N,N-Diethyl-5-iodomethyltetrahydro-1,2-oxazolinium Iodide (V). This compound, with mp 127-128° (acetone-methanol), was obtained in quantitative yield by iodination of IV by the method used to iodinate IIa-e. IR spectrum, cm^{-1}: 1010 (NOC), 1050 (CNO), 3000-2500 ($\geq\overset{+}{N}-$). Found: N 3.7; I 63.6%. $C_8H_{17}I_2NO$. Calculated: N 3.7; I 63.9%.

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ATRANES

XLVIII.* KINETICS AND MECHANISM OF THE HYDROLYSIS OF 1-(α-CHLOROALKYL)SILATRANES

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The kinetics of the hydrolysis of 1-(α-chloroalkyl)silatranes $RSi(OCH_2CH_2)_n[OCH(CH_3)CH_2]_{3-n}N$, (where $R = ClCH_2$, Cl_2CH, and CH_3ClCH, and $n = 1-3$) at 25°C in neutral and acidic aqueous and aqueous alcoholic media with H_2O, ^2H_2O, and $H_2{}^{18}O$ were studied. The rate of hydrolysis in acidic media is considerably higher than in neutral media. The introduction of methyl groups in the 3, 7, and 10 position of the atrane ring and an increase in the electronegativity of the substituent attached to the silicon atom lower the rate of hydrolysis. According to the mass spectrometric data, the triethanolamine formed during hydrolysis in $H_2{}^{18}O$ does not contain ^{18}O, which indicates hydrolytic cleavage of the Si—O bond rather than the O—C bond.

In order to ascertain the effect of the nature of the substituent attached to the silicon atom in the atrane ring on the hydrolytic stability of the molecule, we studied the hydrolysis of 1-(α-chloroalkyl)silatranes with the general formula $RSi(OCH_2CH_2)_n[OCH(CH_3)CH_2]_{3-n}N$, (where $R = ClCH_2$, Cl_2CH and CH_3ClCH, and $n = 1-3$) by polarography.

The silatranes were hydrolyzed at 25° in dilute acidic and neutral aqueous and aqueous alcohol solutions.

The reaction rate in neutral media was calculated from a first-order equation [2], since H_2O is the reagent and the change in its concentration with respect to the substrate is insignificant; the rate in acidic media was measured by a second-order equation [3] because of bonding of HCl with the reaction products.

The rate constants for the hydrolysis of 1-(chloromethyl)silatrane in water and in 25 and 50% (by volume) aqueous ethanol increase rapidly as the water concentration increases both in neutral and acidic media (Table 1).

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*See [1] for communication LXVII.

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TABLE 1. Rate Constants for the Hydrolysis of 1-(Chloromethyl)silatrane in Water and Aqueous Ethanol at 25°C

Parameters	Water concentration, %		
	100	75	50
	Neutral media		
$k_1 \cdot 10^{-6}$ sec^{-1}	9,73±0,02	2,08±0,02	1,31±0,01
	Acidic media		
k_2, liter · mole^{-1} · sec^{-1}	0,87±0,02	0,34±0,01	0,12±0,01

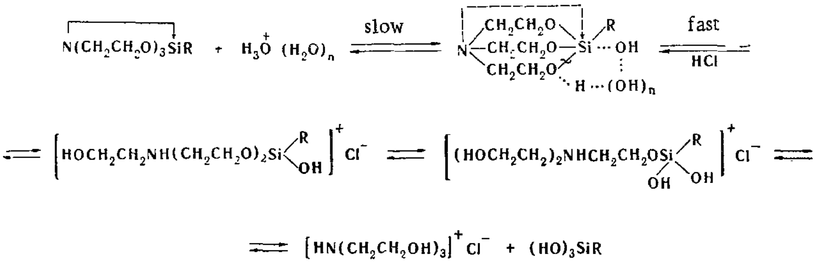
TABLE 2. Rate Constants for the Hydrolysis of 1-(α-Chloroalkyl)silatranes at 25° in Acidic Aqueous Media

	Compound	k_2, liter · mole^{-1} · sec^{-1}		Compound	k_2, liter · mole^{-1} · sec^{-1}
I	$ClCH_2Si(OCH_2CH_2)_3N$	0,87	IV	$ClCH_2Si\langle^{(OCH_2CH_2)_2}_{OCH(CH_3)CH_2}\rangle N$	0,74
II	$Cl_2CHSi(OCH_2CH_2)_3N$	0,20	V	$ClCH_2Si\langle^{(OCH_2CH_2)}_{(OCH(CH_3)CH_2)_2}\rangle N$	0,68
III	$CH_3ClCHSi(OCH_2CH_2)_3N$	1,10	VI	$ClCH_2Si(OCH(CH_3)CH_2)_3N$	0,62

