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Nucleophilic Substitution at Silicon and Germanium: Hydrolysis of Organo-Acetates.

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We have used a titrimetric method to study the rates of hydrolysis of a series of acetates R_3MOAc (M = Si or Ge; R = Ph, iPr, nPr, c-hex, or n-hex) in dioxane. The effects of the concentration of water, temperature and catalysis by potassium acetate have been studied and are discussed in terms of the proposed mechanism for the hydrolysis, in which bond-breaking processes appear to be important. High orders in the water concentration are observed and the germanium acetates are much more reactive than the silicon acetates.

Introduction

Comparative kinetic studies of reactivity at silicon and germanium are rare. The alkaline hydrolysis of triorgano-silanes has received much attention but the corresponding reaction with germanes is too slow to be measured.[1] Acid cleavage rates of aryl silicon and aryl germanium bonds have been compared,[2] but this reaction is rather to be considered as an aromatic electrophilic substitution reaction at carbon than as a nucleophilic substitution at the metal atom. The alkaline cleavage of silicon-carbon and germanium-carbon bonds has also been studied and this reaction is best considered as a nucleophilic attack at the metal with steric effects of great importance.[3] The hydrolysis of triorganochlorosilanes and chlorogermanes has been examined in aqueous acetone solutions using a rapid mixing stopped flow technique.[4] The results obtained were discussed in terms of steric effects and the formation of pπ-dπ bonds between the metal atom and substituent phenyl groups.

The hydrolysis of triphenyl silicon acetate in aqueous dioxane solutions has been studied by Modena and Todesco.[5] Recently, their method has been extended to the study of the hydrolysis and alcoholysis of substituted aryl silicon acetates.[6,7]

We have now examined the hydrolysis of a series of triorganometallic acetates (R_3MOOc-M = Si and Ge; R = Ph, iPr, nPr, c-hex or n-hex) in aqueous dioxane in an effort to indicate further the effects of pπ-dπ bonding and steric factors on nucleophilic substitution at silicon and germanium.

Experimental Section

Materials. Dioxane was purified by first treating with dilute hydrochloric acid, refluxing with sodium and then fractionally distilling.[8] The pure dioxane was used within a week of distillation. Measurement of the rates of identical reactions using different preparations of dioxane were consistent within the experimental error.

Water of conductivity less than 10^{-6} ohm cm.$^{-1}$ was used for all solvolyses. Aqueous solutions were made up by weighing the water directly into 100 ml. volumetric flasks and making up to the mark with dioxane.

The organo-acetates were prepared by methods described in the literature except for $(n\text{-hex})_3SiOAc$ and $(iPr)_3SiOAc$ to which no reference could be found. Trihexyl silicon acetate was prepared from the trihexylsilane (prepared from trichlorosilane and the Grignard reagent from n-hexyl bromide) by treatment with acetic acid in the presence of aluminium and iodine.[9] Distillation using a spinning band column gave a high boiling liquid, b.p. 126°C at approximately 0.02 mm. pressure. Tri-isopropyl silicon acetate was prepared from the silanol[10] by refluxing with acetic anhydride. The product was twice vacuum distilled to give a liquid b.p. 97-99°C at 11.5 mm. Triphenyl silicon acetate was prepared both by refluxing the silanol with acetic anhydride and by stirring the chlorosilane with sodium acetate in benzene. All the silicon and germanium acetates prepared had a strong absorption in the infrared at about 1720 cm.$^{-1}$ and 1700 cm.$^{-1}$ respectively.

Apparatus and Kinetic Measurement. The rates of hydrolysis were determined by a method similar to that described by Modena and Todesco. The organo-acetates were weighed into 50 ml. volumetric flasks and 25 ml. dioxane added to give between 0.02 and 0.04 *M* solution: 25 ml. of the aqueous solution were rapidly

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(9) B. N. Dolgov, N. P. Kharitonov and M. G. Voronkov, *Zhur. Obshchei Khim.*, *24*, 861 (1954).

