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The Hydride Addition of Organohydrosiloxanes to Compounds with a Multiple Carbon-Carbon Bond

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Reactions leading to the formation of an Si-C bond—the hydrosilylation of unsaturated organic compounds by organohydrosiloxanes and the hydride addition of organohydrosiloxanes to organosilicon compounds containing multiple carbon-carbon bonds—are examined. Factors influencing the course of the reaction and the properties of the addition products are discussed. The bibliography includes 153 references.

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I. INTRODUCTION

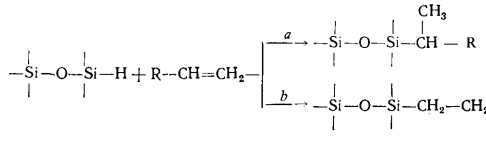
Hydride addition reactions are common in organic and organoelemental chemistry. Using these reactions, a wide variety of numerous organosilicon compounds have been synthesised. The addition of hydrogen-containing organosilicon compounds to compounds with a multiple carbon–carbon bond, the so-called hydride addition or hydrosilylation reaction, constitutes one of the methods for the formation of an Si–C bond[1-3].

The hydride addition reaction has been widely used recently not only for the synthesis of organosilicon monomers and oligomers but also for the conversion of linear and branched organoelemental polymers into polymers with a network structure. The hydride addition reaction has also acquired great importance for the synthesis of polycarbo-organosiloxanes.

Since studies on the hydride addition of organohydrosiloxanes to various organic and organosilicon unsaturated compounds published up to 1964 have already been examined in a monograph[2], studies published from 1964 to 1976 are discussed in the present review.

II. THE HYDRIDE ADDITION OF ORGANOHYDROSILOXANES TO COMPOUNDS WITH A MULTIPLE CARBON–CARBON BOND

The addition of organohydrosiloxanes as well as other hydrogen-containing organosilicon compounds to unsaturated compounds can proceed with formation of α- and β-addition products. Consequently this reaction can proceed both in accordance with the Markovnikov rule (pathway *a*) and contrary to this rule, i.e. in accordance with Farmer's rule (pathway *b*):



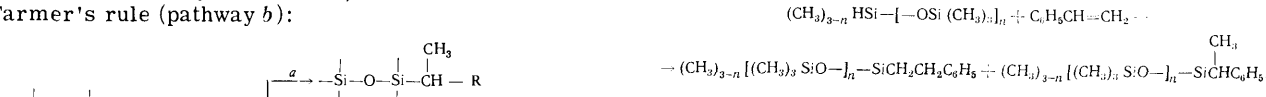
The hydrosilylation of hex-1-ene, hex-2-ene, and hex-3-ene by 1,1,3,3-tetramethyldisiloxane has been investigated[4]. As a result of this reaction, hex-1-ene gives rise exclusively to the 1-hexyl adduct, while hex-2-ene and hex-3-ene lead to a mixture of isomers. At the same time the hexenes themselves isomerise. The hydrosilylation reaction was carried out at 100°C for several days and the addition products obtained were converted into $(CH_3)_3SiC_6H_{13}$. The proportions of the isomers in the final products are illustrated in the Table.

The content of $(CH_3)_3SiC_6H_{13}$ isomers as a function of the structure of the initial olefin.

Initial olefin	Content of $(CH_3)_3SiC_6H_{13}$ isomers, %		
	1-hexyl	2-hexyl	3-hexyl
Hex-3-ene	76	10	14
Hex-2-ene	88	7	5
Hex-1-ene	99	traces	0

The hydride addition of pentamethyldisiloxane to hex-1-ene in the presence of various catalysts (Group VIII transition metals) has been investigated[5]. It has been shown that this reaction is effectively accelerated by rhodium and platinum complexes; palladium and nickel complexes do not catalyse this reaction.

In the hydrosilylation of styrene by methylhydrosiloxanes having the general formula $(CH_3)_{3-n}HSi-[-OSi(CH_3)_3]_n$, where $n = 0-3$, in the presence of chloroplatinic acid in isopropyl alcohol (the Speier catalyst), both α- and β-addition products are formed[6]:



The fraction of β-addition products varies from 80 to 100% depending on the structure of the methylhydrosiloxanes. The tendency of methylhydrosiloxanes to form a β-adduct decreases in the following sequence as a function of the number of trimethylsiloxy-groups (n): $0 > 3 > 2 > 1$.

It has been found[7] that in the presence of the Speier catalyst, the main reaction involving the hydrosilylation of hex-2-ene by bis(trimethylsiloxy)methylsilane is accompanied by the disproportionation of the silane, i.e. the

exchange of methyl and trimethylsiloxy-groups in accordance with the mechanism

$$(CH_3)_2HSi-[-OSi(CH_3)_3]_2 \rightarrow (CH_3)_2HSiOSi(CH_3)_3 + [(CH_3)_3SiO-]_3-SiH.$$

As a result of the above hydrosilylation reaction at 138°C for 10 h with subsequent fractionation of the products, a mixture consisting of 56.6% $[(CH_3)_3SiO]_2Si(CH_3)(C_6H_{13})$, 14.5% $[(CH_3)_3SiO]_3SiH$, and 12.5% $(CH_3)_3SiOSi(CH_3)_2(C_6H_{13})$ was obtained. In addition 6.4% of $\{[(CH_3)_3SiO]_2SiCH_3\}_2O$ (the product of the oxidation of the initial silane) was also isolated.

The hydrosilylation of 3-oxapentadiene by 1,1,3,3-tetramethyldisiloxane leads to 1,1,3,3-tetramethyl-1-(3-vinyloxyethyl)disiloxane in yields up to 15%:[8]

$$CH_2=CHOCH=CH_2 + H(CH_3)_2SiOSi(CH_3)_2H \xrightarrow{H_2PtCl_6} \rightarrow H(CH_3)_2SiOSi(CH_3)_2CH_2CH_2OCH=CH_2.$$

The low yield of the adduct and the large amount of the non-distilling residue makes 1,1,3,3-tetramethyldisiloxane relatively unpromising, according to Voronkov et al.[8], as a hydrosilylating agent.

The hydrosilylation of phenylacetylene and *p*-diethynylbenzene by 1,1,3,3-tetramethyldisiloxane in the presence of chloroplatinic acid yielded phenyl-substituted 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentanes[9]:

$$[(CH_3)_2HSi]_2O + C_6H_5C\equiv CR \rightarrow (CH_3)_2Si\langle \text{C}_6\text{H}_5\text{R}\ \text{CH}-\text{CH}\ \text{O}\rangle Si(CH_3)_2 ;$$

R = H or C_6H_5.

The hydrosilylation of phenyl-substituted acetylenes by 1,3-diethyl-1,3-dimethyl-disiloxane proceeds similarly.

It has been found[10] that certain organosiloxycycloalkanes are capable of polymerising spontaneously. The polyaddition of 1,1,3,3-tetramethyldisiloxane to phenylacetylene and *p*-diethynylbenzene in the presence of H_2PtCl_6 in THF has been reported recently[11,12]. It has been shown that this process consists of consecutive-parallel reactions and is accompanied by the appearance of branching centres:

$$C_6H_5C\equiv CR + H-Si\langle \rightarrow C_6H_5CH=CRSi\langle + C_6H_5C=CHR$$

cis-, *trans-*

$$C_6H_5CH_2-CR(Si\langle)_2 \quad C_6H_5-CH(Si\langle)-CHR(Si\langle) \quad C_6H_5C(Si\langle)-CH_2R ;$$

R = H or C_6H_5.

