ATRANES

XVIII. Kinetics of the Hydrolysis of 1-Alkyl- and 1-Alkoxysilatranes*

M. G. Voronkov and G. I. Zelchan

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 3, pp. 450–455, 1969

UDC 546.287:542.938

The kinetics of the hydrolysis of 15 1-alkyl-, 1-alkoxy- and 1-hydrosilatranes in an aqueous medium has been studied. The hydrolysis reaction is described by a first-order kinetic equation. 1-Hydrosilatrane is hydrolyzed most readily and 1-isopropyl- and 1-tert-butoxysilatranes with the greatest difficulty. A correlation has been drawn up of the logarithms of the rate constants of the hydrolysis of the silatranes and the σ^* constants of the substituents, the influence of the latter on the reaction has been discussed, and a scheme for its mechanism has been put forward.

The capacity of the alkoxysilanes for readily undergoing hydrolysis is well known and is widely used in practice. The hydrolysis reaction of these compounds has been studied qualitatively on numerous examples but its kinetics has been investigated quite inadequately. In the majority of papers the rate of hydrolysis of the alkoxysilanes is characterized only by approximate figures for the yield of the polymeric products of hydrolytic condensation as a function of the time of the process.

Direct kinetic data are given only in a few papers in which the rates of hydrolysis of the alkoxysilanes were studied from the change in the electrical conductivity [2], from the change in the refractive index and density [3, 4], from the change in the content of water determined with CaH_2 or Al_4C_3 [3, 4] or by titration with the Karl Fischer reagent [5], or from the amount of alcohol formed, determined chromatographically [6]. It has been reported [5] that the hydrolysis of the tetraalkoxysilanes in the presence of acid catalysts is a second-order reaction while in the presence of basic catalysts it is a first-order reaction. The kinetics of the hydrolysis of the alkoxyaminosilanes and of the silatranes has not previously been studied.

We have already shown [7] that the silatranes are relatively stable to atmospheric moisture and hydrolyze with considerably more difficulty than the Si-substituted trialkoxysilanes $RSi(OCH_2CH_3)_3$ and tris(2-aminoalkoxy)silanes $RSi(OCH_2CH_2NH_2)_3$ of analogous structure. We considered it to be of interest to study the dependence of the rate of hydrolysis of the silatranes $\overset{\frown}{N(CH_2CH_2O)_3}SiX$ (I) on the nature of the substituent X on the silicon atom. For this purpose we have studied the kinetics of the hydrolysis of the Si-substituted silatranes (I, X = H, alkyl, vinyl, phenyl, alkoxyl) in dilute aqueous solutions at 20° C in the absence of catalysts (see also [8]).

The hydrolysis of I, which is a combination of a series of parallel-successive reactions, is, under these conditions, on the whole, well described by a first-order kinetic equation (Fig. 1). The rate constants (k) of the pseudomonomolecular hydrolysis reaction of I taking place in the presence of a considerable excess of water that have been calculated from the experimental results obtained are given in the table. A comparison of these constants shows that with a change in the substituent X on the silicon atom the rate of hydrolysis of the silatranes falls in the following sequences:

1) $H \gg CH_2=CH > CH_3 > CH_3(CH_2)_2 = C_6H_5 > CH_3CH_2 > (CH_3)_2CH$;
2) $CH_3O > CH_3CH_2O > CH_3(CH_2)_3O > CH_3(CH_2)_2O > (CH_3)_2CHO > CH_3CH_2(CH_3)CHO > (CH_3)_2CHCH_2O \gg (CH_3)_3CO$.

On passing from silatrane itself (X = H) with $t_{1/2}$ = = 1.7 hr to 1-isopropylsilatrane (X = i-C_3H_7) with $t_{1/2}$ = = 177.7 hr, the rate constant of the hydrolysis reaction decreases 108-fold. This difference in the rates of the hydrolysis of these compounds shows their great sensitivity to the polar effect of the substituent on the sil-

*For part XVII, see [1].

