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THE ACID CATALYSED SOLVOLYSIS OF 1-ORGANOSILATRANES

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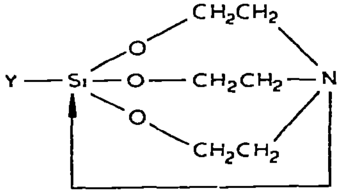
Summary

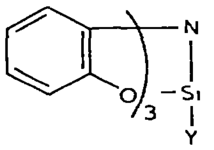
A kinetic study has been made of the reaction of some 1-organosilatranes with aqueous-methanolic hydrochloric acid. The reaction is of first-order in both silatrane and acid, and for XC_6H_4-silatranes electron release by X assists the reaction. For acid catalysis in water or in water/dioxan, the rate is effectively the same irrespective of whether protium oxide or deuterium oxide is used. It is suggested that the rate-determining step involves protonation of the nitrogen atom concerted with breaking of the Si—N bond, the protonation being almost complete at the transition state.

Introduction

Voronkov and Zelchan [1] have measured the rates of hydrolysis of some 1-substituted silatranes, 1-organo-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecanes (I), in neutral water. They observed that electron-release by the 1-substituent hindered reaction, and interpreted the results in terms of nucleophilic attack by water at silicon. Both Frye, who pioneered the studies of the chemistry of silatranes [2] and related 5-coordinate silicon species [3], and Voronkov observed that the silatranes reacted fairly slowly with acids, but the acid-catalysed decomposition seems not to have been studied mechanistically until now. However, Timms has examined the acid-catalysed hydrolysis



(I)



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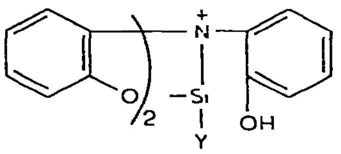

(III)

of nitrilotriphenoxysilanes (II) in aqueous dioxan, and concluded that for Y = Me, Ph, and p-MeC$_6$H$_4$ the rate-determining step is the unimolecular fission of an Si—O bond, to give III, follwing a rapid protonation of one of the oxygen atoms [4]. We describe below the results of a brief study of the acid-catalysed solvolysis of 1-benzylsilatrane and some 1-arylsilatranes.

Results and discussion

The rates of decomposition of the 1-organosilatranes in a mixture of methanol (10 vol.) and aqueous hydrochloric acid (1 vol.) were measured by monitoring the change in the UV absorption in the 260-280 nm region associated with the aromatic rings. In each case the spectrum changes at a measurable rate to become virtually identical with that of the solution obtained by dissolving the corresponding RSi(OMe)$_3$ compound in the same medium, and since the conditions are much too mild to cause cleavage of the R—Si bonds in the latter compounds, we can reasonably assume that with the silatranes we are following the destruction of the silatrane ring system without loss of the R—Si bond. Good first-order kinetics are observed during a run, and the observed first-order rate constant for 1-phenylsilatrane (I, R = Ph) is proportional to the concentration of acid (Table 1), so that the reaction is of first-order in both acid and silatrane. The rate constants at 30.0° and 50.0° for the 1-phenylsilatrane correspond with an approximate value of 22 kcal mole^{-1} for the activation energy.

The observed pseudo first-order rate constants for a series of compounds at a fixed acid concentration at 30° are shown in Table 2. For the compounds 1-XC$_6$H$_4$-silatrane, electron release by X increases, and electron withdrawal by X decreases the rate. A plot of log k against σ shows a marked curvature; a plot against σ^+ is a better straight line, and a Yukawa—Tsuno plot against $[\sigma + r(\sigma^+ - \sigma)]$ with $r = 0.5$ defines a fairly good straight line with a slope, ρ, of ca. —0.35, but only very limited significance can be attached to these plots since the points for X = H, m-Cl, and m-NO$_2$ do not themselves define a good straight line, which they should do in satisfactory Hammett or Yukawa—Tsuno plots.