It has been found[11] that the rate of this reaction is determined by the equation $v = K[\equiv Si-H][C_6H_5C\equiv CR][Cat]^{0.5}$ and the apparent activation energy is 11–18 kcal mole^{-1}. The addition of pyridine in amounts comparable to the amount of the catalyst inhibits this reaction, which is believed[11] to be due to the formation of inactive platinum–pyridine complexes.

The hydrosilylation of styrene, α-methylstyrene, methyl methacrylate, and allyl cyanide by dimethyl(methylhydro)cyclosiloxanes in the presence of chloroplatinic acid has been investigated[13]. It follows from ^{1}H NMR data that the product of the addition of tetramethylcyclotetrasiloxane to α-methylstyrene has the structure $[(CH_3)\cdot(C_6H_5\underset{CH_3}{\underset{|}{C}}HCH_2)SiO]_4$, i.e. the reaction proceeds in accordance with Farmer's rule.

The hydrosilylation of non-1-ene, α-methylstyrene, methyl methacrylate, and allylamine by heptamethylcyclotetrasiloxane as well as the hydrosilylation of methyl methacrylate by tetramethylcyclotetrasiloxane (in the presence of chloroplatinic acid as the catalyst) has been achieved[14]. Analysis of the reaction products by infrared and ^{1}H NMR spectroscopy established, that, regardless of the nature of the unsaturated compound, the addition takes place in accordance with Farmer's rule without the opening of the initial cyclotetrasiloxane fragment.

Data have been published[15] on the hydrosilylation of allyl cyanide, styrene, α-methylstyrene, and methyl acrylate by tetramethyl- and tetraethyl-cyclotetrasiloxanes in the presence of chloroplatinic acid. The addition products were studied by infared and ^{1}H NMR spectroscopy; in contrast to the data of Reikhsfel'd and Grigor'eva[13] and Borisov[14], it was observed that in all cases the addition products are mixtures of α- and β-adducts with similar boiling points.

Andrianov et al.[16] examined the hydrosilylation by pentamethyldisiloxane and bis(trimethylsiloxy)methylsilane of a number of unsaturated compounds in the presence of H_2PtCl_6: hept-1-ene, cyclohexene, styrene, indene, allyl bromide, acrylonitrile, dicyanoethylene, 2-vinylpyridine, hept-1-yne, isopropylacetylene, 2,5-dimethylhex-3-yne-2,5-diol, isoprene, 1,4-dichlorobut-2-yne, cyclopentadiene, and dichloromethylvinylsilane. It was noted that the above methyl hydrosiloxanes do not add to acrylonitrile in dicyanoethylene. Apart from H_2PtCl_6, amines and their derivatives and Pd/C were also tried as catalysts of the addition reaction. Here too the addition does not occur, which has been explained by steric hindrance. When methylhydrosiloxanes were allowed to add to cyclopentadiene, the dimerisation of the latter was observed. Allyl bromide does not add to pentamethyldisiloxane and the interaction of these compounds leads to the formation of pentamethylbromodisiloxane.

The occurrence of side reactions was observed[17] in the addition of methylhydrosiloxanes having the general formula $(CH_3)_{3-n}HSi[OSi(CH_3)_3]_n$ to β-methylallyl chloride in the presence of chloroplatinic acid:

$$\equiv Si-H + CH_2=\underset{CH_3}{\underset{|}{C}}-CH_2Cl \rightarrow \underset{(I)}{\equiv SiCH_2\underset{CH_3}{\underset{|}{C}}HCH_2Cl} + \underset{(II)}{\equiv SiCl} + \underset{(III)}{\equiv SiCH_2\underset{CH_3}{\underset{|}{C}}=CH_2}.$$

Depending on the structure of the initial methylhydrosiloxane, different amounts of reaction products are formed. Thus pentamethyldisiloxane forms only addition products (I) in 97% yield. Bis(trimethylsiloxy)methylsilane gives rise to 34% of (I), 18% of (II), and 9% of (III). Tris(trimethylsiloxy)silane forms the following products: 14% of (I), 42% of (II), and 23% of (III). According to the current ideas[18] about the mechanism of the hydrosilylation reaction in the presence of H_2PtCl_6, the stability of the intermediate complex with the catalyst should increase with increasing amount of the electronegative trimethylsiloxy-groups in the methylhydrosiloxane molecule; this should lead to an increase of the reactivity of the methylhydrosiloxanes, but the role of steric factors in this reaction is also important, so that the reactivity of methylhydrosiloxanes is determined by both factors. The authors suggest that chloromethylsilanes of type (II) are formed as a result of the destabilising effect of methylhydrosiloxanes on the π-allyl complex. Silylmethylallyl derivatives (III) are probably formed from the intermediate complex of the olefin, methylhydrosiloxane, and platinum.

It has been established[19] that, when methylhydrosiloxanes react with unsaturated compounds, side reactions occur together with hydrosilylation:

$$(CH_3)_3SiOSi(CH_3)_2H + CH_2=CH-CH(OCH_3)_2 \xrightarrow{H_2PtCl_6} \rightarrow (CH_3)_3SiOSi(CH_3)_2CH_2CH_2(OCH_3)_2 + (CH_3)_3SiOSi(CH_3)_2(OCH_3) + + (CH_3)CH=CH(OCH_3) .$$

The addition of 1,1,3,3-tetramethyldisiloxane takes place similarly, the β-adducts being formed in both cases.

The addition of linear organohydrosiloxanes to allylamine has been investigated[20]. In the presence of H_2PtCl_6 or the complex of platinum with the vinylpyridine ligand $[(C_5H_5NCH=CH_2)Cl]_2Pt$ allylamine reacts with pentamethyldisiloxane and 1,3-dimethyl-1,3-diphenyldisiloxane to give at 150°C addition products containing the amino-group in the γ-position in the organic group relative to the silicon atom.

The hydrosilylation of allylamine by α,ω-bis(hydromethylsiloxy)methylphenylsiloxane leads to α,ω-bis(γ-aminopropyldimethylsiloxy)methylphenylsiloxanes[21]. On polycondensation with dicarboxylic acids of the dimethylsiloxane series, the latter give rise to elastic organosilicon polyamides, which are soluble in organic solvents.

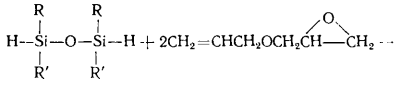
Monoaddition products have been obtained by the reaction of alkyldiallylamines $RN(CH_2CH=CH_2)$, where $R = CH_3$, C_2H_5, or $n\text{-}C_4H_9$, with 1,1,3,3-tetramethyldisiloxane[22]. Kinetic studies[22] have shown that 1,1,3,3-tetramethyldisilazane is less reactive than 1,1,3,3-tetramethyldisiloxane in the hydrosilylation of diallylethylamine.

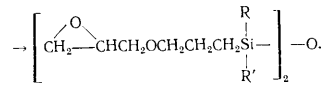
It is noteworthy that pentamethyldisiloxane and 1,1,3,3-tetramethyldisiloxane react with 2-vinylpyridine to form α-addition products only, while heptamethyl-, hexamethyl-, pentamethyl-, and tetramethyl-cyclotetrasiloxanes give rise to a mixture of α- and β-addition products under these conditions[23].

A convenient method for the synthesis of nitroaryl(alkyl)siloxanes involves the hydrosilylation of *m*-nitrostyrene by organohydrosiloxanes[24]. The reaction of 1,1,3,3-tetramethyldisiloxane and heptamethylcyclotetrasiloxane with *o*-, *m*-, and *p*-aminostyrenes in the presence of the Speier catalyst yielded the corresponding aminoaryl(alkyl)siloxanes[25]. ^1H NMR and gas–liquid chromatography (GLC) established that hydrogen and the silicon atom in methylhydrosiloxanes adds to both α- and β-carbon atoms of the C=C bond in aminostyrenes. The addition of 1,1,3,3-tetramethyldisiloxane to thienylmethylphenylvinylsilane has been achieved in the presence of the Speier catalyst[26]. Mono- and di-addition products, which are β-adducts, are formed as a result.

