

MECHANISM OF REVERSIBLE CLEAVAGE OF ACETOXYSILANES TO SILOXANES AND ACETANHYDRIDE*

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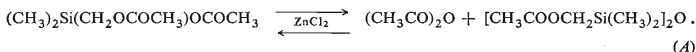
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Rates of the decomposition of acetoxy silanes $XCH_2Si(CH_3)_n(OCOCH_3)_{3-n}$ ($X = H, Cl, OCOCH_3; n = 0-2$) catalysed by $ZnCl_2$ were determined. The extent of interaction of these compounds with the catalyst was estimated by IR spectroscopy as a difference, $\Delta\nu(C=O)$, between $\nu(C=O)$ of the carbonyl group in free acetoxy silane and $\nu(C=O)$ in its complex with $ZnCl_2$. Mechanism of the reaction is discussed.

Linear and cyclic siloxanes are cleaved by carboxylic acid anhydrides in the presence of Lewis acids as well as in their absence to corresponding acyloxysilanes. The preparative utility of this reaction was first demonstrated by Valade¹ on the example of the cleavage of hexamethyldisiloxane with acetanhydride, and later by Snyder and O'Connor² who generalized the course of the reaction. A more detailed study of the cleavage of cyclic siloxanes with acetanhydride was made by Sviridova and coworkers³⁻⁵. The authors found that the catalyst ($FeCl_3, ZnCl_2$) markedly decreases the necessary reaction temperature. On the basis of the analysis of reaction products they suggested reaction scheme involving a set of consecutive reversible reactions. According to the authors the cleavage of siloxanes with acetanhydride proceeds *via* six-membered cyclic "coordination complex" consisting of the siloxane and either acetanhydride or its complex with catalyst (*I*). The higher reactivity of cyclosiloxanes $(CH_3RSiO)_x$ ($R = CF_3CH_2, CH_2=CH, C_2H_5; x = 3, 4, 5$), compared to $[(CH_3)_2SiO]_x$, observed in their catalysed reaction with acetanhydride was accounted for by the influence of the inductive and steric effects of the group R in the transition state of the reaction. Their explanation was based on the assumed irreversibility of the reaction despite of the fact that reversible process was postulated³ in their works as a part of the reaction scheme and reversibility of the cleavage of siloxanes with acetanhydride had been established. Andrianov and coworkers⁶ were the first to report thermal decomposition of $CH_3 \cdot (C_6H_5)Si(OCOCH_3)_2$ to polyorganosiloxanes and acetanhydride. Later, Sviridova and coworkers⁶ have found that α, ω -diacetoxyoligodimethylsiloxanes and dimethyldiacetoxy silane are cleaved in the presence of $FeCl_3$ (ref.⁷), and at the higher temperature also in the absence of this catalyst⁸, to give siloxane oligomers and acetanhydride. However, reactivity differences observed in the series $CH_3COO[Si(CH_3)_2O]_xCOCH_3$ ($x = 2-5$) were directly related to differences in the amount of these compounds in the reaction mixture after the "completion" of the reaction, regardless of the complex character of the cleavage. We have recently observed⁹ that the (acetoxy methyl)methyl(acetoxy)silanes $CH_3COOCH_2Si(OCOCH_3)_n(CH_3)_{3-n}$ ($n =$

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= 1-3) are cleaved in the presence of $ZnCl_2$ to give acetanhydride and polysiloxanes, the product of one of these reactions, $[CH_3COOCH_2Si(CH_3)_2]_2O$, reacts with acetanhydride in the presence of $ZnCl_2$ at an elevated temperature to form $CH_3COOCH_2Si(CH_3)_2OCOCH_3$. The course of reaction (A) can be affected by both an excess of acetanhydride, and its removal (by distillation) from the reaction mixture.



A similar effect of the removal of acetanhydride was observed also by Sviridova and coworkers⁷ in the cleavage of $(CH_3)_2Si(OCOCH_3)_2$. The reversible system $R_3SiOCOCH_3 \rightleftharpoons (CH_3CO)_2O + (R_3Si)_2O$ was kinetically studied only by Andrianov and coworkers⁶. The authors used, however, not quite adequate method, following the decrease of the total concentration of the acetoxy groups bonded to silicon in dependence on time in the investigation of thermal cleavage of $C_6H_5 \cdot (CH_3)_2Si(OCOCH_3)_2$.

