Kinetic Studies for the Acyloxy Exchange Reactions of Acyloxytrimethylsilanes with Carboxylic Acids

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(Received September 22, 1978)

The acyloxy exchange reactions of acyloxysilane with carboxylic acids have been studied kinetically. The rate of reaction has been found to proceed faster with a stronger attacking acid and more basic leaving acyloxy group. The rate was markedly accelerated by the addition of base. The steric effect due to substituents on the silicon atom and hydrogen-deuterium kinetic isotope effects have been examined. A mechanism involving the 5-coordination of the silicon atom prior to the rate-determining proton transfer has been suggested.

A number of organic synthesis recently developed have included the silylation-desilylation reactions of functional groups.[1] An advantage of this reaction is the selectivity which has been demonstrated by the monothioketalization of dicarbonyl compounds[2] and the kinetic study of the silylations of hydroxyl groups.[3] In connection with this, the greater the knowledge of the mechanism of silylation or kinetics may make the reaction more applicable to organic synthesis. Thus, a kinetic study of the proton-silyl exchange reaction *i.e.*, the acyloxy exchange reaction of acyloxysilanes with carboxylic acids as one of the most simple model reactions for the trans-silylation reaction has been carried out. The aims has been to ascertain the kinetics of the exchange reaction and to clarify the mechanism.

Results and Discussion

The acyloxy exchange reaction was found to proceed almost quantitatively if the entering carboxylic acid was stronger than the leaving acid. The rate of

$$\mathrm{RCOOSiR'_3 + R''COOH \longrightarrow R''COOSiR'_3 + RCOOH}$$
$$\mathrm{p}K_\mathrm{a}\ \mathrm{RCOOH > R''COOH}$$

acyloxy exchange for acetoxytrimethylsilane with two equivalents of formic acid in chloroform-*d* was measured by monitoring the decrease ^{1}H NMR trimethyl signal of the starting acetoxysilane (δ 0.28 ppm) and the increase in the product *i.e.*, formyloxytrimethylsilane (δ 0.32 ppm): the rate constant found to be second order. Under the same conditions, the rate of the reverse reaction was too small to affect the kinetics since the exchange was found to proceed almost quantitatively and the reverse reaction of formyloxytrimethylsilane with acetic acid gave no acetoxytrimethylsilane. The rate of reaction with other carboxylic acids was similarly measured and the kinetic results are given in Table 1. The reaction was found to proceed faster with a stronger acid and the rates correlated well with the σ^* parameters with a ρ^* value $+1.10$ as shown in Fig. 1 formic acid was the exception. The deviation in rate for the reaction of formic acid may be ascribed to the release of the steric crowding change in the acyloxy moiety from the acetoxy to the formyloxy group. The effect of the leaving acyloxy groups of acyloxytrimethylsilanes reversed the rates of exchange *i.e.*, in the trimethylsilylations of trifluoroacetic acid by various acyloxytrimethylsilanes, the rates decreased in the order acetoxy, chloroacetoxy, and dichloroace-

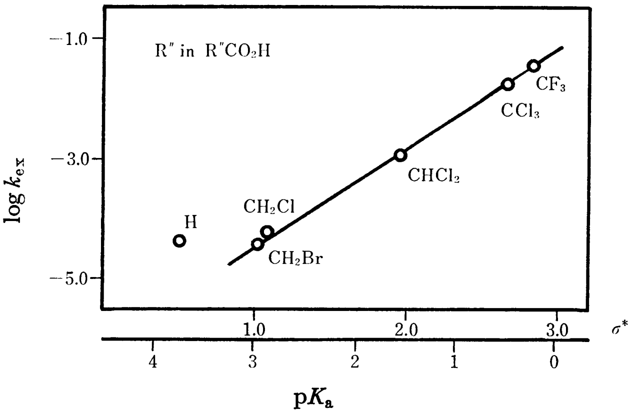


Fig. 1. Plot of the acyloxy exchange rate of acetoxytrimethylsilane *vs.* acid strength.