The corresponding organosilicon derivatives have been obtained by the addition of bis(trimethylsiloxy)methylsilane to *N*-propargylpiperidine, perhydroazepine, and morpholine in the presence of H_2PtCl_6.[27] Mono- and di-substituted acetyl- and γ-chloropropyl derivatives of disiloxane have been obtained by the hydrosilylation of vinyl acetate and allyl chloride respectively with 1,3-dimethyl-1,3-diphenyldisiloxane in the presence of H_2PtCl_6.[28]

The reaction of dihydromethylsiloxanearylenes with epoxy-compounds containing an unsaturated bond yielded organosilicon epoxy-derivatives in yields up to 80%. The reaction was carried out at 60–70°C in the presence of chloroplatinic acid[29]. Organosilicon epoxy-compounds with various substituents at the silicon atom have also been obtained by the addition of 1,1,3,3-tetraorganodisiloxanes to unsaturated epoxides in the presence of the Pt/C catalyst[30]:





It has been recommended[30] that the diaddition products be used as modifying additives to epoxy-resins and also to phenolic, alkyd, and polyester resins in order to increase their thermal stability. Following their addition to organosilicon resins, the diaddition products improve the adhesion of the former and their mechanical properties[30].

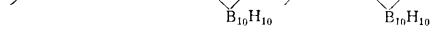
Compounds of the type

$$(CH_3)_3SiO-[-(CH_3)Si-[-(CH_2)_xO(C_2H_4O)_y-]-AO-]_n-Si(CH_3)_3,$$
$$A = H \text{ or } COR,$$

have been obtained by the addition of methylhydrosiloxanes to polyethers containing an unsaturated group, in the presence of H_2PtCl_6. The products are recommended as additives to polyurethane foam plastics[31]. Products with an analogous structure, recommended as foam stabilisers in the manufacture of flexible polyetherpolyurethanes, have also been described in patents[32,33].

Hydrosilylation of acrylic[34,35], and methacrylic[36] acids by α,ω-dihydromethyl(methylphenyl)siloxanes in the presence of the Speier catalyst yielded the corresponding organosiloxane-α,ω-dicarboxylic acids. It has been established by infrared spectroscopy that these reactions give rise to β-addition products.

Carbaborane derivatives of silicon have been obtained by the addition of 1,3-dichlorotrimethyldisiloxane and heptamethylcyclotetrasiloxane to unsaturated carbaborane derivatives[37]:



Isopropenylcarbaborane also adds to linear polyalkylhydrosiloxanes with formation of linear polycarbaboranesiloxanes[38].

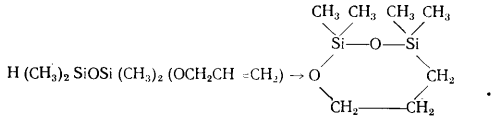
Polyorganosiloxanes containing the $\geq Si-H$ groups react with various organic compounds via the hydrosilylation mechanism[39]. It has been shown, for vinyl derivatives of styrene and divinylbenzene, that the addition of polyorganohydrosiloxanes proceeds in accordance with Farmer's rule.

The hydride addition of polyorganohydrosiloxanes to allyl acetate in the presence of platinum catalysts yielded liquids which are suitable for hydraulic shock absorbers in motor cars[40].

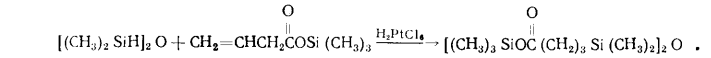
Reactions involving the hydride addition of organohydrosiloxanes to various organosilicon compounds containing unsaturated organic groups as well as the addition of hydrogen-containing organosilicon compounds to organosiloxanes with unsaturated organic substituents have been reported[2]. The addition of chloromethylhydro- and chloroethylhydro-silanes to methylvinylcyclosiloxanes has been described[41,42]. In the presence of the Speier catalyst these reactions yielded compounds capable of being converted further via their hydrolytic condensation. The addition reactions proceed with formation of β-addition products. The hydride addition of 1,1,3,3-tetramethyldisiloxane and tetramethylcyclotetrasiloxane to chloromethylvinyl- and methoxy-silanes in the presence of H_2PtCl_6 have been used to synthesise the initial compounds for the preparation of oxadisilacyclopentanes[43].

It has been shown[44] that, when allyloxyhydromethylsiloxanes are heated in the preeence of the Speier catalyst, intramolecular cyclisation takes place with formation of

methyloxasilacycloalkanes, for example:

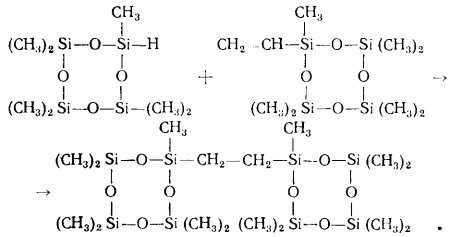


The addition of 1,1,3,3-tetramethyldisiloxane to trimethylsilyl vinylacetate has also been achieved[45]:



2-Silalactones have been obtained by the hydrolysis of the product.

A bicyclic organosiloxane has been obtained by the reaction of heptamethylvinylcyclotetrasiloxane and heptamethylcyclotetrasiloxane in the presence of chloroplatinic acid[46]:

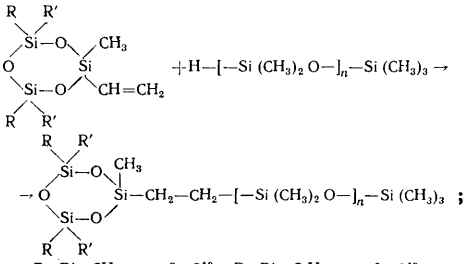


A bicyclic product of the addition of hexamethylphenylcyclotetrasiloxane to heptamethylvinylcyclotetrasiloxane has been obtained similarly[46].

The addition of pentamethyldisiloxane to heptamethylvinylcyclotetrasiloxane in the presence of various complex catalysts based on Group VIII transition metals has been investigated in detail[5,47]. The addition products were isolated by preparative GLC; analysis of the infrared and ^{1}H NMR spectra showed that, in the presence of platinum and rhodium compounds, this reaction proceeds mainly with formation of β-adducts.

The addition of pentamethyldisiloxane and 1-hydroheptamethyltrisiloxane to bis(methylphenyl)bis(methylvinyl)-cyclotetrasiloxane yielded the corresponding organocyclotetrasiloxanes containing dimethylsiloxane chains with terminal trimethylsiloxy-groups as a framework surrounding the silicon atom[48]. Infrared and ^{1}H NMR data led to the conclusion that the addition products are β-adducts. They do not polymerise under the influence of anionic catalysts [KOH at 140°C; $(CH_3)_4NOH$ at 80°C]. The addition of sulphuric acid (1%) induces structure formation in these adducts at 50°C in the course of 3 h with formation of cross-linked polymers.

The addition of vinylorganocyclotrisiloxanes to compounds having the general formula $H-[-Si(CH_3)_2O-]_n-Si(CH_3)_3$, which results in the formation of organocyclotrisiloxanes with methylsiloxane-ethylene groups at the silicon atom, has also been investigated[49,50]:



Dimethylcyclotrisiloxanes with methylsiloxane-ethylene branches give rise to cross-linked polymers in the presence of tetramethylammonium polydimethylsiloxanolate at temperatures from 20° to 75°C. This has been attributed[50] to chain transfer to siloxane-ethylene groups under the conditions of block polymerisation. Diphenylcyclotrisiloxanes with methylsiloxane-ethylene branches form polymers with a molecular weight of 187 000 under these conditions, the size of the siloxane-ethylene group in the initial compounds having little influence on the rate of formation of polymers.