In this work the cleavage of acetoxy silanes catalysed by $ZnCl_2$ was studied, using the compounds $XCH_2(CH_3)_nSi(OCOCH_3)_{3-n}$ ($X = H, Cl, CH_3COO$; $n = 0-2$) for which the rates of their decomposition were determined and the electron donor ability of their carbonyl group in the interaction with the catalyst was estimated.

EXPERIMENTAL

Methylacetoxy silanes $(CH_3)_nSi(OCOCH_3)_{4-n}$ ($n = 1-3$) were prepared by reaction of appropriate methylchlorosilanes $(CH_3)_nSiCl_{4-n}$ (freshly distilled with dry pyridine) with acetanhydride in a nitrogen atmosphere. The reaction mixture was refluxed for 20 h, the acetyl chloride was distilled off, and the methylacetoxy silanes were obtained in high yields (yield % for $n = 1, 78$; $n = 2, 83$; $n = 3, 76$) by fractional distillation. The purity of these and other acetoxy silanes prepared, except $CH_3COOCH_2Si(OCOCH_3)$, was checked by g.l.c. (a glass column, 1 m long, filled with 18.5% dinonylphthalate on Chromosorb W). Trimethylacetoxy silane, b.p. 103°C (ref.¹⁰ b.p. 102-103°C). For $SiC_5H_{12}O_2$ (132.2) found: 20.85% Si, m.w. 133; calculated: 21.24% Si. Dimethyldiacetoxy silane, b.p. 164.5°C (ref.¹¹ b.p. 165°C). For $SiC_6H_{12}O_4$ (176.3) found: 15.90% Si, m.w. 176; calculated: 15.94% Si. Methyltriacetoxy silane, b.p. 89°C/3 Torr (ref.¹² b.p. 110-112°C/17 Torr). For $SiC_7H_{12}O_6$ (220.3) found: 12.77% Si, m.w. 223; calculated: 12.75% Si.

Preparation of the acetoxy silanes $XCH_2Si(CH_3)_n(OCOCH_3)_{3-n}$ ($X = Cl, OCOCH_3$; $n = 0-2$) was reported earlier¹³.

Complexes of acetoxy silanes with $ZnCl_2$ were prepared under nitrogen. The complexes $(CH_3)_3 \cdot SiOCOCH_3 \cdot ZnCl_2$, $(CH_3)_2Si(OCOCH_3)_2 \cdot ZnCl_2$, and $ClCH_2Si(CH_3)_2OCOCH_3 \cdot ZnCl_2$ were freed of the excess acetoxy silane by filtration and washing several times with dry benzene, and traces of the benzene and the acetoxy silane were removed by drying the samples in a vacuum at room temperature. The analysis of the content of Cl and Zn agreed with the above mentioned structures. The other complexes were difficult to isolate in the pure state, due to nonquantitative evaporation of starting acetoxy silanes, which were of higher molecular weight, at room temperature. Even the use of a high vacuum did not avoid heating the samples at an elevated temperature during evaporation, which caused the cleavage of acetoxy silane to acetanhydride and the siloxane. Saturated solutions of $ZnCl_2$ in the acetoxy silanes $XCH_2Si(OCOCH_3)_3$ ($X = H, Cl, OCOCH_3$) decompose during standing for several days at room temperature to a mixture of siloxanes and acetanhydride.

Molecular weights of acetoxysilanes $(\text{CH}_3)_n\text{Si}(\text{OCOCH}_3)_{4-n}$ ($n = 1-3$) and $\text{XCH}_2\text{Si}(\text{CH}_3)_n \cdot (\text{OCOCH}_3)_{3-n}$ (for $\text{X} = \text{OCOCH}_3$, $n = 1, 2$; for $\text{X} = \text{Cl}$, $n = 0-2$) were determined cryoscopically with a Knauer instrument in dry rectified benzene. With all the compounds, the experimental data agreed with the values calculated for monomer; maximum deviations did not exceed 2% of the total value. The molecular weight of $\text{CH}_3\text{COOCH}_2\text{Si}(\text{OCOCH}_3)_3$ could not be measured due to sparse solubility of this compound.