Table 1. Rate constants for acyloxy exchange reactions of acetoxytrimethylsilane with carboxylic acids in $\mathrm{CDCl_3}$[a]

R'' in R''COOH	Temp °C	k_2 l mol^{-1} s^{-1}	ΔH^* kcal/mol	ΔS^* e.u.
H	34	1.32×10^{-4}		
$\mathrm{CH_2Br}$	34	4.00×10^{-5}		
$\mathrm{CH_2Cl}$	27	5.30×10^{-5}		
$\mathrm{CH_2Cl}$	34	6.30×10^{-5}		
$\mathrm{CH_2Cl}$	37	1.00×10^{-4}	11.2	−40.8
$\mathrm{CH_2Cl}$	45	1.70×10^{-4}		
$\mathrm{CHCl_2}$	34	1.30×10^{-3}		
$\mathrm{CCl_3}$	34	$1.8\ \times10^{-2}$		
$\mathrm{CF_3}$	34	$4.0\ \times10^{-2}$		

a) Concentrations are: $\mathrm{Me_3SiOAc}=0.58$ M, R''COOH $=1.21$ M.

Table 2. Rate constants for the reaction of acyloxytrimethylsilane with carboxylic acids in $\mathrm{CDCl_3}$ at 34°C[a]

R'' in the used R''COOH	k_2, l mol^{-1} s^{-1} R in the starting $\mathrm{RCOOSiMe_3}$		
	$\mathrm{CH_3}$	$\mathrm{CH_2Cl}$	$\mathrm{CHCl_2}$
$\mathrm{CF_3}$	2.11×10^{-2}	3.40×10^{-3}	9.22×10^{-4}
$\mathrm{CCl_3}$	1.60×10^{-2}	2.58×10^{-3}	6.61×10^{-4}
$\mathrm{CHCl_2}$	0.13×10^{-2}	0.21×10^{-3}	

a) Concentrations are: $\mathrm{Me_3SiOCOR}=0.57$M, R''COOH $=1.48$ M.

Table 3. Rate constants for the reaction of substituted acetoxysilane with $CHCl_2COOH$ and $CHCl_2COOD$[a] in $CDCl_3$ at 34 °C[b]

	R′ in the starting $Me_2R'SiOAc$			
	CH_3	C_2H_5	$C_6H_5CH_2$	C_6H_5
k_2 (H) $l\,mol^{-1}\,s^{-1}$	1.3×10^{-3}	6.9×10^{-4}	5.4×10^{-4}	4.9×10^{-4}
k_2 (D) $l\,mol^{-1}\,s^{-1}$	8.0×10^{-4}	4.3×10^{-4}	3.3×10^{-4}	
k_H/k_D	1.6	1.6	1.7	

a) 90% D content. b) Concentrations are: $Me_2R'SiOAc=0.70\,M$, $CHCl_2COOH(D)=1.20\,M$.

Table 4. Effect of base on the rate of reaction of acetoxytrimethylsilane with $CH_2ClCOOH$ in $CDCl_3$ at 34 °C[a]

Base	Mole ratio Base/Silane	k_2 $l\,mol^{-1}\,s^{-1}$
None	0	6.30×10^{-5}
Et_3N	0.2	very fast
C_5H_5N	0.2	4.7×10^{-2}

a) Concentrations are: $Me_3SiOAc=0.58\,M$, $CH_2ClCOOH=1.21\,M$.

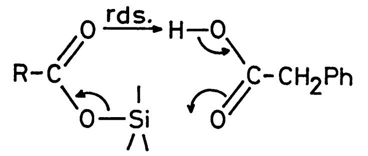
toxytrimethylsilanes as the starting materials; similar results were obtained for the silylations of the dichloro and trichloroacetic acids. The results are given in Table 2 and together with the negative assertion to support free silicenium ion[4)] would rule out prior ionization of the substrate to exchange acyloxy group.

The effect of the silyl-substituent on the rate of the exchange was examined and it was found that the rate was depressed by the bulky substituent on the silicon atom as observed in the acyloxy exchange reactions of acetoxytrimethyl-, ethyldimethyl, benzyldimethyl, and dimethylphenylsilanes with dichloroacetic acid. The results together with the hydrogen-deuterium kinetic isotope effect observed in the exchange reactions are given in Table 3. The small isotope effect is in accordance with the rate determining proton transfer reaction of the carboxylic acid by a intramolecular cyclic process.[5)]

