THE SOLVENT EFFECTS ON KINETICS AND MECHANISM OF ZINC OR CADMIUM HALIDE CATALYZED REACTIONS OF HYDROSILANES WITH HYDROXYLIC REAGENTS

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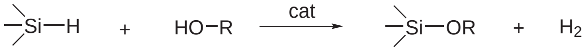
This paper is dedicated to Professor Otto Exner on the occasion of his 80th birthday, in appreciation of his outstanding contribution to the studies of reaction mechanisms.

The effect of solvent composition on reaction rates was studied by a kinetic method for reactions of Et_3SiH with $Ph_2Si(OH)_2$ in the presence of $ZnCl_2$ in a mixture of DMF and THF or Et_3SiH with PhCOOH and cadmium bromide $CdBr_2$ in DMF–1,4-dioxane and DMF–THF. A decrease in reaction rates with decreasing polarity of the medium (and its dielectric constant) has been observed. The kinetic order of dehydrocoupling reaction with respect to DMF was determined from kinetic studies. The constants of nucleophilic catalysis with DMF (λ) were found. The role of DMF in the mechanism of dehydrocoupling of hydrosilanes with hydroxylic reagents in the presence of ZnX_2 and CdX_2 halides (X = Cl, Br, I) is discussed.

Keywords: Hydrosilanes; Silanes; Silanols; Hydroxylic reagents; Dehydrocoupling; Solvent effects; Reaction mechanisms; Nucleophilic substitutions.

In recent fifty years a particularly great attention has been paid to the studies of the mechanism of nucleophilic substitution of different leaving groups at silicon. This area of research has been reviewed by Eaborn[1], Sommer[2,3], Prince[4], Corriu[5–10] and Bassindale[11]. A brilliant contribution to the stereochemistry of substitution and its mechanistic consequences has been done especially by Sommer's[2,3] and Corriu's[7,8] research groups. The Si–H containing silicon compounds have been very often used in these studies.

The dehydrocoupling reaction of of hydrosilanes with nucleophiles containing hydroxy group



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is one of the methods of synthesis of alkoxysilanes, acetoxysilanes, silanols, and block siloxanes[12], and crosslinking of three-component silicon elastomers at room temperature[13]. Recently this reaction catalyzed with rhodium or palladium catalysts was applied to preparation from polymethylhydrosiloxanes of poly[(methyl)alkoxy(crown ether)siloxanes], silyl esters, grafted silicones[14], and poly(methylsiloxanes) containing fluorescent groups[15].

The structure of hydrosilanes strongly affects reaction rates of their solvolysis. Steric and inductive effects of electron-withdrawing and electron-donating groups R in H-silanes of general formula R_3SiH on their reactivity, both in acidic and basic media, were extensively studied[16–19]. Precious contributions to acid catalyzed solvolysis of hydrosilanes were made by Eaborn[1] and Chvalovský[19], and to the base catalyzed solvolysis of H-silanes by Schowen[20] and Eaborn[21]. Only some monoorganosilanes, diorganosilanes and arylfluorosilanes undergo dehydrocoupling with alcohols in electron-donating solvents in the absence of catalysts. Usually the reaction is catalyzed either with nucleophilic or electrophilic catalysts: bases, acids, metals, metal and tetralkylammonium salts, and metal complexes[12]. We have carried out studies of the mechanism of dehydrocoupling (dehydrogenative coupling, dehydrocondensation) of hydrosilanes with hydroxylic reagents by kinetic methods in dimethylformamide (DMF) medium, in the presence of zinc and cadmium halides as catalysts[22–26]. The effect of substituents (Y = *p*-Me_2N, *p*-MeO, *p*-Me, *p*-Cl, H, *m*-Me, and *m*-Cl) bound to the aromatic ring of (aryl)dimethylsilanes $YC_6H_5SiMe_2H$ (in reactions with Ph_3SiOH, methanol and water) is linearly dependent on their Hammett constants σ, although in DMF in the presence of Zn(II) chloride the best correlation was found with σ^+ constants[25]. Dehydrocoupling proceeds through a new mechanism because of zero order with respect to hydroxy groups. It has been found to be of the first order in H-silanes and catalyst. This has been a new example of the mechanism of the nucleophilic substitution of the Si–H bond with reagents containing the hydroxy group. This kind of kinetics is in agreement with a slow formation of an unstable complex intermediate silane–catalyst followed by a fast nucleophilic attack with a hydroxylic reagent, formation of a new Si–O bond and evolution of hydrogen[24]. The driving force of the reaction is an electrophilic attack of active ionic forms of catalysts (Zn^{2+} or Cd^{2+}) on hydrogen atom of the Si–H bond, as it was concluded from investigations of the effect of a common anion with the catalyst on reaction rates[26]. The reaction is enthalpy controlled. The high negative entropy of activation implies a highly complex and polar structure of the transition state[24]. The low negative Hammett reaction constant ($\rho = -0.12$) and the low deuterium kinetic isotope effect

(k_H/k_D = 1.4–1.5) suggested that the intermediate complex has an unsymmetrical non-linear (bent) structure, and a high bond order of the Si–H [22]. Both for base and acid catalyzed solvolysis of hydrosilanes positive values of ρ = 2–5 [21,27] and ρ = 0–0.5 [19], respectively, were reported.

