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Radiation Chlorination of Certain Organochlorosilanes and Organopolysiloxanes

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It is known that the mechanism and the final products of chemical reactions carried out with the aid of ionizing radiation may differ from the mechanism of the same reactions initiated by ordinary methods. Thus, radiation polymerization of certain monomers at low temperature proceeds by an ionic mechanism, and at elevated temperature by a radical mechanism. The processes of radiation chlorination of organic compounds have been studied relatively little, and radiation chlorination of organosilicon compounds has not been studied by anyone at all. Since organosilicon compounds differ substantially in their properties from their carbon analogs, the study of their radiation chlorination is, in our opinion, of considerable interest. The results of radiation chlorination of certain organopolysiloxanes and organochlorosilanes are given below.

Polydimethylsiloxane rubber $-[(CH_3)_2SiO]_n$ (molecular weight $400\,000 \div 500\,000$) was chlorinated at 0° in the form of a 4% solution in CCl_4. The radiation source was Co^{60} with an activity of 800 g-eq radium. At a dose rate of 4200 rad/min, a product containing $50 \div 55\%$ chlorine was obtained. Increasing the integral dose above $1.25 \cdot 10^5$ rad led to an insignificant increase in the chlorine content and was accompanied by destruction of the polymer. The optimum reaction time was 15-30 min.

On chlorination of polyphenylmethylsiloxane $[C_6H_5(CH_3)SiO]_n$ under the same conditions, a product with a chlorine content up to 56.1% was obtained. About 80% of the chlorine that reacted was consumed in the addition reaction at the double bonds of the aromatic nucleus, and $\sim 20\%$ entered into the reaction of replacement of hydrogen in the methyl group.

Table 1

Chlorination of CH_3SiCl_3 and $(CH_3)_2SiCl_2$

Experiment No.	Name of substance	Molar ratio chl. : silane	Temperature, °C	Dose rate, rad/min	Irradiation duration, min	Total chloride content in mixture, %	Monochlorides content in mixture, %	Higher chlorides content in mixture, %
1	CH_3SiCl_3	0.20	20	60	120	18.9	9.2	9.7
2	CH_3SiCl_3	0.20	0	3000	60	18.9	7.9	11.0
3	CH_3SiCl_3	0.20	20	3000	20	17.9	8.6	9.3
4	CH_3SiCl_3	0.47	20	3000	40	32.1	9.0	23.1
5	CH_3SiCl_3	0.81	20	3000	60	44.9	9.1	35.8
6	$(CH_3)_2SiCl_2$	0.30	0	7200	2	34.6	30.0	4.6
7	$(CH_3)_2SiCl_2$	0.50	0	7200	2	47.5	30.6	16.9
8	$(CH_3)_2SiCl_2$	0.20	0	900	15	22.4	18.7	3.7
9	$(CH_3)_2SiCl_2$	0.30	0	900	15	30.6	23.6	7.3
10	$(CH_3)_2SiCl_2$	0.40	0	900	20	40.2	20.2	20.0
11	$(CH_3)_2SiCl_2$	0.20	−30	900	30	23.0	19.1	3.9

On chlorination of ethyltrichlorosilane (molar ratio $Cl_2 : C_2H_5SiCl_3 = 0.15 \div 0.35$, 0°, 900 rad/min), β- and α-monochloro derivatives are formed in a ratio of 1.7 : 1, which coincides with the results of vapor-phase photochemical chlorination of $C_2H_5SiCl_3$ (1).

In the chlorination of methyltrichlorosilane and dimethyldichlorosilane (Table 1), the content of monochloro derivative in the reaction mixture does not depend on the molar ratio of the reagents. A change in the dose rate does not affect the composition of the chlorination products of CH_3SiCl_3; when the temperature is lowered from 20 to 0°, the yield of $CH_2ClSiCl_3$ decreases somewhat.

The average rate of the chlorination reaction of CH_3SiCl_3 does not depend on the chlorine concentration and is, at 0° and 3300 rad/min, 0.148 ± 0.030 mol/l • min. Its magnitude is proportional to the square root of the dose rate and decreases in the presence of atmospheric oxygen. The radiation-chemical yield of the chlorination reactions of CH_3SiCl_3 and $(CH_3)_2SiCl_2$ is $10^4 \div 10^5$ molecules per 100 eV. The activation energies of these reactions are, respectively, ~7300 and ~6100 cal/mol. Thus, the radiation chlorination of CH_3SiCl_3 and $(CH_3)_2SiCl_2$ is a typical radical-chain process and proceeds in the same way as the photochemical (1) and thermally initiated (2) chlorination of these compounds.