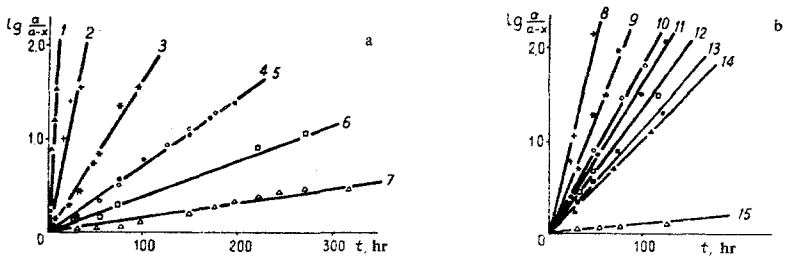


Fig. 1. Log a/(a – x) as a function of the time for the hydrolysis of the silatranes: a: X = H(▲ 1), CH_2 = CH (+2), CH_3 (*3), n-C_3H_7 (○ 4), C_6H_5 (● 5), C_2H_5 (□ 6), i-C_3H_7 (△ 7); b: X = CH_3O (+8), C_2H_5O (*9), n-C_4H_9O (○ 10), n-C_3H_7O (● 11), i-C_3H_7O (□ 12), s-C_4H_9O (■ 13), i-C_4H_9O (▲ 14), t-C_4H_9O (△ 15).

icon atom. It is extremely remarkable that the 1-alkoxysilatranes containing a secondary or tertiary

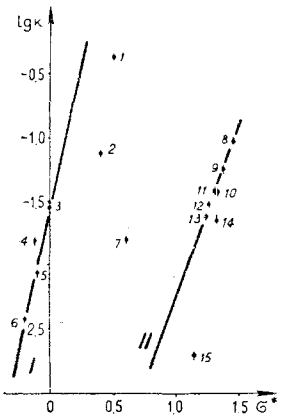


Fig. 2. Logarithms of the hydrolysis rate constants of the silatranes as functions of the induction constant of the substituent X on the silicon atom (σ^*_X): X = H (1), CH_2 = = CH (2), CH_3 (3), n-C_3H_7 (4), C_2H_5 (5), i-C_3H_7 (6), C_6H_5 (7), CH_3O (8), C_2H_5O (9), n-C_3H_7O (10), n-C_4H_9O (11), i-C_3H_7O (12), s-C_4H_9O (13), i-C_4H_9O (14), t-C_4H_9O (15).

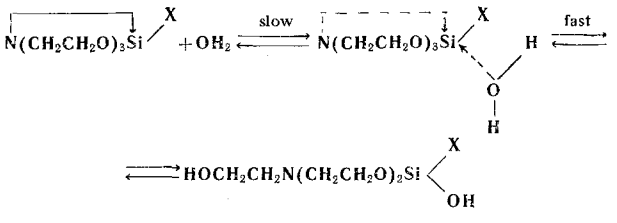
alkyl radical hydrolyze at approximately the same rate as 1-methylsilatrane ($t_{1/2}$ = 22.4-27.7 hr). Of the silatranes studied, compound I with X = $(CH_3)_3CO$ hydrolyzes with the greatest difficulty ($t_{1/2}$ = 346.5 hr).

The quantitative evaluation of the dependence of the relative rates of the hydrolysis of the silatranes on the nature of the substituent X on the silicon atom can be made on the basis of Taft's equation [9, 10].

$$\lg \frac{\kappa}{\kappa_0} = \rho^* \sigma^*_X \text{ or } \lg \kappa = \lg \kappa_0 + \rho^* \sigma^*_X,$$

where σ^*_X is the induction constant of the substituent X and ρ^* is the reaction constant. The correlation between log κ and σ^*_X is illustrated graphically in Fig. 2. This shows that the silatranes studied can be subdivided into two reaction series: I with X = R (alkyl) and II with X = RO (alkoxyl) in each of which there is a fairly good linear correlation between the values of log κ and σ^*_X.

In the reaction series of the alkylsilatranes (R = = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7), an increase in the induction constant of the radical R accelerates the hydrolysis process ($\rho^* > 0$). This shows that the over-all rate of the multistage hydrolysis of the alkylsilatranes is determined by the nucleophilic attack on the reaction center of the molecule of I by a water molecule (or a hydrated HO^- ion), which is the slowest stage of the process:



The high absolute value of the reaction constant ρ^* (+4.76) shows the considerable degree of polarity of the transition state in the kinetic stage of the process in which the reaction center (the silicon atom) acquires a considerable negative charge. The spatial influence of the substituent on the rate of hydrolysis of the 1-alkylsilatranes apparently has no fundamental influence (the point corresponding to I with X = i-C_3H_7 lies on the correlation curve).