We have also found that DMF plays an essential role in the mechanism of this reaction since it does not take place in other less polar solvents (benzene, toluene, ether, THF) in the absence of DMF, even at reflux. In this paper, results of studies of the effect of DMF concentration on the rates of reactions of triethylsilane with diphenylsilanediol or benzoic acid in the presence of $ZnCl_2$ or $CdBr_2$ in DMF–THF or DMF–1,4-dioxane solutions are presented.

EXPERIMENTAL

Reagents

Syntheses and purification of triethylsilane and diphenylsilanediol, purification of DMF and preparation of $ZnCl_2$ and $CdBr_2$ solutions are described elsewhere[24,26]. THF and 1,4-dioxane were dried and distilled over sodium/benzophenone. Benzoic acid (p.a.) was used without further purification.

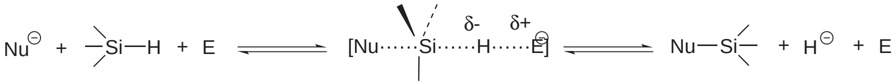
$Ph_2Si(OH)_2$: m.p. 163–165 °C. ^{1}H NMR (CD_3COCD_3): 5.96 s, 2 H (Si-OH); 7.29–7.43 m, 6 H (C_6H_5, *m*-, *p*-); 7.67–7.77 m, 4 H (C_6H_5, *o*-). ^{13}C NMR (CD_3COCD_3): 128.96, 130.99, 135.80, 138.77 (C_6H_5). ^{29}Si NMR (CD_3COCD_3): –32.39 s.

Kinetic Method

Substrates (Et_3SiH, $Ph_2Si(OH)_2$ and PhCOOH) were dissolved in a mixture of DMF with THF or 1,4-dioxane (1:1, v/v). Catalysts were dissolved in DMF. Reaction progress was monitored by a gasometric method – the volume of liberated hydrogen was measured in a thermostatted device at ambient pressure. Kinetic data from experimental measurements were plotted according to the first order equation[24].

RESULTS AND DISCUSSION

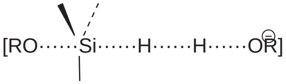
The Si–H bond has only a very slight ionic character (≈2%)[1]. The hydride ion H^- is a poor leaving group, because of its high basicity. Contrary to the common leaving groups, such as HO^-, RO^-, X^- (halide), hydrogen bound to silicon has no free electron pair which could coordinate to an electrophile, thus also molecules of a nucleophile participate in transition states of these reactions[1,23].



(2)

It was assumed that in the case of base solvolysis the attacking nucleophile is the solvent which forms a specific type of hydrogen bonding with a substrate, perhaps having character of a charge transfer complex. As a consequence the hydrogen molecule is formed.

Both base and acid solvolyses of H-silanes were intensively studied. The participation of the solvent molecules in the above processes was very often postulated in a literature. In the case of base solvolysis solvent molecules take part in electrophilic assistance of the departure of hydride anion, with formation of the transition state of structure[1,27]



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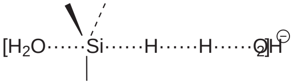
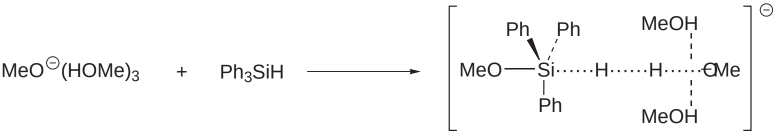
where R = H, organyl.

The transition state of acid catalyzed hydrolysis has a structure[1,28]



(*4*)

in which solvent molecules solvate both silicon atom and proton which directly attacks hydrogen of the Si–H bond. Schowen et al. concluded from the solvent isotope effect studies that in the base catalyzed solvolysis of Ph_3SiH, the solvent molecule (MeOH) donating proton to the hydride ion of the Si–H is solvated by two additional molecules of methanol[20].



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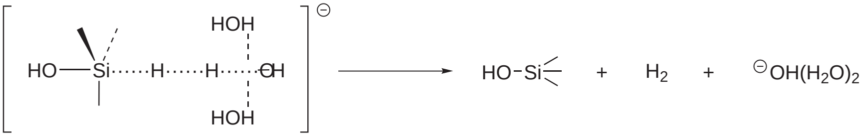
This fact is in agreement with results from the hydrolysis of $MeO(CH_2)_2O$-$(CH_2)_3SiMe_2(H)$, catalyzed with Me_4NOH in the system dioxane–water, studied by the independent kinetic method of Steward[29]. Water was used as the solvent and reagent. Similar transition state to that of Schowen[20] was proposed.



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Presumably two additional molecules of water form hydrogen bonds with a third molecule of H_2O and solvate a regenerating hydroxide anion. It seems that such solvation is strongly stabilized by a resonance.

In the case of alcoholysis of diorganosilanes in dimethylformamide, participation of DMF in the intermediate complex was suggested. The effect of DMF on reaction kinetics was stronger at low temperature[30].