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added by inversion of a 25 ml. pipette.* At known time intervals, 5 ml. aliquots of the reaction mixture were pipetted into 25 ml. of A.R. 60-80 petrol ether and extracted successively with 20 ml. and 10 ml. of water. The combined aqueous layers were titrated with standard sodium hydroxide solution using phenolphthalein as indicator. Tests using acetic acid solutions showed the method to be accurate to within 3%. Infinite time was taken as equal to at least ten half lives. Reactions were pseudo-first order over the whole reaction, except for $(n\text{-}Pr)_3GeOAc$ and $(n\text{-}hex)_3GeOAc$ which approached hydrolytic equilibrium. Rate constants were calculated by the method of least squares and the errors given are standard deviations.

The temperature of the reaction was controlled to within 0.1°C and corrections have been applied to the measured rate constants to allow for the expansion of the dioxane solution with temperature.

Results and Discussion

The overall reaction studied is:

$$R_3MOAc + H_2O = R_3MOH + AcOH$$

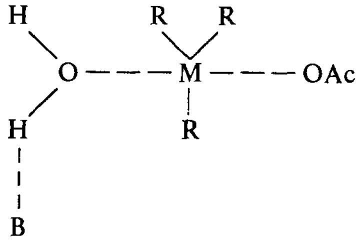
The aqueous solutions are best considered as ordered lattices of water and dioxane molecules. We propose to discuss our results in terms of reaction between an ordered group of water molecules, or water polymer, and the organo-acetate. Solvolysis reactions of this type have recently been discussed.[11] Although it is more convenient to discuss the mechanism in terms of reaction with a preformed water polymer:

$$nH_2O \rightleftharpoons (H_2O)_n$$
$$(H_2O)_n + R_3MOAc \rightarrow R_3MOH + (H_2O)_{n-1} + AcOH$$

it may be that the reaction is better considered as an initial solvation stage followed by reaction of the organo-acetate with its solvation shell: **

$$\text{solvent} + R_3MOAc \longrightarrow (R_3MOAc)_{\text{solvated}} \longrightarrow (R_3MOH)_{\text{solv.}} + (AcOH)_{\text{solv.}}$$

Measurements of heats of solution might enable a distinction to be made between these two alternative mechanisms. Thus our model for the transition state of the reaction is:



with B generally a water polymer or solvation shell but capable of replacement or assistance by any general base. H_2O^{18} experiments with Ph_3SiOAc indicate that Si-O fission occurs during the hydrolysis and we have assumed metal-oxygen fission to be involved in all the reactions studied. We have now confirmed by H_2O^{18} experiments on other silicon and selected germanium acetates that M-O fission does occur with these also. Formation of such a transition state from the solvated ground state of the molecule will involve considerable ordering of solvent molecules which play no direct part in the reaction. We shall discuss the effect of temperature on the reaction using the formula

$$\Delta H_{obs} = \Delta H_{act} - \Delta H(1-\alpha)/[1+(n-1)\alpha]$$

as derived by Chipperfield and Prince.[4]

(a) *Reaction Order.* First order rate constants at various water concentrations are given in Table I. It was not possible to measure the rates of reaction of every compound at a single concentration of water, owing to the large rate variation involved, especially between the silicon and germanium acetates.

Plots of $\log(H_2O)$ against $\log(k_1)$ show good linearity over wide ranges of water concentration indicating an equation of the form.

$$k_1 = k[H_2O]^n$$

The results obtained for $(n\text{-}Pr)_3SiOAc$ over the range 5% to 25% are shown plotted in Fig. 1. For all the silicon acetates studied, «n» had a value close to 4.5 over the range of water concentrations, 5% to 50%. Modena and Todesco measured the hydrolysis of Ph_3SiOAc from 5% to 20%. Although we find good agreement with their data at 15% and less good at 20%, the plot of log k against $\log(H_2O)$ using their data

