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Abstract

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CHEMISTRY

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ON THE MECHANISM OF THE INTERACTION OF SILICON HYDRIDES WITH ORGANIC HALIDES IN THE GAS PHASE

In a number of works it has been shown ($^{1-18}$) that the reaction between silicon hydrides and organic halides at a temperature of 500–700° in the gas phase at atmospheric pressure is a new general method for obtaining aryl- and alkenylhalosilanes. In investigating this interaction it was shown that the reaction proceeds almost quantitatively according to the scheme:

$$R_{nCl_{3-n}}SiH + R'Cl \rightarrow R_{nCl_{3-n}}SiR' + R_{nCl_{4-n}}Si + R'H + HCl.$$

In order to elucidate the reaction mechanism, the material balance of the reaction was studied in the present work. A mixture of chlorobenzene and trichlorosilane was passed through a reactor at 580° with a contact time of the components in the reaction zone of 32 sec. The cube residue amounted to 1.7 g; from it a small amount of diphenyl was isolated; losses, 3.0 g.

Table 1

Reaction	Starting compounds	Starting compounds	Products obtained	Products obtained	Products obtained	Products obtained	Products obtained	Products obtained
I	C_6H_5Cl $\frac{771}{86.8}$	$HSiCl_3$ $\frac{278}{37.7}$	HCl $\frac{130}{4.7}$	$C_6H_5SiCl_3$ $\frac{132}{28.1}$	$SiCl_4$ $\frac{59.0}{10.1}$	C_6H_6 $\frac{55.5}{4.3}$	$HSiCl_3$ $\frac{66.8}{9.1}$	C_6H_5Cl $\frac{565}{63.5}$
II	C_6H_5Cl $\frac{556}{62.6}$	CH_3SiHCl_2 $\frac{278}{31.9}$	HCl $\frac{74.8}{2.72}$	$C_6H_5SiCl_2CH_3$ $\frac{76.5}{14.6}$	CH_3SiCl_3 $\frac{78.2}{11.7}$	C_6H_6 $\frac{74.4}{5.76}$	CH_3SiHCl_2 $\frac{94.7}{10.9}$	C_6H_5Cl $\frac{369}{41.5}$
	$CH_3C_6H_4Cl$	$HSiCl_3$	HCl	$CH_3C_6H_4SiCl_3$	$SiCl_4$	$CH_3C_6H_5$	$HSiCl_3$	$CH_3C_6H_4Cl$

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Reaction	Starting compounds	Starting compounds	Products obtained	Products obtained	Products obtained	Products obtained	Products obtained	Products obtained
III	$\frac{556}{70.4}$	$\frac{278}{37.7}$	$\frac{124.2}{4.5}$	$\frac{125}{28.2}$	$\frac{48}{8.2}$	$\frac{46.4}{4.27}$	$\frac{83.8}{11.2}$	$\frac{359.2}{45.5}$

Note. Values above the line are the amount of substance in millimoles; below the line, in grams.

The study of the material balance of the reactions between chlorobenzene and trichlorosilane (I), *o*-chlorotoluene and trichlorosilane (II), and also between chlorobenzene and methyldichlorosilane (III) led to the following results (see Table 1). The gaseous products of the reaction amounted to 1-2% of the weight of the reagents. From the data presented it is evident that the molar amounts of the hydrogen chloride formed and of the organochlorosilane, on the one hand, and of silicon tetrachloride (or methyltrichlorosilane) and the corresponding hydrocarbon, on the other, are close. It is natural to suppose that each of these pairs compounds was formed by a separate reaction. A certain excess of silicon tetrachloride (or methyltrichlorosilane) over the corresponding hydrocarbon is explained by slight pyrolysis of trichlorosilane (or methyldichlorosilane):

$$4Cl_3SiH \rightarrow 3SiCl_4 + Si + 2H_2.$$

Theoretically, it might be assumed that the above-mentioned pairs of compounds are formed as a result of secondary reactions, and not from the starting compounds; for example, for the interaction of chlorobenzene and trichlorosilane one might suppose the secondary reactions:

$$C_6H_5SiCl_3 + HCl \rightarrow C_6H_6 + SiCl_4$$

or

$$C_6H_6 + SiCl_4 \rightarrow C_6H_5SiCl_3 + HCl.$$

Specially designed experiments showed that neither of these reactions occurs under the conditions of the interaction being studied. In addition, it turned out that, at the given temperature and ratio of the initial reagents, the ratio between the above-mentioned pairs of compounds remains practically unchanged.

