

SILYL-PROTON EXCHANGE REACTION BETWEEN ACYLOXYTRIMETHYLSILANES AND PHENYLACETIC ACID*

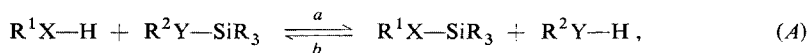
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Equilibrium constants of a proton-silyl exchange reaction between acyloxytrimethylsilanes $\text{RC(O)OSi(CH}_3)_3$ and phenylacetic acid in CCl_4 were determined by NMR spectroscopy. The equilibrium of this reaction is established immediately after mixing both components. Transfer of the silyl group is facilitated by electron-donating groups R. The trimethylsilyl group exchange in trimethylsilyl esters of acetic and thioacetic acid proceeds with similar ease. Mechanism of the reaction is discussed.

Increasing use of silylating agents in the organic chemistry requires the deeper knowledge of mechanism of silylation reactions to ensure the appropriate application and maximum effectiveness of these compounds. Transition state of these "proton-silyl exchange" equilibrium reactions (A) has been recently discussed for silyl amides¹ ($\text{Y} = -\text{C(O)N}=\text{O}$):



(X = e.g. O, S, N; Y = also halogen).

In connection with the knowledge of mechanism of the reactions of types *a* and *b* (see²⁻⁴ and references cited therein), transition state involves nucleophilic attack of the fragment X of R^1XH on the silicon atom of R^2YSiR_3 . In the acid-base catalysed reaction a catalyst activates the reagents by increasing either the nucleophilicity of X or the electron-donor ability of the silicon atom. The reactivity of silylating agents depends above all on the nature of the Si—Y bond that can be strongly influenced by the rest of the molecule. Thus, for example, an increased silylating effectiveness of silyl amides compared to silyl amines was ascribed to activation of the Si—N bond by the carbonyl group^{1,5}. The silylating ability of silyl amides is further increased by electro-negative substituents¹.

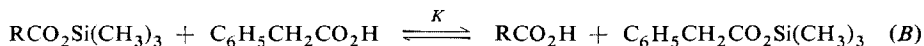
The effect of substitution on the ease of transfer of the silyl group from acyloxy-silanes to ROH and H_2O can be demonstrated by the reactivities of acyloxysilanes in their solvolysis^{7,23} or hydrolysis⁸. By the study of these reactions⁷⁻⁹ it was established that migration of the silyl group is facilitated by electronegative substituents, in agreement with formation of transition state initiated by nucleophilic attack. The aim

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of this work was to ascertain how substitution in the acyloxy group affects silyl group transfer from acyloxysilanes to the more acidic substrates, carboxylic acids and to contribute to the knowledge of the mechanism of this "proton-silyl exchange" reaction.

EXPERIMENTAL

All the compounds $\text{RC(O)OSi(CH}_3)_3$ ($\text{R} = \text{H, CH}_3, \text{C}_2\text{H}_5, \text{i-C}_3\text{H}_7, (\text{CH}_3)_2\text{CHCH}_2, (\text{CH}_3)_3\text{CCH}_2, (\text{CH}_3)_3\text{SiCH}_2, \text{CH}_3\text{C(O)(CH}_2)_2, \text{ClCH}_2, \text{Cl}_2\text{CH, Cl}_3\text{C, NCCCH}_2, \text{C}_6\text{H}_5, \text{and CF}_3$) were prepared by treatment of an appropriate acid with trimethylchlorosilane in the presence of stoichiometric amounts of pyridine in dry diethyl ether and were obtained in 70 to 85% yields by rectification. Their purity was checked by gas chromatography and their identity was verified by NMR spectroscopy. Physical constants of the acyloxytrimethylsilanes and thioacetoxymethyltrimethylsilane are presented in Table I. Equilibrium constants of acyloxysilane-phenylacetic acid systems were determined by NMR spectroscopy (a modified Tesla BS-477 spectrometer working at 60 MHz with the use of internal lock). Solutions (5 ml) of essentially stoichiometric amounts of phenylacetic acid and acyloxytrimethylsilane ($1 \cdot 10^{-2}$ mol) in CCl_4 were allowed to stand for 2 days and then the intensities of resolved signals of CH_3Si groups of both acyloxysilanes, $\text{RCO}_2\text{Si(CH}_3)_3$ and $\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2\text{S(CH}_3)_3$, were measured by integrating and planimetric signals. Each mixture was evaluated 2–3 times. The equilibrium constant K (Equation (B)) was calculated from