The unsubstituted 1-hydrosilane (X = H) must also be assigned to the reaction series I. Some deviation of the value of log κ from the correlation curve must probably be ascribed to the fact that in the hydrolysis of this compound it is not only the Si—O—C bond but also, in part, the Si—H bond that is cleaved (as is confirmed by the evolution of bubbles of hydrogen during the reaction).

The values of log κ for 1-vinyl- and, particularly, 1-phenylatranes deviate considerably from the correlation curve of I, and the rates of their hydrolysis are far lower than expected. We are inclined to explain this effect by the p_π-d_π interaction of the substituents mentioned with the central silicon atom, as a result of which their electron-accepting effect (σ^*_X = 0.40 and 0.60, respectively) is considerably lowered (to $\sigma^*_{eff} \approx$ $\approx$ 0.10 and −0.05, respectively). This is also confirmed by the fact that the linear correlation of the acidity of the triorganylsilanols with the magnitude $\Sigma\sigma^*$ of the substituents on the silicon atom is disturbed in the case of phenyl-substituted compounds, which possess a lower acidity than could have been expected on the basis of the value $\sigma^*_{C_6H_5}$ = 0.600 [10].

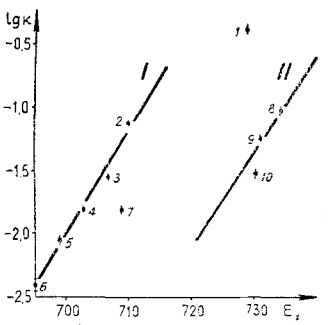


Fig. 3. Relationship between the logarithms of the rate constants for the hydrolysis of the silatranes and the spectroscopic induction constant of the substituent X on the silicon atom (E_X): X = H (1), CH_2 = CH (2), CH_3 (3), n-C_3H_7 (4), C_2H_5 (5), i-C_3H_7 (6), C_6H_5 (7), CH_3O (8), C_2H_5O (9), i-C_3H_7O (10).

In reaction series II (alkoxysilatranes), the reaction constant ρ^* = +2.60 proved to be lower than in series I*. This once again indicates the nucleophilic nature of

*In the calculation of the parameters of Taft's equation, it was assumed that $\sigma^*_{OR} = \sigma^*_R + 1.45$ (this is equivalent to performing the correlation of log κ for I (X = OR) with σ^*_R).

Rates of Hydrolysis of the Silatranes $XSi(OCH_2CH_2)_3N$ and Polar Constants of the Substituents X

X	Found		Calculated		Difference		$t_{1/2}$, hr	σ^*_X	E_X
	$\kappa \cdot 10^2$, hr^{-1}	$\log k_{mean}$	$\kappa \cdot 10^2$, hr^{-1}	$\log \kappa$	$\Delta\kappa$	$\log \kappa$			
Series I, $\log k = 1.54 + 6.76\sigma^*x$									
H	42.0±4.2	−0.38	62.3	0.79	20.3	1.17	1.7	0.49	729.0
CH_3	2.9±0.2	−1.54	2.9	−1.54	0.0	0.00	23.9	0.00	706.7
C_2H_5	0.9±0.1	−2.05	1.0	−2.01	0.1	0.04	77.0	−0.10	699.0
n-C_3H_7	1.6±0.1	−1.80	0.8	−2.11	−0.8	−0.31	43.3	−0.12	702.7
i-C_3H_7	0.39±0.04	−2.41	0.36	−2.44	−0.03	−0.03	177.7	−0.19	695.0
CH_2=CH	7.7±0.8	−1.11	2.3	0.37	−5.4	1.48	9.0	0.40	710.0
C_6H_5	1.6±0.1	−1.80	20.7	1.32	19.1	3.12	43.3	0.60	708.8
Series II, $\log k = 4.81 + 2.60\sigma^*x$									
CH_3O	9.5±1.0	−1.02	9.1	−1.04	−0.4	−0.02	7.3	1.45	734.3
C_2H_5O	5.8±0.6	−1.24	5.7	−1.25	−0.1	−0.01	11.9	1.37	731.0
n-C_3H_7O	3.8±0.3	−1.42	4.5	−1.35	0.7	0.07	18.2	1.33	
i-C_3H_7O	3.1±0.3	−1.51	2.9	−1.53	−0.2	−0.02	22.4	1.26	730.3
n-C_4H_9O	3.9±0.4	−1.41	4.2	−1.38	0.3	0.03	17.8	1.32	
i-C_4H_9O	2.3±0.2	−1.64	4.2	−1.38	1.9	0.26	30.1	1.32	
s-C_4H_9O	2.5±0.2	−1.60	2.6	−1.59	0.1	0.01	27.7	1.24	
t-C_4H_9O	0.20±0.02	−2.70	1.5	−1.82	1.3	0.82	346.5	1.15	