The results described above do not enable a choice to be made between, on the one hand, a rate-determining protonation of the nitrogen atom of the silatrane system, with synchronous cleavage of the N—Si bond, and, on the other, a rapid protonation of an oxygen atom followed by slow fission of an Si—O bond, as proposed by Timms [4] for the nitrilotriphenoxysilanes, with subsequent rapid complete breakdown to RSi(OH)$_3$ and its derivatives, since

TABLE 1

DEPENDENCE OF THE PSEUDO FIRST-ORDER RATE CONSTANT, k, ON ACID CONCENTRATION FOR THE REACTION OF 1-PHENYLSILATRANE IN A MIXTURE OF METHANOL (10 VOL.) AND AQUEOUS HYDROCHLORIC ACID (1 VOL.) AT 30.0°[a]

[aq. HCl] (M)	0.500	0.200	0.145	0.100
10^2k(s^{-1})	66	25.7	19.4	13.3
10^2k/[aq. HCl]	132	129	127	133

[a] A rate constant of 6.8 × 10^{-3} s^{-1} was observed at 50.0°.

TABLE 2

REACTIONS OF 1-ORGANOSILATRANES WITH A MIXTURE OF METHANOL (10 VOL.) AND 0.10 *M* AQUEOUS HYDROCHLORIC ACID (1 VOL.) AT 30.0°

Substituents in silatrane	Conc.[a] (*M*)	λ(nm)[b]	$10^3k(s^{-1})$[c]	k_{rel}[d]
1-C_6H_5	2×10^{-3}	271	1.33	1.0
1-(*m*-ClC_6H_4)	2×10^{-3}	273	0.91	0.68
1-(*m*-$NO_2C_6H_4$)	2×10^{-4}	285	0.81	0.61
1-(*p*-$MeOC_6H_4$)	1×10^{-3}	246.8	2.02	1.52
1-(*p*-MeC_6H_4)	1×10^{-3}	262	1.69	1.27
1-($C_6H_5CH_2$)	1×10^{-3}	268	2.48	1.86
1-Ph-3,7,10-Me_3-	2×10^{-3}	271	0.90	0.68

[a] Approx. concn. of the silatrane. [b] Wavelength used to follow progress of reaction. [c] Observed first-order rate constant. [d] Rate relative to that of 1-phenylsilatrane.

reaction by either mechanism would be facilitated by electron release towards silicon from the groups R. In an attempt to decide between these possibilities we examined the deuterium solvent isotope effect, since rapid preequilibrium protonation of oxygen followed by rate-determining fission of the Si—O bond should be clearly faster (probably by a factor of 1.5-3.5) in deuterium oxide than in protium oxide (see, e.g., refs. 5 and 6), whereas slow protonation of the nitrogen would be expected probably to be slower in the deuterated than in the non-deuterated medium, the magnitude of the solvent isotope effect, k_{H_2O}/k_{D_2O}, depending on the degree of proton transfer at the transition state [6]. The reaction of 1-phenylsilatrane in aqueous acid (trifluoroacetic acid was used for convenience) was too fast at 30.0° for convenient measurement under pseudo first-order conditions, i.e., with at least a 10-fold excess of the acid present, and reduction of the acid concentration leads to more complex kinetics since a significant amount of the acid is then removed by the product triethanolamine. However, it was observed that the reaction—time curves for the deuterated and non-deuterated media were superimposable within the experimental error, indicating that the k_{H_2O}/k_{D_2O} ratio lay between 0.9 and 1.1. Rates were then measured at 30.0° for the 1-phenylsilatrane in dioxan/water (ca. 30 vol. % water) containing hydrogen chloride (2.00×10^{-2} *M*); again the rate constants were identical within experimental error for protium and deuterium oxide, indicating a k_{H_2O}/k_{D_2O} ratio of 1.00 ± 0.05. This solvent isotope effect of unity is at first sight somewhat surprising, since there can be no doubt that a proton transfer is involved either before or in the rate-determining step. The absence of a clear inverse isotope effect argues fairly strongly against a mechanism of the Timms type, involving slow unimolecular fission of the Si—O bond following rapid pre-equilibrium protonation of the oxygen. While for rate-determining proton transfer to nitrogen we expected a definite normal isotope effect, the observed result is consistent with such transfer provided the attachment of the proton to the nitrogen atom is almost complete in the transition state. This is because an inverse secondary isotope effect can balance out the primary isotope effect for the proton transfer. Application of Schowen's approximate treatment [6] to the general reaction of type (1), in which L = H or D (which effectively covers the silatrane reaction, since the fact that the nitrogen is initially four-coordinate in the latter has no significance in the isotope effect calculations), indicates that for an H—N bond order in the transition state in the region of 0.9, the primary isotope effect, k_H/k_D, of ca. 2 will be countered by a secondary isotope effect of ca. 1/2, to give an overall solvent isotope effect of about unity.