Solvent Effects on Reaction Rate

In our studies of solvent effects on reaction rate we have applied Steward's approach[29], which involves determination of rate constants at different concentrations of the examined solvent. The dependence of rate constant k on solvent concentration [L] is described by the equation

$$k = \lambda[\mathrm{L}]^n \,, \tag{7}$$

where n is reaction order with respect to a solvent and λ is rate constant of nucleophilic catalysis by solvent.

$$\lambda = k/[\mathrm{L}]^n \tag{8}$$

In the logarithmic form it gives the expression

$$\log k = \log \lambda + n \log [\mathrm{L}] \,. \tag{9}$$

Alternatively, experimental results could be analyzed according to Eq. (*10*)

$$\log k = A + n \log [\mathrm{L}] + B/\varepsilon \,, \tag{10}$$

where A and B are adjustable coefficients and ε is dielectric constant of the medium.

The term B/ε concerns the effect of the change in the dielectric constant of the solvent system on the rate constant k.

We chose the solvent systems DMF–THF and DMF–1,4-dioxane for our studies of dehydrocoupling reactions. Tetrahydrofuran and 1,4-dioxane dissolve very well in DMF and both are less polar than DMF, which has a relatively high donor number (DN) and relatively low acceptor number[31] (AN) (Table I).

The composition of solvents, values of ε and results of rate measurements are presented in Tables II–IV. Dielectric constants ε of solvent mixtures were calculated taking into consideration additivity of dielectric constants of components and their volume fraction. The observed rate constants k_{obs} were determined from plots of the relationship log (V_∞ – V) = $f(t)$ as a tangens of a slope of kinetics curves (V_∞ is hydrogen volume equivalent to the initial concentration of Si–H, V is hydrogen volume measured at time t). Catalytic rate constants k' were calculated from the relationship

$$k' = k_{obs}/[\mathrm{cat}]\ . \qquad (11)$$

Reaction orders with respect to DMF were determined as a tangens of an angle of inclination of kinetic lines drawn according to the relationship log k' = f(log [DMF]) (Figs 1–3 plotted from data presented in Tables II, III and IV, respectively).

The increase in THF or 1,4-dioxane content in their mixtures with DMF caused a proportional decrease in the catalytic rate constants k'. The relationship $k' = f(100/\varepsilon)$ (Fig. 4, line *1*) retains rectilinearity up to ≈50% content of THF. Above 60% fraction of THF in the system (at $\varepsilon = 19$) a complete inhibition of dehydrogenation reaction of triethylsilane with diphenylsilanediol was observed, presumably because of further decrease in the dielectric constant of the reaction medium, which could stop dissociation of the catalyst ($ZnCl_2$). As it is shown in Fig. 1, the reaction order with respect to DMF in this case is very close to 2. Thus it seems that at least two molecules of DMF take part in the transition state of dehydrocoupling. Additional molecules of DMF may solvate Zn^{2+} ions, but they should not affect reaction kinetics. In the activated complex, Zn(II) cations probably have coordination numbers 4–6 and tetrahedral or octahedral structures[32–34]. The values of rate constant of nucleophilic catalysis by DMF (λ) calculated for the second reaction order with respect to DMF ($n_{DMF} = 2$) from the relationship

$$\lambda = k'[\mathrm{DMF}]^2\ , \qquad (12)$$

TABLE I
Dielectric constants, dipole moments, DN and AN of solvents used in this work

Solvent	ε	μ	DN	AN
DMF	36.7	3.24	26.6	16.0
THF	7.4	1.75	20.0	8.0
1,4-Dioxane	2.2	0	14.8	10.8

TABLE II
Solvent effects on reaction kinetics of dehydrocoupling of Et_3SiH with $Ph_2Si(OH)_2$ in the presence of $ZnCl_2$ in DMF–THF at 25.0 °C

No.	$[SiH]_0$	$[OH]_0$	$[ZnCl_2]$	[DMF]	DMF	THF	ε	100/ε	$k_{obs} \times 10^5$	$k' \times 10^4$	$5 + \log k'$	$\lambda_{DMF} \times 10^6$ [a]
	mol dm^{-3}				%				s^{-1}	$mol^{-1}\ dm^3\ s^{-1}$		$mol^{-3}\ dm^9\ s^{-1}$
1	0.2500	0.2500	0.2394	13.921	100	0.0	36.7	2.72	4.285	1.720	1.2355	1.03
2	0.0750	0.0750	0.1870	12.060	90.7	9.3	34.2	2.92	2.799	1.496	1.1752	1.02
3	0.0750	0.0750	0.1870	11.376	85.6	14.4	32.8	3.05	2.287	1.223	1.0874	0.95
4	0.1875	0.1875	0.1870	9.809	76.1	23.9	29.9	3.34	1.946	1.041	1.0174	1.08
5	0.1875	0.1875	0.1870	8.440	65.5	34.5	26.8	3.73	1.381	0.738	0.8681	1.03
6	0.1875	0.1875	0.1870	6.990	55.0	45.0	23.7	4.22	1.077	0.576	0.7604	1.18
7	0.1875	0.1875	0.1870	6.389	49.5	50.5	22.1	4.53	0.858	0.459	0.6665	1.12
8	0.0750	0.0750	0.1870	5.050	39.2	60.8	19.0	5.26	[b]	[b]	[b]	[b]

[a] λ_{DMF}, rate constant of nucleophilic catalysis with DMF: $\lambda_{DMF} = k'/[DMF]^2$. [b] No reaction.