Recently, Pola *et al.* reported the equilibrium constants of proton-silyl exchange *i.e.*, for the acyloxy exchange reaction between acyloxytrimethylsilanes and phenylacetic acid in carbon tetrachloride.[6)] It was

$$RCOOSiMe_3 + PhCH_2COOH \overset{K}{\rightleftharpoons} RCOOH + PhCH_2COOSiMe_3$$

reported that the silylating ability of acyloxysilanes decreased with increasing electronegativity of the R group in the acyloxy moiety and the equilibrium constants were successfully correlated with the σ^* constants of the R groups giving a ρ^* value of −0.57. On the basis of these results, it was suggested that a transition state, similar to the carboxylic acid dimer existed in which proton transfer was the rate determining step. Similar results have been observed in the present kinetic study *i.e.*, the less electronegative acyloxy groups of the starting acyloxysilanes facilitate exchange (Table 2), reactions with stronger acids proceed faster (Fig. 1) and the positive kinetic isotope effect is in accordance with the rate determining proton transfer. The base catalysis of the reaction, however, as shown in Table 4, suggests a nucleophilic attack on the silicon atom which occurrs before or at the rate determining step. Since a kinetic isotope effect was observed, nucleophilic attack would be expected to occurr before the rate determining step.



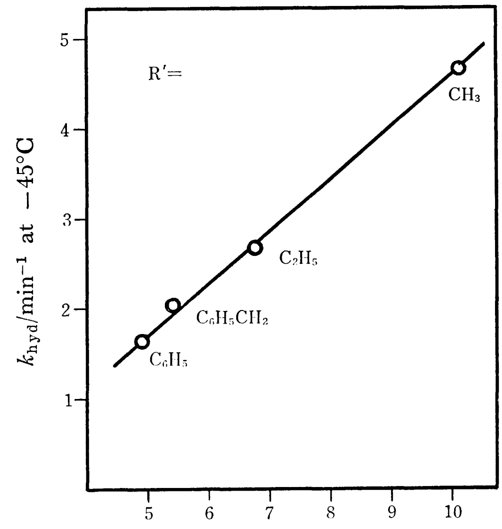
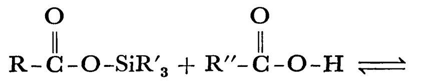
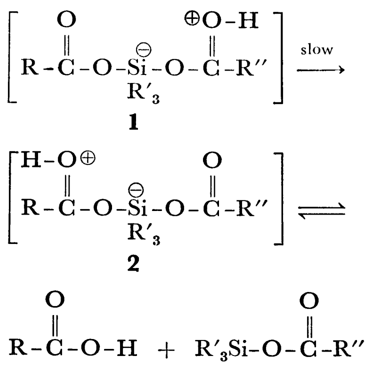


Fig. 2. Plot of rates of hydrolyses of $Me_2R'SiCl$ *vs.* rates of exchange reactions of $Me_2R'SiOAc$ with $CHCl_2CO_2H$.

Nucleophlic attack finds further support when the results given in Table 3 are compared with the rates of the hydrolyses of the corresponding chlorosilanes which proceed *via* a 5-coordinated intermediate.[7)] As shown in Fig. 2, the rates of acyloxy exchange correlate linearly to the hydrolyses of the corresponding chlorosilanes. This suggests that the two reactions are very similar in mechanism *i.e.*, 5-coordination of the silicon atom. The large negative entropy value observed in the present study is also in agreement with a 5-coordination mechanism.[8)]

Based on the above considerations, the most plausible mechanism for acyloxy exchange is as follows:


$$R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}SiR'_3 + R''\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}H \rightleftharpoons$$



$$\left[\mathrm{R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}\underset{R'_3}{\overset{\ominus}{Si}}{-}O{-}\overset{\displaystyle \oplus O{-}H}{\overset{\|}{C}}{-}R''}\right] \xrightarrow{\text{slow}}$$

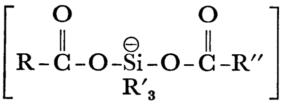
1

$$\left[\mathrm{R{-}\overset{\displaystyle H{-}O\oplus}{\overset{\|}{C}}{-}O{-}\underset{R'_3}{\overset{\ominus}{Si}}{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R''}\right] \rightleftharpoons$$

2

$$\mathrm{R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}H} + \mathrm{R'_3Si{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R''}$$

