

2. Measures which prevent the formation of an inhibitor result in the good agreement of the calculated and experimentally observed induction periods.

3. An oscillating mode of combustion of hydrogen only occurs when contaminants are present in the reactor system; fluttering of the flame apparently arises as a result of the interaction of the active sites with the surface on which the extraneous substances are sorbed.

#### LITERATURE CITED

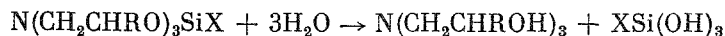
1. N. N. Semenov, Some Problems in Chemical Kinetics and Reactivity [in Russian], Izd. Akad. Nauk SSSR, Moscow (1958).
2. L. V. Karmilova, A. B. Nalbandyan, and N. N. Semenov, Zh. Fiz. Khim., 32, 1193 (1958).
3. V. V. Azatyan, E. N. Aleksandrov, and M. S. Khachatryan, Fiz. Goreniya Vzryva, 9, 426 (1973).
4. V. V. Azatyan, Khim. Fiz., No. 4, 491 (1982).
5. V. V. Azatyan, Dissertation, Moscow (1981).
6. E. N. Aleksandrov, V. S. Arutyunov, I. V. Dubrovina, and S. N. Kozlov, Izv. Akad. Nauk SSSR, Ser. Khim., 652 (1983).
7. E. N. Aleksandrov, V. S. Arutyunov, I. V. Dubrovina, and S. N. Kozlov, Zh. Fiz. Khim., 57, 2448 (1983).
8. T. A. Garibyan, R. R. Grigoryan, A. A. Mantashyan, and A. B. Nalbandyan, Arm. Khim. Zh., 25, 95 (1972).
9. T. A. Garibyan, Dissertation, Moscow (1971).
10. V. V. Azatyan, Kinet. Katal., 23, 1301 (1982).
11. V. V. Azatyan, E. N. Aleksandrov, and A. F. Troshin, Kinet. Katal., 16, 306 (1975).
12. V. N. Kondrat'ev, Rate Constants of Gas Phase Reactions [in Russian], Nauka, Moscow (1970).
13. E. N. Aleksandrov, Kinet. Katal., 18, 1382 (1977).
14. E. N. Aleksandrov, Dissertation, Moscow (1975).

#### KINETICS OF HYDROLYSIS OF SILATRANES IN A NEUTRAL MEDIUM

M. G. Voronkov, D-S. D. Toryashinova,  
V. P. Baryshok, B. A. Shainyan, and  
É. I. Brodskaya

UDC 541.127:542.938:547.1'128

The study of the kinetics and mechanism of hydrolysis of silatranes is interesting for evaluating the instability in water (which is very important in their study as biologically active compounds) and the relationship between the structure and reactivity. The hydrolysis of 1-substituted silatranes  $XSi(OCHRCH_2)_3N$  proceeds irreversibly and quantitatively with the formation of the corresponding tri(2-hydroxyalkyl)amine (THA) and a Si-substituted silanetriol by the following scheme [1, p. 102; 2]:



As the result of the study of the hydrolysis of 1-organyl- and 1-organoxylylsiltranes in an acidic medium, the following schemes of mechanism of the process have been proposed, which include at the limiting stage: 1) an electrophilic attack at the reaction center ( $SiO_3$ ) by a hydroxonium ion [1, p. 98]; 2) cleavage of the Si-O bond, following rapid protonation of one of the oxygen atoms of the silatrane ring [3]; 3) protonation of nitrogen atom with synchronous cleavage of the transannular Si-N bond [4]. Later, it was suggested that in the hydrolysis of 1-aroxy-silatranes in both acidic and alkaline media, the cleavage of the Si-O-Ar bond is the rate-determining stage [5].

The neutral hydrolysis of silatranes has already been studied by acidimetric titration [1, p. 95]. Since the acid added can be bound not only by the THA formed in the hydrolysis, but can also react with silatrane itself, sufficiently accurate kinetic curves cannot be obtained [6].

---

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 12, pp. 2673-2676, December, 1984. Original article submitted September 7, 1983.