TABLE 3. Mass Numbers of the Most Characteristic Fragment Ions of Tris(2-hydroxyalkyl)amines

Structure	m/e							
$N(CH_2CH_2OH)_3$			149	118	104	74	56	43
$N(CH_2CH_2OH)_2CH(CH_3)CH_2OH$		163	132	118	88	74	56	43
$N(CH(CH_3)CH_2OH)_2CH_2CH_2OH$	177	146	132	118	88	74	56	43

The rate of hydrolysis of 1-(chloromethyl)silatrane in acidic media is considerably higher than in neutral media and is satisfactory linearly related to [HCl] ([HCl] $= 1 \cdot 10^{-3}$, $1.5 \cdot 10^{-3}$, and $2 \cdot 10^{-3}$ mole/liter; $k_2^{25} = 0.44 \pm 0.01$, 0.66 ± 0.01, and 0.87 ± 0.02 liter · mole^{-1} · sec^{-1}, respectively). This large change in the rate in the presence of HCl constitutes evidence that the rate-determining step is electrophilic attack of the reaction center by the hydronium ion with simultaneous transfer of the hydration shell to the silicon atom.



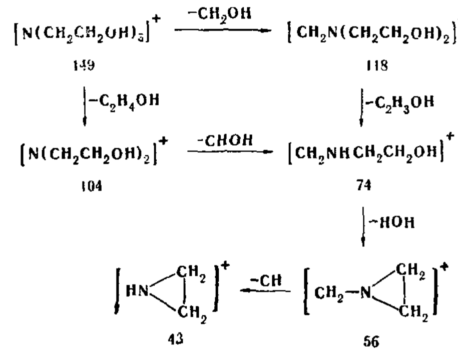
The next steps in the hydrolysis of the Si–O–C bonds of the silatrane ring proceed very rapidly. The products have practically no effect on the rate during the reaction.

An electronegative substituent attached to the silicon atom of the silatrane should increase its electrophilicity and, consequently, its reactivity. Table 2 shows that the rate constants for the hydrolysis of 1-(α-chloroalkyl)silatranes are reduced considerably as the electronegativity of the substituent bonded to the silicon atom increases; this is associated with the attendant increase in the $p_\pi - d_\pi$ character of the Si–O bonds.

The effect of methyl groups in the 3, 7, and 10 positions of the heterocyclic framework of 1-(α-chloroalkyl)silatranes (IV–VI) considerably lowers the rate of hydrolysis, although the steric accessibility of the silicon atom in the molecules remains unchanged.

This provides evidence that the inductive effect of the substituents in the 3, 7, and 10 positions, which raises the order and, consequently, the strength of the Si–O bond, evidently has the principal effect on the reactivity of silatranes.

To confirm the above scheme for the mechanism of the hydrolysis we studied the mass spectra of tris(2-hydroxyalkyl)amines (Table 3), which made it possible to propose a scheme for their dissociative ionization and to isolate from the mass spectrum of the hydrolyzate the characteristic mass numbers of ions belonging to the triethanolamine formed during the hydrolysis of 1-(chloromethyl)silatrane in ^2H_2O and $H_2{}^{18}O$. In this case it was observed that in hydrolysis in $H_2{}^{18}O$, neither the molecular ion of triethanolamine nor the fragment ions formed during its dissociative ionization contains significant amounts of ^{18}O, and this indicates the proposed scheme for the mechanism of the hydrolysis of 1-(α-chloroalkyl)silatranes.



EXPERIMENTAL

The kinetics of the hydrolysis of 1-(α-chloroalkyl)silatranes were studied in aqueous solution in the presence of HCl at 25 ± 0.02°. The initial concentration of the solutions of the investigated compounds was $2 \cdot 10^{-3}$ mole/liter, and the HCl concentration ranged from $1 \cdot 10^{-3}$ to $2 \cdot 10^{-3}$ mole/liter. The reaction rate was followed from the typing up of HCl by means of an Lp-7 polarograph. The accuracy in the establishment of the potential in the apparatus was ±3.5 mV in a total range from +2 to −4 V.

The average hydrolysis rate constants were calculated from no less than 10 measurements, the error in which was no more than 2%.

The mass spectra were recorded with an MKh-1303 spectrometer with $V = 50$ eV and $I = 0.75$ mA at a chamber temperature of 200°. The reaction mixtures contained 80% ^2H_2O and 42% $H_2{}^{18}O$. The spectra were recorded immediately after preparation of the mixtures and after 2 and 24 h.

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