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Nucleophilic Substitution at Silicon and Germanium: II. Hydrolysis of Methyl Substituted Acetates

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Received May 28, 1968

The series of compounds $(n\text{–}Pr)_3MO.CO.CH_{(3-n)}Me_n$ ($M = Si$ and Ge; $n = 0$ to 3) were prepared and the rates of hydrolysis measured in aqueous dioxane. The entropy of activation is shown to be the main factor determining the rate differences. pK_a Values of the substituted acetic acids correlate well with $\log(k_1)$. A transition state similar to a solvated proton and a solvated carboxylate ion is proposed.

Introduction

In our previous paper we discussed the importance of the solvation of the leaving group in determining the rate of hydrolysis of organometallic acetates. Entropies of activation are large and negative for this reaction and it was suggested that the entropy is the most significant activation parameter associated with the hydrolysis.

Furthermore, on plotting $\Delta S°$ for the dissociation of acetic acid in aqueous dioxane solutions[1] against the logarithm of the first-order rate constant for the hydrolysis of Ph_3SiOAc, $(i\text{–}Pr)_3SiOAc$ and $(n\text{–}Pr)_3SiOAc$, good straight lines are observed.[2] This suggests that the entropy changes are similar in the two processes—forming the hydrolytic transition state and dissociating acetic into solvated ions.

To investigate such solvation effects more systematically, we have now measured the rate of hydrolysis of the compounds $(n\text{–}Pr)_3MO.CO.CH_{(3-n)}Me_n$ where $n = Si$ and Ge in aqueous dioxane solutions.

Experimental Section

Preparations. The organosilicon carboxylates were prepared from the appropriate silanes,[3] *e.g.*, 9 g $(n\text{–}Pr)_3SiH$ were added to 10 ml iso-butyric acid and 0.1 g aluminum powder and 1.5 g iodine added. After the initial reaction had subsided, the temperature was slowly raised until the mixture refluxed gently. After refluxing for one hour, a little copper powder was added and the mixture fractionated on a Nester Faust spinning band column.

The germanium carboxylates were prepared from $(n\text{–}Pr)_3GeOAc$[4] by exchange with the appropriate acid, *e.g.*, 5 g $(n\text{–}Pr)_3GeOAc$ were refluxed with 10 ml iso-butyric acid for one hour on a spinning band column. The mixture was slowly distilled at 60 mm. pressure keeping the distillation flask at 110°C. When all the acetic acid and excess isobutyric acid had distilled, the remaining liquid was fractionated carefully at 100 mm. pressure.

Analyses and boiling points are given in Table I.

Rate Measurements. The method used was as described previously (Part 1) except that with iso-butyric and pivalic acids, extraction with one extra and two extra 10 ml aliquots of water was necessary for complete separation. All solutions were made up at the temperature of the reaction. At 2% w/v H_2O the germanium carboxylates react to equilibrium and this has been allowed for in calculating first-order rate constants, k_1. All the data given are uncorrected for the small mixing error discussed in Part I. This error

Table I.

Compound	B. Pt.	%C	%H	M.W.	%C	%H	M.W.
$(n\text{–}Pr)_3SiO.COCH_3$	93°/ 9 mm	61.1	11.1	216	61.3	10.4	214
$(n\text{–}Pr)_3SiO.COCH_2Me$	105°/ 9 mm	62.6	11.3	230	62.4	10.8	229
$(n\text{–}Pr)_3SiO.CO.CHMe_2$	112°/13 mm	63.9	11.5	244	64.0	11.2	259
$(n\text{–}Pr)_3SiO.CO.CMe_3$	111°/10 mm	65.1	11.6	258	65.5	11.9	262
$(n.Pr)_3GeO.CO.CH_3$	115°/14 mm	50.6	9.2	261	50.7	9.2	252
$(n\text{–}Pr)_3GeO.CO.CH_2Me$ [a]	111°/10 mm	52.4	9.5	275	51.7	—	254
$(n\text{–}Pr)_3GeO.CO.CHMe_2$	109°/10 mm	54.0	9.7	289	54.0	9.8	275
$(n\text{–}Pr)_3GeO.CO.CMe_3$	120°/10 mm	55.5	9.9	303	56.1	10.0	320

[a] Contaminated with propionic acid. Re-distilled before use.

(*) Part 1: R. H. Prince and R. E. Timms, *Inorg. Chim. Acta, 1*, 129 (1967).

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(2) R. E. Timms, Ph. D. Thesis, Cambridge (1967).

(3) B. N. Dolgov, N. P. Kharitonov, and M. G. Voronkov, *Zhur. Obshchei Khim., 24*, 861 (1964); *Chem. Abs., 49*, 80941 (1955).

