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THE ALCOHOLYSIS OF HYDROSILANES

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1. INTRODUCTION

A special feature of hydrosilanes is their ability to undergo alcoholysis leading to alkoxysilanes and gaseous hydrogen (the reaction of dehydrocondensation) [1,2]:

$$\equiv SiH + HOR \longrightarrow \equiv SiOR + H_2$$

The rate of dehydrocondensation significantly depends on the extent of Si-H bond polarization in the silanes, the reaction being generally conducted in the presence either of nucleophilic or electrophilic catalysts [1].

Only some hydrosilanes, such as monoorganosilanes [3,4], diorganosilanes [5] and arylfluorosilanes [6] undergo dehydrocondensation with alcohols in the absence of catalysts. However, no reaction occurs when triethylsilane is boiled with anhydrous ethanol in a quartz vessel for 24 hrs [2].

The heating of a mixture of triethoxysilane with ethanol in a sealed tube at 100°C during 125 hrs brings about a 50% conversion of triethoxysilane to tetraethoxysilane [7]. Slow evolution of hydrogen was noted in the reaction of triethoxysilane and ethanol in the absence of catalysts and solvents at lower temperatures [8]. In these cases, the alkali contained in the glass surface, possibly acts as catalyst.

The dehydrocondensation of alkoxysilanes with amino alcohols is catalyzed by the amino alcohol itself [9,10], whereas the aminoalkylhydrosilanes react with alcohols autocatalytically [11,12].

Potassium and sodium hydroxides [13-31], alkaline metal alcoholates [20,32-48], organic bases [49-66], hydrogen chloride [67-72], cationites [73-75], group IB [76-78] and group VIII [79-87] metals, salts of metals [88-96, 99-104] and tetraalkylammonium [96-98], and metal complexes [105-136] have been used as catalysts for the dehydrocondensation of hydrosilanes with alcohols.

2. THE ALCOHOLYSIS OF HYDROSILANES IN THE ABSENCE OF CATALYSTS

Monoorganosilanes [3,4] and diorganosilanes [5] undergo dehydrocondensation with alcohols in electron-donating solvents without catalysts.

A study of the kinetics of the three-stage parallel-consecutive reactions of monoorganosilanes with alcohols of different structure in dimethylformamide has demonstrated that alcohol reactivity in this reaction rises with increasing nucleophility of the alcohol oxygen [3]:

$$RSiH_3 + R'OH \xrightarrow[-H_2]{k_1} RSiH_2(OR') \xrightarrow[\substack{+R'OH \\ -H_2}]{k_2} RSiH(OR')_2 \longrightarrow$$

$$\xrightarrow[+R'OH]{k_3} RSi(OR')_3 + H_2$$

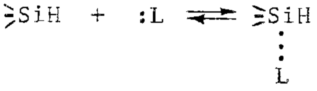
In the reactions of phenylsilane with allyl, propyl and branched alcohols as well in those of parachlorophenylsilane with propyl, benzyl and branched alcohols the ratio $k_1/k_2 < 1$, i.e. the reactivity grows from $RSiH_3$ to $RSiH_2(OR')$. This is in contrast to other alcohols where $k_1/k_2 > 1$. The ratio $k_2/k_3 \gg 1$ in all cases. Steric factors apparently play a crucial role at the third stage of the reaction.

A study of the kinetics of dehydrocondensation of diorganosilanes with alcohols in dimethylformamide has shown that the reactivity of silanes falls in the sequence [5] :

$$Ph_2SiH_2 > PhC_6H_{13}SiH_2 > Bu_2SiH_2,$$

i.e. with increasing electron density on the silicon atom. In the reactions of diphenylsilane with 2-phenylethyl and benzyl alcohols the ratio $k_2/k_1 > 1$. Dimethylformamide possibly participates in the formation of the intermediate complex.

The effects exerted by the solvent and temperature on the reaction kinetics of organosilanes with nucleophilic agents suggest that at low temperatures the reaction rate is determined by the associate formation:



$$\geq SiH + :L \rightleftharpoons \underset{\underset{L}{\vdots}}{\geq SiH}$$

The effect of solvent can be reduced to a minimum if the reaction is conducted at temperatures when the dissociation rate of silane-solvent associates prevails over the rate of their formation [4].

3. THE ALCOHOLYSIS OF HYDROSILANES IN THE PRESENCE OF ALKALINE CATALYSTS

3.1. Potassium and sodium hydroxides

The alcoholysis of hydrosilanes in the presence of alkaline catalysts has been studied in more detail than to the reactions with other catalysts. However, it must be pointed out that KOH- and NaOH-catalyzed solvolysis is frequently carried out in alcohol containing 5-7 vol % of water leading to the alcoholysis and hydrolysis of hydrosilanes simultaneously [13-20, 22-28].

Numerous investigations have been dedicated to the kinetics of the alkaline solvolysis of hydrosilanes. As far back as 1947 [13], the effect of silane structure on the solvolysis of trialkylsilanes in 95% ethanol (catalyzed by KOH) was studied to give the following series of relative rates ($k^{34,4}$):

Et_3SiH	Et_2MeSiH	Me_2n-PrSiH	Men-Pr_2SiH	n-Pr_3SiH
100	169	391	115	44

This variation in the reaction rate constants is accounted for mainly by the steric effects of the substituents at the silicon atom.

A similar sequence was obtained for the reaction of trialkylsilanes with 94.5% ethyl alcohol in the presence of NaOH [15] ($k^{34,9}$):

Et_3SiH	n-Pr_3SiH	n-Bu_3SiH	i-Bu_3SiH	i-Pr_3SiH
100	40	27	4.1	1.6

Although the inductive and steric effects of these substituents at the silicon atom act in the same direction, the decisive role is assigned to the steric factors [15].

The determination of relative rates for the solvolysis of fluoroalkylsilanes RR'$(CH_3)SiH$ in 93.7% ethanol and KOH used as catalyst revealed the predominance of the inductive effects of $CF_3CH_2CH_2$ and $CF_3CF_2CH_2$ groups over the steric effects [16]:

R	R'	$k^o_{rel.}$
$CH_3CH_2CH_2$	CH_3	1.0
$CF_3CH_2CH_2$	CH_3	59
$CF_3CH_2CH_2CH_2$	CH_3	8.3
$CF_3CF_2CH_2CH_2$	CH_3	83
$CF_3CH_2CH_2$	$CF_3CH_2CH_2$	2100

The kinetics of alkaline (KOH) solvolysis in the series of ω-cyanoalkyl-, ω-phenylalkyl-, fluoroalkyl- and alkylsilanes in 93.7% ethanol at 0^oC was examined [17]. The correlation of the rate constants with Taft's constants σ^* was described by a linear relationship ($\rho^* = 4.27$; r=0.998). However, the points for ω-phenylalkylsilanes deviate considerably from the correlation line according to these authors, due to the steric effects of the phenyl group.

A study of the kinetics of solvolysis of arylsilanes $RC_6H_4Me_2SiH$ (where R = m-CF_3, p-Cl, H, p-Me, p-MeO, p-NMe_2) in 95% ethanol (KOH) demonstrated a linear relationship between the logarithms of rate constants and constants σ^o ($\sigma^o = \sigma_1 + \sigma^o_R$), where σ_1 and σ^o_R describe the inductive and mesomeric effects of the substituents, respectively [19].

Relative rate constants for the solvolysis of vinylsilanes were obtained [19]:

Silane	$k^o_{rel.}$
Et_3SiH	1
$(CH_2{=}CH)Et_2SiH$	21
$(CH_2{=}CH)_2EtSiH$	310
$(CH_2{=}CH)_3SiH$	3800

It has been concluded [19] that the p_π-d_π interaction of the phenyl and vinyl groups with the silicon atom fails to affect the reactivity of aryldimethyl- and vinylsilanes. However, a comparison of the relative rate constants for the solvolysis of vinylsilanes shows that an increase in the rate constant from triethylsilane to trivinylsilane is not constant, indicating a certain influence exerted by the p_π-d_π interaction of the vinyl groups with the silicon atom.