On the basis of the data obtained, it was established that in the sequence of reactions:

$$\mathrm{CH_3SiCl_3} \xrightarrow[\mathrm{M}]{k_1} \cdot\mathrm{CH_2SiCl_3} + \mathrm{H}; \quad \mathrm{Cl_2} \xrightarrow[\mathrm{M}]{k_1'} 2\mathrm{Cl}, \tag{1}$$

$$\cdot\,\mathrm{CH_2SiCl_3} + \mathrm{Cl_2} \xrightarrow{k_2} \mathrm{ClCH_2SiCl_3} + \mathrm{Cl}, \tag{2}$$

$$\mathrm{CH_3SiCl_3} + \mathrm{Cl} \xrightarrow{k_3} \cdot\mathrm{CH_2SiCl_3} + \mathrm{HCl}, \tag{3}$$

$$\mathrm{ClCH_2SiCl_3} + \mathrm{Cl} \xrightarrow{k_4} \cdot\mathrm{CHClSiCl_3} + \mathrm{HCl}, \tag{4}$$

$$\cdot\,\mathrm{CHClSiCl_3} + \mathrm{Cl_2} \xrightarrow{k_5} \mathrm{CHCl_2SiCl_3} + \mathrm{Cl} \tag{5}$$

stage (3) determines the rate of the entire reaction as a whole; the ratio of the rate constants of the chlorination reactions of $CH_2ClSiCl_3$ and CH_3SiCl_3 is $k_4 : k_3 \simeq 10$.

Phenyltrichlorosilane and phenylmethyldichlorosilane were chlorinated at temperatures of 0-150° and dose rates of 5900 rad/min (in ampoules) and 800 rad/min (with chlorine passed through). In the chlorination of $C_6H_5SiCl_3$ and $C_6H_5(CH_3)SiCl_2$ at 0-20°, chlorine addition to the double bonds of the aromatic ring predominates, leading to the formation of $C_6H_5Cl_6SiCl_3$ and $C_6H_5Cl_6(CH_3)SiCl_2$. Additive chlorination of $C_6H_5(CH_3)SiCl_2$ at 20-22° is accompanied by a parallel substitution reaction of hydrogen atoms by chlorine in the methyl group, with the ratio of addition and substitution products being 4:1. Thus, the radiation chlorination of $C_6H_5SiCl_3$ and $C_6H_5(CH_3)SiCl_2$ at 0-20° proceeds analogously to the photochemical process ([3],[4]).

Radiation chlorination of $C_6H_5(CH_3)SiCl_2$ at 50° leads to the formation of a mixture of products of substitution in the methyl group, in the aromatic ring, and of the addition product:

$$\mathrm{C_6H_5(CH_3)SiCl_2} \xrightarrow[\mathrm{W}]{\mathrm{Cl_2};\ 50^\circ} \begin{cases} \mathrm{C_6H_5Cl_6(CH_3)SiCl_2}, \\ \mathrm{C_6H_5(CH_{3-n}Cl_n)SiCl_2}, \\ \mathrm{C_6H_{5-n}Cl_n(CH_3)SiCl_2}. \end{cases} \tag{6}$$

At 75-150°, substitution in the aromatic ring predominates; the product of chlorine addition to the double bonds is not formed under these conditions, while the products of substitution in the CH_3 group amount to 6-12% of the total quantity of chlorides formed.

The products of radiation chlorination of phenylmethyldichlorosilane obtained at 75-150° are identical to the chlorination products formed in the presence of ionic-type catalysts—$SbCl_3$ and I_2 ([5]). The reaction is not inhibited by atmospheric oxygen, and its rate is proportional to the first power of the dose rate. Addition to the irradiated system of 0.005-0.04% of the radical initiator porophor suppresses substitution in the aromatic ring and accelerates substitution in the methyl group. The totality of these facts indicates that the radiation chlorination of $C_6H_5(CH_3)SiCl_2$ at 75-150° proceeds by an ionic mechanism.

It is known that when ionizing radiation interacts with a substance, the principal primary processes are excitation and ionization of the molecules of the absorbing medium. It is believed, however, that in the liquid phase at temperatures above zero the electrons recombine so rapidly with the parent positive ions that the latter do not have time to enter into any reactions. At low temperatures ($< -40^\circ$), ionic radiation processes in the liquid phase are possible, for example ionic polymerization.

According to Mage' s assumptions (6), the lifetime of positive ions may increase not only with decreasing temperature, but also in the presence of substances possessing a considerable electron affinity and an increased cross section for the capture of thermal electrons, such as, for example, halides and oxygen. If, in the present case, the presence of chlorine in the system promotes an ionic reaction, then, evidently, quite a large number of compounds may be found—including those not containing silicon—which under analogous conditions will be capable of ionic radiation chlorination. There are, however, indications that silicon compounds may possess a considerable electron affinity (7). If the acceptor of free thermal electrons proves to be phenylmethyldichlorosilane itself, then it is quite possible that precisely this circumstance accounts for the ionic mechanism of its chlorination at $75 \div 150^\circ$. In that case, substances possessing analogous properties, i.e. the ability to capture electrons, may prove capable of ionic radiation chlorination. Investigation of the radiation chlorination of various aromatic compounds will make it possible to clarify this question.