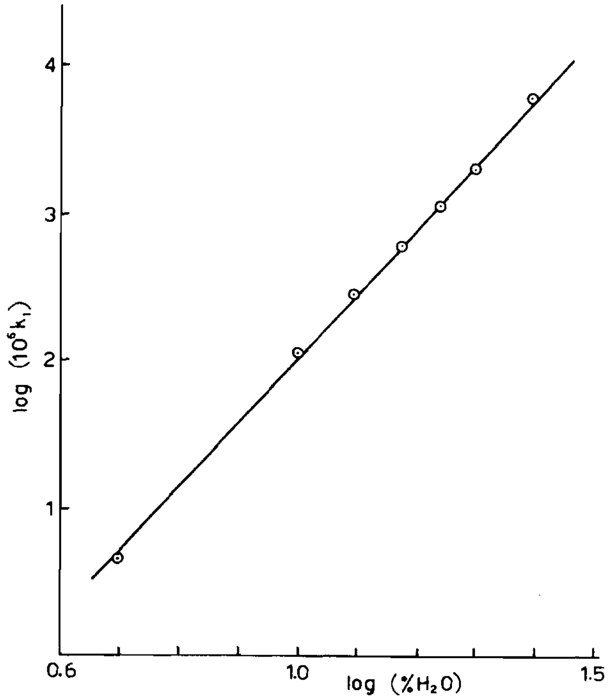


Figure 1. Effect of % water concentration on rate of hydrolysis of $(n\text{-}Pr)_3SiOAc$ in dioxane at 25°C.

(*) Since the very high orders in water magnify the slight error introduced by this method of mixing, all the measured rate constants have been corrected to allow for the slight volume error.

(**) In other words, it is not possible from the kinetics to deduce the rate sequences by which a group of water molecules becomes ordered around the transition state but we are able to state that (a) such a group does form, (b) the kinetics show this, (c) groups of the same size do not always function in the transition state, the size or range of sizes, depending upon the nature of the reacting substrate.

(11) R. F. Hudson, *J. Chem. Soc.*, B, 761 (1966).

Table I. (a) First order Rate Constants at 25°C, $k_1 \times 10^4$ sec.$^{-1}$, for R_3SiOAc hydrolysis

% H_2O (mls of water per 100 mls solution)	R Ph	nPr	iPr	n-hex	c-hex
5		.047 ± .001			
10		1.15 ± .01			
12.5		2.91 ± .03			
15	.53 ± .01	6.03 ± .04			
17.5		11.7 ± .1			
20	1.78 ± .05	20.0 ± .2	.122 ± .001	2.85 ± .05	
25		61 ± 3			
30	9.9 ± .2		.66 ± .01		.085 ± .005*
40	40.8 ± .6		2.13 ± .05		
50			4.3 ± .2		

(b) First order Rate Constants at 25°C, $k_1 \times 10^4$ sec^{-1}, for R_3GeOAc hydrolysis

% H_2O (mls of water per 100 mls solution)	R Ph	nPr	iPr	n-hex	c-hex
1		1.55 ± .06			
1.5		3.1 ± .2		1.73 ± .06	
2		4.4 ± .2			
3		19 ± 3		11.8 ± .9	
5	58 ± 4		1.37 ± .02	84 ± 5	
6	107 ± 6		3.67 ± .03		
7	295 ± 15		7.66 ± .20		
8	540 ± 20		18.4 ± .3		2.6 ± .1
9			32.4 ± .6		
10			70 ± 2		9.3 ± .4
12.5					31 ± 2

* During the final stages of this reaction, prior to measurement of the infinite time titre, $(c\text{-hex})_3SiOH$ was precipitated and identified by its melting point.

is not linear; though the slope of the curve at 20% H_2O is approximately 4.5, equal to our value of «n». Both our preparations of Ph_3SiOAc gave the same results within experimental error. The germanium acetates studied had «n» close to 5.6, although for $(n\text{-}Pr)_3GeOAc$ and $(n\text{-}hex)_3GeOAc$ which were studied at water concentrations below 5%, plots of log(% H_2O) against log(k_1) show curvature. We consider this curvature to be due to the formation of water polymers of lower order, concomitant with a change in the structure of the solvent, possibly resulting in participation of dioxane molecules in the transition state.

We should emphasise that «n» is not in general equal to the number of water molecules specifically solvating the transition state but is related to this number through the liquid structure; i.e., significance may be given to «n» by considering the solvent structure together with the kinetics as we have done above and in reference 4.