A comparison of the relative rate constants obtained for the solvolysis of hydrosiloxanes in 95% ethanol catalyzed by KOH has revealed that the influence of the trimethylsiloxy group results from at least three contributions: -I, steric and p_π-d_π interaction of the oxygen atom with the reactive centre, however, the observed results do not allow to discriminate between the individual contributions of each effect [20]:

Silane	$k^{o}_{rel.}$
Me_3SiH	1.7
$EtMe_2SiH$	1
Me_3SiOMe_2SiH	130
$Me_3SiOEtMeSiH$	90
$[Me_3SiO]_2MeSiH$	550
$[Me_3SiO]_2EtSiH$	115
$[Me_3SiO]_3SiH$	129

A study of the reactivity of silanes $R_nMe_{3-n}SiH$ (where $R = Me_3CO$, Me_3CCH_2, $n = 0-3$) has found that the steric influences of the tert-butoxy- and neopentyl groups are similar, but the results cannot be described by the polar and steric effects only. The authors however, fail to interpret this point [20].

The kinetics of methanolysis in the monoorganosilane series (dimethylformamide - solvent, KOH - catalyst) was examined [21]:

$$RSiH_3 + 3CH_3OH \xrightarrow[-3H_2]{k_1,\ k_2,\ k_3} RSi(OCH_3)_3$$

R = i-Bu; $Ph(CH_2)_2$; $PhCH_2$; $NC(CH_2)_3$; Ph, $NC(CH_2)_2$

Within the series of compounds containing an equal number of Si-H bonds the rate of the reaction grows with the increasing -I-effect of the substituents. Due to the influence of the extremely electronegative methoxy group ($\sigma^* = 1.45$), stage 2 of the reaction proceeds faster than stage 1 ($k_2 > k_1$).

At stage 3, despite the two CH_3O-groups already present in the silane molecule, the reaction rate declines markedly, apparently due to the steric effects. The dependencies of the logarithms of rate constants on σ^* constants are linear comprising without any considerable deviation the points for the compounds with a phenyl group, whose effect of the $p_\pi - d_\pi$ interaction with the silicon atom is not displayed here. It has been shown that in the methanolysis in the $RSiH_2(OCH_3)$ series, the inductive effect of the methoxy group is approximately by 40% outweighed by the opposite effect of $p_\pi - d_\pi$ interaction.

The effect of the silane structure on the rate of solvolysis in aqueous ethanol with KOH present has been studied quantitatively [22-27]. The alkylsilanes were found to react slower than the arylsilanes, and the rate of dehydrocondensation decreased with the elongation and branching of the carbon chain in the substituent at the silicon atom [22]. The logarithms of the rate constants of the para-substituted triphenylsilanes plotted vs. Hammet's constants σ do not give a linear relationship. Therefore constants $\sigma_{(Si)} = \sigma_1 + 0.75\,\sigma_m$ were applied to obtain a good correlation.

However, later the data reported in [22] were reevaluated to infer that the use of σ_{Si} constants is not justified [19]. A good correlation is also observed in the case of σ^o constants. Furthermore, constants σ_{Si} have no definite physical sense:

Constant	k_o	ρ	r
σ_{Si}	-0.61	5.48	0.997
σ^o	-0.61	5.48	0.999

The logarithms of the rate constants for the solvolysis (96.5% ethanol, catalyst - KOH) of meta-substituted arylsilanes $(X\text{-}C_6H_4)_nMe_{3-n}SiH$ ($n = 1, 2, 3$, X = m-Me, H, m-MeO, m-F, m-Cl, m-Br) are linearly correlated with the σ_m^o constants of the substituents. However, this linearity breaks down in the triarylsilanes $(m\text{-}X\text{-}C_6H_4)_3SiH$, where X = F, Cl, Br, which react slower than expected according to their inductive constants [24].

In the case of ethanolysis of tetraalkyl- and tetraaryldisilanes the logarithms of the rate constants show a good correlation with constants $\sigma^o{}_{(Si_2)}{}^{I} = 1.25\ \sigma_1 + \sigma_m^o$ or $\sigma^o{}_{(Si_2)}{}^{II} = \sigma_1 + 0.8\,\sigma_m^o$, but not with Hammett's constants [25].

The rate of ethanolysis of alkoxysilanes decreases from dialkoxysilanes to trialkoxysilanes [20,26]. The authors [26] believe that when three electron-acceptor alkoxy groups are present in the molecule the reaction rate diminishes owing to the increase in the degree of $p_\pi - d_\pi$ interaction.

A good correlation was established between the rate of ethanolysis of phenylsilanes and benzylsilanes and σ^o [27], the latter reacting slower than the arylsilanes.

3.2. Alkaline metal alcoholates

The dehydrocondensation of trialkylsilanes with alkanols in the presence of alkaline metals is a convenient and simple procedure for the synthesis of trialkylalkoxysilanes in high yields [2]. The rate of the reaction and the product yields increase with growing alkaline metal number (from lithium to rubidium). The same was observed during the dehydrocondensation of trialkylsilanes with glycols [37].

Under normal pressure the trialkylsilanes in the presence of lithium alcoholates react only with primary alcohols. In the presence of sodium alcoholates the trialkylsilanes react with secondary alcohols too, however, the reaction proceeds slower and the product yields are low as compared to the reaction with primary alcohols. In the presence of potassium alcoholates the reaction occurs readily both with the primary and secondary alcohols. Tertiary alcohols react with trialkylsilanes only when rubidium alcoholates are present, whereas the corresponding lithium, sodium and potassium alcoholates do not act as catalysts. This may due to the rise in the degree of ionization of alcoholates with increasing metal number and alkoxyl ion concentration [2].

By conducting the reaction in an autoclave ($200-210^{o}$) in the presence of sodium alcoholates the trialkylsilanes react readily with the primary, secondary and tertiary alcohols.

The rate of reaction of hydrosilanes R_3SiH and alcohols falls with the elongation of the alkyl radicals R. For example, the theoretically estimated amount of hydrogen in the reaction of n-butyl alcohol with triethylsilane in the presence of 8% mol of sodium butylate is evolved during 4 hours, while in the reaction with tri-n-propylsilane 10 hrs are required [2].

The rate of the reaction declines with the elongation and branching of the alkyl group in the primary alcohols as well as from the secondary to tertiary alcohols.

A study of the kinetics of ethanolysis of propylethoxysilanes in the presence of sodium ethylate has given the relative rate constants as follows [20]:

Silane	$k_{rel.}^{10^{\circ}}$
Pr_3SiH	1
$(EtO)Pr_2SiH$	688
$(EtO)_2PrSiH$	6860
$(EtO)_3SiH$	1490

The investigators believe that the influence of the ethoxy groups is not restricted only to the polar and steric effects, although they do not give a definite reason for the reduced reactivity of triethoxysilane.

The dehydrocondensation of silatrane $\overrightarrow{N(CH_2CH_2O)_3Si}H$ and triethoxysilane with alcohols in the presence of the corresponding sodium alcoholates demonstrate that the rate of the reaction grows with increasing acidity of the alcohols in the hydrosilane series [42]:

$$Et_3SiH \leqslant \overrightarrow{N(CH_2CH_2O)_3Si}H < (EtO)_3SiH$$

The attack of the alkoxyl ion on the silicon atom in the silatrane cannot take place on the opposite side of the Si-H bond due to the specific steric properties of the silatrane. Therefore the authors postulate that the nucleophilic attack on the silicon in the silatrane by the RO^- group during alcoholysis occurs "from the flank" and results in an intermediate complex containing a sixcovalent octahedral silicon atom formed through the interaction between its 3d-orbitals and RO^- anion [42].

The kinetic isotope effects were determined for triorganosilanes and methanol in the methanolysis in the presence of sodium methoxide [43-46]. The kinetic isotope effects in the methanolysis of Ph_3SiH, $(PhCH_2)_3SiH$ and Bu_3SiH, and their deuterated analogues were found to be small and only slightly dependent on the structure of the silane ($k_{SiH}/k_{SiD} = 1.2$, 1.35 and 1.4, respectively) [44].

From the above results a transition state was proposed in the reaction:

$$N — Si---H \ldots\ldots\ldots\ldots H — A$$

The bonding between the silicon and the nucleophilic agent is extremely strong, the silicon-hydrogen bond is somewhat weakened, bond H-A in methanol is comparatively strong, and bond H•••H is weak. It has been suggested that the removal of protons Si-H and H-A occurs simultaneously. The leaving hydrogen ion (Si-H) interacts inefficiently with the methanol proton. This model has been subject to criticism. It was shown, for instance, that bond H-A in the methanol is considerably weakened, the transition complex has a nonlinear structure, while the reaction follows a two-stage mechanism [46].