the hydrolysis of the silatranes with X = OR but with a lower negative charge of the reaction center in the transition state.

The values of log κ for the alkoxysilatranes possessing an i-C_4H_9O and, particularly, a t-C_4H_9O group on the silicon atom deviate considerably from the correlation curve II. This must be ascribed to a steric effect. The calculation of the steric hindrance created by such substituents using a modified Taft equation [9, 10, 12].

$$\lg \frac{\kappa}{\kappa_0} = E_s + \sigma^* x \rho^*,$$

where E_S is the steric constant of the substituent, leads to values of E_S for the iso- and tert-butoxy groups on the silicon atom in the silatranes of −0.26 and −0.88, respectively.

The rate of hydrolysis of the 1-alkoxysilatranes proves to be considerably lower than could have been expected on the basis of the correlation curve I. This is the case in spite of the fact that electron-accepting OR groups on the silicon atoms in the silatranes must raise its electrophilicity considerably in comparison with the alkylsilatranes and that the molecule of a 1-alkoxysilatrane contains not three but four Si—O—C bonds capable of undergoing hydrolysis. It may be assumed that in the 1-alkoxysilatranes a Si—O—C bond present in the silatrane skeleton of the molecule, and not that in the alkoxy group, is hydrolyzed first. This is confirmed by the fact that, as we shall show in subsequent papers, the introduction of alkyl substituents in the positions 3, 7, and 10 of the heterocyclic skeleton of the silatrane molecule considerably lowers the rate of their hydrolysis, although this does not change the steric accessibility of the silicon atom in these compounds. Furthermore, all our attempts to obtain 1-hydroxysilatrane (I, X = OH) by the hydrolysis of 1-alkoxysilatranes with the equivalent amount of water under various conditions led to the production of polymeric substances formed through the cleavage of the Si—O—C bonds in the silatrane skeleton.

In our opinion, the cause of such a high hydrolytic stability of the 1-organoxysilatranes is not to be sought only in the presence of the Si ← N transannular coordination bond in their molecule, creating a considerable negative charge on the silicon atom which prevents the nucleophilic attack of a water molecule or a HO^- ion. The considerable displacement to the right of the correlation curve II as compared with curve I must also be explained by the considerable effect of the p_π-d_π of the oxygen atoms in the alkoxy groups with the central silicon atom, in this case, as a result of which σ^*_{eff} proves to be smaller than σ^*_{OR} by ~1.2 units. Thus, for example, for the OCH_3 and OC_2H_5 groups the values of σ^*_{eff} characterizing their over-all electronic influence on the central silicon atom should, on the basis of curve I, be, +0.25 and +0.17, respectively. Such a low electron-accepting effect of the alkoxy groups on the silicon atom is convincingly confirmed by the results of nuclear quadrupole resonance (NQR) [13], which show that the p-electron densities on the chlorine atoms in the molecules $(CH_3)_3SiCl$ and $(C_2H_5O)_3SiCl$, for example, are practically identical*.

Figure 3 shows the existence of a linear correlation between the values of log κ and the spectroscopic induction constants E_X of the substituents X in the alkyl- and alkoxysilatranes. In this case, again, a pattern similar to that shown in Fig. 2 is found. The two correlation curves I (alkylsilatranes) and II (alkoxysilatranes) in Fig. 3 correspond to the equations:

$$\lg \kappa = -58.0 + 0.08\, E_R$$

$$\lg \kappa = -81.7 + 0.11\, E_{OR}.$$

The values of E_R characterizing the inductive influence of the substituents directly connected with the silicon atom are correlated with the values of log κ even better than the values of σ^*_X—log κ for 1-vinylsilatrane falls on the correlation curve and log κ for

*In the spectra of these two compounds, the NQR frequencies of the ^{35}Cl—Si bond (ν), which are linearly connected with the total inductive effect of the other substituents on the silicon atom [14–16], are practically the same (ν^{77} = 16.457 ± 0.006 MHz). For $(CH_3O)_3SiCl$, ν^{77} = 16.87 MHz.