TABLE III
Kinetic measurements for the reaction of Et_3SiH with PhCOOH catalyzed with $CdBr_2$ in DMF–1,4-dioxane at 25.0 °C

No.	DMF vol.%	ε[a]	100/ε	[DMF] mol dm^{-3}	log [DMF]	$k' \times 10^3$ mol^{-1} dm^3 s^{-1}	4 + log k'
9	100	36.70	2.72	12.921	1.1113	6.068	1.7830
10	84.2	31.25	3.20	10.880	1.0366	5.649	1.7520
11	73.4	27.33	3.63	9.484	0.9770	5.248	1.7200
12	54.7	21.08	4.74	7.068	0.8493	4.563	1.6593
13	46.0	18.07	5.53	5.944	0.7741	4.019	1.6041
14	39.8	15.92	6.28	5.136	0.7106	3.332	1.5227
15	32.9	13.55	7.38	4.248	0.6282	2.945	1.4691
16	31.8	13.16	7.60	4.11	0.6139	2.091	1.3203
17	30.0	12.55	7.97	3.87	0.5881	1.996	1.3002
18	26.2	11.25	8.89	3.39	0.5298	1.633	1.2130
19	22.1	9.81	10.19	2.85	0.4547	1.259	1.1000
20	19.9	9.09	11.01	2.58	0.4110	1.033	1.0142
21	19.7	9.00	11.11	2.54	0.4053	0.992	0.9965

[a] ε, dielectric constant of the solvents mixture.

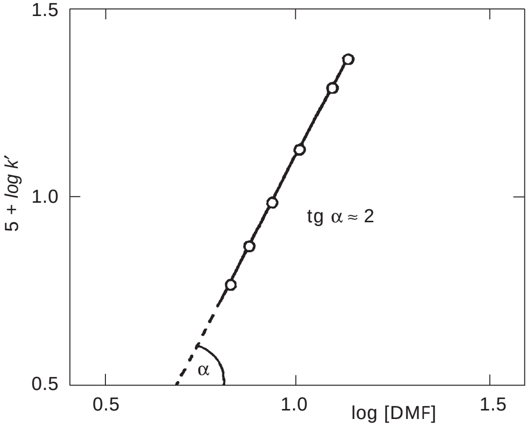


FIG. 1
Values of log k' vs log [DMF] (at 25.0 °C) for dehydrocoupling of Et_3SiH with Ph_3SiOH in solution of DMF–THF in the presence of $ZnCl_2$

TABLE IV
Kinetic measurements for the reaction of Et_3SiH with PhCOOH catalyzed with $CdBr_2$ in DMF–THF at 25.0 °C

No.	DMF vol.%	ε[a]	100/ε	[DMF] mol dm^{-3}	log [DMF]	$k' \times 10^3$ mol^{-1} dm^3 s^{-1}	4 + log k'
9	100	36.70	2.72	12.921	1.1113	6.068	1.7830
22	84.2	32.0	3.12	10.87	1.0364	5.37	1.7302
23	73.4	28.1	3.56	9.48	0.9768	4.72	1.6741
24	54.7	21.2	4.71	7.07	0.8494	3.90	1.5916
25	46.0	18.5	5.54	5.95	0.7744	3.35	1.5248
26	42.2	16.65	6.00	5.45	0.7362	2.99	1.4758
27	39.7	15.74	6.35	5.13	0.7104	3.07	1.4866
28	29.9	12.14	8.23	3.87	0.5876	2.08	1.3190
29	26.2	10.78	9.27	3.38	0.5293	1.79	1.2539
30	22.0	9.24	10.82	2.85	0.4542	1.57	1.1954
31	19.9	8.47	11.80	2.57	0.4106	1.44	1.1590
32	16.5	7.22	13.84	2.14	0.3298	0.94	0.8996

[a] ε, dielectric constant of the solvents mixture.

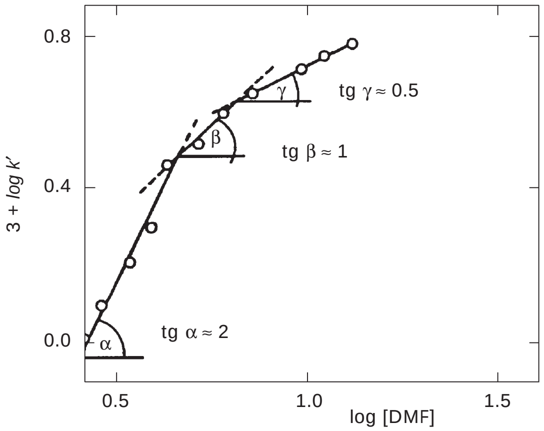


FIG. 2
Values of log k' vs log [DMF] (at 25.0 °C) for dehydrocoupling of Et_3SiH with PhCOOH in solution of DMF–1,4-dioxane in the presence of $CdBr_2$

were constant, within an experimental error ($\lambda = (0.94–1.16) \times 10^{-6}$ mol^{-3} dm^{9} s^{-1}), and independent of the THF concentration in the system (see Table II); the ratio of both catalytic rate constants was following: $\lambda/k' = 0.0061$ (Tables II and V).