The methanolysis of Ph_3SiH in a mixture of CH_3OH and CH_3OD revealed that the primary isotope effect of methanol $k_H/k_D = 6$ [45].

The ratio of the hydrogen isotopes (product) was measured in the reaction of Et_3SiH, $(PhCH_2)_3SiH$ and triarylsilanes

$(XC_6H_4)_3SiH$ (X = H, p-Me, p-OMe, p-Cl, CF_3) with a mixture of CH_3OH and CH_3OD [46]. It was found that the isotope effect of the product (IEP) rose with increasing reactivity of R_3SiH, the tris(pentafluorophenyl)silane being an exception.

R	IEP	R	IEP
Et	2.30	Ph	3.95
$PhCH_2$	2.55	p-ClC_6H_4	4.32
p-MeC_6H_4	3.00	m-$CF_3C_6H_4$	5.03
p-$MeOC_6H_4$	3.40	C_6F_5	3.98

The relatively high values of IEP indicate that bond $H\text{-}OCH_3$ is substantially weakened in the transition complex.

There are two possible mechanisms for the alkaline alcoholysis of hydrosilanes [1,13,14,17,46]:

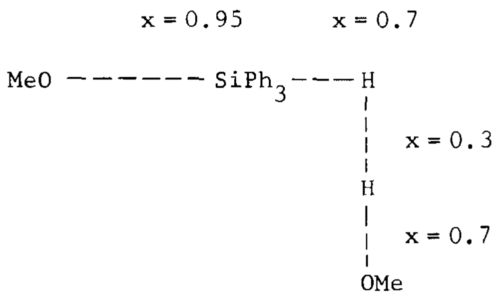
$$\left.\begin{array}{lll} MeO^- + R_3SiH & \rightleftharpoons & \underset{(I)}{[MeOSiR_3H]^-} \quad (a) \\ [MeOSiR_3H]^- + MeOH & \longrightarrow & MeOSiR_3 + H_2 + MeO^- \quad (b) \end{array}\right\} (1)$$

$$MeO^- + R_3SiH + HOMe \longrightarrow MeOSiR_3 + H_2 + MeO^- \qquad (2)$$

The first one involves a two-step process (1), the second one is concerted (2).

The data presented in [46] are discussed in terms of mechanism 1, where the rate-determining cleavage of Si-H bond follows the rapid, reversible formation of a five-coordinate silicon intermediate.

A nonlinear Si-H-H arrangement is suggested for the transition state [46]:



where x is the order of bond breakage or formation.

3.3. Organic bases

The applicability of piperidine as catalyst for the dehydrocondensation of triphenylsilane with some alcohols has been described in [49], however, the use of moist reagents would lead to reduced yields of triphenylalkoxysilanes and sometimes to their complete absence from the reaction products. When the reaction is conducted in anhydrous medium, the triarylalkoxysilanes are obtained in good yield [50]. Piperidine is capable of catalyzing the alcoholysis of not only aryl-, but also heteroaryl- (furyl-, thienyl-), alkoxy- and even alkylsilanes, if their molecules contain strong electron-withdrawing groups [50-62]. The catalytic properties are possessed also by other amines whose $pK_a > 7$ [50,60]. The rate of the reaction of methyldi(2-furyl)-, methyldi(2-thienyl)- and triethoxysilane with ethanol in the presence of amines increases with growing basicity of the amine [50,60].

The choice of catalyst for the dehydrocondensation of furyl- and thienylsilanes plays an essential role because of the side reactions taking place in the presence of alkali, alcoholates of alkaline metals, metal halides, acids, group VIII metals and their derivatives [61]. By contrast, in the presence of amines no side reactions occurred. The only product obtained in the reaction of methyldi(2-thienyl)silane with propargyl alcohol in the presence of piperidine was methyldi(2-thienyl)propargyloxysilane, whereas hexachloroplatinic acid brings about the hydrosilylation of the triple bond in the propargyl alcohol. The yields of di- and triheteroarylethoxysilanes and triphenylethoxysilane reach 80% [61].

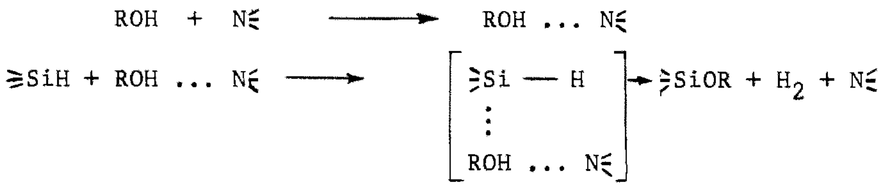
The effect of structure studied for 13 alcohols on the rate of dehydrocondensation of methyldi(2-furyl)-, methyldi-(2-thienyl)-, triethoxy-, methyldi(p-chlorophenyl)- and triphenylsilanes reveals that the rate of the reaction rises with growing -I-effect of the substituents in the alcohol molecule. The logarithms of the rate constants plotted against the Taft's constants of the substituents give two straight lines: one for electron-acceptor and the other for electron-donor substituents. These lines can be described by Taft's equation. Using a two-parameter correlation that accounts for the inductive and steric effects of the substituents by comparing ρ and δ' values, it has been concluded that the inductive effect is dominant [60].

Depending on the radicals at the silicon atom, the rate of alcoholysis of hydrosilanes diminishes in the order:
2-furyl > 2-thienyl > phenyl > α-naphthyl > 2-(4,5-dihydrofuryl) > 3-furyl [50,62].

The rate of the reaction and the yields of products increase with increase in the number of aryl and heteroaryl groups in the silane molecule. The logarithms of the rate constants of 14 aryl- and heteroarylsilanes with propargyl alcohol are satisfactorily correlated with the sum of Taft's constants of substituents at the silicon atom in the hydrosilanes and with the spin-spin coupling constants $^{1}J_{SiH}$ [50,62]:

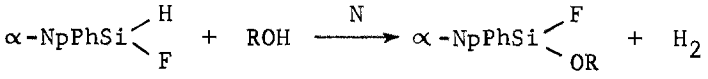
$$\log k = -2.72 + 1.37\,\Sigma\,\sigma^{*}_{R} \qquad r = 0.982;\quad s = 0.05$$
$$\log k = -33.5 + 0.17\,{}^{1}J_{SiH} \qquad r = 0.975;\quad s = 0.1$$

The molecular mechanism for the formation of intermediates containing a five-coordinated silicon atom has been proposed for the dehydrocondensation of aryl-, furyl- and thienylsilanes with alcohols in the presence of amines [50,62].



$$\mathrm{ROH} + \mathrm{N}{\lessgtr} \longrightarrow \mathrm{ROH} \ldots \mathrm{N}{\lessgtr}$$
$$\gtrless\mathrm{SiH} + \mathrm{ROH} \ldots \mathrm{N}{\lessgtr} \longrightarrow \left[\begin{array}{l}\gtrless\mathrm{Si} - \mathrm{H} \\ \vdots \\ \mathrm{ROH} \ldots \mathrm{N}{\lessgtr}\end{array}\right] \rightarrow \gtrless\mathrm{SiOR} + \mathrm{H_2} + \mathrm{N}{\lessgtr}$$

Fluorine-containing hydrosilanes, such as α-naphthylphenylfluorosilane , in the presence of nucleophilic agents (organic bases included) react readily with alcohols [63]:



$$\alpha\text{-NpPhSi}\genfrac{}{}{0pt}{}{\diagup \mathrm{H}}{\diagdown \mathrm{F}} + \mathrm{ROH} \xrightarrow{\mathrm{N}} \alpha\text{-NpPhSi}\genfrac{}{}{0pt}{}{\diagup \mathrm{F}}{\diagdown \mathrm{OR}} + \mathrm{H_2}$$

However, both the hydrogen and fluorine atom become substitutedby an alkoxy group during the reaction.

The rate of the reaction increases in the following sequence of catalysts: dimethylsulphoxide < hexamethylphosphorotriamide < triethylamine < tetramethylethylenediamine.