1-phenylsilatrane deviates from it to a considerably smaller extent than from the corresponding curve in Fig. 2. Nevertheless, the existence of this deviation confirms the conclusion drawn previously of the inhibiting influence of p_π-d_π conjugation between the silicon atom and the phenyl group on the rate of hydrolysis of 1-phenylsilatrane.

EXPERIMENTAL

The kinetics of the hydrolysis of the silatranes were studied in 0.01-molar aqueous solutions. The vessel with the prepared solution was thermostated at 20.00 ± 0.05° C, and 10.00-ml samples were taken from it after predetermined intervals of time and were titrated with 0.05 N HCl (with Methyl Orange as indicator). The degree of hydrolysis of the silatrane was determined from the amount of hydrochloric acid consumed in the titration.

The order of the reaction was determined graphically (Fig. 1), and the hydrolysis rate constant κ was calculated from the equation for first-order reactions:

$$k = \frac{2.3}{t} \lg \frac{v_\infty}{v_\infty - v_t},$$

where t is the time from the beginning of the reaction to the moment of withdrawal of the sample in hours, v_t is the number of milliliters of hydrochloric acid consumed in the titration of the sample, and v_∞ is the number of milliliters of HCl consumed in the titration of the completely hydrolyzed sample.

The time of half hydrolysis, $t_{1/2}$, was calculated from the relation

$$t_{1/2} = \frac{0.693}{k}.$$

REFERENCES

1. V. A. Chetverikova, V. A. Kogan, G. I. Zelchan, M. G. Voronkov, and O. A. Osipov, KhGS [Chemistry of Heterocyclic Compounds], 5, 446, 1969.

2. H. Reuther, Z. anorg. Chem., 272, 122, 1953.

3. M. G. Voronkov and L. A. Zhagata, Izv. AN Latv. SSR, ser. khim., 452, 1967.

4. M. G. Voronkov and L. A. Zhagata, ZhOKh, 37, 1156, 2551, 1967.

5. R. Aelion, A. Loebel, and F. Eirich, J. Am. Chem. Soc., 72, 5705, 1950; Rec. Trav. chim. Pays-Bas, 69, 61, 1950.

6. V. A. Vekhov, E. N. Dudnik, and E. I. Rumyantseva, ZhNKh, 10, 2359, 1965.

7. M. G. Voronkov and G. I. Zelchan, KhGS [Chemistry of Heterocyclic Compounds], 1, 51, 1965.

8. M. G. Woronkow, G. I. Seltschans, A. F. Lapsina, and W. A. Pestunowitsch, Z. Chem., 8, 214, 1968.

9. Yu. A. Zhdanov and V. I. Minkin, Correlation Analysis in Organic Chemistry [in Russian], Izd-vo RGU, 1966.

10. Ya. K. Syrkin, Izv. AN SSSR. OKhN, 389, 401, 1959.

11. R. H. Baney, O. W. Steward, and O. R. Pierce, J. Am. Chem. Soc., 83, 4932, 1961.

12. V. A. Pal'm, Usp. khim., 30, 1069, 1961; Principles of the Quantitative Theory of Organic Reactions [in Russian], Khimiya, Leningrad, 1967.

13. I. P. Biryukov, M. G. Voronkov, and I. A. Safin, Izv. AN LatvSSR, ser. khim., 638, 1966.

14. I. P. Biryukov, M. G. Voronkov, and I. A. Safin, DAN, 165, 857, 1965.

15. I. P. Biryukov, M. G. Voronkov, and I. A. Safin, TEKh [Theoretical and Experimental Chemistry], 1, 373, 1965.

16. I. P. Birjukoo and M. G. Voronkov, Intern. Symp. on Organosilicon Chem., Prague, p. 204, 1961.

21 January 1967

Institute of Organic Synthesis
AS Latvian SSR, Riga