To study the mechanism of the hydrolytic splitting of silatranes, we investigated their hydrolysis in a neutral medium by UV spectroscopy. This method has already been used in the study of the acidic and alkaline hydrolysis of 1-aryl- and 1-aryloxysilatranes from the change in intensity of the  $\pi \rightarrow \pi^*$  transition band at 250-300 nm [3-5]. In contrast to these papers, we controlled the course of the reaction from increase in intensity of  $n \rightarrow \sigma^*$  transition band with participation of the unshared electron pair on the nitrogen atom in THA in the 200-220-nm region. A similar band in the UV spectra of the aqueous solutions of silatrane is present in a shorter wave region (below 190 nm) than in the spectra of THA and triethylamine [7]. The corresponding Si-substituted derivatives of silanetriol formed in the hydrolysis and the products of their anhydro-condensation do not absorb above 190 nm. Thus, increase in optical density in the 200-220-nm region characterizes the accumulation of THA or monocyclic elimination products formed in the hydrolysis of silatranes.

#### EXPERIMENTAL

The silatranes studied were obtained by methods already described and were purified by subliming twice in vacuo [1, p. 8; 2].

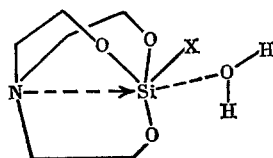
The kinetic measurements were carried out on the "Specord UV-VIS" spectrophotometer with a thermostated cuvette, 0.2 cm thick. The accuracy of thermostating was  $\pm 0.1^\circ\text{C}$ . The concentration of the silatranes was 0.01-0.03 mole/liter. The curves of the  $D = f(t)$  dependence ( $D$  is optical density,  $t$  is time) were recorded at the descent of the  $n \rightarrow \sigma^*$ -transition band in THA at 217 nm and at 40-80°C. The optical density of THA at a given concentration and temperature, coinciding with the final absorption of the product obtained after complete hydrolysis, was taken as  $D_\infty$ .

Twice-distilled water and a phosphate buffer ( $\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ ) at pH 7.15 (25°) were used in the experiments.

#### DISCUSSION OF RESULTS

The time dependence of the logarithm of optical density in the UV spectra of the aqueous solutions of silatranes, shown in Fig. 1, does not obey a first-order equation. The accumulation of the THA is more rapid than follows from the equation of pseudomonomolecular process of hydrolysis. Since in a simple system such as the silatrane-water system it is impossible to present the slow pre-equilibrium stage without participation of silatrane, the zero order as a mechanical alternative is excluded. The observed acceleration of the process is obviously due to the autocatalytic influence of the THA base separating out. In fact, in hydrolysis in a neutral buffer, the  $D = D(t)$  dependence corresponds well to the kinetic first-order equation (see Fig. 1). Therefore, all further measurements were carried out in a neutral phosphate buffer (pH 7.15).

The values of the reaction rate constants obtained are listed in Table 1. The following reaction mechanisms of neutral hydrolysis of silatranes can be assumed: 1) a rate-determining electrophilic attack of a water molecule at the oxygen or nitrogen atom followed by rapid ring opening of the silatrane skeleton (cleavage of the transannular Si  $\leftarrow$  N bond; 2) a nucleophilic attack of water molecule at the silicon atom with simultaneous cleavage of the transannular Si  $\leftarrow$  N bond and opening of one of the half-rings; 3) a rapid pre-equilibrium stage of formation of the  $\text{H}-\text{O}-\text{H}\dots\text{O}-\text{Si}$  bond followed by slow opening of the silatrane skeleton; 4) a stage with the formation of a four-centered intermediate state in the form



with synchronous or subsequent opening of the silatranes skeleton.

In the neutral hydrolysis reaction, there is no salt effect (0.1 M KCl and LiCl), as already observed for this process in an acidic medium [1, p. 97]. When the hydrolysis is carried out in  $\text{D}_2\text{O}$ , an inappreciable kinetic isotopic effect (KIE) is observed ( $k^{\text{H}}/k^{\text{D}} = 1.25$  for  $\text{X} = \text{EtO}$ ). However, for acidic hydrolysis reaction this effect is practically absent [4]. These data indicate the absence of a noticeable contribution of the  $\text{HO}\dots\text{H}(\text{D})$  cleavage to the rate of the determining stage.