Hydroxylamine and N-substituted hydroxylamines have been also used as catalysts in the dehydrocondensation reaction [64,65].

The reaction of 1,1,5,5-tetrahydro-1,5-dimethyl-3,3-diphenyltrisiloxane with methanol in the presence of Et_2NOH affords 1,1,5,5-tetramethoxy-1,5-dimethyl-3,3-diphenyltrisiloxane [64].

In the reaction of dehydrocondensation of aminoalkylsilanes the role of the catalyst is assumed by the silane itself. For example, ω-aminoalkylsubstituted silanes $Me_2N(CH_2)_nSiRH_2$ (where $n = 1,3,5$; $R = Me$, Ph) participate readily in the reaction of dehydrocondensation with nucleophilic agents in the absence of catalysts [11,12,66]. The reaction of $Me_2N(CH_2)_3SiMeH_2$ and menthol , for one, proceeds in dimethylacetamide solution without catalyst upon heating in a water bath [12]:

$$Me_2N(CH_2)_3SiMeH_2 + Ment\text{-}OH \xrightarrow[-H_2]{} Me_2N(CH_2)_3SiHMe(OMent)$$

The substitution of the second hydrogen atom by the menthoxyl group fails to occur in these conditions due to steric hindrance and reduced acceptor properties of the silicon atom.

The kinetics of alcoholysis of aminoalkylsilanes $Me_2N(CH_2)_nSiRH_2$ studied in dimethylacetamide [66] showed that the reactivity of aminoalkylsilanes declines with increasing number of methylene groups between the nitrogen and silicon atoms:

$$Me_2NCH_2SiMeH_2 > Me_2N(CH_2)_3SiPhH_2 > Me_2N(CH_2)_3SiMeH_2 >$$
$$> Me_2N(CH_2)_5SiMeH_2$$

A comparison of log k_1 and substituent constants σ^* in the alcohols indicates a correlation characterized by positive ρ values, however, the data for cinnamic and benzyl alcohols depart from this correlation. Addition of an OR' group negatively affects the reactivity of Si-H bond ($k_2/k_1 < 1$), apparently due to the steric factor.

4. THE ALCOHOLYSIS OF HYDROSILANES IN THE PRESENCE OF ACIDIC CATALYSTS

4.1. Hydrogen chloride

The alcoholysis of hydrosilanes in the presence of hydrogen chloride is rather poorly documented in the literature [67-72].

The reactions were conducted in absolute ethanol [67,70, 71] and in aqueous ethanol [68-72].

It was found that the rate of acidic ethanolysis of triethylsilane was proportional to the square of the mean activity of hydrogen chloride [67], however, the proportionality is retained only over a restricted range of hydrogen chloride concentrations [68].

The reactivity of silanes in the reaction with aqueous ethanol falls in the sequence [68]:

$C_6H_{11}SiH_3$	Pr_2SiH_2	Et_3SiH
120	22	1

(in the first two cases the elimination of the first hydrogen atom is taken into account).

The rate of the loss of the first hydrogen atom for Pr_2SiH_2 is 18 times that of the second one.

The data showing the effect of the silane structure on the rate of acidic solvolysis of silanes R_3SiH in 95% ethanol are summarized in the table:

R_3	$k_{rel.}^{34.9^\circ}$	R_3	$k_{rel.}^{34.9^\circ}$
Et_3	100	Ph_3	30
$n\text{-}Pr_3$	63	$(p\text{-}ClC_6H_4)_3$	130
$n\text{-}Bu_3$	59	$(p\text{-}ClC_6H_4)Me_2$	220
$i\text{-}Bu_3$	17	$PhMe_2$	180
$i\text{-}Pr_3$	6	$(p\text{-}MeC_6H_4)Me_2$	150

The low reactivity of $i\text{-}Pr_3SiH$, as compared to Pr_3SiH, is accounted for by the steric effect.

The kinetic isotope effects suggest that the bond O-H is broken at the stage determining the rate of the process.

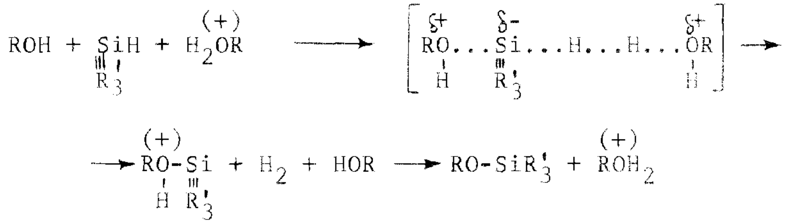
Electron-acceptor substituents were found to enhance the reaction, when the effect of substituents in the hydrosilane molecule was studied on the reaction rate of mono-, di- and triorganosilanes with 95% ethanol at 34.8°. The logarithms of the rate constants are correlated with the sum of σ^* values for the substituents at the silicon atom; nevertheless, three individual lines are attained for the tri-, di- and monoorganosilanes [69], the ρ^* values in Taft's equation being equal to 0.77. However, departures from the correlation line (lower location of points) are observed for some triorganosilanes. In the case of triisopropylsilane and triisobutylsilane this is explained by steric factors, although deviations are also present in the case of chloromethyldimethylsilane, triphenylsilane and phenyldimethylsilane. For phenylsilanes this may be the result of additional π-bonding which reduces the -I-effect of the phenyl group. The departure from the plotted line observed for chloromethyldimethylsilane is due to the α-effect of the chloromethyl group leading to an increase in the electronic density on the silicon atom.

The kinetics of dehydrocondensation of silanes $RC_6H_4SiHMe_2$ (where R = p-Me, H, m-MeO, p-Br, m-Cl, m-CF_3, p-CF_3) with ethanol has been investigated in the presence of hydrogen chloride (0.05-0.8 M), the concentration of water in alcohol being 0.1, 5 and 20 vol.% [70]. It has been found that the rate of the reaction is only slightly dependent on the inductive effects of the substituents (by contrast to alkaline catalysis). For absolute ethanol, constant ρ in Hammett's equation is not related to HCl concentration and is practically equal to zero. With increasing water concentration in alcohol, value ρ rises to 0.5. If the content of water in the ethanol is increased, to decrease the value of constant ρ to zero, one has to increase the concentration of HCl. This may be explained by the solvation of HCl and protons (the latter are produced as a result of HCl dissociation) by H_2O molecules which leads to a decrease in H_2O concentration. Therefore, the observed variation in ρ values is related to changes in the hydrolysis/ethanolysis ratio in this process.

Dehydrocondensation of Et_3SiH, $PhSiHMe_2$ and $C_6H_{11}SiH_3$ with absolute and 95% ethanol reveals a linear correlation between the logarithms of rate constants and acidity function indicating the involvement of protons in the formation of intermediates [71].

The ethanolysis of Si-H-containing penta- and tetramethyldisiloxanes demonstrates that the reaction rate increases with HCl concentration [72].

The above findings can be explained by the scheme [68,70]:



$$ROH + \underset{R_3}{SiH} + \overset{(+)}{H_2OR} \longrightarrow \left[\overset{\delta+}{\underset{H}{RO}}\cdots\overset{\delta-}{\underset{R'_3}{Si}}\cdots H\cdots H\cdots\overset{\delta+}{\underset{H}{OR}}\right] \longrightarrow$$

$$\longrightarrow \overset{(+)}{\underset{H\ \ R'_3}{RO-Si}} + H_2 + HOR \longrightarrow RO-SiR'_3 + \overset{(+)}{ROH_2}$$

The reaction simultaneously involves the nucleophilic attack by ROH on the silicon atom and the electrophilic attack by the $\overset{(+)}{H_2OR}$ species on the hydrogen. However, the negative charge at the silicon atom indicates that the nucleophilic and electrophilic attacks are not strictly synchronous.

4.2. Cationites

The sulphocationite KU-2-8 acts as catalyst in the reaction of hydrogen substitution in triethylsilane by nucleophilic agents [73-75]. The kinetics of triethylsilane alcoholysis studied in dibutyl ether [74] has revealed that:

(1) the reaction occurs at the catalyst surface,

(2) reaction rate logarithms plotted against σ^* constants in the alcohol molecule are characterized by two arms, with

positive and negative ρ values, respectively; this is due to the presence of cationite in the system, i.e. to competitive sorption of alcohols and the solvent by the cationite, not reflected by the σ^* constants;

(3) a criterion of alcohol reactivity in the reaction is its sorption by the catalyst;

(4) the reaction follows the scheme:

$$R_3SiH + H^+:L \longrightarrow [R_3SiH_2]^+L$$

$$[R_3SiH_2]^+L + R'OH \longrightarrow R_3SiOR' + H_2 + H^+L$$

Proton transfer from the cationite to the silane is accomplished by solvent molecules (**L**).

