention times (sec), ethyl chloride (309), 1,1-dichloroethane (370), 1,2-dichloroethane (442), 1-dichloropropane (506, standard).

Propane: column A; 60° (12 psi); 2-chloropropane (464), 1-chloropropane (506), 1-chlorobutane (610, standard).

***n*-Butane:** column A; 80° (12 psi); 2-chlorobutane (365), 1-chlorobutane (395), *tert*-butyl chloride (331, standard), 1,2-dichlorobutane (711), 1,3-dichlorobutane (769).

Isobutane: column A; 80° (12 psi); *tert*-butyl chloride (331), isobutyl chloride (371), 1-chlorobutane (395, standard).

Neopentane: column A; 80° (20 psi); neopentyl chloride (265), 1,1-dichloro-2,2-dimethylpropane (650), norbornane (380, standard).

Cyclohexane: (B) stainless steel open tubular column, 150 ft × .01 in.; stationary phase, *m*-bis(*m*-phenoxyphenoxy)benzene + Apiezon L; column temperature 80°; helium pressure 30 psi; cyclohexyl chloride (357), cyclohexyl bromide (610, standard).

Norbornane: (C) stainless steel open tubular column, 150 ft × 0.01 in.; stationary phase, Carbowax 1540; column temperature 60°; helium pressure 30 psi; 7-chloronorbornane (552), *exo*-2-chloronorbornane (571), *endo*-2-chloronorbornane (593), norbornane (167, used as standard).

Adamantane: (D) stainless steel open tubular column, 150 ft × .01 in.; stationary phase, butanediolsuccinate; column temperature 80°; helium pressure 20 psi; 1-chloroadamantane (175), 2-chloroadamantane (190), adamantane (30, used as standard).

General Procedure for Chlorination of Alkylaromatics without Solvent. The individual arylaromatics (100 mmol) and (10 PCl_5 (10 mmol) were placed into the reaction flask. A slow stream of finely dispersed chlorine gas (dried by H_2SO_4) was passed through the reaction mixture for 30 min in the dark (by external cooling the temperature was kept at 25°). Excess chlorine was removed by passing nitrogen through the reaction mixture, which was then several times washed with water and dried, and the reaction products were analyzed by glc or nmr spectroscopy.

In Nitromethane as Solvent. The same amount of aromatics and PCl_5 was dissolved in a 20-fold excess of nitromethane and for 30 min a slow stream of finely dispersed chlorine gas was passed through the cooled (25°) solution in the dark. The washed and dried nitromethane solutions were analyzed by glc (after addition of a known amount of internal standard).

Gas-Liquid Chromatographic Analysis. Side-Chain Chlorinated Aromatics: (G) stainless steel packed column, 12 ft × 1/8 in.; stationary phase, 5% Benton and 5% silicon oil DC 200 on acid washed Chromosorb W, 60–80 mesh; column temperature 130°; helium pressure 25 psi; benzyl chloride (348), α-chloroethylbenzene (396), β-chloroethylbenzene (510), α-chlorocumene (decomposition product α-methylstyrene 300), β-chlorocumene (552). Column E; 100° (30 psi); α-chlorocumene (decomposition product, α-methylstyrene 505), β-chlorocumene (1163).

Ring-Chlorinated Aromatics: (E) stainless steel open tubular column, 150 ft × .01 in.; stationary phase, *m*-bis(*m*-phenoxyphenoxy)benzene + Apiezon L; column temperature 100°; helium pressure 30 psi; chlorotoluenes,[28] o (321), m (331), p (331); chloroethylbenzenes, o (430), m (479), p (479); chlorocumenes, o (591), m (681), p (733); chloro-*tert*-butyl-benzenes, o (830), m (883), p (923); chloro-o-xylenes (80° (30 psi)), 3 (1188), 4 (1230); chloro-*m*-xylenes (80° (30 psi)), 2 (921), 4 (961); 2-chloro-*p*-xylene (100° (30 psi), 535); 2-chloromesitylene (100° (30 psi), 1302).

Determination of Relative Substrate Selectivity. In a typical experiment 8.4 g (0.1 mol) of cyclohexane, 9.2 g (0.1 mol) of toluene, 4.06 g (0.02 mol) of PCl_5, and 1.4 g (20 mmol) of chlorine were reacted in the dark for 10 hr at 25°. Glc analysis of the reaction products on column G: 100° (40 psi); benzyl chloride (345), cyclohexyl chloride (900). Ethylbenzene–toluene (1:1) and cumene–toluene (1:1) were reacted in the same way. The reaction products were analyzed by glc on column G (130° (25 psi)).

Determination of Substrate and Positional Selectivity of Ring Chlorination in Nitromethane. Mixtures (1:1) of benzene and alkylbenzenes were dissolved in a 20-fold amount of nitromethane, 20 mol % of PCl_5 (based on the amount of the aromatics) was added and then chlorine gas (10 mol %) was introduced into the well stirred solution at 25°. The work-up and glc analysis was performed as described (column E).

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Registry No.—PCl_5, 10026-13-8; PCl_3, 7719-12-2.

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Radical Reactions. II.[1] Lewis Base Catalyzed Anti-Markovnikov Addition of Hydrogen Bromide to Alkenes

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Lewis base catalysts such as PBr_3 and $POCl_3$ promote anti-Markovnikov addition of hydrogen bromide to alkenes. Inhibitor effects, as well as observed isomerization of *cis*-stilbene, further illustrate the homolytic nature of the reactions. An initiation mechanism is proposed involving initial interaction of hydrogen bromide with the Lewis base type catalysts leading subsequently to homolytic cleavage of the weakened hydrogen–bromine bond.

The mechanism of the free-radical addition of hydrogen bromide to alkenes was first clarified by Kharasch and Mayo.[2] Following the development of the chain reaction concept in additions of hydrogen bromide,[3,4] numerous in-