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Effect of Substituents on the Silicon Atom on Etherification of Organochlorosilanes with Ethanol

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Abstract—The kinetics of etherification of organochlorosilanes with various substituents on the silicon atom with ethanol were studied. The etherification rate is mostly controlled by the inductive constants of the substituents and increases as the electron-acceptor power of the substituents increases. The ρ^* value in the Taft equation for etherification of organochlorosilanes with ethanol was determined.

There have been only a few works [1–4] on the kinetics and mechanism of organochlorosilane etherification, which is obviously explained by the fact that such fast reactions are difficult to study. In the present work we studied the kinetics of etherification of five organochlorosilanes. We focused on the effect of substituents on the silicon atom on the rate of this reaction. For more reliable etherification rate constants, we used organochlorosilanes with a monochlorinated silicon atom: chloro(chloromethyl)diethoxysilane (**Ia**), chlorodiethoxyvinylsilane (**Ib**), chloro(chloromethyl)ethoxymethylsilane (**Ic**), chlorodiethoxymethylsilane (**Id**), and chlorotrimethylsilane (**Ie**). The etherifying agent was ethanol. Compounds **Ia**–**Id** were prepared by disproportionation of the corresponding chloro- and alkoxysilanes.

$$\mathrm{RSiCl_3 + 2RSi(OEt)_3 \longrightarrow 3RSi(OEt)_2Cl},$$
$$\mathrm{R = Vin,\ ClCH_2,\ Me;}$$
$$\mathrm{ClCH_2(Me)SiCl_2 + ClCH_2(Me)Si(OEt)_2}$$
$$\mathrm{\longrightarrow ClCH_2(Me)Si(OEt)Cl.}$$

The etherification of organochlorosilanes occurs with hydrogen chloride evolution.

$$\mathrm{R^1R^2R^3SiCl + EtOH \longrightarrow R^1R^2R^3SiOEt + HCl.}$$

The concentration of HCl was determined conductometrically. The kinetic investigation was performed by the stopped-flow technique [5, 6]. The etherification rate constants of compounds **Ia**–**Ie** are listed in Table 1. As seen from the table, the rate constants vary in a fairly wide range: from 7.56 l $\mathrm{mol^{-1}\,s^{-1}}$ for compound **Ia** to 0.766 l $\mathrm{mol^{-1}\,s^{-1}}$ for compound **Ie**. Obviously, the reactivity of organochlorosilanes is determined by substituents on the silicon atom.

For a more detailed analysis of the substituent effect, we used in the consideration the etherification rate constants for chlorophenylsilanes and chloromethylsilanes, obtained in [2, 3]. Table 2 lists the etherification rate constants for 10 organochlorosilanes with various substituents on the silicon atom.

To assess the effect of inductive factors in this reaction, we turned to the simplest Taft equation for compounds with several substituents [7, 8].

$$\log (k/k_0) = \rho^* \Sigma\sigma^*.$$

Here k/k_0 is the ratio of rate constants, and $\Sigma\sigma^*$ is the sum of the inductive constants of the substituents. This equation is known to reasonably fit many organosilicon reactions [8]. Table 2 also contains $\Sigma\sigma^*$ and $\log (k/k_0)$ values. The σ^* values for Cl (2.94), OEt (1.366), $\mathrm{ClCH_2}$ (1.05), Vin (0.653), Ph (0.600), and Me (0.00) were taken from the handbook [9]. For

Table 1. Rate constants of the direct (k) and reverse (k') reactions of etherification of organochlorosilanes with ethanol at 20 ± 0.5°C

Comp. no.	Rate constant, l $\mathrm{mol^{-1}\,s^{-1}}$		Equilibrium constant K
	k	k'	
Ia	7.56	0.890	8.49
Ib	4.79	0.771	6.21
Ic	2.91	0.460	6.33
Id	2.43	0.932	2.61
Ie[a]	0.766	–	–

[a] k' and K were not determined.

the standard reaction with the rate constant k_0 we took therification of Me_3SiCl.

$$Me_3SiCl + EtOH \xrightarrow{k_0} Me_3SiOEt + HCl.$$

The figure shows the plot of log (k/k_0) on $\Sigma\sigma^*$. It is seen that for most compounds the correlation is fairly good. The only point that falls out of the correlation is point *10* for $Ph(OEt)_2SiCl$, a compound that has the rather bulky phenyl substituent. Apparently, for this compound we should use a full Taft equation which takes account of both the inductive and steric (E_s) substituent constants. Since $Ph(OEt)_2SiCl$ definitely falled out of the general regularity, we did not include it in the corelation.

The Taft equation for the compounds listed in Table 2 [except for $Ph(OEt)_2SiCl$)], calculated with the log (k/k_0) and $\Sigma\sigma^*$ values (Table 2), has the following form (correlation coefficient r 0.97, rms deviation s 0.020).

$$\log (k/k_0) = 0.014 + 0.221\Sigma\sigma^*.$$

The positive ρ^* value (0.221) gives evidence for the mechanism of bimolecular nucleophilic substitution at silicon SN2–Si, proposed by Sommer [10]. It follows from the above equation that the rate of etherification of organochlorosilanes is mostly controlled by the inductive effects of substituents at the silicon atom. Thus, the stronger electron-acceptors are the substituents, the faster is etherification.