5. THE ALCOHOLYSIS OF HYDROSILANES IN THE PRESENCE OF METALS

5.1. Group IB metals

The catalytic properties of metallic copper were first demonstrated in [2], where triethylsilane reacted with ethyl alcohol in the absence of alkaline catalyst in an autoclave at 200°C to give triethylethoxysilane at 88% yield. Following the reaction, the copper seal and the autoclave walls were found to have suffered from corrosion. It has been also reported that triethylsilane reacts with ethanol in the presence of activated copper powder upon boiling at normal pressure. In this case however, the yield of triethylethoxysilane is low (11%) and the reaction occurs slowly.

Phenylsilane reacts with alcohols in the presence of copper powder or wire [76] at room temperature. Thereby, one, two or three hydrogen atoms can undergo substitutions, the yields of reaction products being low. It was found that the reactivity of alcohols increases in the sequence:

$$\mathrm{MeOH} < \mathrm{EtOH} < \mathrm{PrOH} < \mathrm{BuOH}$$

Metallic copper has been used in the reaction of SiH_4 with methanol to obtain mono-, di- and trimethoxysilanes [77]. The rate of methanolysis of the Si-H bond rises following the addition of methoxy groups at the silicon atom - the electron-acceptor methoxy groups increase the positive charge on the silicon atom thereby making it more vulnerable to nucleophilic attack. This effect apparently prevails over the steric effect of the methoxy group.

The kinetics of the reaction of monoorganosilanes with alcohols was studied in the presence of freshly precipitated copper [78]. Under the conditions employed a two-step reaction is under way:

$$RSiH_3 \xrightarrow[-H_2]{+R'OH} RSiH_2OR' \xrightarrow[-H_2]{+R'OH} RSiH(OR')_2$$

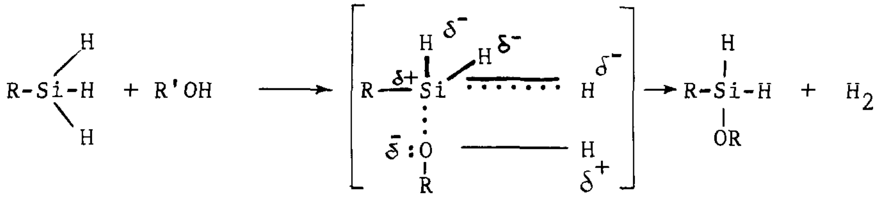
The reactivity of silanes declines in the sequence:

$$C_6H_5SiH_3 > p\text{-}ClC_6H_4SiH_3 > BuSiH_3$$

In the reaction with p-chlorophenylsilane the reactivity of alcohols decreases in the order:

propyl > allyl > propargyl > benzyl alcohol.

Based on the kinetic data, a mechanism has been proposed for the reaction, which is represented in the scheme. According to the scheme, the silicon atom is attacked by the alcohol leading to activated complex formation and subsequent formation of a Si-O bond accompanied by elimination of a hydrogen molecule [78]:



The use of silver as catalyst has been reported by [83,84], but the reaction was not studied in detail.

5.2. Group VIII metals

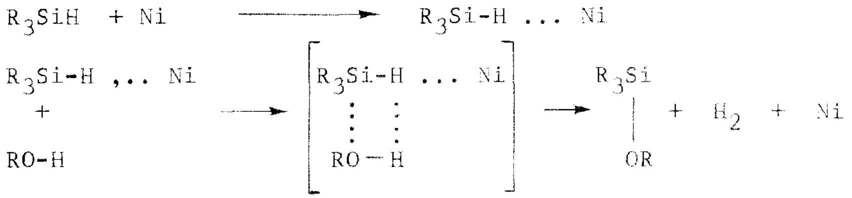
Group VIII metals have been extensively applied for catalytic dehydrocondensation of hydrosilanes with hydroxyl-containing compounds [79-87].

In [79-84], reactions were performed in the presence of either colloid [79-81,84] or Raney [82,83] nickel.

In [84], the reaction of trialkyl(aryl)silanes with cyclohexanol was examined in the presence of various catalysts, including colloidal nickel and palladium. In greater detail was studied the dehydrocondensation reaction catalyzed by nickel. The reaction rate was found to increase with the amount of catalyst and to decrease with elongation and branching of the radical chain attached to the silicon in the silane molecule:

$$Et_3SiH > MeBu_2SiH > MePh_2SiH > Pr_3SiH >$$
$$Bu_3SiH > Me(i\text{-}Bu)_2SiH > i\text{-}Bu_3SiH$$

The following mechanism was suggested for the reaction:



Optically active products were obtained in the reaction of $(+)\overset{*}{R_3}SiH$ with methanol, cyclohexanol, t-butyl alcohol and phenol in the presence of Raney nickel [82]. The reaction proceeds with inversion of configuration at the silicon atom and the methanol reacts faster than other reagents.

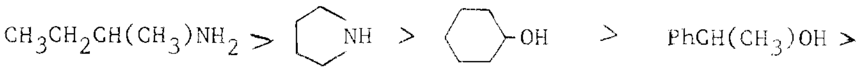
The factors affecting the reaction of optically active silanes $\overset{*}{R_3}SiH$ with hydroxyl-containing compounds in the presence of Raney nickel and palladium on carbon (Pd/C) have been explored in detail [83]. This study makes use of other catalysts, too, such as rhodium on carbon (Rh/C), ruthenium on carbon (Ru/C), $H_2PtCl_6 \cdot 6H_2O$, $PdCl_2 \cdot 2H_2O$, $PdCl \cdot 2H_2O(Et_3N)$.

In the presence of Raney nickel and Pd/C the reactivity of alcohols in the reaction declines in the sequence:

primary > secondary > tertiary.

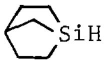
Elongation and branching of the carbon chain in the alcohol reduces the rate of reaction. The relative rates of nucleophilic reagents in the reaction with R_3SiH in the presence of 10% Pd/C were obtained:

$CH_3OH > CH_3CH_2OH \approx PhCH_2OH > PhCH_2CH_2OH >$



$(CH_3)_3COH > CH_3COOH \approx PhOH > PhCOOH$

A study of silane structure reveals that the reaction is enhanced by the electron-withdrawing substituents in the silane molecule:

$MePhMeOSiH > MeEtPhSiH \sim Et_3SiH >$ 

The reaction proceeds with inversion of configuration at the silicon atom. In the case of silabicyclo(2,2,1)heptane where inversion of configuration is impossible, the rate of methanolysis is extremely slow as compared to its acyclic analogue Et_3SiH.

The rate of the reaction in various solvents falls in the order: alkanes (pentane, heptane) > methylene chloride > aromatics (benzene, toluene, p-xylene).

A comparison of catalysts shows that Pd is more effective than Ni. In the case of Pd and Ni, methanolysis occurs with almost complete inversion of configuration, but with Rh and Ru it is less stereospecific.

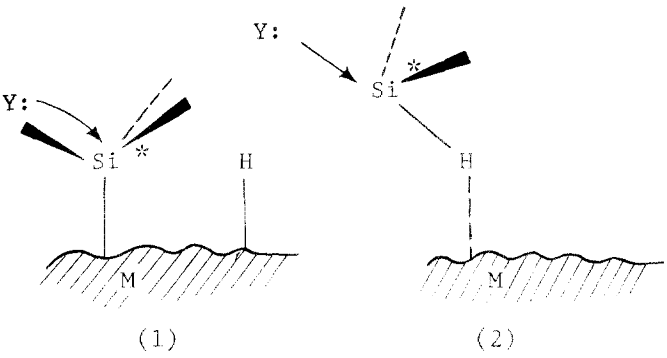
On the basis of stereochemical data it is claimed that the observed inversion of configuration at the silicon atom contradicts the S_Ni-Si mechanism. They believe that the reaction of optically active silane and metal occurs with retention of configuration, whereas that of the intermediate and alcohol occurs with inversion of configuration [83]:

$$R_3\overset{*}{Si}H \xrightarrow[\text{retention}]{(M)} \left[R_3\overset{*}{Si}H(M\ )\right] \xrightarrow[\text{inversion}]{ROH} R_3\overset{*}{Si}OR$$

Two possibilities are conceivable in the case of the intermediate:

(1) Si-M bonds are present,

(2) Si-H bond is retained, but activated by metal



In both cases attack by a nucleophile, Y:, results in inversion of configuration at the silicon center.