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amounts to a decrease in the water concentration of 0.88%, equivalent to a rate decrease of about 4% for the silicon and 4.8% for the germanium acetate hydrolysis in dioxane under the conditions described here.

pK_a Measurements. The pK_a's for the four acids were determined in 2% and 15% H_2O solutions using an indicator method. The most suitable indicator was found to be Methyl red and a commercial sample was recrystallised from toluene before use. Measurements of the optical density were made on buffer solutions containing equal quantities (M/200) of the acid and its sodium salt. The analytical wavelengths used were:

	Acid	Alkaline
15% H_2O:	516 mμ	415 mμ
2% H_2O:	506 mμ	395 mμ

Small corrections to the observed optical densities were made to allow for the absorption of the acid form in the alkaline region and vice versa.

Each acid was freshly distilled from molecular sieve, size 4A, through a 6′ Vigreux column and a small centre fraction used at once.

The pK_a values given in Table II are relative and not absolute thermodynamic values which can only be calculated if the dissociation constant of the indicator in the solvent is known. They are believed to be accurate to within ±.01.

Table II. pK_a Values of carboxylic acids in water/dioxane solutions

Acid	2% H_2O	15% H_2O
Acetic	1.58	0.92
Propionic	1.66	1.11
Iso-butyric	1.73	1.25
Pivalic	1.83	1.51

Results and Discussion

First-order rate constants,* enthalpies, and entropies of activation are given in Table III at 15% H_2O for the silicon carboxylates and at 2% H_2O for the germanium carboxylates. In Table IV the variation of rate with water concentration is given for the silicon series. At 25°C the relative rate ratios are:

	Ac	Pr	i-But	PiV
Si	1	.35	.13	.029
Ge	1	.57	.36	.11

For both metals we observe:

(a) the rate decreases with increasing methyl substitution, more sharply for silicon than germanium;

(b) the relative rate decrease is proportional to the number of methyls substituted, except for the pivalates which are «anomalously» slow;

(c) the value of ΔH* is constant within the experimental error for each element, except for $(n\text{-}Pr)_3SiOPiv$ which is low by 1 kcal though this is probably not a real effect. This confirms that variation of inductive effects is small;

(d) the values of $-\Delta S^*$ increase with methyl substitution though the changes are small relative to the standard deviations. Within the accuracy of the data, changes in ΔS* account for most of the changes in the rate.

Table IV. First-order rate constants for the hydrolysis of $(n\text{-}Pr)_3SiO.COR'$ in dioxane at 25°C (10^4k_1 sec^{-1})

%H_2O	OPr	OiBu	OPiv
15	2.07±.01	.765±.015	.173±.009
20	6.90±.07	2.98 ±.04	.72 ±.03
25	17.2 ±.2	7.50 ±.09	1.82 ±.07
30	42.2 ±.6	16.7 ±.2	4.03 ±.09

Plots of log k_1 against pK_a are shown in the Figure 1. For both the silicon and germanium series excellent straight lines are obtained including even the «anomalous» pivalates. It is also noteworthy that the slopes of the two lines are similar, implying that (a) above is a consequence of the two different elements.**

Since ΔH° for the dissociation of acetic and propionic acids in dioxane is almost constant down to at least 18% H_2O,[1] we may reasonably assume that the pK_a values reflect changes in ΔS° only. Now for the dissociation we may write:

Table III. Hydrolysis of $(n\text{-}Pr)_3MO.CO.CH_{(3-n)}Me_n$ at 25°C in dioxane

M	X	n	10^5k_{25} (sec^{-1})	ΔH* (kcals)	ΔS* (e.u.)
Si at 15% H_2O	OAc	0	59.7 ±1.2	6.3 ±.3	−48 ±1
	OPr	1	20.7 ± .1	6.7 ±.1	−48.9± .5
	OiBu	2	7.65± .15	6.7 ±.2	−50.8± .6
	OPiv	3	1.73± .09	5.25±.06	−58.7± .2
Ge at 2% H_2O	OAc	0	42.8 ±2	3.9 ±.3	−56.5±1
	OPr	1	24.5 ± .9	3.1 ±.5	−60.5±1.5
	OiBu	2	15.3 ± .6	2.9 ±.6	−62 ±2
	OPiv	3	4.9 ± .3	2.5 ±.7	−66 ±2.5

(*) Enthalpies of activation reported in Part. I, ΔH, are in fact activation energies E_a. Since $E_a = \Delta H^* + RT$ true ΔH* and ΔS* may be obtained by substraction of 0.6 kcal and 2.0 e.u. respectively from the values quoted there.