Rates of the cleavage of the acetoxysilanes were measured under identical conditions: the same concentration of all the components of the reaction system, the same temperature, and only to 5% conversion. A reaction flask was always charged with the following amounts of acetoxysilane (10 ± 0.1 mmol), anhydrous ZnCl_2 (catalyst, $6.2 \pm 0.1 \times 10^{-2}$ mmol), and ethylbenzene (1.0 ± 0.02 mmol). Then it was placed into a temperature-controlled oil bath which was maintained at a temperature of 150°C . At fixed time intervals small amounts of the reaction mixture were removed, immediately cooled to room temperature and analysed by g.l.c. (a glass column (1 m long) filled with 18.5% dinonyl phthalate on Chromosorb W, 90°C oven temperature, hydrogen as a carrier gas). The weight content of acetoxysilane was determined by using ethylbenzene as an internal standard. The rate of decomposition of acetoxysilane was determined as the rate of the formation of acetanhydride from the slope of the linear time-dependence (at least 6 experimental points) of the amount of acetanhydride in the reaction mixture. The following values (in mol/min) were obtained, which are the average of two measurements: $(\text{CH}_3)_3\text{SiOCOCH}_3$ $1.87 \pm 0.01 \times 10^{-7}$; $(\text{CH}_3)_2\text{Si}(\text{OCOCH}_3)_2$ $1.36 \pm 0.03 \times 10^{-6}$; $\text{CH}_3\text{Si}(\text{OCOCH}_3)_3$ $4.70 \pm 0.04 \times 10^{-5}$; $\text{CH}_3\text{COOCH}_2\text{Si}(\text{CH}_3)_2\text{OCOCH}_3$ $1.86 \pm 0.01 \times 10^{-7}$; $\text{CH}_3\text{COOCH}_2\text{SiCH}_3 \cdot (\text{OCOCH}_3)_2$ $1.59 \pm 0.04 \times 10^{-6}$; $\text{CH}_3\text{COOCH}_2\text{Si}(\text{OCOCH}_3)_3$ $6.67 \pm 0.06 \times 10^{-5}$; $\text{ClCH}_2\text{Si} \cdot (\text{CH}_3)_2\text{OCOCH}_3$ $1.58 \pm 0.05 \times 10^{-6}$; $\text{ClCH}_2\text{SiCH}_3(\text{OCOCH}_3)_2$ $3.44 \pm 0.12 \times 10^{-5}$; $\text{ClCH}_2 \cdot \text{Si}(\text{OCOCH}_3)_3$ $2.84 \pm 0.80 \times 10^{-4}$. Further discussed are decomposition rates related to the rate of the decomposition of $(\text{CH}_3)_3\text{SiOCOCH}_3$.

Infrared spectra of the model compounds were recorded with a double-beam Zeiss, Model UR-20, spectrophotometer, both in subst., and in solution (CCl_4 , CS_2). The spectra of saturated solutions of ZnCl_2 in acetoxysilanes were measured as capillary layer between KBr plates, the spectra of c. 7% solutions in $\text{CCl}_4(\text{CS}_2)$ were measured in cells thick 0.01 cm. The spectra of the complexes of acetoxysilanes with ZnCl_2 (insoluble in CCl_4) were measured as Nujol or Florube mulls.

RESULTS AND DISCUSSION

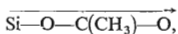
Before reliable mechanism of catalysed cleavage of acetoxysilanes to acetanhydride and siloxanes can be suggested, the character of interaction of acetoxysilanes with the catalyst, ZnCl_2 , should be elucidated. For that reason IR spectra of the complexes of acetoxysilanes (acetanhydride) with ZnCl_2 , or the spectra of saturated solutions of ZnCl_2 with acetoxysilanes in $\text{CCl}_4(\text{CS}_2)$, were measured with the aim to ascertain which oxygen atom of acetoxysilanes interacts with the catalyst. In the spectra of highly viscous saturated ZnCl_2 solutions in acetoxysilanes the following changes were found to occur in the region of the $\text{C}=\text{O}$ and $(\text{Si})-\text{O}-\text{C}$ group absorptions: the absorption maximum due to $\nu(\text{C}=\text{O})$ is usually shifted to lower wavenumbers; in some cases only broadening of this band on the lower wavenumber side is observed,