(b) *Effect of Temperature.* The rates of reaction were measured at three or four temperatures between 14° and 60°C. ΔH_{obs} and ΔS_{obs} the enthalpy and entropy of activation have been calculated in the normal way and are given in Table II. ΔH_{obs} at low water concentrations is close to zero as found for the hydrolysis of chlorogermanes and chlorosilanes in aqueous acetone.[4] At the higher water concentrations we find higher enthalpies of activation tending to essentially «normal» values. In our equation for ΔH_{obs} above, α will tend to unity as the water concentration increases so that ΔH_{obs} tends to ΔH_{act}.

ΔS_{obs} values for the reaction are particularly large and negative owing to the high ordering of the water required by the transition state. With rising water concentration, ΔS_{obs} values tend to fall as the solution becomes more ordered. In solvolysis reactions such as these we consider ΔS_{obs} to be a more meaningful quantity than ΔH_{obs}. In the special case when ΔH_{obs} equals zero, the differences in rates of solvolysis lie solely in the differences in ΔS_{obs}.

Table II.*

M	R	ΔH (k.cals)	ΔS (e.u.)	% H_2O
Si	Ph	11.2±.6	- 38.3±2	20
	n-Pr	6.6±.3	- 48.6±1	20
	n-Pr	6.9±.3	- 50.2±1	15
	i-Pr	9.9±.7	- 44.5±2	30
	c-hex	11.8±.1	- 42.2± .3	30
Ge	Ph	- 0.3±.1	- 69.2± .3	5
	n-Pr	4.6±.3	- 58.6±1	2
	i-Pr	3.4±.5	- 65.0±1.5	5
	c-hex	7.3±.6	- 48.0±2	10

* Errors given are standard deviations obtained from a regression equation of logk against 1/T.

(c) *Effect of varying R and M.* Relative rate constants for the germanium and silicon acetates are given in Table III. The tricyclohexyl acetate rate is taken as

Table III. Relatives Rates at 25°C

		R_3GeOAc at 5% H_2O			
R	Ph	nPr	iPr	n-hex	c-hex
	260	760	7.3	450	1
		R_3SiOAc at 20% H_2O			
R	Ph	nPr	iPr	n-hex	c-hex
	114	1220	7.8	179	1

unity for both series and data measured at other water concentrations has been included by extrapolation to 5% or 20% water.

By extrapolation, we estimate that tricyclohexyl germanium acetate is hydrolysed about 2000 times as rapidly as tricyclohexyl silicon acetate and this figure serves to indicate the considerably greater ease of hydrolysis of the germanium acetates relative to the corresponding silicon acetates. This difference is so great in fact, that the most easily hydrolysed silicon acetate studied, $(nPr)_3SiOAc$, reacts more slowly than the slowest germanium acetate, $(c\text{-}hex)_3GeOAc$. Studies of the acidities of the triphenyl metal hydroxides (Ph_3MOH, M = C to Pb) have been interpreted as indicating much more extensive π-bonding in the Si-O bond than in the Ge-O bond.[12] Measurements of the basicities of alkoxysilanes and siloxanes were interpreted similarly.[13] Comparisons of Si-O and Ge-O bond lengths and energies in organosilanes and germanes are not available although there is little doubt that the Si-O bond is the stronger. If we attribute the large rate differences observed between the silicon and germanium acetates to the formation of strong π-bonds in the Si-O system then, since the product silanols or siloxanes will also contain Si-O bonds strengthened by similar π-bonding, we cannot simply attribute the slow silicon acetate hydrolysis to the greater strenght of the Si-O bond. The hydrolysis of triphenyl fluorosilane may be conveniently studied in 30% water/acetone solution[14] whereas triphenyl fluorogermane is virtually instantly hydrolysed under similar conditions.[15] We have already seen that the kinetic order in water is different for the two elements, suggesting solvation differences. The data quoted above on the kinetics and acidities of silicon and germanium compounds show that the oxygen lone pairs are less available in the Si-O bond than in the Ge-O bond and so for R_3GeOAc we expect greater solvation and hydrogen bonding of the acetate group, making the entropy of activation less negative (for which there is other evidence[15]), the ground state being more ordered. In the transition state the germanium acetate is associated with at least one more water molecule and greater solvation of the leaving acetate group in the transition state may also contribute to a lower activation energy compared with the corresponding silicon compound.