$$L_3O^+ + R_3N \rightarrow L_2O + R_3NL^+ \qquad (1)$$

The fairly high activation energy observed for the reaction (in aqueous methanol) is consistent with a transition state well removed from the ground state, and thus with a considerable degree of protonation of the nitrogen atom and of breaking of the Si—N bond. Once the Si—N bond is broken, subsequent hydrolytic cleavage of the Si—O bonds will be very rapid under these conditions, just as it is for the corresponding $RSi(OMe)_3$ or $RSi(OEt)_3$ compounds. As noted above, the substituent effects in the XC_6H_4-silatranes are consistent with rate-determining protonation at nitrogen. The enhanced reactivity of the 1-phenyl-3,8,9-trimethylsilatrane relative to that of 1-phenylsilatrane is in the expected direction, since the electron release by the methyl groups will assist the protonation. The effect seems rather large to be attributed wholly to inductive effects, and it should be noted that a small electron release to the nearby oxygen atom could result in a rather larger increase in the $(p\rightarrow d)\pi$ bonding between the oxygen and silicon atom, and thus to a weaker Si—N bond and a greater ease of protonation at nitrogen. The lower reactivity of the 1-benzyl- compared with the 1-phenyl-silatrane could not necessarily have been predicted, since inductive electron withdrawal by the phenyl group is greater than of the benzyl group. However, whereas the silicon atom receives electrons back from the phenyl group by $(p\rightarrow d)\pi$ bonding, the CH_2—Si bond of a benzyl—silicon compound strongly releases electrons to the aromatic ring by hyperconjugation (cf. ref. 7), and so the electron density on silicon could be lower for a $PhCH_2Si$ than for the corresponding PhSi system. (Calculations for the analogous $CH_2{=}CHSiH_3$ and $CH_2{=}CHCH_2SiH_3$ systems indicate that a larger degree of positive charge resides on the SiH_3 group in the latter than in the former compound [8].) However, the explanation of the relatively low reactivity of the 1-benzyl- compared with the 1-phenyl-silatrane may lie not so much in the electron densities on the silicon atoms in the ground state as in the fact that with the phenyl compound the loss of the Si—N bond will be partly compensated by increased $(p\rightarrow d)\pi$ bonding between the aromatic ring and the silicon atom, whereas no such effect is possible for the benzyl compound.

As might be expected, the sequence of the ease of the acid-catalysed solvolysis of the 1-organosilatranes is the opposite of that of the ease of their formation from the $RSi(OMe)_3$ compounds and triethanolamine (see Table 3 and ref. 7). Thus, in the preparations from the $XC_6H_4Si(OMe)_3$ compounds, the most rapid reaction was that for X = m-NO_2, which proceeded exothermally on mixing the reactants at room temperature. For X = H and m-Cl the reaction proceeded satisfactorily at higher temperatures without a catalyst, but for X = p-Me and p-OMe, use of a little potassium hydroxide as catalyst was necessary to give a satisfactory rate at comparable temperatures. However, while no catalyst was needed in the preparation of the 1-benzylsilatrane (or of its m- and p-fluoro-derivatives), the reaction was much slower than that to

TABLE 3

PREPARATIONS OF 1-SUBSTITUTED SILATRANES

Substituent	Catalyst	Temp. (°C); Time (h)	Yield (%)	M.p. (°C)	Found (calcd.) (%)		
					C	H	N
C_6H_5	None	100; 2	90	209-210[a]			
m-ClC_6H_4	None	150; 2	75	203-203.5	50.1 (50.4)	5.8 (5 8)	5.2 (4.9)
m-$NO_2C_6H_4$[b]	None	[c]	70	161-161.5	48.4 (48 6)	5.4 (5.4)	9.4 (9.45)
p-MeC_6H_4	KOH[d]	130; 2	78	195-195.5	58.6 (58.8)	7 2 (7 2)	5.4 (5.3)
p-$MeOC_6H_4$	KOH[d]	130; 2	80	192-193	55 2 (55.5)	6.8 (6.8)	5.0 (5.0)

[a] Lit. m.p. 208-209° [2], 210.3-211.3° [1]. [b] See ref. 10. [c] Spontaneous and exothermic on mixing at room temperature. [d] Approx. 0.01 g.

give the *m*-nitrophenyl compound, which is not in accord with the rather similar reactivities of these compounds in the acid solvolysis.