sometimes an additional band appears at the lower wavenumber side of the original band. On the contrary, the absorption band which is characteristic of the $(\text{Si}-)\text{—O—C}$ grouping is shifted to higher wavenumbers. Similar shifts of the $\nu(\text{C=O})$ and $\nu(\text{SiOC})$ bands, relative to those of the free acetoxy silanes, were observed also in the spectra of prepared solid complexes of acetoxy silanes with ZnCl_2 . In accordance with the work¹⁴, these changes can be taken as evidence for the interaction of ZnCl_2 with the carbonyl group oxygen. The possibility that the decrease of $\nu(\text{C=O})$ is due to self-association of acetoxy silanes can be excluded, since the patterns of the spectra of studied compounds measured in solutions (CCl_4 , CS_2) were similar to those obtained in their absence. IR spectroscopy can be used to evaluate the ability of the carbonyl group of acetoxy silanes to act as an electron donor in the interaction of these compounds with ZnCl_2 , since the difference between the wavenumber of $\nu(\text{C=O})$ of some carbonyl compounds and that of the $\nu(\text{C=O})$ of their complexes with some metal halogenides, $\Delta\nu(\text{C=O})$, can be taken as a measure of the interaction of the carbonyl group with the metal (cf.^{15,16}).

The IR spectrum of a solution of ZnCl_2 in $(\text{CH}_3)_3\text{SiOCOCCH}_3$ is identical with the spectrum of trimethylacetoxy silane ($\nu(\text{C=O})$, 1725 cm^{-1} , $\nu(\text{COSi})$ 1267 cm^{-1}), since the complex formed, $(\text{CH}_3)_3\text{SiOCOCCH}_3 \cdot \text{ZnCl}_2$, is practically insoluble in the silane. The spectrum of a suspension of this complex in Florube shows absorption bands at 1622 and 1346 cm^{-1} . The IR spectrum of a solution of ZnCl_2 in $(\text{CH}_3)_2 \cdot \text{Si}(\text{OCOCCH}_3)_2$ shows besides the bands characteristic of dimethyldiacetoxy silane ($\nu(\text{C=O})$ 1732 cm^{-1} , $\nu(\text{COSi})$ 1238 cm^{-1}), also additional bands at 1636 and 1613 cm^{-1} , and a doublet (1334 and 1343 cm^{-1}). Only these bands were observed in the spectrum of a suspension of the complex $(\text{CH}_3)_2\text{Si}(\text{OCOCCH}_3)_2 \cdot \text{ZnCl}_2$ in Nujol. In the spectrum of a solution of ZnCl_2 in $\text{CH}_3\text{Si}(\text{OCOCCH}_3)_3$ (for $\text{CH}_3\text{Si}(\text{OCOCCH}_3)_3$, $\nu(\text{C=O})$ 1745 cm^{-1} , $\nu(\text{COSi})$ 1223 cm^{-1}) the $\nu(\text{C=O})$ band is broadened on the lower wavenumber side. When the sample was allowed to stand for 1 to 4 days, an additional band at 1630 cm^{-1} appeared (its intensity increases with time), and the maximum of the $\nu(\text{COSi})$ band shifted to 1243 cm^{-1} . The increasing intensity of the 1630 cm^{-1} band with time may be explained by slow dissolving of ZnCl_2 in $\text{CH}_3\text{Si}(\text{OCOCCH}_3)_3$, rather than by slow reaction of ZnCl_2 with $\text{CH}_3\text{Si}(\text{OCOCCH}_3)_3$, during which ZnCl_2 and acetoxy silane exchange Cl and acetoxy group, since characteristic bands of the products of this reaction ($\nu(\text{Si—Cl})$, $\nu(\text{C=O})$ for $\text{Zn}(\text{OCOCCH}_3)_2$ 1548 cm^{-1}) are absent in the spectrum. Simultaneous occurrence of the $\nu(\text{C=O})$ band of acetylhydride and the absorption band of its complex with ZnCl_2 , (1567 cm^{-1} , see later) further indicates that the acetoxy silane undergoes cleavage reaction.