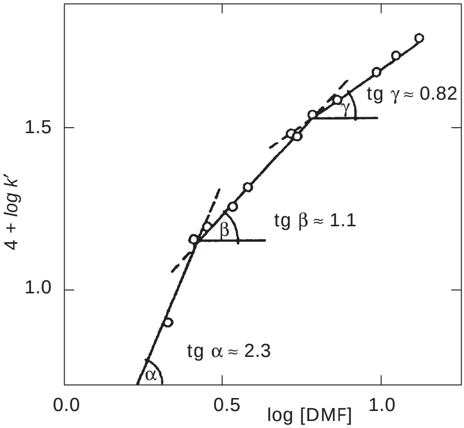


FIG. 3
Values of log k' vs log [DMF] (at 25.0 °C) for dehydrocoupling of Et_3SiH with PhCOOH in solution of DMF–THF in the presence of $CdBr_2$

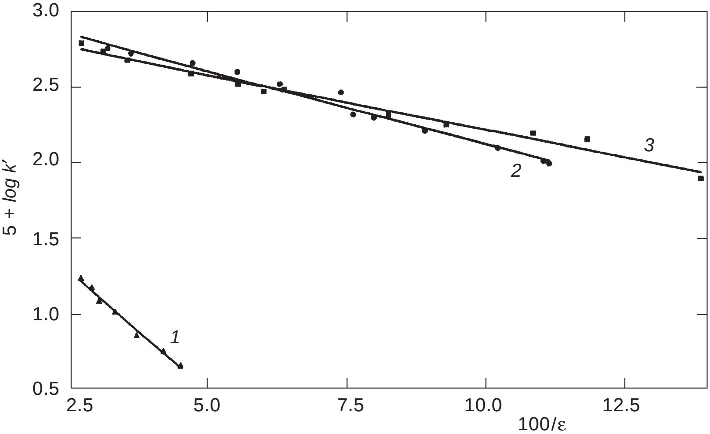


FIG. 4
Relationships of log k' vs 100/ε (at 25.0 °C) for reactions of Et_3SiH with: *1* Ph_3SiOH in solution of DMF–THF in the presence of $ZnCl_2$; *2* PhCOOH in solution of DMF–1,4-dioxane in the presence of $CdBr_2$; *3* PhCOOH in solution of DMF–THF in the presence of $CdBr_2$

For the reaction of Et_3SiH with benzoic acid catalyzed with $CdBr_2$, in DMF–THF or DMF–1,4-dioxane solutions we also observed a decrease in the catalytic rate constants with decreasing dielectric constants of solvent mixtures, although the dependences $\log k' = f(\log [DMF])$ were much more complex than in the reaction of Et_3SiH with $Ph_2Si(OH)_2$, catalyzed with $ZnCl_2$ in DMF–THF. Deflections shown in Figs 2 and 3 enabled us to determine three different reaction orders with respect to DMF for each solvent system: 2.0, 1.0 and 0.50 in DMF–1,4-dioxane, and ≈2.3, 1.1 and 0.82 in DMF–THF.

The reaction order with respect to DMF (n_{DMF}) decreases with increasing concentrations of DMF in the solvent systems used, as we can see from Figs 2 and 3. In the above two cases, the reaction order in DMF was close to 2 only for lower concentrations of DMF in the solvent systems used. Presumably at higher concentrations of DMF, interactions of DMF and 1,4-dioxane (or THF) with the transition state of dehydrocoupling are more complex, or, perhaps the activity of cations depends (i) on the value of the dielectric constant of the medium and (ii) on the concentration of DMF, and increases only to a certain degree. Also interactions of the carbonyl group of the benzoic acid with the transition state of the reaction can play an important role. It seems that further detailed studies, including other hydroxylic reagents, could help to explain the observed phenomena.

For reaction of Et_3SiH with PhCOOH catalyzed with $CdBr_2$, both in DMF–1,4-dioxane and DMF–THF, very close values of rate constants of nucleophilic catalysis with DMF have been calculated only for experiments in which the reaction order $n_{DMF} = 2$ (see Figs 2 and 3): $\lambda \approx 4.8 \times 10^{-5}$ $mol^{-3}\ dm^9\ s^{-1}$. Ratios of the catalytic rate constants: $\lambda/k' = 0.0079$ for PhCOOH are quite close to the value $\lambda/k' = 0.0061$ for $Ph_2Si(OH)_2$ within experimental error (see Tables II–V).

Table V

Rate constants of nucleophilic catalysis with DMF (λ_{DMF}) in dehydrocoupling reactions of Et_3SiH at 25.0 °C

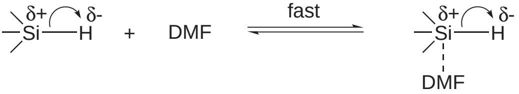
Reagents	Catalyst	Solvents	λ_{DMF} $mol^{-3}\ dm^9\ s^{-1}$	λ_{DMF}/k' [a]
$Et_3SiH + PhSi(OH)_2$	$ZnCl_2$	DMF + THF	1.05×10^{-6} ($\pm 0.11 \times 10^{-6}$)	0.0061
Et_3SiH + PhCOOH	$CdBr_2$	DMF + 1,4-dioxane	$\sim 4.8 \times 10^{-5}$	0.0079
Et_3SiH + PhCOOH	$CdBr_2$	DMF + THF	$\sim 4.8 \times 10^{-5}$	0.0079

[a] k', catalytic rate constants.