Nucleophilic attack of carboxylic acid on the substrate gives a 5-coordinated intermediate (**1**) which transfers a proton (the rate determining step) to give a second intermediate (**2**). The second intermediate collapses into the products. The latter intermediate (**2**) is expected to be more stable than **1** since the proton is bonded to a more basic site. The reverse reaction, for example, giving acetoxytrimethylsilane from formyloxytrimethylsilane and acetic acid would energetically unfavorable since an unstable intermediate would have to be formed from a stable intermediate. In the base catalyzed reaction, an intermediate **3** would be formed



$$\left[\mathrm{R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}\underset{R'_3}{\overset{\ominus}{Si}}{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R''}\right]$$

3

by the attack of a stronger nucleophile, the carboxylate ion. Thus the reaction is enhanced by the addition of base.

Experimental

Materials. Acyloxytrimethylsilanes were prepared from chlorotrimethylsilane and silver or sodium carboxylates.[9] Me$_3$SiOAc; bp 102 °C, (lit,[10] 103.3—105 °C), Me$_3$SiOCOCH$_2$Cl; bp 124—126 °C, (lit,[11] 159 °C), NMR δ (ppm) 0.32 s (9H) 4.02 s (2H), Me$_3$SiOCOCHCl$_2$; bp 80 °C/30 mmHg (133.322Pa), (lit,[12] 63 °C/14 mmHg). Chloro(ethyldimethyl), (benzyldimethyl), and (dimethylphenyl)silanes were prepared from dichlorodimethylsilane and the appropriate Grignard reagent.[7,13] The reactions of the chlorosilanes with sodium acetate gave the corresponding acetoxysilanes. Me$_2$(Et)SiOAC; bp 115 °C, (lit,[14] 125—126 °C), Me$_2$(Ph)SiOAc; bp 85 °C/28 mmHg, (lit,[15] 127—130 °C/44 mmHg), Me$_2$(PhCH$_2$)SiOAc; bp 93—94 °C/4 mmHg, NMR δ (ppm) 0.25 s (6H), 1.98 s (3H), 2.32 s (2H), 6.85—7.20 m (5H), IR (cm^{-1}) 1720, 1260, Me$_2$(Ph)SiOAc; bp 85 °C/28 mmHg, (lit,[15] 127—130 °C/44 mmHg). The deuterated carboxylic acids were obtained by the hydrolysis of the carboxylic anhydrides with deuterium oxide and purified by distillation; the deuterium contents were determined by integration of ^{1}H NMR signals.

Product Analysis. The reaction of acetoxytrimethylsilane (0.27 mmol) with a small excess of the carboxylic acid (0.55 mmol) was conducted in chloroform-*d* (0.37 ml) solution. The mixture was allowed to stand for 5 h. Acyloxytrimethylsilane and acetic acid were detected as products by examination of the ^{1}H NMR spectrum of the solution. A small amount (5—7%) of hexamethyldisiloxane (δ 0.07 ppm) was detected as a side product which was probably formed by the moisture catalyzed decomposition of the acyloxysilane.

$$\mathrm{RCOOSiR'_3 + H_2O \longrightarrow RCOOH + R'_3SiOH}$$

$$\mathrm{2R'_2SiOH \rightleftharpoons R'_3SiOSiR'_3 + H_2O}$$

No other compound was detected in the solution. Dichloroacetoxytrimethylsilane was isolated from the reaction mixture of acetoxytrimethylsilane (7.6 mmol) and dichloroacetic acid (15 mmol) by GLC separation and the structure confirmed by comparison with an authentic sample.

Kinetic Procedure. A typical example is as follows: acetoxytrimethylsilane (35 mg; 0.27 mmol) was dissolved in CDCl$_3$ (0.370 ml) and the solution placed in a sample tube inside a NMR probe (Hitachi-Perkin-Elmer R-20 spectrometer). Dichloroacetic acid (71 mg; 0.55 mmol) was added to the solution and the trimethyl signals recorded at specified time intervals. The reaction temperature was the same as the probe temperature (34 °C). After reaction, the volume of the reaction mixture was measured and the concentrations of the components determined. Good reproduceability for the rate constant was obtained (within ±10%). The activation parameters were obtained using a variable temperature system (JEOL PS-100 spectrometer) and the temperatures measured by observing the chemical shifts of 1,2-ethanediol at that temperatures.

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