Eq. (I) where a and b is the known amount of acyloxysilane and phenylacetic acid, respectively and P is the ratio of the signal of $\text{CH}_3(\text{Si})$ group of phenylacetoxymethyltrimethylsilane to the same signal of acyloxytrimethylsilane $\text{RC(O)Si(CH}_3)_3$. Equilibrium constants K and confidence intervals¹⁰ are given in Table I.

$$K = [aP^2/(1 + P)]/[b - aP/(1 + P)] \quad (I)$$

RESULTS AND DISCUSSION

¹H-NMR measurements show that the reaction of acyloxysilanes with phenylacetic acid (equation (B)) achieves equilibrium immediately after mixing both components. An analogous equilibrium between carboxylic acids and alkoxytrimethylsilanes is established at much slower rate – in the case of the reaction of acetic acid with n-propoxysilane a small amount of n-propanol (8%) was observed only after 10 days⁶. It can be therefore concluded that, similar to aminotrialkylsilanes, also in alkoxytrimethylsilanes the introduction of the carbonyl group between the silicon and the hetero atom facilitates trialkylsilyl group transfer. From position of the equilibria between individual acyloxysilanes and phenylacetic acid (Table I) it follows that in this case thermodynamic silylating ability of acyloxysilanes decreases with increasing electronegativity of groups R.

It remains unclear whether the facility of the silyl group transfer from the acyloxysilanes $\text{RC(O)OSi(CH}_3)_3$ due to electron-donating groups R in their reaction with carboxylic acids distinguishes these compounds from their derivatives, silylacetanilides, the silyl groups of which are transferred to alcohols with greater ease when the benzene ring is substituted by electronegative substituents^{1,20}. The validity of the Taft equation (Eqs (2) and (3)) (the correlation coefficient $r = 0.988$) for $\sigma^* = -0.3$ to 2.65 (Fig. 1) indicates that equilibrium reactions of all the acyloxysilanes proceed by the same mechanism. Since of the two oxygens of an acyloxysilane only the carbonyl oxygen interacts significantly with Lewis acids (interaction of acyloxysilanes with ZnCl_2 leads to the lowering of the $\nu(\text{C=O})$ wavenumber²¹) and since

$$\log K_{\text{rel}} = \rho^* \sigma^* + C \quad (2)$$

$$K_{\text{rel}} = K_{\text{R}}/K_{\text{CH}_3}; \quad \rho^* = -0.567 \quad (3)$$

transition state of the reaction of acyloxysilanes with phenylacetic acid is stabilized by electron-donating substituents R, the rate-determining step seems to be interac-

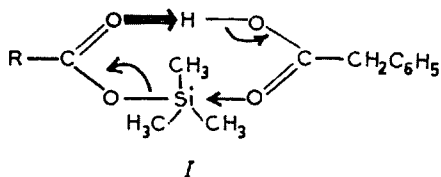
TABLE I

Physical and Equilibrium Data for Acyloxytrimethylsilanes $\text{RC(O)OSi(CH}_3)_3$