Four factors may be of importance in determining the effect of R on the rate : (i) inductive effects, (ii) pπ-dπ bonding, (iii) steric hindrance, (iv) mass or ponderal effects. Inductive effects are likely to be very small for the groups used and will not be further considered. pπ-dπ bonding between the benzene ring and silicon was postulated to account for the orders of reactivity of triphenyl chlorosilane and chlorogermane.[4] In our study, comparison with the other acetates indicates no evidence for such π-bonding. It seems likely that pπ-dπ bonding between silicon and oxygen will lower the ability of the silicon atom to form π-bonds with the aromatic ring.

Steric and ponderal factors are difficult to separate without quantitative calculation. Comparison of the relative rates for the n-propyl and iso-propyl groups would seem to indicate that greater steric hindrance is occurring at silicon whereas a similar comparison for n-hexyl and cyclohexyl would indicate the reverse. In discussing ponderal effects Ingold has pointed out that an added mass is usually more strongly retarding the further off it is from the reaction centre.[16] Further, ponderal effects will be greater for the lighter silicon atom than for the germanium atom. The steric effects produced by the n-propyl and n-hexyl groups are expected to be similar and we conclude that the relative rates

$$(nPr)_3Ge : (n\text{-}hex)_3Ge = 1.7$$
$$\text{and } (nPr)_3Si : (n\text{-}hex)_3Si = 6.8$$

probably indicate the importance of ponderal effects on the rate of hydrolysis. Comparing the iso-propyl and n-propyl groups for silicon and germanium, the ponderal effect will be much less than for the exyl system and steric factors dominate.

(d) *Catalysis by Potassium Acetate.* The hydrolysis is strongly catalysed by potassium acetate as first noted by Modena and Todesco. Plots of the observed rate constants, k_{obs}, against potassium acetate concentration show excellent linearity indicating a rate law of the form:

$$k_{obs} = k_1 + k_c[KOAc]$$

where k_1 is the rate of the uncatalysed reaction and k_c the catalytic constant. Rate constants for the catalysed reactions studied are shown in Table IV.

Comparison with $(iPr)_3SiOAc$ shows Ph_3SiOAc to be extremely sensitive to catalysis under the same conditions though the reason for this is not clear.

In order to determine the effect of solvent composition on the catalysed reaction, $(nPr)_3SiOAc$ was studied at

Table IV. Catalysis of organosilicon and -germanium acetate hydrolysis by potassium acetate

	KOAc × 10^4 (moles/litre)	$k_{obs} \times 10^4$ (sec^{-1})
Ph_3SiOAc	0	9.9 ± .2
in 30% H_2O	2.70	21.5 ± .5
	5.39	31.8 ± .7
$(iPr)_3SiOAc$	0	.66 ± .01
in 30% H_2O	2.70	.67 ± .01
	5.39	.66 ± .01
	26.9	.76 ± .01
$(nPr)_3SiOAc$	0	.047 ± .001
in 5% H_2O	2.70	.227 ± .004
	6.79	.473 ± .005
	10.8	.67 ± .02
$(nPr)_3SiOAc$	0	20.0 ± .2
in 20% H_2O	5.51	21.6 ± .2
	9.51	23.1 ± .2
	13.6	24.5 ± .4
$(iPr)_3GeOAc$	0	1.37 ± .02
in 5% H_2O	1.15	2.04 ± .01
	3.87	3.24 ± .06
	7.46	4.82 ± .05

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both 5% and 20% water concentration. In Fig. 2, k_{obs}/k_1, the relative increase in rate is plotted against potassium acetate concentration and it can be seen that the reactivity of the catalyst is much smaller at the higher water concentration. We attribute this lowered reactivity to the increased base strength of the medium at higher water concentrations, water molecules themselves acting more effectively as the base B in our model above. A similar effect was observed during the hydrolysis of chlorosilanes in the presence of chloride ion[19] although this work has recently been criticised by Petersen and Ross who found no evidence for catalysis by chloride ion and suggested that the reaction is initiated by HCl.[20]