6. THE ALCOHOLYSIS OF HYDROSILANES IN THE PRESENCE OF METAL AND TETRAALKYLAMMONIUM SALTS

The applicability of salts as catalysts for the dehydrocondensation of hydrosilanes with alcohols has been first demonstrated for the ethanolysis of methylpolysiloxane $(MeHSiO)_x$ in the presence of $ZnCl_2$, $MgCl_2$, $Zn(ClO_3)_2$, BF_3 [88]. The reaction yielded a polymer with useful properties; $ZnCl_2$ was found to be the most suitable catalyst.

This reaction underlies the general catalytic procedure for the preparation of trialkyl- and triarylalkoxysilanes where a 95% yield is observed [89]. The best catalysts were the halides of Ni, Co, Cr, Ge, Zn, Sn. Metal halides have been used by several investigators [40,84,88-96,99-103] along with other salts: tetramethylammonium fluoride [97,98], tetraethylammonium fluoride [99], tetrabutylammonium fluoride [96], potassium tartrate, phthalate, formate and rhodanide [101-103], caesium, potassium and lithium acetates [101,102], dodecylammonium propionate [104].

6.1. Effect of catalyst nature

The rate of the reaction of trialkyl silanes with alcohols depends on the nature and amount of metal chlorides [90]. The most active are $ZnCl_2$ and $SnCl_2$ [84,90,91].

The reaction of dipropylethoxysilane and ethanol [40] demonstrates that the rate of dehydrocondensation increases with growing ionic radius of the halogen:

$$ZnF_2 < ZnCl_2 < ZnBr_2 < ZnI_2$$

The rate of the reaction of trialkylsilanes with cyclohexyl alcohol rises with the amount and degree of dissociation of the tin halide [84].

The activity of fluorides and acetates of alkali metals in the reactions of mono- and diorganosilanes increases in the sequences [101,102]:

$$LiF < KF < CsF$$

$$AcOLi < AcOK < AcOCs$$

i.e. with increasing ionic character of the salt.

In [102,103], the activity of salts was arranged in the following order: potassium tartrate < KSCN < HCOOK < < potassium phthalate < KF < CsF.

It has been noted that alcoholysis in the presence of salts is a selective method for the synthesis of alkoxysilanes which, depending on the conditions (salt, temperature, reagent ratio), leads to mono- or dialkoxysilanes [102,103]. For instance, the reaction of α-NpPhSiH$_2$ with heptanol in the presence of KSCN results in monoalkoxysilane, whereas in the presence of HCOOK, KF and potassium phthalate, dialkoxysilane is obtained.

6.2. Effect of alcohol structure

A study of dehydrocondensation of trialkylsilanes with alcohols in the presence of metal chlorides has shown [90] that the rate of the reaction declines with elongation and branching of the alkyl radical.

The reactivity of alcohols in the reaction with diethylsilane in the presence of $ZnCl_2$ diminishes in the order [95]:

$$\text{primary} > \text{secondary} > \text{tertiary}$$

The reactivity of alcohols in the reaction with methyldiphenylsilane in the presence of NMe_4F rises in the sequence [97]:

$$t\text{-BuOH} < MeOH < CH_2{=}CHCH_2OH < PhCH_2OH < HC{\equiv}CCH_2OH$$

The reaction rate of the alkanols used obeys Taft's equation with allowance made for the steric factor.

The reactivity of hydroxyl-containing compounds in the dehydrocondensation with diphenylsilane in the presence of KSCN decreases in the sequence [102]:

$$m\text{-cresol} > n\text{-heptanol} > \text{menthol}$$

In the case of homogeneous catalysis (metal complexes are present) phenols react slower than alcohols [105,112], but in the presence of salts, phenols are more reactive. However, m-cresol reacts slower with diorganosilanes than menthol in the presence of dodecylammonium propionate [104].

6.3. Effect of silane structure

Substitution of one of the ethyl radicals in triethylsilane be methyl, increased the rate of dehydrocondensation with n-butyl alcohol in the presence of $SnCl_2$ and $ZnCl_2$ by 2- and 3.5-fold, respectively [90].

The reactivity of silanes in the reaction with pentaerythritol in the presence of $SnCl_2$ drops in the sequence [91]:

$$Et_3SiH > Pr_3SiH > Bu_3SiH$$

The rate of the reaction of triorganosilanes with cyclohexanol in the presence of tin halides diminishes with increasing +I- and steric effect of the substituents at the silicon atom [84].

The reactivity of hydrosilanes with menthol decreases in the order [102,103]:

$$\alpha\text{-}NpSiH_3 > Ph_2SiH_2 > PhMeSiH_2 > \alpha\text{-}NpPhSiH_2 > Am_2SiH_2$$

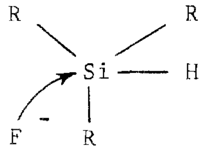
6.4. The mechanism of reaction

An ion-chain S_N2 mechanism has been suggested in [84]:

$$C_6H_{11}OH + SnX_2 \longrightarrow (C_6H_{11}O \ldots SnX_2)^-H^+$$

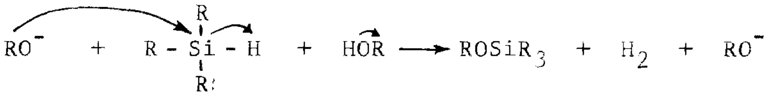
$$(C_6H_{11}O \ldots SnX_2)^-H^+ + \overset{\delta-}{H} \ldots \overset{\delta+}{SiR_3} \longrightarrow C_6H_{11}OSiR_3 + H_2 + SnX_2$$

The catalytic effect of fluorides CsF, KF and $(C_2H_5)_4NF$ has been explained by the attack of the "hard" base F^- on the "hard" silicon atom facilitating the elimination of the "soft" H^- ion [99] :



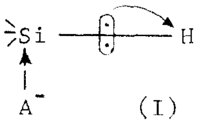
It is indicated in [100] that F^- withdraws a proton from the alcohol molecule:

$$ROH + F^- \longrightarrow RO^- + HF$$

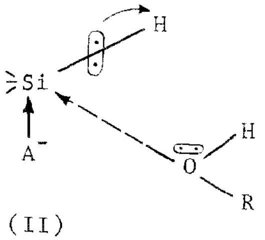


$$RO^- + R-\underset{R}{\overset{R}{Si}}-H + HOR \longrightarrow ROSiR_3 + H_2 + RO^-$$

It is believed [101-103] that the salt acts by activating the silicon atom due to the formation of a pentacoordinated silicon complex (I). The coordination causes displacement of the electron pair of the Si-H bond which is followed by the nucleophilic attack excited by the alcohol molecule on the silicon atom (II):