The data obtained convincingly indicate that the interaction between silicon hydrides and organochlorides in the gas phase at atmospheric pressure proceeds in two parallel directions. For example, for chlorobenzene and trichlorosilane:

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$$C_6H_5Cl + HSiCl_3 \begin{cases} \longrightarrow C_6H_5SiCl_3 + HCl & \text{(I)} \\ \longrightarrow C_6H_6 + SiCl_4 & \text{(II)} \end{cases}$$

We call reaction I the condensation reaction; reaction II, the reduction reaction.

The ratio between the two reactions is determined to a decisive extent by the nature both of the organochloride and of the silicon hydride. We studied the reactions of trichlorosilane with various organohalides and, for each case, determined the ratio (in moles) of the condensation and reduction products. We denote this ratio by K/R. The amount of organotrichlorosilane in moles characterizes the condensation product; the amount of silicon tetrachloride, the reduction product. The experimental data obtained are given in Table 2.

Table 2

Dependence of the ratio of condensation and reduction products on the structure of organohalides in their interaction with trichlorosilane at 580°, $\tau = 27$–30 sec., RHal : HSiCl$_3$=2 : 1

Organohalides	K/R	Organohalides	K/R
C_6H_5Cl	2.4	$CH_2 = CHCl$	17.0
n-$CH_3C_6H_4Cl$	4.2	$Cl_2C = CCl_2$	1.9
o-$CH_3C_6H_4Cl$	2.6	$CH_2 = CH{-}CH_2Cl$	6.7
2,5-$(CH_3)_2C_6H_3Cl$	3.6	C_6H_5Br	0.1
2,4,6-$(CH_3)_3C_6H_2Cl$	3.2	α-$C_{10}H_7Br$	1.1
n-ClC_6H_4Cl	1.9	C_6H_5F	1.0
α-$C_{10}H_7Cl$	6.2	$C_6H_5CH_2Cl$	0
β-$C_{10}H_7Cl$	9.7	CH_3Cl	0
o-$C_6H_5C_6H_4Cl$	0.7	CCl_4	0

As is seen from Table 2, the K/R ratio for aromatic organochlorides is influenced by two factors—the nature of the substituent and steric hindrance. Steric hindrance, namely the presence of the substituent in the ortho position relative to the chlorine atom being attacked, lowers the value of K/R. The same conclusion follows from a comparison of the K/R values for α- and β-chloronaphthalenes. Introduction of electron-donor substituents into the aromatic ring increases the value of K/R. It is interesting to note that in the case

2,4,6-trimethylchlorobenzene, despite the presence of methyl groups in both ortho positions to the chlorine atom, the value of C/R is higher than for o-chlorotoluene. The introduction of electron-acceptor substituents promotes a decrease in C/R. For chloronaphthalenes, C/R is several times higher than for benzene derivatives; C/R is of approximately the same order for allyl chloride as well. Vinyl chloride has the largest C/R value. In the case of saturated aliphatic chlorides, the reaction proceeds practically only according to the reduction scheme, and C/R = 0.

The nature of the halogen in organohalides also has a strong influence on the value of C/R. Replacement of chlorine by either bromine or fluorine leads to a decrease in C/R.

Table 3

Dependence of the ratio of condensation and reduction products on the structure of silicon hydrides in their reaction with chlorobenzene at 540°, $\tau = 28$ sec. $C_6H_5Cl : R^1R^2R^3SiH = 2 : 1$

Silicon hydrides	C/R	Silicon hydrides	C/R
Cl_3SiH	2.4	$C_6H_5SiCl_2H$	1.1
CH_3SiCl_2H	1.0	$(C_6H_5)_3SiH$	0.1
$C_2H_5SiCl_2H$	0.5		

Further investigation showed that the nature of the second component of the reaction—the silicon hydride—also has a strong influence on the value of C/R. As can be seen from the data in Table 3, replacement of chlorine atoms in trichlorosilane by alkyl or aryl radicals promotes a relative increase in the reduction reaction. Moreover, the more chlorine atoms are replaced by radicals, the more strongly the interaction proceeds according to the reduction scheme.