Organosiloxanes with a cyclolinear structure have been obtained by the addition of pentamethyldisiloxane to hexamethyldivinylcyclotetrasiloxane in the presence of tris(triphenylphosphine)rhodium chloride[51]. It has been established with the aid of infrared and ^{1}H NMR spectroscopy that they are products of β-addition with an admixture (up to 10%) of α-addition products. GLC showed that both monoaddition and diaddition products are a mixture of stereoisomers. Cyclolinear organosiloxanes have also been obtained by the addition of α,ω-dihydrodimethylsiloxanes having the general formula $HSi(CH_3)_2O-[-Si(CH_3)_2O-]_n-Si(CH_3)_2H$ ($n = 0-3$) to heptamethylvinylcyclotetrasiloxane in the presence of tris(triphenylphosphine)rhodium chloride[52]. Analysis of the addition products with the aid of infrared and ^{1}H NMR spectroscopy established that the reaction proceeds preferentially in accordance with Farmer's rule

Reactions involving the addition of pentamethyldisiloxane to methylvinylsiloxanes having the general formula $(CH_3)_{3-n}(CH_2{=}CH)Si-[-OSi(CH_3)_3]_n$, where $n = 0-3$,[53] as well as reactions involving the addition of heptamethylvinyldisiloxane to methylhydrosiloxanes having the general formuls $(CH_3)_{3-n}HSi-[-OSi(CH_3)_3]_n$, where $n = 0-3$, have been described[54]. It has been shown that in the presence of platinum and rhodium compounds these reactions proceed with the preferential formation of β-adducts.

Organosiloxanes with ferrocene groups[55] have been obtained by the reaction of organosilicon ferrocene derivatives containing the $\geq Si-H$ bond with allylorganosiloxanes.

III. THE HYDRIDE POLYADDITION OF ORGANODIHYDROSILOXANES TO DI- AND POLYFUNCTIONAL UNSATURATED COMPOUNDS

This section deals with methods for the preparation of polycarbaorganosiloxanes using the hydride polyaddition of organohydrosiloxanes to organoalkenylsiloxanes and to organoalkenylhydrosiloxanes. Various organosilicon oligomers and polymers have been synthesised by the hydride polyaddition reaction[2,3,38]. There are two main methods for the preparation of oligomers and polymers of this kind.

1. Polyaddition of organosilicon compounds containing both an $\geq Si-H$ linkage and an unsaturated group in the molecule:

where R are various organic groups and R′ is an organic group with $n \geq 0$.

2. Polyaddition of organosilicon compounds containing two or more $\geq$Si–H linkages to bifunctional or polyfunctional unsaturated compounds (a) or to acetylene and its derivatives (b):

a) $$m\,H-(-SiR_2O-)_n-SiR_2H + m\,(CH_2=CH)_2A \xrightarrow{cat.} \rightarrow -[(-SiR_2O-)_n-SiR_2(CH_2)_2A(CH_2)_2-]_m- ,$$

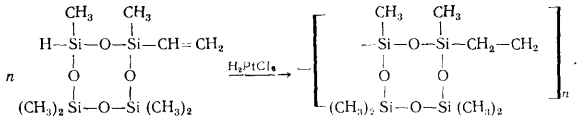
where R are various organic groups, A is an organic or organoelemental group, and $n \geq 0$;

b) $$m\,H-(-SiR_2O-)_n-SiR_2H + m\,CH\equiv CH \xrightarrow{cat.} \rightarrow -[(-SiR_2O-)_n-SiR_2-CH_2-CH_2-]_m- ,$$

where R are various organic groups and $n \geq 0$.

The possibility of synthesising linear polymeric products by the polyaddition reaction of *p*-vinylphenylmethylhydrosiloxanes having the general formula $CH_2=CHC_6H_4.Si(CH_3)_2-[-OSi(CH_3)_2-]_n-H$, where $n = 1-4$, has been demonstrated[56]. Polycarbaorganocyclosiloxanes have been obtained by the polyaddition of organohydrocyclotetrasiloxanes, containing vinyl and allyl groups, in the presence of H_2PtCl_6.[57,58]

The polyaddition reaction of hexamethylvinylcyclotetrasiloxane, whose polymeric products contain methylcyclotetrasiloxane units in the main chain linked by ethylene bridges, has been studied in greater detail[59]:



The reaction was carried out in carbon tetrachloride solution at 75°C in the presence of H_2PtCl_6. The products were viscous liquids with a molecular weight of 2200, which dissolved in benzene and other organic solvents. The infrared and ^{1}H NMR spectra of the addition products did not reveal the presence of the $\rangle$CH–CH$_3$ group, which led the authors[59] to the conclusion that the polyaddition reaction takes place with formation of β-adducts. Kinetic measurements at 50–80°C and a catalyst concentration of $(1.4-4.2)\times10^{-4}$ mole/mole showed that the reaction is described satisfactorily by a second order equation with respect to the monomer with first-order control with respect to the catalyst. It was shown that the reaction proceeds via a state involving the formation of an intermediate compound of the monomer and the catalyst.

Methods have been developed for the synthesis of polycarbaorganosiloxanes by the polyaddition of dihydroorganosiloxanes to dialkenylorganosiloxanes. This work was initiated by a study[60] of the addition of 1,3-diethyl-1,3-dimethyldisiloxane to 1,3-diethyl-1,3-dimethyl-1,3-divinyldisiloxane and to 1,3-diallyl-1,1,3,3-tetramethyldisiloxane in the presence of H_2PtCl_6. Next mention should be made of studies involving the polyaddition of α,ω-dihydrodimethylsiloxanes to α,ω-divinyl- and α,ω-diallyldimethylsiloxanes in the presence of Pt/C.[56,61] The products were linear polymers having the general formula

$$R(CH_3)_2Si-\{[-OSi(CH_3)_2-]_n-(CH_2)_m-\}_x-Si(CH_3)_2-[-OSi(CH_3)_2-]_n-R';$$

R=R′=–CH=CH$_2$ or H, m=2, n=2, 4, 5, x=3–250;

R=R′=–CH$_2$–CH=CH$_2$ or H, m=3, n=1, 2, x=3–250.

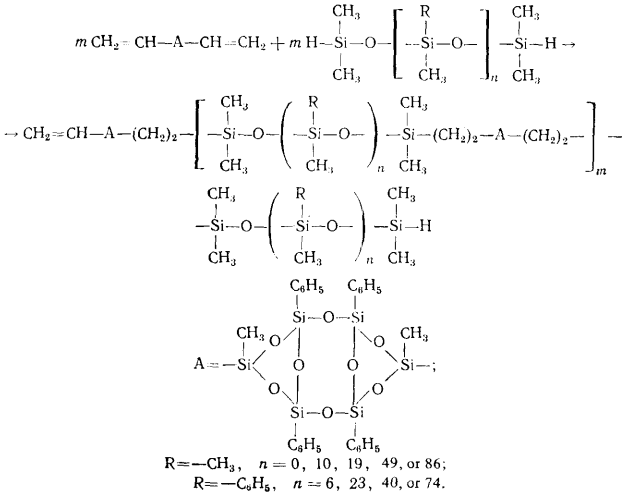
Their molecular weights, determined cryoscopically and on the basis of the content of the end groups, were 1000 to 25 000. The polyaddition products consisted of viscous liquids or gel-like substances. Infrared spectra led to the conclusion[56,61] that these are β-polyaddition products without $\rangle$CH–CH$_3$ groups.