A^- - salt anion

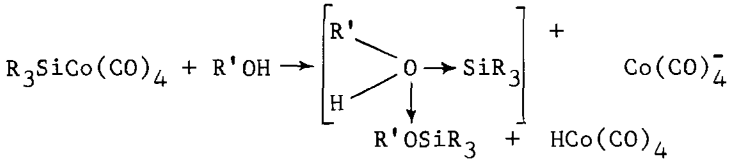


7. THE ALCOHOLYSIS OF HYDROSILANES IN THE PRESENCE OF METAL COMPLEXES

7.1. Iron and cobalt complexes

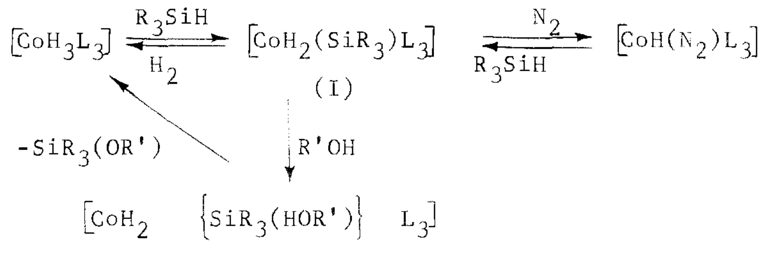
Dicobalt octacarbonyl $Co_2(CO)_8$, a new catalyst, was proposed in 1970 for the silylation of alcohols with triethylsilane [105,106]. In its presence, the dehydrocondensation of triethylsilane with ethanol continues for several hours at 25°C to yield 90% of triethylethoxysilane. $Co_2(CO)_8$ can be applied for selective silylation of alcohols. The reaction follows the scheme:

$$Co_2(CO)_8 + 2R_3SiH \longrightarrow 2R_3SiCo(CO)_4 + H_2$$



The reaction of triethoxysilane with ethanol in the presence of $(Ph_3P)_3Co(N_2)H$ or $(Ph_3P)_3CoH_3$ proceeds during 2.5 hours with 80% yield or tetraethoxysilane [107]. With these two catalysts present, methanol reacts with triethoxysilane three times as fast as ethanol, whereas butanol fails to react [108]. Under the same conditions, triethylsilane does not react with alkanols, but the dehydrocondensation of polysiloxane $Me_3Si[OSi(H)Me]_n$ takes place easily.

Dehydrocondensation in the presence of cobalt complexes proceeds according to the scheme:



$L = Ph_3P; \quad R = OEt$

The attack of alcohol on the complex (I) determines the rate of the reaction, the hydrogen being formed inhibits the reaction.

The use of iron complexes was studied later than of cobalt complexes.

It was found that the iron complexes $[FeH_2(PMePh_2)_4]$ and $[FeH_2(N_2)(PEtPh_2)_3]$ catalyzed the reaction of alcohols with the hydrosilanes $(EtO)_3SiH$ and Ph_2SiH_2 at room temperature [109]. The reaction had an induction period and failed to occur with the silanes Et_3SiH, Ph_2SiHMe, Ph_3SiH.

By means of chromatography and IR-spectroscopy it was demonstrated that the two hydrogen atoms in the silane Ph_2SiH_2 were reactive (dialkoxy derivatives were formed). In the case of $(EtO)_3SiH$, transesterification also takes place to give $Si(OEt)_n(OR)_{4-n}$.

Complex $[Fe(C_2H_4)(Ph_2PCH_2CH_2PPh_2)_2]$ also catalyzes dehydrocondensation, but rapidly loses its activity because of the side reactions.

A study of kinetics of the reaction of $(EtO)_3SiH$ with ethanol suggests the following scheme which resembles the dehydrocondensation in the presence of cobalt complexes:

$$[FeH_2L_4] \longrightarrow [FeH_2L_3] + L$$

$$[FeH_2L_3] + R_3SiH \longrightarrow [FeH_3(SiR_3)L_3]$$

$$[FeH_3(SiR_3)L_3] + EtOH \longrightarrow [FeH_3(SiR_3\cdot EtOH)L_3]$$

$$[FeH_3(SiR_3\cdot EtOH)L_3] \longrightarrow [FeH_4L_3] + R_3SiOEt$$

$$[FeH_4L_3] \xrightarrow{fast} [FeH_2L_3] + H_2$$

L - $PMePh_2$; R -OEt

7.2. Ruthenium, rhodium and palladium complexes

Rhodium complexes have been most frequently applied, $(Ph_3P)_3RhCl$ being the most effective among them [110-115]. $(Ph_3P)_3RhCl$ is a selective catalyst for the alcoholysis of diarylsilanes [112] (it is much more active than $Co_2(CO)_8$ [110,112]).

$(Ph_3P)_3RhCl$ in combination with hydrosilane is a strong silylating agent for OH-groups [114], hence it can be used for protection of OH-groups in terpenes, carbohydrates, etc. In this fashion were obtained O-diethylsilylmenthol, -borneol, -geraniol, bis-triethylsilylmandelic acid and other compounds in quantitative yield.

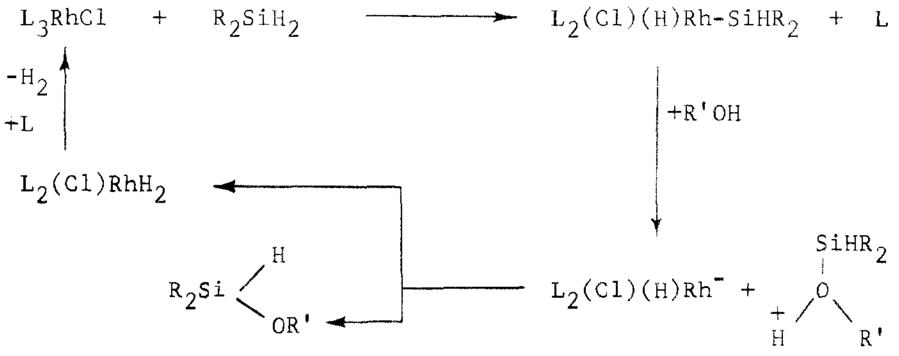
The reactivity of alcohols in the reaction with triethylsilane in the presence of $(Ph_3P)_3RhCl$ diminishes in the order [114]:

MeOH (100) > EtOH (64) > i-PrOH (11) > t-BuOH (0.8)

The reactivity of hydrosilanes decreases from monoorgano- to triorganosilanes [114]. E.g., CH_3SiH_3 with 2-propanol, unlike $(CH_3)_3SiH$, reacts already at -56°C.

Dehydrocondensation with diorganosilanes also proceeds much more rapidly than with triorganosilanes [112]. The alcoholysis of chiral silanes occurs with retention of configuration at the silicon atom [112].

The results of these investigations are illustrated by the scheme [112]:



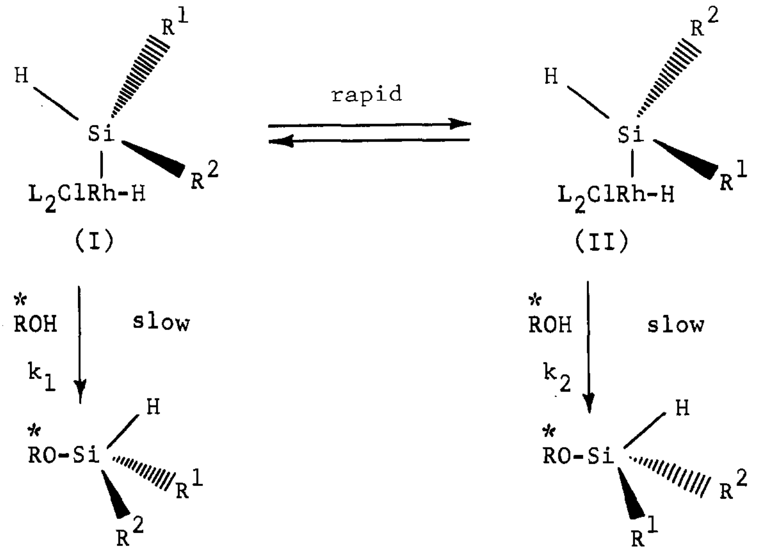
L = PPh_3

The complexes $(C_8H_{14})_2RhCl_2$ [111,113,116] and $[(C_6H_{11})_3P]_2RhCl$ [113] have been also used as catalysts.

In asymmetric alcoholysis of prochiral organosilanes the complexes $(PPh_3)_3RhCl$, $[(C_8H_{14})_2RhCl]_2$ and optically active [(+)-diop] RhCl, [(-)-diop] RhCl, $(NMDPP)_2RhCl$, $(MDPP)_2RhCl$, [where diop is 2,3-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane, NMDPP neomenthyldiphenylphosphine, MDPP menthyldiphenylphosphine], have been employed [115].

The use of these catalysts resulted in alkoxysilanes with optical yields up to 57%. The optical yield largely depends on the structure of the organosilane and alcohol but is only slightly affected by the nature of organic ligands in the rhodium complexes.

A reaction scheme was suggested on the basis of the results obtained where rapid and reversible activation of the silane is followed by slow interaction with the alcohol:



No specific activation of alcohol by the catalyst was detected.