The revealed regularity readily explains the known fact that the rate of etherification of organochlorosilanes decreases ($k_1 > k_2 > k_3$) with successive substitution of chlorines by ethoxy groups [2–4].

$$RSiCl_3 + EtOH \xrightarrow{k_1} RSi(OEt)Cl_2 + HCl, \quad (1)$$

$$RSi(OEt)Cl_2 + EtOH \xrightarrow{k_2} RSi(OEt)_2Cl + HCl, \quad (2)$$

$$RSi(OEt)_2Cl + EtOH \xrightarrow{k_3} RSi(OEt)_3 + HCl. \quad (3)$$

Reactions (1)–(3) involve successive subsitution of chlorines (σ^* 2.9) by ethoxy groups (σ^* 1.366); $\Sigma\sigma^*$ is thus reduced, and the reaction slows down. Therefore, the last stage, reaction (3), is the slowest and, consequently, limiting stage. Therewith, the first two reactions are almost irreversible, and the last stage is reversible [2].

Table 2. Effect of substituents R^1, R^2, and R^3 on etherification of organochlorosilanes $R^1R^2R^3SiCl$ with ethanol

Run no.	R^1	R^2	R^3	$\Sigma\sigma^*$	k, l mol^{-1} s^{-1}	log (k/k_0)
1	Me	Me	Me	0	0.766^a	0
2	CH_2Cl	Me	OEt	2.416	2.91^a	0.580
3	Me	OEt	OEt	2.733	2.43^a	0.502
4	Vin	OEt	OEt	3.385	4.79^a	0.796
5	CH_2Cl	OEt	OEt	3.782	7.56^a	0.994
6	Me	OEt	Cl	4.266	5.84^b	0.882
7	Ph	OEt	Cl	4.866	12.1^c	1.198
8	Me	Cl	Cl	5.800	20.5^b	1.428
9	Ph	Cl	Cl	6.400	13.7^c	1.252
10	Ph	OEt	OEt	3.332	0.343^c	–0.350

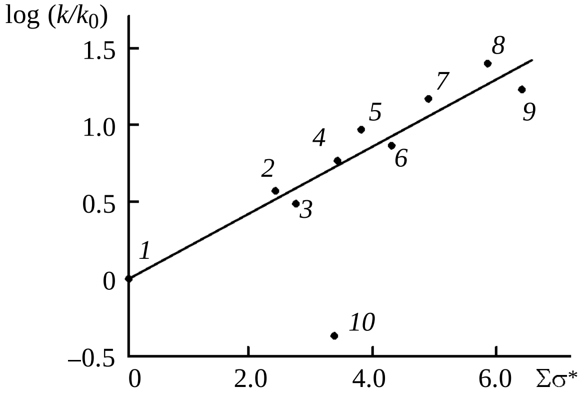
Notes: The k value was determined in: [a] the present work, [b] in [3], and [c] in [2].

The etherification rate only slightly depends on temperature. Thus, the rate constants of etherification of $VinSi(OEt)_2Cl$ with ethanol at 8, 20, and 30°C are 3.38, 4.79, and 6.30 l mol^{-1} s^{-1}, respectively. With these rate constants, we obtained the following Arrhenius equation: $k = 10^{4.30} \times e^{-20.3}/RT$, l mol^{-1} s^{-1}, and estimated the activation energy at 20.3 kJ/mol.

EXPERIMENTAL

The kinetics of etherification were studied by a stopped-flow technique [5] on the apparatus described in [6]. Solutions of the reactants (organochlorosilanes and ethanol) were simultaneously delivered with two syringes into the reaction cell equipped with an electroconductivity detector. The concentration of HCl evolved was determined conductometrically with a high-speed conductometer specially designed for the apparatus used (scan time 10^{-4} s).

Kinetic measurements were performed with a large excess of alcohol; therefore, computer treatment of



Plot log (k/k_0) on $\Sigma\sigma^*$ for etherification of organochlorosilanes with ethanol. The point numbers correspond to the entry numbers in Table 2.

the conductometric data gave apparent first-order rate constants (k_{app}). The computer treatment was performed using a special program. The computed k_{app} values nicely fitted those estimated manually by the Guggenheim method [11].

The k values listed in Table 1 were determined by the equation $k_{app} = kc_{ROH}$ (k is the etherification rate constant and c_{ROH} is the concentration of ethanol) using the k_{app} values obtained at the reaction onset, when the reverse etherification reaction could be neglected.

For the reactions of compounds **Ia**–**Id** from the equilibrium chemical compositions of the starting and final products we determined equilibrium constants K. From the equation $K = k/k'$ (k and k' the rates of the direct and reverse reactions) we obtained the k' values listed in Table 1. The errors in k, k', K for a 95% confidence level did not exceed ±12%.

Compounds **Ia**–**Id** were prepared by disproportionation from the corresponding chlorosilanes and ethoxysilanes in a 1:2 molar ratio at room temperature (1–2 days) and isolated by rectification on a column of a 10000 plates efficiency. Compound **Ie** was isolated from the products of direct synthesis of chloromethylsilanes. Further purification, when required, was performed by preparative GLC. The purity of compounds used in kinetic studies was no less than 99% (by GLC).

Gas chromatography was performed on an LKhM-72 chromatograph, detector katharometer, carrier gas helium (60 ml/min). Stainless-steel columns (0.3 × 200 cm) were packed with Chromaton N-AW-DMCS (0.25–0.31 mm); liquid phase E-301 or PMS-20000 (15 wt %). Injector temperature 390°C, detector temperature 300°C. The oven temperature was programmed from 30 to 200°C at a rate of 15 deg/min. Kinetic measurements were performed with acetone solutions of organochlorosilanes and ethanol (0.01–0.02 and 0.9–1.1 M, respectively).

The reaction temperature was maintained within ±0.5°C. The solutions were prepared using ultrapure grade acetone distilled over P_2O_5 and handled over 3 Å molecular seives.

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