From the experimental values of $\Delta\nu(\text{C=O})$ for the series $(\text{CH}_3)_n\text{Si}(\text{OCOCCH}_3)_{4-n}$ ($n = 1, 2, 3$; $\nu(\text{C=O})$ (cm^{-1}) = 115, 107, 103) it may be concluded that the ability of these acetoxy silanes to interact by their carbonyl group with ZnCl_2 increases with increasing number of the acetoxy groups. With regard to the fact that increasing number of the acetoxy groups brings about an increase in the $\nu(\text{C=O})$ wavenumber,

one can conclude that the factor determining formation of the complex of acetoxysilanes with ZnCl_2 is the polarisability of acetoxy group in the direction



which should be increased by increasing number of the acetoxy groups.

The rate of the cleavage of chloromethyl(acetoxy)methylsilanes is markedly higher than the rate of analogous reaction of methylacetoxysilanes. In order to estimate the effect of the chlorine atom of these compounds on their interaction with ZnCl_2 , the spectra of $\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{OCOCH}_3$ and $\text{ClCH}_2\text{Si}(\text{CH}_3)(\text{OCOCH}_3)_2$ were measured and compared with the spectra of solid $\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{OCOCH}_3 \cdot \text{ZnCl}_2$ and the solution of ZnCl_2 in $\text{ClCH}_2\text{Si}(\text{CH}_3)(\text{OCOCH}_3)_2$, respectively. The spectra of a solution of ZnCl_2 in $\text{ClCH}_2\text{Si}(\text{OCOCH}_3)_3$ and the spectrum of $\text{ClCH}_2\text{Si}(\text{OCOCH}_3)_3$ could not be measured, since in the solution of ZnCl_2 in $\text{ClCH}_2\text{Si}(\text{OCOCH}_3)_3$ fast decomposition of the acetoxysilane to acetanhydride and acetylchloride was taking place already at room temperature. The IR spectrum of a suspension of the complex $\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{OCOCH}_3 \cdot \text{ZnCl}_2$ in Florube (for free acetoxysilane $\nu(\text{C}=\text{O})$ 1725 cm^{-1} , $\nu(\text{COSi})$ 1258 cm^{-1} overlapped with $\delta(\text{Si}-\text{CH}_3)$ exhibits absorption bands at 1625 and 1350 cm^{-1} . When the solution of ZnCl_2 in $\text{ClCH}_2\text{Si}(\text{CH}_3)(\text{OCOCH}_3)_2$ (for acetoxysilane $\nu(\text{C}=\text{O})$ 1715 , 1730 , 1742 cm^{-1} , $\nu(\text{COSi})$ 1235 cm^{-1}) was allowed to stand for some time an additional absorption band at 1635 cm^{-1} has appeared, and the $\nu(\text{COSi})$ band was shifted towards higher wavenumbers; the latter band overlapped with the $\delta(\text{Si}-\text{CH}_3)$ band. Other bands observed were those corresponding to acetyl chloride ($\nu(\text{C}=\text{O})$ 1805 cm^{-1}) and acetanhydride ($\nu(\text{C}=\text{O})$ 1825 cm^{-1}) and a band at 1567 cm^{-1} which was assigned to the complex of acetanhydride with ZnCl_2 , since the complex of ZnCl_2 with acetyl chloride is characterized by the band at 1620 cm^{-1} .