The polyaddition of linear dihydromethylsiloxanes to methyldivinylsiloxanes with terminal trimethylsiloxy-groups has been studied in the presence of the Speier catalyst[62]. Products with a molecular weight <2000, consisting of slightly viscous liquids, were obtained. Comparison of the rates of addition of $[(CH_3)_2SiH]_2O$ and $(CH_3)_3SiO-[-(CH_3)HSiO-]_2-Si(CH_3)_3$ to $(CH_3)_3SiO-[-(CH_3).(CH_2=CH)SiO-]_2-Si(CH_3)_3$ established that 1,1,3,3-tetramethyldisiloxane adds 100 times faster than methyldisiloxane with terminal trimethylsiloxy-groups. The difference between the rates of addition is attributed to steric hindrance. It has been shown by ^{1}H NMR that β-addition products are formed.

The polyaddition of α,ω-dihydro-organosiloxanes to α,ω-divinylorganosiloxanes with methyl, ethyl, and phenyl groups at the silicon atoms has also been studied[63]. It was established that, for both α,ω-divinylorganosiloxanes and α,ω-dihydro-organosiloxanes, the rate of reaction decreases when the methyl group is replaced by the more electronegative phenyl group. Together with electronic factors, the rate of reaction is influenced also by steric factors.

Linear polycarbadiorganosiloxanes with methylcyclotetrasiloxane fragments in the polymer chain have been obtained by the polyaddition of α,ω-dihydrodimethylsiloxanes to hexamethyldivinylcyclotetrasiloxane[64]. The polyaddition reaction was carried out in an atmosphere of argon with an equimolar ratio of the initial components at 100–110°C for 50–160 h. The catalyst was chloroplatinic acid in an amount of $(1-1.5)\times10^{-5}$ g per gramme of the initial mixture. Part of the catalyst was introduced before the start of the reaction and the rest after 25–140 h. The products were viscous colourless transparent liquids whose molecular weight increased from 75 000 to 471 000, depending on the molecular weight of the initial α,ω-dihydrodimethylsiloxane. When the addition products were heated in the presence of 0.0001–0.1% of an anionic polymerisation catalyst, the viscosity increased sharply and a gel was formed.

Polyorganosiloxanes with linear and cyclic fragments in the chain have been obtained[65] by the addition of 1,7-dimethyl-3,5,9,11-tetraphenyl-1,7-divinyltricyclohexasiloxane to α,ω-dihydrodimethyl(methylphenyl)-siloxanes in the presence of H_2PtCl_6 in THF:



R=–CH$_3$, n = 0, 10, 19, 49, or 86;
R=–C$_6$H$_5$, n = 6, 23, 40, or 74.

Polymers with linear dimethylsiloxane and aromatic fragments in the chain have been synthesised by the addition of diallyl isophthalate to α,ω-dihydrodimethylsiloxanes[65]. It was established[65] that, with increase of

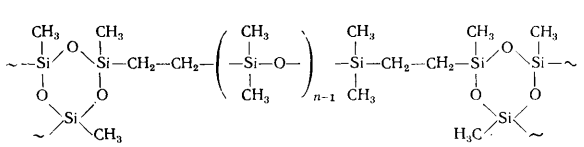
the fraction of siloxane tricyclic and aromatic fragments in the linear siloxane chain, the glass points of the polymers increase. Thermogravimetric analysis showed that the stability of the polymers in relation to thermo-oxidative degradation increases with increasing fraction of aromatic fragments in the linear dimethylsiloxane chain.

Three-dimensional polymers have been obtained by the polyaddition of tetramethylcyclotetrasiloxane to tetramethyltetravinylcyclotetrasiloxane in the presence of chloroplatinic acid[66], while polyaddition of α,ω-dihydrodimethylsiloxanes having the general formula $H(CH_3)_2SiO-[-Si(CH_3)_2O-]_n-Si(CH_3)_2H$, where $n = 0-200$, to tetramethyltetravinylcyclotetrasiloxane yielded cross-linked polycarbadiorganosiloxanes with a regular structure[67]. In the latter case the polyaddition reaction was carried out at 100–110°C in the presence of H_2PtCl_6. Depending on the ratio of the initial components, liquid or solid, infusible products, partly soluble in organic solvents, were obtained. The study of the properties of the products established that their thermo-oxidative stability decreases with increasing length of linear organosiloxane units. The authors explain[67] this phenomenon by the fact that, when the products are heated above 200°C, the rings in the polymer structure apparently open with a consequent increase in network density. This process results in an inhibition of degradation. The relatively low temperature of the onset of thermo-oxidative degradation of polymers, which is 310°C for $n = 0$ in the initial α,ω-dihydrodimethylsiloxane or 200°C for $n = 200$, is attributed to the presence of the platinum catalyst in the products.

The mechanical properties of cross-linked organosilicon polymers obtained by the polyaddition of 1,5-dihydrohexamethyltricyclosiloxane to trimethyltrivinylcyclotrisiloxane and to tetramethyltetravinylcyclotetrasiloxane have been investigated[68]. The existence of structural formations, which decompose as a result of slight deformations and under the influence of temperature, was noted.

Polymers have been synthesised by the addition of tetramethylcyclotetrasiloxane to trimethyltrivinylcyclotrisiloxane, to tetramethyltetravinylcyclotetrasiloxane, and to tetraphenyltetravinylcyclotetrasiloxane in the presence of H_2PtCl_6.[69] Thermogravimetric analysis of the products in oxidising (in air) and inert (in a stream of argon) atmospheres showed that the thermal and thermo-oxidative stabilities of the polymers, determined by the temperature of the onset of decomposition of the polymer in the course of dynamic heating, are independent of the nature of the groups surrounding the silicon atom. However, the temperature at which 10% of the weight of the polymer is lost depends on the nature of the organic groups at the silicon atom in both inert and oxidising atmospheres. For polymers with methyl groups, this temperature is higher than for polymers with phenyl groups.

The influence of the crystallisation of cross-linked polycarbadimethylsiloxanes with rings at the nodes of the network, of the type



$n = 36, 60, 150$,

on longitudinal NMR relaxation has been investigated[70]; it was shown that, with increase of the extent of the linear dimethylsiloxane chains, i.e. in the sequence $n = 36$, 60, 150, the segmental mobility of the chains between the network nodes increases.

It follows from the foregoing that the hydride addition of organohydrosiloxanes to organoalkenylsiloxanes is widely used to synthesise a wide variety of monomers, oligomers, and polymers. The reaction is also used for the hardening of organosilicon resins, the vulcanisation of siloxane elastomers, and the synthesis of various compositions.

The preparation of cross-linked polymers by the addition of polyhydro-organosiloxanes to polyvinylorganosiloxanes has been studied[71,72] in the presence of H_2PtCl_6 and it has been established that the replacement of methyl groups by phenyl groups in the initial polyorganosiloxanes leads to a decrease of the degree of hardening of the products due to steric hindrance, which interferes with the polyaddition reaction. Compared with their polyorganosiloxane analogues, polymers with disilylethylene groups exhibit a smaller thermo-oxidative stability but a greater thermal stability under conditions which rule out the dissociation of the C–C bond as a result of oxidation, i.e. in the absence of atmospheric oxygen[71,72].

The vulcanisation of linear polyorganosiloxanes with vinylsiloxy-units in the chain has been achieved by the hydride addition reaction; various organohydrosiloxanes were then used as structure-forming agents[73]. The vulcanisation was as a rule carried out at 50–100°C, which led to the formation of disilylethylene groups, which then functioned as cross-linking units in the formation of linear diorganosiloxane macromolecules. The use of polyorganosiloxanes containing vinyl groups makes it possible to obtain polymeric coatings with an enhanced strength and flexibility[74]. Elastic compositions suitable as adhesives and current-conducting materials have been obtained on the basis of the above cross-linking agents[75] using various hydrosilylation catalysts, in the first place H_2PtCl_6 and platinum complexes[74,76].