R	K	$2KnR^a$	B.p., °C/Torr		n_D^{20}	
			found	reported	found	reported
$(\text{CH}_3)_3\text{C}$	1.51	0.40	86/94	—	1.3923	—
$(\text{CH}_3)_3\text{SiCH}_2$	1.64	0.46	65/8	61/11 ^b	1.4141	1.4170 ^b
i-C ₃ H ₇	1.34	0.40	77/76	44/20 ^c	1.3936	1.3950 ^c
$(\text{CH}_3)_3\text{CCH}_2$	1.0	0.20	114/100	—	1.4055	—
$(\text{CH}_3)_2\text{CHCH}_2$	1.30	0.12	76/37	—	1.4007	—
C ₂ H ₅	1.27	0.60	71/47	122–123 ^c	1.3935	1.3931 ^c
CH ₃	1.08	0.60	104	103 ^d	1.3885	1.3890 ^e
H	0.48	0.18	86	86.5 ^f	1.3804	—
$\text{CH}_3\text{C(O)(CH}_2)_2$	0.92	0.40	81/15	—	1.4217	—
C ₆ H ₅ CH ₂	—	—	84/2	92/2.5 ^g	1.4759	—
C ₆ H ₅	0.65	0.20	68/2	40–42/0.1 ^h	1.4843	1.4817 ^h
ClCH ₂	0.35	0.20	87/40	159 ⁱ	1.4216	1.4231 ⁱ
CNCH ₂	0.30	0.10	87/8	—	1.4189	—
Cl ₂ CH	0.090	0.060	71/15	—	1.4300	—
F ₃ C	0.024	0.020	88	90.2 ⁱ	1.3379	1.338 ^j
Cl ₃ C	0.036	0.020	108/52	—	1.3923	—
CH ₃ ^k	0.88	0.50	100	—	1.3881	—

^a Confidence interval. ^b Ref.¹¹, ^c Ref.¹², ^d Ref.¹³, ^e Ref.¹⁴, ^f Ref.¹⁵, ^g Ref.¹⁶, ^h Ref.¹⁷, ⁱ Ref.¹⁸, ^j Ref.¹⁹. ^k $\text{CH}_3\text{C(O)SSi(CH}_3)_3$.

tion of the carbonyl oxygen of the acyloxysilane with the progressively dissociating hydrogen of phenylacetic acid. Transition state of the reaction can be best visualized by structure *I* that has an analogy in dimerisation of carboxylic acids; as a result of the primary attack $C=O \rightarrow H$, transfer of the silyl group to the carbonyl oxygen of the acid is made easier by increasing electron density on the carbonyl oxygen of the acid and by increasing electron deficiency on the silicon of the silyl group.



It is known that hydrolysis and alcoholysis of acyloxysilanes^{7,8,23} is facilitated by electronegative substituents. The rate-determining step of these reactions is formation of transition state by the attack of nucleophile on silicon. In reaction of acyloxysilanes with carboxylic acids the reaction mechanism is changed due to increasing relative importance of one of the two centers of the amphiprotic reagent that are both capable of acid-base interaction.

The knowledge of equilibrium constants of the reaction of trimethylsilyl esters of acetic and thioacetic acids with phenylacetic acid renders it possible to compare the silylating effectiveness of the trimethylsilyl group attached to oxygen and to sulphur. The values of these constants for both compounds $CH_3C(O)XSi(CH_3)_3$ ($X = O, S$) are approximately the same. As replacement of the ether oxygen of acetoxytrimethylsilane by sulphur does not affect significantly the $C=O$ group ($\nu(C=O)$)

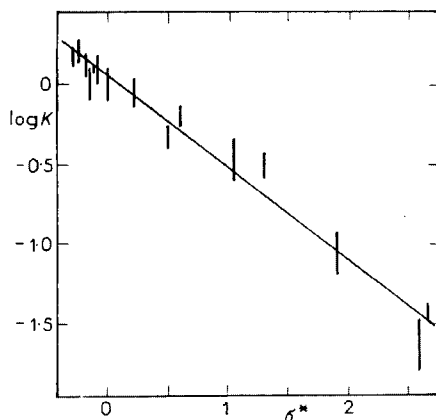


FIG. 1

Plot of $\log K$ of Equilibrium Reaction of Acyloxytrimethylsilanes $RC(O)OSi(CH_3)_3$ with Phenylacetic Acid versus σ^* Constant of Group R

for both $\text{CH}_3\text{C}(\text{O})\text{OSi}(\text{CH}_3)_3$ and $(\text{CH}_3)_3\text{C}(\text{O})\text{SSi}(\text{CH}_3)_3$ in CCl_4 is 1722 cm^{-1} (ref.⁶), and because of the generally accepted less important $(p-d)_\pi$ character of the Si—S bond²², the above fact can be ascribed to the higher polarisability of sulphur due to which the positive charge arising in transition state (structure I) affects the silyl group less extensively.

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