(**) Si-O and Ge-O cleavage has recently been proved to occur for both aryl and alkyl silicon and germanium acetates.[2] Thus the mechanism of reaction is the same for both elements.

$$\Delta S^\circ = S^\circ_{\mathrm{O\bar{A}c(solvd.)}} + S^\circ_{\mathrm{H^+(solvd.)}} - S^\circ_{\mathrm{AcOH(solvd.)}} - S^\circ_{\mathrm{Solvent}}$$

where $S^\circ_{\mathrm{Solvent}}$ is an entropy term for the solvent involved in the dissociation.

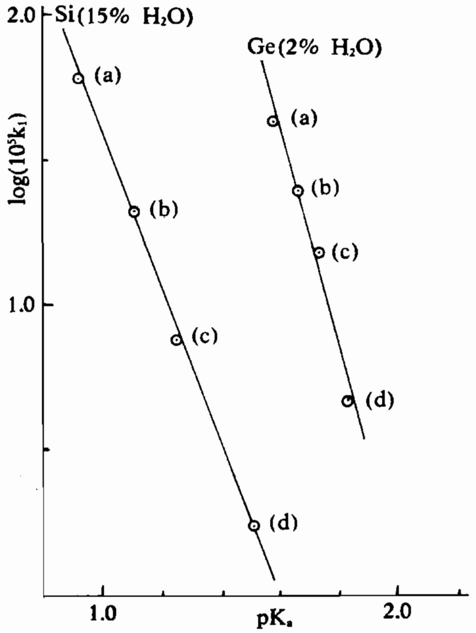

Figure 1. The correlation between hydrolysis rate and pK_a in dioxan/water solutions at 25°C. R in $nPr_3SiO.CO.R$: (a) CH_3 (b) CH_3CH_2 (c) $(CH_3)_2CH$ (d) $(CH_3)_3C$

Similarly, for the hydrolysis:

$$\Delta S^\circ = S^\circ_{\mathrm{t.s.(solvd.)}} - S^\circ_{\mathrm{R_3MOAc(solvd.)}} - S^{\circ\prime}_{\mathrm{Solvent}}$$

Now the solvation of R_3MOAc and acetic acid are likely to be similar in nature and the change in entropy of solvation with water concentration, of similar magnitude. Assuming our $S^\circ_{\mathrm{Solvent}}$ and $S^{\circ\prime}_{\mathrm{Solvent}}$ terms are similar we conclude that

$$S^\circ_{\mathrm{t.s.(solvd.)}} \propto S^\circ_{\mathrm{O\bar{A}c(solvd.)}} + S^\circ_{\mathrm{H^+(solvd.)}}$$

and changes in ΔS^* (and hence the rate since ΔH^* is practically constant) parallel changes in ΔS°. From this analysis, the transition state is similar to a solvated proton and a solvated acetate ion, in good agreement with the conclusion that «considerable ionic stretching has taken place in the transition state placing substantial negative charge on X».[5]

From the data in Table IV and the data for $(n{-}Pr)_3SiOAc$ given in Part I, we have calculated the order in water for each hydrolysis (a least squares method was used and the errors given are standard deviations).

Leaving Group	OAc	OPr	OiBu	OPiV
Order	4.39±.06	4.31±.11	4.43±.09	4.52±.14
Correlation Coefficient	.9995	.9993	.9996	.9991

Thus the order in water is the same for all four leaving groups. It may well be argued that these leaving groups are little different in kind and therefore this result is not surprising. However the hydrolysis of both Ph_3SiNH_2 and $(Me_3Si)_2NH$ in dioxane also show an order of about 4.4.[6] Further, the hydrolysis of tri-organochlorosilanes in acetone proceeds with an order of about 3.5,[7] in agreement with our order for the hydrolysis of $(n{-}Pr)_3SiOAc$ in acetone.

We suggest that to a good approximation the order in water is: (a) independent of the leaving group; (b) dependent on the solvent and the metal.

Most of the solvation by water molecules in the transition state will be centred on the incipient proton and the effect of changing the leaving group on the overall solvation by the water may well be small. Changing the metal will affect the extent of bond-breaking/bond-making and the amount of charge on the incipient proton and leaving group, thus changing the composition of the solvation shell.

There is evidence that the dissociation of acetic acid involves the «freezing» of about four water molecules around the proton:

$$AcOH + 4H_2O \rightleftharpoons AcO^- + H^+(H_2O)_4$$

This value of four, like our order in water, has no precise significance but must represent an average over all the water molecules affected by the proton, however slightly. Thus, although we do not consider that an observed order of 4.4 indicates participation of 4.4 water molecules in the transition state, we do consider that the order bears some relation to the number of water molecules involved. More exactly we postulate that the greater the observed order the greater number of water molecules associated with the transition state.

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