Polyorganosiloxanes which are effective foam stabilisers for the preparation of fire resistant polyurethane foam plastics have been synthesised by hydride addition in the presence of the above catalysts[77].

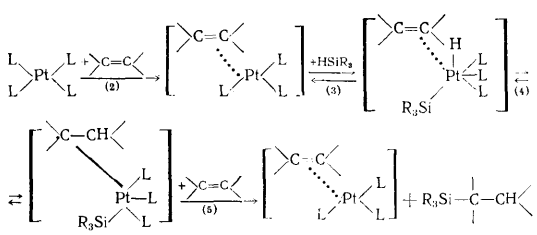
IV. THE PRINCIPAL FACTORS INFLUENCING THE COURSE OF THE HYDRIDE ADDITION REACTION

The addition of organohydrosiloxane to organovinylsiloxanes is a special case of the hydride addition reaction and obeys the general rules governing the latter. The hydride addition reaction is influenced, together with general factors (concentrations of the reactants, reaction temperature and time, the nature of the solvent, etc.), also by specific factors such as the type of catalyst used and the structure of the unsaturated and hydrogen-containing organosilicon compounds. This section deals with the effects of such specific factors.

The hydride addition reaction can be carried out in the absence of catalysts; for example, the addition of trichlorosilane to olefins at 300°C takes place without a catalyst[78,79]. Various initiators and hydride addition catalysts are used to reduce the temperature, to increase the rate of reaction, to increase the yield of addition products, and to suppress undesirable side reactions. The initiating effect of ultraviolet light, γ-radiation, various peroxy-compounds and other substances readily forming free radicals, as well as organic electron-donating compounds such as amines, amides, phosphines has been demonstrated[2,3].

Group VIII metals fixed on carriers or forming part of the composition of various compounds are effective catalysts of the hydride addition reaction. Compounds of other metals (copper, zinc, zirconium, chromium, molybdenum, etc.) are also known to exhibit a catalytic activity. The most active catalyst is chloroplatinic acid[80], which is used in the form of a solution in isopropyl alcohol (the so-called Speier catalyst). By virtue of the ease of its use and high catalytic effect, chloroplatinic acid is the most common catalyst of reactions of this type. However, its application also suffers from certain disadvantages, namely an induction period necessary for the manifestation of catalytic action, in some cases an acceleration of side reactions, and insolubility of the catalyst in many organic solvents.

On the basis of detailed studies of hydride addition[18] and by analogy with other homogeneous-catalytic processes, a mechanism has been proposed for the hydride addition reaction catalysed by H_2PtCl_6,[81] the first stage of which involves the formation of a platinum complex $Pt(L)_4$ with replacement of chlorine atoms by hydrogen; R_3SiH is the source of hydrogen. Next the reaction proceeds in accordance with the following scheme:

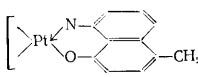


where L = Cl, H, or a coordinated solvent molecule.

Thus the hydride addition reaction consists of the following stages: (1) reduction of H_2PtCl_6 by the organosilicon hydride; (2) π-coordination of the unsaturated component with simultaneous displacement of one of the ligands; (3) oxidative addition of the organosilicon hydride with formation of an unstable hexacoordinate platinum complex with inclusion in the inner sphere of hydrogen and the silyl group; (4) displacement of a hydrogen atom from platinum to the coordinated olefin and the formation of an alkyl–platinum σ bond; (5) reductive displacement of the alkylsilane via the coordination of another molecule of the unsaturated component.

The catalytic effect of Group VIII transition metal complexes has been recently examined in many studies of the hydride addition reactions. The use of complexes of various metals in different oxidation states and coordinated to a wide variety of ligands as catalysts has been described. On the basis of the mechanism proposed above, which has been extended[18] to Group VIII transition metal complexes, a distinct catalytic effect is to be expected for compounds which satisfy the following requirements: (a) unsaturated reagents can coordinate to them; (b) they activate the hydrogen-containing organosilicon reagent, i.e. they cleave the $\geq$Si–H bond and at the same time both fragments formed can be coordinated to them; (c) they are not reduced by hydrogen-containing organosilicon compounds with formation of the free metal.

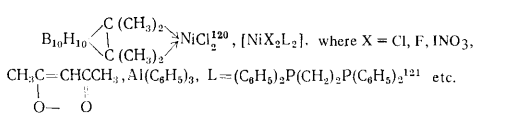
The following platinum complexes can be used as catalysts of the hydrosilylation reaction: $\{[(C_6H_5)_3P]_2.Pt(C_2H_4)\}$[82] and $[(C_6H_5)_3P]_4Pt$[83–85]—i.e. compounds containing zerovalent platinum; $(alkene)_2PtCl_2$,[86–88] $[(C_6H_5)_3P]_2PtCl_2$,[89] $(CH_3CN)_2PtCl_2$ and $(C_6H_5CN)_2PtCl_2$,[90] *trans*-$[(C_2H_5)_2OSC_2]_2.PtCl_2$,[91] *cis*-$(CO)_2PtCl_2$,[92] $[(CH_3)_3Si(CH_2)_nP(C_4H_9)_2]_2PtCl_2$ with $n = 1-3$,[93] $(cyclo\text{-}C_6H_{11})_2PtCl_2$,[94] and di-iodohexamethyldipyridineplatinum[95]—i.e. compounds containing bivalent platinum; $[Pt(CH_3)_3]_2$ and $(CH_3)_3PtI$[96]—i.e. compounds containing quadrivalent platinum; the polymeric chelate complex[97]



complexes of platinum chlorides with olefins, compounds of the pyridine series, thioimides, alkylthioureas, phosphines, and nitriles[98], platinum complexes with olefins or cyclopropane[99], as well as platinum complexes stabilised by phosphines and nitriles[100].

Palladium complexes have also recently begun to be used as catalysts of the hydride addition reaction, although they are readily reduced by the hydrogen-containing compounds. The complexes $[(C_6H_5)_3P]_4Pd$,[101,102] metallic palladium, and bivalent palladium complexes with ligands such as trialkyl(aryl)phosphines[101], $Pd(PR_3)_mL_n$, where R is an aliphatic, aromatic or alicyclic group, L is another ligand or an acid residue, $m = 1-4$, and $n + m = 4$,[103] nitrile complexes of bivalent palladium halides[104,105], $(R_3P)_2PdCl_2$,[106] $[(CH_3)_3SiCH_2P.(C_4H_9)_2]_2PdCl_2$,[93] a polymeric chelate complex containing palladium[97], the complex $[PdCl(\pi\text{-}C_5H_5)_2]$,[107] and other palladium complexes also exhibit effective catalytic properties.