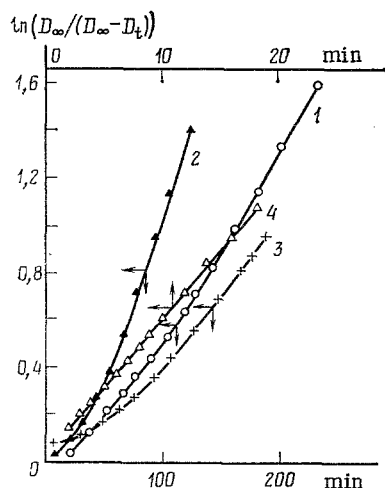


Fig. 1. Dependence of  $\ln D_{\infty}/(D_{\infty} - D_t)$  on time in neutral hydrolysis of  $XSi(OCH_2CH_2)_3N$  in water: X = Me (1),  $ClCH_2$  (2), EtO (3), and in phosphate buffer at pH 7.15, X = Me (4).

The hydrolytic stability of the silatranes studied in a neutral buffer decreases in the following order of change in substituent:  $Me_2CH > Me_2CHO \geq EtO \geq CH_2Cl \geq Me > CH_2=CH$ .

By successively introducing methyl groups into positions 3, 3, 7, and 3, 7, 10 of the silatrane, and also by introducing an ethyl group at position 4, additional information can be obtained on the limiting stage of hydrolysis of silatranes. In the successive methylation of the silatrane skeleton the reaction is inhibited nonmonotonically (see Table 1). In the series of  $MeSi(OCH_2CH_2)_n(OCHMeCH_2)_{3-n}N$ , on transition from 1-methylsilatrane ( $n = 3$ ) to 1,3-dimethylsilatrane ( $n = 2$ ), the reaction is inhibited by a factor of 2.6. On further transition from 1,3,7-trimethylsilatrane ( $n = 1$ ) to 1,3,7,10-tetramethylsilatrane ( $n = 0$ ), the reaction is inhibited by a factor of 2.5. However, on transition from 1,3-dimethylsilatrane ( $n = 2$ ) to 1,3,7-trimethylsilatrane ( $n = 1$ ), the reaction is accelerated 1.7 times.

When methyl groups are introduced at positions 3, 7, 10, or Et at position 4 of the silatrane skeleton, the basic properties of the oxygen atoms practically do not change [8]. This means that there is no noticeable inductive effect of these substituents on the basicity of the oxygen atoms in the silatrane skeleton. The Si-N distance, determining the degree of the transannular interaction between the silicon and nitrogen atoms, remains unchanged when methyl groups are introduced at positions 3, 7 [9] and 3, 7, 10 of the silatrane skeleton. The inhibition of the reaction on introduction of a  $C_2H_5$  group at position 4 of 1-methylsilatrane is much stronger than when the  $CH_3$  group is introduced at the 3-position (by a factor of 8 and 2.6, respectively). These data indicate the determining role of conformational strains arising in the opening of the silatrane skeleton.

The not-very-high values of enthalpy ( $\Delta H^\ddagger$ ) and high negative values of entropy of activation ( $\Delta S^\ddagger$ ) indicate that combination of stages limiting the hydrolysis process includes bind-

TABLE 1. Hydrolysis Rate Constants of Si- and C-Substituted Silatranes

Compound	C, mole/liter	$k \cdot 10^4$ , sec <sup>-1</sup>	T, °C
MeSi(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N (I)	0,02030	5,8	40
	0,02086	10,6	50
	0,02029	19,8	60
	0,01985	34,8	70
MeSi(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> (OCHMeCH <sub>2</sub> )N (II)	0,02066	2,1	40
	0,01967	4,1	50
	0,02066	6,8	60
	0,01948	12,3	70
MeSi(OCH <sub>2</sub> CH <sub>2</sub> )(OCHMeCH <sub>2</sub> ) <sub>2</sub> N (III)	0,01900	7,0	50
MeSi(OCHMeCH <sub>2</sub> ) <sub>3</sub> N (IV)	0,01193	2,7	50
MeSi(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> (OCH <sub>2</sub> CHEt)N (V)	0,02034	1,3	50
	0,02052	2,9	60
	0,01988	4,75	70
<i>i</i> -PrSi(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N (VI)	0,019785	9,35	80
	0,02089	1,45	50
	EtOSi(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N (VII)	0,02854	7,55
<i>i</i> -PrOSi(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N (VIII)	0,01470	6,6	50
ClCH <sub>2</sub> Si(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N (IX)	0,01967	8,4	50
CH <sub>2</sub> =CHSi(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N (X)	0,01043	19,55	50