It was of interest to find which type of the acetoxy group in acetoxysilanes $(\text{CH}_3)_2\text{Si}(\text{OCOCH}_3)\text{CH}_2\text{OCOCH}_3$ and $\text{CH}_3\text{Si}(\text{OCOCH}_3)_2\text{CH}_2\text{OCOCH}_3$ is involved in interaction with ZnCl_2 . For this purpose we measured the spectra of solutions of ZnCl_2 in these compounds and in $(\text{CH}_3)_3\text{SiCH}_2\text{OCOCH}_3$ ($\nu(\text{C}=\text{O})$ 1740 cm^{-1}). In the spectrum of the solution of ZnCl_2 in trimethylacetoxymethylsilane the attention has been paid only to changes in the region of the carbonyl absorption, because of very complicated structure of the bands in the $1200-1400 \text{ cm}^{-1}$ region. The intensity of the $\nu(\text{C}=\text{O})$ band at 1740 cm^{-1} strongly decreased and a new, broad band has appeared at 1630 cm^{-1} . In the spectra of solutions of both acetoxymethyl(acetoxy)silanes there occurs a broadening of the bands corresponding to the $\text{Si}-\text{O}-\text{C}$ arrangement (with distinct shift to higher wavenumber), and the $\nu(\text{C}=\text{O})$ band maxima are shifted towards lower wavenumbers. The spectrum of a solution of ZnCl_2 in $(\text{CH}_3)_2\text{Si}(\text{OCOCH}_3)\text{CH}_2\text{OCOCH}_3$ showed an additional band at 1577 cm^{-1} and a shoulder at 1660 cm^{-1} . These data are difficult to interpret. However, it seems likely that the extraordinarily high value of $\Delta\nu(\text{C}=\text{O})$ in the case of $(\text{CH}_3)_2\text{Si}$.

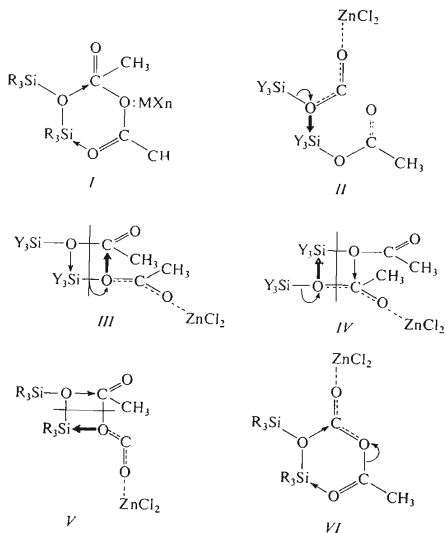
$.(OCOCH_3)CH_2OCOCH_3$ (152 cm^{-1} , resp. 166 cm^{-1}) may be due to an intramolecular interaction of both types of acetoxy groups, which results in an increase of the electron donor ability of one and in a decrease of the electron ability of the other group.

In the spectrum of solution of $ZnCl_2$ in acetanhydride there occurs after one to two days a broadening of the bands in the carbonyl region, the shift of their maxima to lower wavenumbers, a broadening of the $\nu(COC)$ bands and the shift of their maxima to higher wavenumbers. The spectrum shows also an additional band at 1567 cm^{-1} ; its intensity increases with time. This can be also explained rather by slow dissolution of $ZnCl_2$ in acetanhydride, than by slow reaction between these two compounds to give acetyl chloride and zinc acetate, since the absorption band of $Zn.(OCOCH_3)_2$ at 1548 cm^{-1} is absent in the spectrum of acetanhydride solution of $ZnCl_2$. This indicates that acetanhydride, too, interacts with $ZnCl_2$ by its carbonyl group, and not by its ether oxygen, since the latter interaction should shift ($\nu C=O$) bands to higher wavenumbers, contrary to the observed case.

There is no reason why the mechanism of catalysed decomposition of acetoxy-silanes could not be regarded to be general for all acetoxy-silanes. It may be assumed that transition state of this reaction is formed by bimolecular interaction of the molecule of acetoxy-silane with the nucleophilic complex containing acetoxy-silane and the catalyst (further called only complex). As from the spectroscopic data it follows that in the complex the catalyst is bonded to the carbonyl oxygen of acetoxy-silane, it can further be assumed that in the course of nucleophilic attack the complex acquires ion-pair character, $Y_3Si^{\delta+} \dots /O=C(CH_3)=O \dots ZnCl_2/\delta^-$ ($Y = OCOCH_3$ or XCH_2 ; $X = H, Cl, CH_3COO$), and its nucleophilicity is enhanced by stabilisation of its positively charged component by polarisable acetoxy groups. The increase of relative rates of catalysed decomposition of acetoxy-silanes in the order