A catalytic activity in hydrosilylation reactions has been noted for certain nickel complexes. In particular, nickel carbonyl compounds $Ni(CO)_4$ [108] and $[(\pi\text{-}C_5H_5)_2Ni(CO)]_2$,[109] phosphine complexes of nickel $(R_3P)_2NCl_2$ and $\{[C_6H_5)_3P]_2Ni(C_2H_4)\}$,[110–112] $(C_5H_5N)_2NiCl_2$, $Ni(Cp)_2$, and $\{[(C_6H_5)_3P]Ni(Cp)(C_2H_5)\}$, where Cp is the cyclopentadienyl ligand[113], $Ni(acac)_2 + Al(C_2H_5)_3$,[114–118] $Ni(COD)_2$ and the $NiCl_2$ (or $NiBr_2$) + PR_3 + sodium bis-(2-methoxyethoxy)-hydroaluminate[119], a polymeric chelate complex (whose structure is analogous to that of the chelate complex of platinum mentioned above)[97], the complexes $[(CH_3)_3Si.(CH_2)_nPR_2]_2NiX_2$, where $n = 1$ or 2, R = C_4H_9 or C_6H_5, and X = Cl or Br,[93] and



It is believed[122] that the mechanism of the addition of organohydrochlorosilanes to olefins in the presence of phosphine complexes of nickel is analogous to the mechanism of the hydrosilylation reaction in the presence of H_2PtCl_6. The hydrosilylation reaction in the presence of phosphine complexes of nickel takes place at a temperature >90°C and most effectively at ~120°C.[122] It is accompanied by the exchange of hydrogen and chlorine atoms:

$$2RCH{=}CH_2 + 3R'_2SiHCl \xrightarrow{Ni^{II}} RCH_2CH_2SiR'_2Cl + RCH_2CH_2SiR'_2H + R'_2SiCl_2.$$

The exchange is faster and more extensive the more pronounced are the electro-accepting properties of the phosphorus-containing ligands. It has been found[122] that the addition takes place *cis*-stereospecifically. As in catalysis by H_2PtCl_6, the reactivities of chloromethylhydrosilanes decrease in the sequence

$$HSiCl_3 > (CH_3)HSiCl_2 > (CH_3)_2HSiCl \gg HSi(CH_3)_3.$$

It is of interest that the catalytic action of nickel(II) complexes is characterised by a longer induction period than the action of the zerovalent complexes. Among

cobalt complexes, the carbonyl compounds have been widely used as catalysts of the hydrosilylation reaction. These are primarily dicobalt octacarbonyl and π-cyclopentadienyldicobalt dicarbonyl[123], in the presence of which the hydrosilylation reaction sometimes takes place even at room temperature.

It has been established[124] that, in the presence of dicobalt octacarbonyl, the addition of $\geq$Si–H to olefins is directed to form β-adducts, this being accompanied by the isomerisation of the initial olefin. In view of the low thermal stability of dicobalt octacarbonyl, when the reaction is carried out at a temperature >60°C, the yield of addition product falls. It is believed[125] that the reaction includes the following stages:

$$R_3SiH + Co_2(CO)_8 \rightarrow R_3SiCo(CO)_4 + HCo(CO)_4 ,$$

$$HCo(CO)_4 + R'CH=CH_2 \rightarrow R'CH_2CH_2Co(CO)_4 ,$$

$$R'CH_2CH_2Co(CO)_4 + R_3SiH \rightarrow R'CH_2CH_2SiR_3 + HCo(CO)_4 ,$$

$$R'CH_2CH_2Co(CO)_4 + R_3SiCo(CO)_4 \rightarrow R'CH_2CH_2SiR_3 + Co_2(CO)_8 .$$

There is also a possibility of the reactions

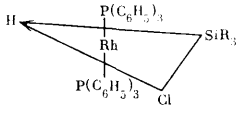
$$2HCo(CO)_4 \rightarrow Co_2(CO)_8 + H_2 ,$$
$$HCo(CO)_4 + R_3SiH \rightarrow R_3SiCo(CO)_4 + H_2 .$$

The latter are undesirable and so is the formation of the complex $R_3SiCo(CO)_4$, which is catalytically inactive. An excess of the unsaturated compound is necessary to suppress these undesirable reactions.

The hydrosilylation reaction has been achieved in the presence of the phosphine complexes of cobalt $[(C_6H_5)_3P].CoH_3$, $[(C_6H_5)_3P]CoH(N)$,[126] a two-component system of the Ziegler type $Co(acac)_2 + Al(C_2H_5)_3$,[115-118] etc.

Rhodium complexes are highly active as catalysts of the hydrosilylation reaction. These are primarily the phosphine complexes $[(C_6H_5)_3P]_3RhCl$ (the so-called Wilkinson catalyst),[127-129], $[(C_6H_5)_2PH]_3RhCl$,[130] $\{[(C_6H_5)_3P]_4RhH\}$,[131] $\{[Rh(1,5\text{-}C_6H_{12})Cl]_2\} + L$, where L = P(cyclo-$C_6H_{11})_3$, $P(CH_3)_2C_6H_5$, $PCH_3(C_6H_5)_2$, $P(C_6H_5)_3$, $P(OC_4H_9\text{-}n)_3$, $P(OC_6H_5)_3$, or $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$,[132] $\{L_2RhH[Si(OC_2H_5)_3]Cl\}$, where L = $(C_6H_5)_3P$, $(p\text{-}CH_3C_6H_4).(C_6H_5)_2P$, C_6H_5 (cyclo-$C_6H_{11})_2P$, or $(C_6H_5)_2$(cyclo-$C_6H_{11})P$,[133] the carbonyl complexes $[(CO)_4Rh_2Cl_2]$,[125] $\{[(C_6H_5)_3P]_2.Rh(CO)Cl\}$, and $\{[(C_6H_5)_3P]_3RhH(CO)\}$,[85,125,132] the olefin complex $[(C_2H_4)_2Rh_2Cl_2]$, a polymeric chelate complex containing rhodium[97], and others.

The same mechanism, in principle, has been proposed for the hydrosilylation reaction in the presence of rhodium complexes as in the presence of H_2PtCl_6.[18] The pentacoordinate rhodium complex[127]



is believed to be catalytically active[127]. This complex is formed as a result of the reaction

$$[(C_6H_5)_3P]_3RhCl + R_3SiH \rightleftarrows [(C_6H_5)_3P]_2Rh(SiR_3)HCl + (C_6H_5)_3P.$$

Its stability under the conditions obtaining in the reactions of chloroethylhydrosilanes depends on the nature of the groups SiR_3 and decreases in the sequence

$$-Si(C_2H_5)_3 < -SiCl(C_2H_5)_2 < -SiCl_2(C_2H_5) < -SiCl_3.$$

Among other transition metal complexes proposed as catalysts of the hydrosilylation reaction, mention should be made of iron carbonyls[135], a two-component catalyst of the Ziegler–Natta type $Fe(acac)_2 + Al(C_2H_5)_3$,[115] manganese[136,137], ruthenium[138], and iridium[127] complexes, and $Co(CO)_6$ (the last complex is used in combination with ultraviolet irradiation)[139].

Together with the homogeneous catalysts indicated above, which are used in the form of solutions, catalysts based on transition metals bound to carriers have been developed recently. These forms of catalysts are interesting because they combine the advantages of homogeneous and heterogeneous catalysts, namely high catalytic activity, the possibility of the repeated use of the catalyst, and applicability to continuous processes. Thus the preparation of phosphine complexes of rhodium chemically bound to organic polymeric materials, for example, on a butadiene–styrene copolymer, and their application in hydrosilylation reactions have been described[140]. The catalyst $[Rh(CO)_2Cl]_2$ deposited on a modified styrene–divinylbenzene copolymer has also been proposed[141]. Alumina, glass, molecular sieves, silica, and other materials are also employed as catalyst carriers[140,142].

Platinised ion-exchange resins can be used as catalysts of the hydrosilylation reaction[143,144].

The catalytic activities of various platinum, rhodium, palladium, nickel, and cobalt compounds in reactions involving the addition of pentamethyldisiloxane to methylvinylsiloxanes with linear and cyclic structures have been investigated[5,145]. The palladium and nickel compounds hardly catalyse the above reactions, while the platinum and rhodium compounds exhibit a high catalytic activity. It was noted that the rhodium compounds ensure a greater β-selectivity of the addition process. Dicobalt octacarbonyl exhibits a high catalytic activity at higher concentrations.