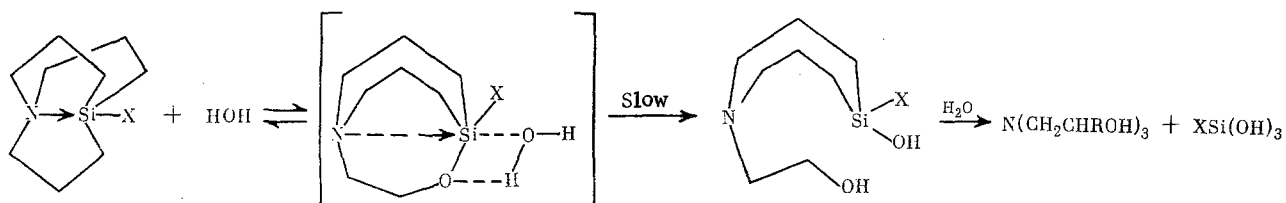
\*Error in the determination of  $k$  is  $\pm 10\%$ .

TABLE 2. Activation Parameters of 1-Methylsilatrane and Its 3-Methyl and 4-Ethyl-Substituted Derivatives

Compound	$\Delta H^\ddagger$ , kJ/mole	$\Delta S^\ddagger$ , J/mole·deg
(I)	50,6±4,1	-144,8
(II)	48,9±3,8	-157,7
(V)	57,7±5,9	-140,2

ing the silatrane molecules and water, while the low value of KIE (1.25) probably indicates the equilibrium character of this reaction (Table 2). The considerable (by almost one order of magnitude) difference in the rate of hydrolysis of 1-methyl- and 1-isopropylsilatrane (see Table 1) indicates the important role of the steric availability of the reaction center.

The data obtained suggest the following scheme of mechanism of neutral hydrolysis of silatranes



#### CONCLUSIONS

1. The kinetics of hydrolysis of 1-organyl- and 1-alkoxylsilatranes in a neutral medium was studied by UV spectroscopy.

2. A scheme has been proposed for the neutral hydrolysis of silatranes with the formation of a four-centered intermediate at the first stage, followed by slow opening of the silatrane skeleton.

#### LITERATURE CITED

1. M. G. Voronkov and V. M. D'yakov, Silatranes [in Russian], Nauka, Novosibirsk (1978).
2. M. G. Voronkov, V. M. Dyakov, and S. V. Kirpichenko, *J. Organomet. Chem.*, **233**, 1 (1982).
3. R. E. Timms, *J. Chem. Soc., A*, 1969 (1971).
4. A. Daneshrad, C. Eaborn, R. Eidenschink, and D. R. M. Walton, *J. Organomet. Chem.*, **90**, 139 (1975).
5. J. Lukasiak and Z. Jamrogiewicz, *Acta Chim. Acad. Sci. Hung.*, **105**, 19 (1980).
6. M. G. Voronkov, S. G. Shevchenko, É. I. Brodskaya, Yu. L. Frolov, V. P. Baryshok, N. M. Deriglazov, E. S. Deriglazova, and V. M. D'yakov, *Dokl. Akad. Nauk SSSR*, **230**, 627 (1976).
7. M. G. Voronkov, É. I. Brodskaya, N. M. Deriglazov, V. P. Baryshok, and V. V. Belyaeva, *J. Organomet. Chem.*, **225**, 193 (1982).
8. M. G. Voronkov, É. I. Brodskaya, V. V. Belyaeva, V. P. Baryshok, M. S. Sorokin, and O. G. Yarosh, *Dokl. Akad. Nauk SSSR*, **267**, 654 (1982).
9. M. G. Voronkov, M. P. Demidov, V. E. Shklover, V. P. Baryshok, V. M. D'yakov, and Yu. L. Frolov, *Zh. Strukt. Khim.*, **21**, 100 (1980).