The radiation-chemical yield of substitution products in the C_6H_5-group during chlorination of $C_6H_5(CH_3)SiCl_2$ is $10^4 \div 10^5$ molecules per 100 eV. Such a high yield is possible only if not only primary ions participate in the reaction. In the case under consideration, the integral doses did not exceed $2 \cdot 10^{20}$ eV, and per 100 eV of absorbed energy an average of about three ion pairs is formed. Consequently, there must exist some other source of formation of the ions that carry the reaction.

At present it is considered that catalytic chlorination of aromatic compounds proceeds with the participation of Cl^+ ions:

$$\mathrm{MeCl_3 + Cl_2 \rightarrow MeCl_4^- + Cl^+}, \tag{7}$$

$$\mathrm{C_6H_6 + Cl^+ \rightarrow C_6H_5Cl + H^+}, \tag{8}$$

$$\mathrm{MeCl_4^- + H^+ \rightarrow MeCl_3 + HCl}, \tag{9}$$

where $MeCl_3$ is a catalyst of the $SbCl_3$ or $AlCl_3$ type. According to this scheme, Cl^+ ions are regenerated on the catalyst, which itself remains unchanged.

In radiation chlorination, primary Cl^+ ions may be formed in several ways. First, they are obtained directly upon radiolysis of dissolved chlorine:

$$\mathrm{Cl_2} \rightsquigarrow \begin{cases} \mathrm{Cl_2^+ + e^-} \\ \mathrm{Cl^+ + Cl + e^-} \end{cases} \tag{10}$$

A second source of Cl^+ ions may be the organochlorosilane itself. Under electron impact on $C_6H_5SiCl_3$ and $C_6H_5(CH_3)SiCl_2$ in a mass spectrometer (10), 13.2 and 6.5% of all ions formed, respectively, are Cl^+ ions.

Finally, one can envisage a reaction between molecular or fragment ions and a chlorine molecule:

$$\mathrm{[Ion]^+ + Cl_2 \rightarrow [Ion]Cl + Cl^+}, \tag{11}$$

if the lifetime of the positive ions in solution is sufficient for them to participate in secondary reactions.

Primary Cl^+ ions can further enter into reaction with the silane molecule:

$$\mathrm{C_6H_5(CH_3)SiCl_2 + Cl^+ \rightarrow C_6H_4Cl(CH_3)SiCl_2 + H^+}. \tag{12}$$

The H^+ ions, reacting with molecular chlorine, liberate new chlorine ions:

$$\mathrm{H^+ + Cl_2 \rightarrow HCl + Cl^+ + 2.5\ eV}. \tag{13}$$

Energetically, reaction (13) is quite possible. The process of regeneration of Cl^+ ions by reaction (13) may continue until one of them recombines with a negative ion.

Naturally, the above considerations can be valid only if the lifetime of positive ions in solution is sufficiently long. The proposed mechanism is not the only possible one; however, it appears to us to be quite plausible.

As already stated, radiation chlorination of phenyltrichlorosilane at 0–20° proceeds exclusively by addition of chlorine to the aromatic nucleus. At 50°, along with additive chlorination, a substitution reaction also occurs to a slight extent (~8.0% of the chlorides consists of $ClC_6H_4SiCl_3$ and ~65.0% of $C_6H_5Cl_6SiCl_3$). At 100 and 150° chlorination proceeds exclusively as a reaction of substitution of hydrogen atoms by chlorine; the addition product is not detected under these conditions. Investigation of the composition of the chlorination products by spectroscopic and chromatographic methods showed that the mixture of monochloro derivatives contains ~70% meta-, ~20% ortho-, and ~10% para-$ClC_6H_4SiCl_3$, while 2,5-dichlorophenyltrichlorosilane predominates in the mixture of dichlorides (70-80%).

Attempts to determine the average rate of chlorination of $C_6H_5SiCl_3$ by the same method as in the case of chlorination of $C_6H_5(CH_3)SiCl_2$, i.e., by measuring the density at specified time intervals, did not give reproducible results, which is associated with the low rate of chlorination of $C_6H_5SiCl_3$. On the basis of the data obtained, it can definitely be asserted that chlorination of $C_6H_5SiCl_3$ at 100-150° is not inhibited by oxygen (or is inhibited only partially), and, consequently, it may be assumed that the ionic mechanism plays the main role in this reaction.

In connection with the foregoing, it is of interest to investigate, under analogous conditions, the radiation chlorination of other aromatic compounds containing substituents other than Si. Thus, according to preliminary data obtained by us, nitrobenzene is not chlorinated at 100° and an integral dose of about $1.9 \cdot 10^5$ rad. Chlorobenzene is chlorinated at 80–100°, and the reaction is inhibited by atmospheric oxygen.

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