The structure of unsaturated and hydrogen-containing organosilicon compounds exerts an appreciable influence on the rate and direction of the hydrosilylation reaction. The relative rate constants for the addition of trichlorosilane to various unsaturated compounds have been determined by the method of competition kinetics[146]. It was established that the reactivity of the unsaturated compounds depends mainly on the electron density at the double bond and sometimes on steric factors. The reactivities of the test compounds in the reaction under consideration decrease in the sequence hept-1-ene > *cis*-hept-2-ene > allylbenzene > t-butylethylene > dec-1-ene > styrene > allyl chloride > cyclohexene.

The reactivity of unsaturated compounds in relation to alkylhydrocyclosiloxanes decreases in the sequence[147] styrene > α-methylstyrene > methyl methacrylate > allyl cyanide. The decrease is correlated with the decrease of the electron density of the double bond. α-Methylstyrene, where the influence of steric factors is significant, constitutes an exception.

The rate of hydrosilylation of halogeno-olefins decreases in the following sequence in the presence of H_2PtCl_6:[148]

$$CH_2=CH_2 > CH_2=CF_2 > CF_2=CFCl > CF_2=CF_2.$$

Attack by the olefin on the $\geq$Si–H bond is easier the greater the electron density in the double bond[149]. Hydrogenation of the unsaturated component is facilitated simultaneously.

The reactivity of methylvinylsiloxanes having the general formula $(CH_2=CH)(CH_3)_{3-n}Si[OSi(CH_3)_3]_n$ decreases with increase of the number of trimethylsiloxy-groups (n was varied from 3 to 1) when sulphur compounds are added to them in the presence of H_2PtCl_6.[18]

The reactivity of methylvinylsiloxanes having the general formula $(CH_3)_{3-n}(CH_2{=}CH)Si[OSi(CH_3)_3]_n$, where $n = 0-3$, in relation to pentamethyldisiloxane in the presence of tris(triphenylphosphine)rhodium chloride has been investigated by the method of competition kinetics[53]. It was established that, with increase of the number of trimethylsiloxy-groups in methylvinylsiloxanes, the reactivity of the latter decreases in the sequence[53]

$$(CH_3)_3(CH_2{=}CH)Si > (CH_3)_2(CH_2{=}CH)SiOSi(CH_3)_3 > CH_3(CH_2{=}CH)Si[OSi(CH_3)_3]_2 > CH_2{=}CHSi[OSi(CH_3)_3]_3.$$

The influence of substituents at the silicon atom bound to the vinyl group on the reactivity of linear α,ω-divinyldiorganosiloxanes in the addition reactions of α,ω-dihydrodiorganosiloxanes has been investigated[63]. The observed rate constants for the addition reaction show that the replacement of the methyl group by the more electronegative phenyl group reduces the reactivity of vinylorganosiloxanes. The steric influence of the phenyl groups has also been noted in isolated instances.

Thus the reactivity of unsaturated compounds is higher the greater the electron density in the double bond. Naturally, in the presence of steric hindrance due to bulky substituents, the reactivity of unsaturated compounds can decrease.

The reactivity of hydrogen-containing organosilicon compounds in reactions involving addition to unsaturated compounds also depends on structural factors. Thus the reactivity of chloroethylhydrosilanes in reactions involving addition to hept-1-ene in the presence of H_2PtCl_6 increases in the following sequence[150]:

$$(C_2H_5)_3SiH < (C_2H_5)_2SiHCl < C_2H_5SiHCl_2 < HSiCl_3.$$

The observed increase of the reactivity of chloroethylhydrosilanes is due to the decrease of the electron density in the $\rangle Si-H$ bond when ethyl groups are replaced by the electronegative chlorine atoms. A similar behaviour has been observed in the study of the addition of chloroethylhydrosilanes to hept-1-ene in the presence of dicobalt octacarbonyl[151].

In the addition of hydrogen-containing organosilicon compounds to diethyl allylmalonate in the presence of H_2PtCl_6 the amount of adduct formed increases with increase of the number of electronegative substituents at the silicon atom[152]:

$$R_3SiH < R_2SiHCl < RSiHCl_2 < HSiCl_3;$$
$$R_3SiH < R_2SiH(OR') < RSiH(OR')_2 < HSi(OR')_3.$$

The reactivity of organochlorosilanes in relation to acrylonitrile decreases in the sequence[153]

$$HSiCl_3 > (C_6H_5)HSiCl_2 > (CH_3)HSiCl_2 > (C_6H_5)_2HSiCl > (C_6H_5)(CH_3)SiHCl \gg (CH_3)_2HSiCl.$$

Comparison of the relative rate constants for the addition of ethoxypropylhydrosilanes $(C_3H_7)_nHSi(OC_2H_5)_{3-n}$ to hex-1-ene in the presence of tris-(triphenylphosphine)-rhodium chloride and dicobalt octacarbonyl (determined by the method of competition kinetics) shows that the observed increase of the reactivity of ethoxypropylhydrosilanes with increasing content of ethoxy-groups takes place in the following sequence: tripropylsilane < ethoxydipropylsilane < diethoxypropylsilane < triethoxysilane[151].

There are relatively few data concerning the influence of the structure of organohydrosiloxanes on their reactivity in reactions involving addition to unsaturated compounds. The study of the kinetics of the addition of 1,1,3,3-tetramethyldisiloxane and octamethyl-3,5-dihydrotetrasiloxane to heptamethyl-3-vinyltrisiloxane showed that the introduction of the trimethylsiloxy-group into methylhydrosiloxanes hinders the reaction appreciably[62].

The reactivity of methylhydrosiloxanes having the general formula $(CH_3)_{3-n}HSi[OSi(CH_3)_3]_n$, where $n = 1-3$, in the reaction involving addition to hex-1-ene and heptamethylvinylcyclotetrasiloxane in the presence of H_2PtCl_6 is determined predominantly by steric factors[51,145]. The methylhydrosiloxanes investigated can be arranged in the following sequence in terms of the decrease of their reactivity in the above hydride addition reactions:

$$(CH_3)_2HSiOSi(CH_3)_3 > (CH_3)HSi[OSi(CH_3)_3]_2 > HSi[OSi(CH_3)_3]_3.$$

It has been established by the method of competition kinetics[52] that the reactivities of dimethyl-α,ω-dihydrosiloxanes having the general formula $H-Si(CH_3)_2O-.[-Si(CH_3)_2O-]_n-Si(CH_3)_2-H$, where $n = 0-3$, in reactions involving addition to hept-1-ene in the presence of tris-(triphenylphosphine)rhodium chloride decrease with increase of molecular weight. This can be accounted for by the decrease of molecular mobility and probably by differences in the stability of the intermediate compound involving the catalyst.

It has also been shown[52] that the replacement of the methyl group in dimethyl-α,ω-dihydrosiloxanes by the electronegative phenyl group does not increase the reactivity in reactions involving addition to methylvinylsiloxanes. The reactivity actually decreases owing to steric hindrance.

Thus the reactivity of hydrogen-containing organosilicon compounds in reactions involving addition to unsaturated compounds is determined by steric and electronic factors. In particular, the introduction of electronegative groups and the associated increase of the positive charge on the silicon atom promote the dissociation of the hydrogen atom as a proton. This is manifested by an increase of the reactivity of hydrogen-containing organosilicon compounds.

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The data reviewed show that there have been many studies on the hydrosilylation of unsaturated organic compounds and on the hydride addition of organohydrosiloxanes to organosilicon compounds containing multiple carbon–carbon bonds. It has been established that the hydrosilylation reaction is important for the synthesis of a wide variety of organosilicon compounds. Hydride addition constitutes a convenient method for the synthesis of high-molecular-weight compounds and gives rise to extensive possibilities for their modification in order to convert them into systems with three-dimensional and cross-linked structures.

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