is consistent with this assumption. On the basis of this assumption it may further be assumed that in the initial stage of the formation of the transition state the activated oxygen of the $Si-O-C$ bond of the complex approaches the molecule of acetoxy-silane which, of the two cyclic transition states, the four-membered and the six-membered one, prefers the former. Regardless of the higher activation entropy of the six-membered transition state, the tendency of the complex to acquire ion-pair character particularly *via* this type results in the cleavage of the $Si-O$ bond, not in the formation of siloxane *II*. According to the type of the center of nucleophilic attack in the molecule of acetoxy-silane, it is possible to distinguish between the two four-membered transition states *III* and *IV*. As increasing number of polarisable acetoxy groups in the molecule of acetoxy-silane should, moreover, lead to much higher increase of electron acceptor ability of the silicon (than of the carbonyl carbon)



of acetoxysilane during formation of the transition state, with respect to the observed reactivity order the transition state *IV* seems to be more likely. In the ground state the electronic shielding of the silicon apparently increases with increasing number of acetoxy groups, since the wavenumber of the $\nu(\text{C}=\text{O})$ band¹⁷ of the silanes $(\text{CH}_3)_n\text{Si}(\text{OCOCH}_3)_{4-n}$ increases with decreasing n . The fact that increasing number of acetoxy groups increases somewhat also the strength of their interaction with the catalyst affects the reaction rate probably less significantly.

From comparison of analogous acetoxysilanes (with the same number of acetoxy groups at silicon) of the three series ($X = \text{H}, \text{Cl}, \text{CH}_3\text{COO}$) it follows that the substitution of CH_3 group of $(\text{CH}_3)_n\text{Si}(\text{OCOCH}_3)$ for Cl — or CH_3COO — group increases the relative rate of the decomposition the greater, the higher is the number of the acetoxy groups attached to silicon:

$\text{CH}_3\text{COOCH}_2\text{Si}(\text{CH}_3)_2\text{OCOCH}_3$	1.0	$\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{OCOCH}_3$	8.4
$\text{CH}_3\text{COOCH}_2\text{SiCH}_3(\text{OCOCH}_3)_2$	8.5	$\text{ClCH}_2\text{SiCH}_3(\text{OCOCH}_3)_2$	184
$\text{CH}_3\text{COOCH}_2\text{Si}(\text{OCOCH}_3)_3$	357	$\text{ClCH}_2\text{Si}(\text{OCOCH}_3)_3$	1 518

The above groups could both contribute to stabilisation of ion-pair character of the complex (α -effect) and increase the electron-accepting ability of the silicon of acetoxy-

silane. However, when compared to the other two series, the chloromethyl(methyl)-acetoxysilanes are decomposed in more complex way, since reaction products contain besides acetanhydride also acetyl chloride, which is present already at 5% conversion of the starting compound. As it was shown in the introduction, the catalytic decomposition of acetoxysilanes is reversible. The transition state of catalytic cleavage of siloxanes with acetanhydride was assumed by the Russian authors^{3,5} to be six-membered cyclic species *I* which is formed by interaction of siloxane with the complex containing acetanhydride coordinated to the catalyst (further only complex). In this complex the catalyst (FeCl_3 , ZnCl_2) is bonded to the C—O—C oxygen of acetanhydride. An interaction of this oxygen with the catalyst should decrease the nucleophilicity of the carbonyl oxygen of the complex which attacks the silicon of siloxane. In such a case the formation of the transition state would be more difficult than in the case of uncatalysed reaction. In harmony with the finding that ZnCl_2 coordinates to the oxygen of the carbonyl group of acetanhydride, it may be assumed that the transition state of the catalysed cleavage of siloxanes with acetanhydride is best represented by structure *V*. In six-membered cyclic transition state, which would be formed by interaction of the complex in which the catalyst is bonded to the carbonyl (structure *VI*), the metal halogenide would exert inhibiting effect. Moreover, the decomposition of such a transition state would not result in the formation of the expected products, acetoxysilanes.

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