The homolytic character of the reaction studied was demonstrated earlier ([1,3,4]) and, obviously, cannot be disputed. The results obtained in the present work make it possible to deepen our understanding of the mechanism of this reaction and to put forward several new propositions.

The initiation of radicals evidently occurs by thermal dissociation of the Si—H bond, for example:

$$HSiCl_3 \rightarrow \dot{H} + \dot{S}iCl_3.$$

We shall consider the case of the reaction of trichlorosilane with chlorobenzene. It is unlikely that the reaction begins with decomposition of the organochloride molecule, where the C—Cl bond energy is considerably higher. The ease of decomposition of the silicon hydride molecule leads to constant generation of radicals. Along with this, chain propagation must play a significant role in radical generation. During chain transfer, only the radical $\dot{S}iCl_3$ is regenerated, since any radical, acting on a silicon hydride molecule, whose concentration is relatively high, must abstract a hydrogen atom with liberation of a silyl radical. Thus, during development of the process the active species is the silyl radical.

Obviously, both parallel reactions occur as a result of attack by the silyl radical on the organochloride molecule, but at different sites.

When the $\dot{\mathrm{S}}\mathrm{iCl}_3$ radical attacks the chlorine atom of the chlorobenzene molecule, abstraction of the chlorine atom occurs and silicon tetrachloride and the phenyl radical are formed; the latter, reacting with trichlorosilane, again gives the radical $\dot{\mathrm{S}}\mathrm{iCl}_3$:

$$\mathrm{C_6H_5Cl} + \dot{\mathrm{S}}\mathrm{iCl_3} \rightarrow \mathrm{SiCl_4} + \dot{\mathrm{C}}_6\mathrm{H_5},$$

$$\dot{\mathrm{C}}_6\mathrm{H_5} + \mathrm{HSiCl_3} \rightarrow \mathrm{C_6H_6} + \dot{\mathrm{S}}\mathrm{iCl_3}.$$

Such is the scheme of the reduction reaction. The occurrence of $\mathrm{C_6}\dot{\mathrm{H}}_5$ in the course of the reaction is evidenced by the isolation from the cube residue of diphenyl, formed, evidently, by recombination of phenyl radicals.

For the condensation reaction to occur, it is necessary that in the organochloride the C—Cl bond be at a carbon bound to a neighboring carbon—

with a π bond. The attack of the silyl radical may be directed at such a bond with formation of a so-called π-complex, for example:

$$\mathrm{Cl_3Si}^{\bullet} + \mathrm{C_6H_5Cl} \longrightarrow [\mathrm{C_6H_5Cl(SiCl_3)}]^{\bullet}$$

The formation of intermediate σ-complexes must be excluded, since reactions with various aryl chlorides never led to the formation of isomers; moreover, the amount of gaseous reaction products at such a high temperature is very small ($\sim 1\%$), which indicates the absence of disruption of the aromatic system.

Upon collision of the intermediate π-complex with a molecule of trichlorosilane, aryltrichlorosilane and hydrogen chloride are formed, and a silyl radical is generated:

$$[\mathrm{C_6H_5Cl(SiCl_3)}]^{\bullet} + \mathrm{HSiCl_3} \longrightarrow \mathrm{C_6H_5SiCl_3} + \mathrm{HCl} + {}^{\bullet}\mathrm{SiCl_3}$$

Thus, the essence of the condensation and reduction mechanism is reduced to competition between attack by the silyl radical on the chlorine atom and on the π-electron bond of the organochloride molecule. The proposed hypothesis for the mechanism of the condensation and reduction reactions satisfactorily explains the experimental data obtained by us, namely: the increase in K/B in the presence of electron-donating substituents in chlorobenzene and its decrease with electron-accepting substituents; the increase in K/B in the reaction with chloronaphthalenes; the occurrence only of the reduction reaction with saturated aliphatic chlorides, etc.

The experimental procedure has been described previously ([1]).

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