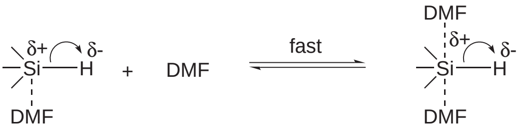
Reikhsfeld et al.[35] concluded on a basis of results of high resolution ^1H NMR studies of $PhSiH_3$–DMF solutions in $CDCl_3$ that nitrogen atom of DMF coordinates to silicon in $PhSiH_3$. The intermediacy of molecular complexes of (alkoxy)hydrosilanes with DMF and other solvents in pre-equilibriumm steps of reactions of the Si–H bond was proposed by Marciniec and Gulińska on the basis of IR study of trialkoxysilane–solvent interactions[36]. According to Voronkov such coordination of a solvent molecule to the silane takes place only when an electron-withdrawing substituent is present at the silicon atom[37]. Five-, hexa-, and higher-hypercoordinated silicon species were established as intermediates in nucleophilic substitutions at silicon by Corriu et al.[5,9,10]. West, Corriu et al.[38] concluded that the high reactivity of {2-[(dimethylamino)methyl]-phenyl}(1-naphthyl)silane, $2\text{-}(Me_2NCH_2)C_6H_4(C_{10}H_7)SiH_2$, with alcohols and acids was associated with intramolecular penta-coordination, which supported earlier hypothesis that the Si–H bond is activated for substitution by coordinative expansion of the silicon atom. Activation of the Si–H bond by nucleophiles (e.g., in CsF catalyzed reactions of H-silanes with alcohols and carbonyl compounds) is associated with coordination to the silicon atom giving more reactive penta-coordinative species[10]. Hydrogen atom has the lowest ability to penta-coordination among functional groups at silicon[8]. Five-coordinate hydrido-[39] and dihydridosilicates[40] were prepared and characterized by ^{29}Si NMR spectroscopy, e.g. $[HSi(OEt)_4]^-K^+$, $[H_2Si(OEt)_3]^-K^+$. Five-coordinate silicon hydrides were postulated as intermediates of reactions of trihydridosilanes with NaH, KH and $LiAlH_4$ [41]. The formation of penta-coordinated complexes of H-silanes containing electronegative ligands was studied by Bassindale by ^{29}Si NMR spectroscopy[42]. In some cases cationic penta-coordinated complexes $[Nu_2SiMe_2H]^+X^-$ (X = Cl, I, OSO_2CF_3) were isolated as pure compounds[43]. $HSi(OEt)_3$ reacts rapidly with α-hydroxy acids with the formation of H_2, while no reaction was observed in the absence of catalysts with many alcohols and organic acids. It was concluded that intramolecular coordination (in THF) and intermolecular extra-coordination (in DMSO) at silicon raised the nucleophilicity of silicon hydrides[44].

The Role of DMF in Reaction Mechanism

DMF presumably forms molecular complexes with hydrosilanes in fast reactions, prior to the formation (in a rate-determining step) of active complex with catalysts (ZnX_2, CdX_2, X = Cl, Br, I).

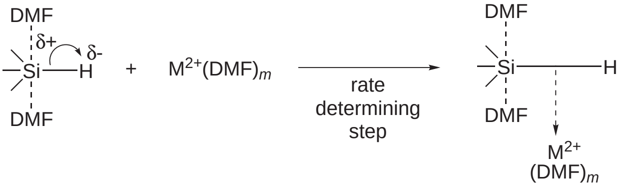


(*13*)



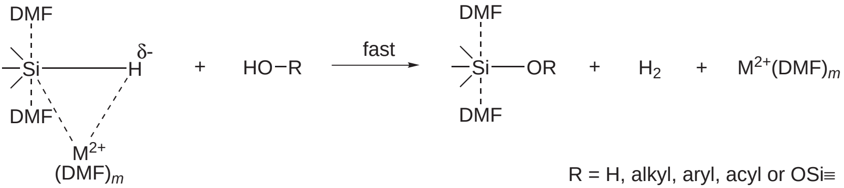
(*14*)

As a result of interactions of DMF with silicon atom in H-silanes, polarization of the Si–H bond can be distinctly increased, before it receives an electrophilic assistance from the active forms of the metal catalysts (M^{2+})[24,45], leading to the formation of the active complex.



(*15*)

The formation of hexa-coordinated species is consistent with the second order of dehydrocoupling with respect to DMF. Its molecules could neutralize a very slight positive charge on silicon atom in the transition state, which results from the studies of the Hammett free energy relationship (ρ = –0.12)[22]. Results of investigations of the primary kinetic isotope effect (k_H/k_D = 1.4–1.5) suggested a non-linear, bent structure of the activated complex[22]. Alternatively the intermediate product of the oxidative addition of the Si–H bond to M^{2+} may have three-centre transition metal–hydrogen–silicon two-electron structure[46], in which the hydride ion is replaced by oxygen atom of alcohol, silanol, carboxylic acid or water in a fast consecutive step.



(*16*)

Many examples of non-classical interactions of hydrosilanes with transition metal complexes were found, some of them are stable compounds[47].

In order to confirm the presence of DMF molecules in the active complex of reaction, we have also conducted studies of interactions of H-silanes with DMF by ^{29}Si NMR spectroscopy. Their results will be presented in a next paper. Some common features of the reaction mechanisms with hydride transfer to carbenium ion[48] will be also discussed.