While we favour slow protonation of the nitrogen atom in the solvolysis of the 1-organosilatranes, it is possible that rapid protonation of an oxygen atom followed by unimolecular fission of the relevant Si—O bond does occur in the case of the nitrilotriphenoxysilanes, as suggested by Timms [4]. However, in our view his experimental observations are equally consistent with slow protonation of the nitrogen atom concerted with breaking of the N—Si bond. While in both the silatranes and the nitrilotriphenoxysilanes the (reversible) protonation of an oxygen atom will certainly be rapid, there is no reason to assume that the subsequent unimolecular Si—O breaking will occur especially readily. Indeed, this process has the disadvantage of leading to what must be a fairly high-energy product of a type, such as III (which Timms would describe as a siliconium ion, but which is better regarded as an ammonium ion), in which a four-coordinate silicon atom, which would prefer to be tetrahedral, has all its bonds tied back on one side in a strained cage-structure. In contrast, the products from the process involving protonation of the nitrogen atom concerted with cleavage of the Si—N bond involve normal tetrahedral, four-coordinate silicon systems, which will subsequently undergo rapid solvolysis, just as do the comparable $RSi(OEt)_3$ compounds.

Experimental

Preparation of 1-organosilatranes (cf. ref. 2)

The preparations of some of the silatranes have been described previously [3]. Usually, a stirred mixture of the appropriate organotrimethoxysilane (0.1 mol) and triethanolamine (0.2 mol), sometimes in the presence of a little potassium hydroxide, was heated, by means of an oil bath maintained at the temperature shown, for the time specified in Table 3, the formed methanol being removed continuously through a short column. The solid residue was recrystallized from chloroform. Yields, m.p.'s and analyses are shown in Table 3.

When *m*-nitrophenyltrimethoxysilane (0.025 mol) and triethanolamine (0.025 mol) were mixed, a vigorous exothermic reaction took place, with expulsion of methanol, to give a solid. This was recrystallized twice from chloroform.

Rates of solvolyses in aqueous methanolic hydrochloric acid

Aqueous hydrochloric acid, in most cases 0.10 M (1 vol.), was added to a solution (10 vol.) of the organosilatrane of the concentration specified in Table 1, and the mixture was well shaken. Some of it was transferred to a stoppered 1 cm quartz cell, which was placed in the thermostatted cell compartment of a Unicam 500 spectrophotometer. The mixture was allowed to reach the equilibrium temperature, then optical density measurements were begun at an appropriate wavelength which was pre-selected by examining the change brought about by the reaction over the spectral range 230-300 nm.

Good first-order kinetics were obtained for more than 90 % of reaction. The first-order rate constants are shown in Tables 1 and 2.

Solvent isotope effects

(a). In a typical set of runs in aqueous solution, a small volume of anhydrous trifluoracetic acid was injected into a 2×10^{-3} M solution of 1-phenylsilatrane in water at 30° to give a mixture containing 4×10^{-3} M acid. The progress of the reaction at 30.0° was followed spectrophotometrically as above. The percentage-reaction—time curves in protium oxide and deuterium oxide, respectively, were superimposable, implying a solvent isotope effect of 1.0 ± 0.1.

(b). For runs in aqueous dioxan, a mixture containing water and dioxan in 1/0.495 mole ratio and 2.0×10^{-3} M 1-phenylsilatrane was made up by mixing 70 vol. of a solution of the silatrane with 30 vol. of protium oxide or 30.1 vol. of deuterium oxide. A very small volume of 8.00 M hydrochloric acid was injected into the mixture maintained at 30° to give an initial acid concentration of 2.0×10^{-2} M. Rates were measured spectrophotometrically at 30°, as above, a wavelength of 269.3 being used. Good first-order kinetics were observed, with a pseudo first-order rate constant of 2.1×10^{-3} s^{-1} in both cases.

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