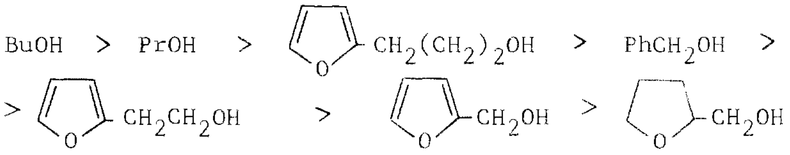
Among ruthenium complexes only one catalyst, viz. $(Ph_3P)_3RuCl_2$ [110,112] was reported, although more detailed investigations are not available.

Recently, palladium complexes have been also used:

$[Pd(dppe)(ROH)_2](ClO_4)_2$ (R = H, Me, Et) [116] and $[Pd(dppe)(Me_2CO)_2]$ $(ClO_4)_2$ [117], where dppe = $(CH_2PPh_2)_2$.

7.3. Iridium and platinum complexes

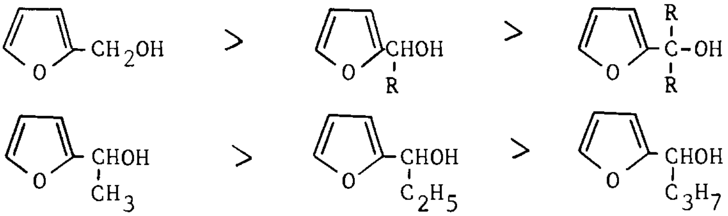
Many investigators [48,82,83,118-134] describe chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) catalysis of dehydrocondensation. Despite the wide application of H_2PtCl_6 in synthetic processes the factors affecting these reactions are poorly understood. The kinetic study reported by [124] is an exception, where the dehydrocondensation of triethylsilane with various alcohols was examined in the presence of $H_2PtCl_6 \cdot 6H_2O$ in different solvents. It was shown that the reactivity of primary alcohols toward triethylsilane in toluene solution at 25°C falls in the sequence:



The above pattern of variation indicates that the reactivity of alcohols increases with the +I-effect of substituents in the alcohol molecule (with increasing electron density on the hydroxyl oxygen in the alcohol molecule). The rate of dehydrocondensation drops with hydrocarbon radical branching in the alcohol and also from primary to secondary and tertiary alcohols. The reactivity of butanol isomers in the reaction with triethylsilane in toluene and dioxan at 40°C diminishes as follows:

n-BuOH > i-BuOH > s-BuOH > t-BuOH

In the furan series:

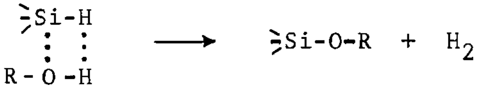


Consequently, the reactivity of alcohols depends on electronic and steric factors.

The rate of the reaction as a function of solvent drops in the order: toluene > dioxan ≫ pyridine, dimethylformamide.

The rate of the process grows with increasing amount of the catalyst.

The reaction is assumed to occur via a cyclic intermediate:



$$\begin{matrix} \geq Si-H \\ \vdots \quad \vdots \\ R-O-H \end{matrix} \longrightarrow \geq Si-O-R + H_2$$

However, the stereochemical evidence obtained later contradicts this scheme [83], since racemic products were obtained in the reaction of the silanes $R_3\overset{*}{Si}H$ with methanol in the presence of $H_2PtCl_6 \cdot 6H_2O$ in methylene chloride.

Iridium complexes as catalysts of dehydrocondensation were reported only recently [135,136].

The iridium complexes (I)IrX(CO)L_2, IrCl(N_2)(PPh_3)$_2$, IrClL_2, [IrCl(C_8H_{14})$_2$]$_2$ (X - halogen, L - tertiary phosphine or arsine) effectively catalyse the dehydrocondensation of silanes R_3SiH($R=Ph$, Et, OEt) with alcohols R'OH (R'=Et, Me) [135].

The reactivity of alkanols in reaction with $(EtO)_3SiH$ in the presence of $IrCl(CO)(Ph_3P)_2$ diminishes in the order:

$$MeOH\ (3.5) > EtOH\ (1.0) > t\text{-}BuOH\ (0.5)$$

The polysiloxane $Me_3SiO[SiH(Me)O]_nSiMe_3$ ($n \sim 50$) reacts with ethanol extremely rapidly giving hydrogen in 95% yield during 20 sec.

Iridium complexes are more effective than tin-containing catalysts [135]. For instance, in the reaction of EtOH: $(EtO)_3SiH=5:1$, the product yield is 50-100% in the presence of $IrCl(N_2)(Ph_3P)_2$ at 23°C during 25-50 min, but in the presence of $Bu_2Sn(OAc)_2$ at 60°C the reaction requires 70-500 min to occur.

Iridium complexes $IrCl(CO)L_2$ ($L = Ph_2P(CH_2)_2Si(OEt)_3$) and $IrClL_2$ (prepared "in situ" from $[IrCl(C_8H_{14})_2]_2 + 4L$) on silica gel have been used, as heterogeneous catalysts in reactions of $HSiR_3$ (R = Et, OEt) and $Me_3SiO[Si(H)(Me)O]_nSiMe_3$ (PS1, n = 1; PS50, $n \sim 50$) with primary alcohols [136]. The complex $IrCl(CO)[Ph_2P(CH_2)_2Si(OEt)_3]_2$ quickly loses its activity. A more effective catalyst is obtained if silica gel is first treated with $Ph_2P(CH_2)_2Si(OEt)_3$ and then with $[IrCl(C_8H_{14})_2]_2$.

The reactivity of silanes towards ethanol in the presence of $IrCl(CO)L_2$ decreases in the sequence:

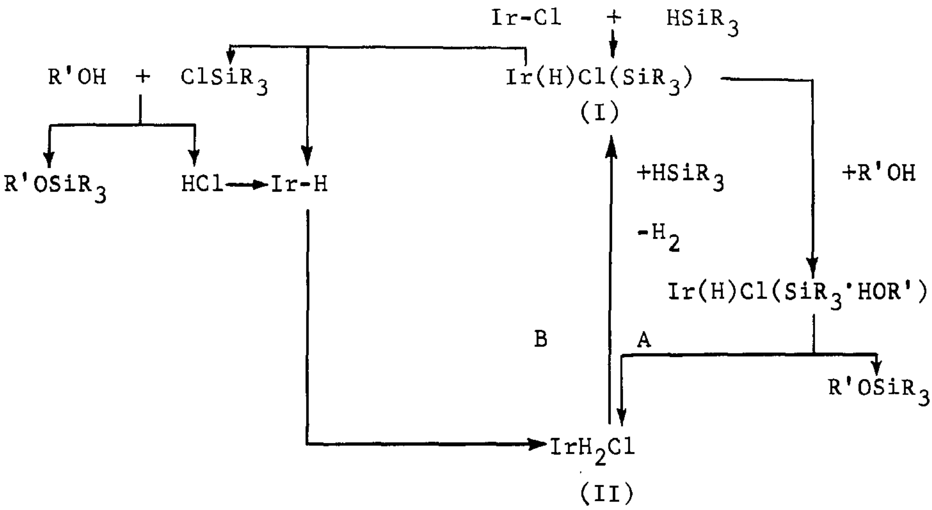
$$PS50 \gg HSi(OEt)_3 > HSiEt_3 \gg PS1$$

The reactivity of alcohols in the reaction with $(EtO)_3SiH$ diminishes as follows:

MeOH > EtOH > i-PrOH; t-BuOH

Using a wider range of alcohols in the case of PS50 the reaction rate drops in the order:

EtOH ≫ citronelol, geraniol, p-anisyl alcohol, 2-phenylethanol > menthol > 2-ethylhexane-1,3-diol > > eugenol.



Two major mechanisms (the phosphine ligands are omitted from the scheme), both of them involving the formation of complex (I), are possible in the case of O-silylation of alcohols or other hydroxyl-containing compounds in the presence of transition metals. Complex (I) may further react with R'OH (route A) or split off chlorosilane, which reacts with R'OH (route B). In both cases, complex (II) is formed which in reaction with the silane regenerates complex (I). It can be assumed that mechanism B is operable in the case of the catalyst $IrCl(CO)L_2$ and mechanism A in the case of $IrClL_2$ [135,136], as well as with iron and cobalt complexes.

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