CONCLUSIONS

1. Dehydrocoupling of tertiary hydrosilanes with hydroxylic reagents does not take place in the presence of Zn(II) and Cd(II) halides without co-catalysis by DMF molecules.

2. Reaction is the second order with respect to DMF for reactions of: Et_3SiH with $Ph_2Si(OH)_2$, catalyzed with $ZnCl_2$, carried out at 25 °C in DMF–THF; Et_3SiH with PhCOOH, catalyzed with $CdBr_2$, carried out at 25 °C in DMF–1,4-dioxane and in DMF–THF. In two last cases, only at lower concentrations of DMF.

3. Rate constants of the nucleophilic catalysis with DMF (λ) were calculated (according to Eq. (*13*)) for the first reaction: $\lambda = (1.05 \pm 0.11) \times 10^{-6}$ mol^{-3} dm^{9} s^{-1} (see Table II), and for the second and third reactions: $\lambda \approx 4.8 \times 10^{-5}$ mol^{-3} dm^{9} s^{-1} (only for experiments in which reaction order $n_{DMF} = 2$).

4. It is concluded on the basis of the kinetic studies that molecular complexes of DMF with H-silanes are formed in fast equilibria, prior to the rate-determining step, involving the electrophilic assistance of the active forms of the catalysts (Zn^{2+} and Cd^{2+}) to hydrogen atom of the Si–H bond.

REFERENCES

1. Eaborn C.: *Organosilicon Compounds*. Butterworth, London 1960.
2. Sommer L. H.: *Stereochemistry, Mechanism and Silicon*. McGraw–Hill, New York 1965.
3. Sommer L. H.: *Intra-Sci. Chem. Rep.* **1973**, *7*, 1.
4. Prince H.: *Int. Rev. Sci., Inorg. Chem., Ser. One* **1973**, *9*, 353.
5. Corriu R. J. P., Henner M.: *J. Organomet. Chem.* **1974**, *74*, 1.
6. a) Corriu R. J. P., Guerin C.: *J. Organomet. Chem.* **1980**, *198*, 231; b) Corriu R. J. P., Guerin C.: *Adv. Organomet. Chem.* **1982**, *20*, 265.
7. Corriu R. J. P., Guerin C., Moreau J. J. E.: *Top. Stereochem.* **1984**, *15*, 43.
8. Corriu R. J. P., Guerin C., Moreau J. J. E. in: *The Chemistry of Organic Silicon Compounds* (S. Patai and Z. Rappoport, Eds), p. 305. Wiley & Sons, Chichester, New York, Brisbane, Toronto, Singapore 1989.