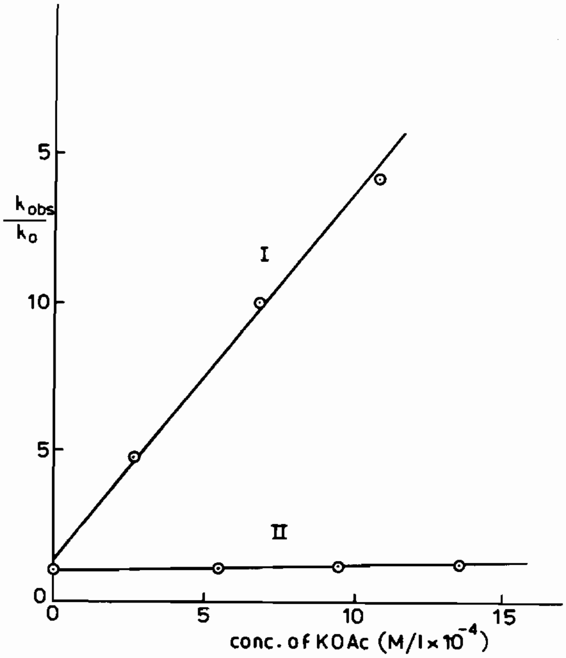

Figure 2. I, 5% H_2O; II, 20%, H_2O.

(e) *Effect of Deuterium Oxide.* For the compound $(iPr)_3GeOAc$, we have measured the variation of rate with D_2O concentration and the effect of temperature on the rate at 5% D_2O. The results are given in Table V. In Fig. 3, the data for both light and heavy water are compared graphically. The reaction order «n», with D_2O is significantly lower at 5.0, than with H_2O. Although the enthalpy of activation is greater, as expected from zero point energy considerations, the entropy of activation is significantly lower than for the comparable reaction involving H_2O. The structure of D_2O, at a temperature T, has been described as that of water at a lower temperature, T-ΔT;[17] i.e. D_2O possess a more ordered structure than H_2O. Furthermore, the «hydrogen» bonding in D_2O has been observed[18] to be stronger than in H_2O. Thus we conclude that the entropy change to form the highly ordered transition state will be less in the more ordered heavy water as observed. Consideration of the isotope effect in terms of

$$\frac{k_{H_2O}}{k_{D_2O}}$$

or the enthalpy of activation does not seem rewarding in view of the lack of knowledge concerning the structure of the solvolytic transition state.

Table V. Reaction of $(iPr)_3GeOAc$ with D_2O

% D_20*	$k \times 10^4$ sec^{-1}, at 25°C	k_{H_2O}/k_{D_2O}
5	.965 ± .01	1.42
6.5	3.53 ± .08	—
8	9.65 ± .1	1.91
10	30.5 ± 1	2.29
ΔH = 5.7±.6 k.cals	ΔS = —57.8±2 e.u.	in 5% D_2O

* «x% D_2O» indicates that the solution was equimolar with an x% solution of H_2O. In terms of percentage by volume the difference is very small owing to the greater density of heavy water.

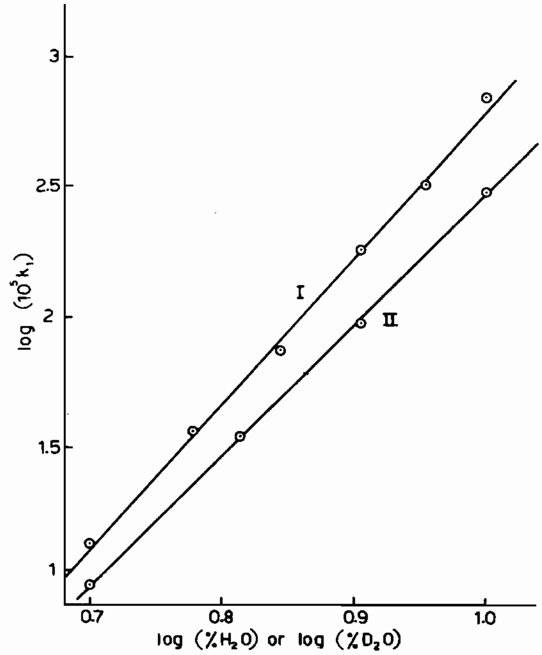

Figure 3. I, H_2O; II, D_2O.

In order to clarify the observed rate changes caused by variation of solvent composition, which we have discussed in terms of the structure of the solvent and entropy changes, it is hoped to carry out further studies on a selected compound over a wide range of solvent composition.

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