9. Corriu R. J. P., Guerin C., Moreau J. J. E. in: *The Chemistry of Organic Silicon Compounds* (S. Patai and Z. Rappoport, Eds), p. 1241. Wiley & Sons, Chichester, New York, Brisbane, Toronto, Singapore 1989.
10. Chuit C., Corriu R. J. P., Reye C., Young C.: *Chem. Rev.* **1993**, *93*, 1371.
11. a) Bassindale A. R., Taylor P. G. in: *The Chemistry of Organic Silicon Compounds* (S. Patai and Z. Rappoport, Eds), p. 839. Wiley & Sons, Chichester, New York, Brisbane, Toronto, Singapore 1989; b) Bassindale A. R. in: *Organosilicon Chemistry, Proceedings of the Xth International Symposium, Poznań 1993* (B. Marciniec and J. Chojnowski, Eds), p. 191. Gordon & Breach Sci. Publ., Amsterdam 1995.
12. Lukevics E., Dzintara M.: *J. Organomet. Chem.* **1978**, *144*, 147.
13. Noll W.: *Chemie und Technologie der Silicone*, 2nd ed. Verlag Chemie, GmbH, Weinheim 1968.
14. a) Chauhan B. P. S., Boudjouk P.: *Tetrahedron Lett.* **1999**, *40*, 4127; b) Chauhan M., Chauhan B. P. S., Boudjouk P.: *Org. Lett.* **2000**, *2*, 1027; c) Chauhan B. P. S., Ready T., Al-Badri Z., Boudjouk P.: *Organometallics* **2001**, *20*, 2725.
15. Toulokhonova I., Bjerke-Kroll B., West R.: *J. Organomet. Chem.* **2003**, *686*, 101.
16. Price F. P.: *J. Am. Chem. Soc.* **1947**, *69*, 2600.
17. Baines J. E., Eaborn C.: *J. Chem. Soc.* **1955**, 4023.
18. a) Hetflejš J., Mareš F.: *Collect. Czech. Chem. Commun.* **1965**, *30*, 1643; b) Hetflejš J., Mareš F.: *Collect. Czech. Chem. Commun.* **1966**, *31*, 586.
19. a) Náhlovský B., Chvalovský V.: *Collect. Czech. Chem. Commun.* **1968**, *33*, 3131; b) Náhlovský B., Chvalovský V.: *Collect. Czech. Chem. Commun.* **1968**, *33*, 3391.
20. O'Donnel K., Bacon R., Chellappa R. L., Schowen R. L., Lee J. K.: *J. Am. Chem. Soc.* **1972**, *94*, 2500.
21. Eaborn C., Jenkins I. D.: *J. Organomet. Chem.* **1974**, *69*, 185.
22. Chruściel J., Lasocki Z.: *Main Group Met. Chem.* **1989**, *12*, 129.
23. Lasocki Z., Chruściel J., Graczyk T., Kulpiński J., Piechucki S.: *Acta Chim. Hung.* **1974**, *81*, 223.
24. Chruściel J., Lasocki Z.: *Pol. J. Chem.* **1983**, *57*, 113; *Chem. Abstr.* **1984**, *101*, 7260.
25. Chruściel J., Lasocki Z.: *Pol. J. Chem.* **1983**, *57*, 121; *Chem. Abstr.* **1984**, *101*, 72791.
26. Chruściel J.: *Pol. J. Chem.* **1997**, *71*, 977; *Chem. Abstr.* **1997**, *127*, 135846.
27. a) Kaplan L., Wilzbach K. E.: *J. Am. Chem. Soc.* **1952**, *74*, 6152; b) Gilman H., Dunn G. E., Hammond G. S.: *J. Am. Chem. Soc.* **1951**, *73*, 4499; c) Kaplan L., Wilzbach K. E.: *J. Am. Chem. Soc.* **1955**, *77*, 1297; d) Brynko C., Dunn G. E., Gilman H., Hammond G. S.: *J. Am. Chem. Soc.* **1956**, *78*, 4909.
28. a) Gilman H., Dunn G. E.: *J. Am. Chem. Soc.* **1951**, *73*, 3404; b) Baines J. E., Eaborn C.: *J. Chem. Soc.* **1956**, 1436.
29. Steward O. W., Lutkus A. G., Greenshields J. B.: *J. Organomet. Chem.* **1985**, *295*, 265.
30. Saratov I. E., Reikhsfeld V. O., Ivanov V. A.: *Zh. Obshch. Khim.* **1970**, *40*, 2622.
31. Gutman V.: *Coord. Chem. Rev.* **1976**, *18*, 225.
32. Ishiguro S., Ozutsumi K., Ohtaki H.: *Bull. Chem. Soc. Jpn.* **1987**, *60*, 531.
33. Cotton F. A., Wilkinson G.: *Advanced Inorganic Chemistry*, 5th ed., p. 607. Wiley & Sons, Chichester, Brisbane, Toronto, Singapore 1988.
34. Kęcki Z., Kołos W., Libuś W., Minc S., Stolarczyk L.: *Spektralne badania roztworów elektrolitów*. PWN, Warsaw 1969.
35. Saratov I. E., Reikhsfeld V. O.: *Zh. Obshch. Khim.* **1966**, *36*, 1069.
36. Marciniec B., Gulinska H.: *J. Organomet. Chem.* **1978**, *146*, 1.

37. a) Lebedeva G. I., Voronkov M. G.: *Izv. Akad. Nauk SSSR* **1973**, 2574; b) Voronkov M. G., Lebedeva G. I.: *Izv. Akad. Nauk SSSR* **1973**, 2597; c) Voronkov M. G., Lebedeva G. I.: *Zh. Obshch. Khim.* **1973**, 2597.
38. Helmer B. J., West R., Corriu R. J. P., Poirier M., Royo G., Saxce A. D.: *J. Organomet. Chem.* **1983**, *251*, 295.
39. a) Corriu R. J. P., Guerin C., Henner M., Wong Chi Man W. W. C.: *Organometallics* **1988**, *7*, 237; b) Becker B., Corriu R. J. P., Guerin C., Henner M., Wang Q.: *J. Organomet. Chem.* **1989**, *359*, C33.
40. Corriu R. J. P., Guerin C., Henner M., Wang Q.: *Organometallics* **1991**, *10*, 2297.
41. a) Corriu R. J. P., Guerin C., Henner M., Wang Q.: *Organometallics* **1991**, *10*, 3574; b) Becker B., Corriu R. J. P., Guerin C., Henner M.: *J. Organomet. Chem.* **1989**, *369*, 147; c) Chuit C., Corriu R. J. P., Reye C. in: *Chemistry of Hypervalent Compounds* (Kin-ya Akiba, Ed.). Wiley-VCH Inc., New York 1999.
42. Bassindale A. R., Jiang J.: *J. Organomet. Chem.* **1993**, *446*, C3.
43. Bassindale A. R., Stout T.: *J. Chem. Soc., Chem. Commun.* **1984**, 1387.
44. Roth M. J., Brook M. A., Penny H. B.: *J. Organomet. Chem.* **1996**, *521*, 65.
45. Chruściel J.: *Can. J. Chem.*, in press.
46. Schubert U.: *Transition Met. Chem. (London)* **1991**, *16*, 136; and references therein.
47. a) Corey J. Y., Braddock-Wilking J.: *Main Group Chem. News* **1996**, *4(3)*, 6, and references therein; b) Corey J. Y., Braddock-Wilking J.: *Chem. Rev.* **1999**, *99*, 175.
48. a) Chojnowski J., Fortuniak W., Stańczyk W.: *J. Am. Chem. Soc.* **1987**, *109*, 7776; b) Chojnowski J., Stańczyk W.: *Adv. Organomet. Chem.* **1990**, *30*, 243; c) Chojnowski J., Stańczyk W.: *Main Group Chem. News* **1994**, *2(1)*, 6.