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THE MECHANISM OF SOLVOLYSIS OF β-KETOSILANES

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Summary

Rates of cleavages of compounds of the type $XC_6H_4COCH_2SiR_3$ have been measured spectrophotometrically at various temperatures. The cleavage of the Si–C bond occurs readily in THF/H_2O alone but it is also catalyzed by NaOH. The effects of substituents X correlate with their Hammett σ constants ($\rho = 2.2$ and 0.77 in the neutral and the basic medium, respectively). The rate isotope effect (r.i.e.), the effect of substitution at Si and the activation parameters are reported and discussed. The data in the neutral medium are consistent with a cyclic mechanism in which transfer of a proton from a H_2O molecule to the oxygen of the C=O is synchronous with the formation of the Si–O bond and probably with the breaking of the C–Si bond, whereas in basic medium the most likely mechanism involves formation of a Si^V intermediate in the rate determining step of the reaction.

Introduction

The mechanism of the base-catalyzed cleavage of the α-ketosilanes has been the subject of detailed studies [1a–e], which have indicated various possible mechanistic pathways for the reaction. In contrast, there have been only a few mechanistic studies of the β-ketosilanes $XC_6H_4COCH_2SiR_3$, and these were concerned exclusively with the rearrangement reaction [2a–d].

The aim of this study was to get a clear understanding of the route taken by the spontaneous and base-catalyzed cleavage of the Si–C bonds of the title compounds in aqueous media, with special reference to the site of nucleophilic attack by the base.

Results and discussion

For this study a series of substituted β-ketosilanes were synthesized, and the rates of solvolysis (eq. 1) were measured for various substituents X and various alkyl

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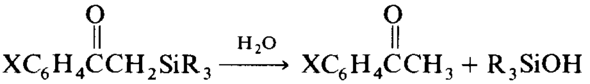
groups R.



$$XC_6H_4\overset{O}{\overset{\|}{C}}CH_2SiR_3 \xrightarrow{H_2O} XC_6H_4\overset{O}{\overset{\|}{C}}CH_3 + R_3SiOH \quad (1)$$

Aqueous THF (1/2, v/v) was used for all the kinetic experiments. The effects of the substituents on the rates of the spontaneous and base-catalyzed reactions are shown separately in Tables 1 and 2 as first-order rate constants k, specific rate

TABLE 1

RATE CONSTANTS FOR CLEAVAGE OF $XC_6H_4COCH_2SiR_3$ IN THF/WATER (2/1, v/v) AT 24°C

R	X	λ [a] (nm)	10^4k [b] (s^{-1})	k_{rel} [c]
CH_3	p-OCH_3	320	1.60	0.276
	p-CH_3	315	2.95	0.509
	m-CH_3	320	5.06	0.872
	H	315	5.80	1.000
C_2H_5	H	315	0.142	0.024
CH_3	p-Cl	345	28.0	4.83
	m-Cl	340	38.6	6.66

[a] Wavelength used for rate measurements. [b] Observed first order rate constant [c] Rate constant relative to that for X = H, R = CH_3.

TABLE 2

RATE CONSTANTS FOR CLEAVAGE OF $XC_6H_4COCH_2SiR_3$ BY SODIUM HYDROXIDE (0.0033 M) IN THF/WATER (2/1, v/v) AT 24°C

R	X	λ [a] (nm)	10^2k [b] (s^{-1})	k_s [c] ($l\ mol^{-1}\ s^{-1}$)	k_{rel} [d]
CH_3	p-OCH_3	320	1.25	3.79	0.619
	p-CH_3	315	1.57	4.76	0.778
	m-CH_3	315	1.84	5.58	0.911
	H	315	2.02	6.12	1.000
C_2H_5	H	315	0.0153	0.046	0.0076
CH_3	m-Cl	340	3.94	11.94	1.95

[a] Wavelength used for rate measurements. [b] Observed first order rate constant. [c] Specific rate constant, i.e. k/[NaOH]. [d] Rate constant relative to that for X = H, R = CH_3.

TABLE 3

ACTIVATION PARAMETERS FOR NEUTRAL AND BASE-CATALYZED CLEAVAGES OF $C_6H_5COCH_2SiMe_3$

T (°C)	10^3[NaOH] (M)	10^4k (s^{-1})	$\Delta H^\ddagger$ ($kcal\ mol^{-1}$)	$\Delta S^\ddagger$ ($cal\ mol^{-1}\ deg^{-1}$)
18.0	0.00	4.21		
24.0	0.00	5.80	8.45	−45.0
35.4	0.00	10.10		
18.0	3.30	153		
24.0	3.30	202	6.69	−43.8
35.1	3.30	312		

TABLE 4

SOLVENT ISOTOPE EFFECTS IN NEUTRAL AND BASE-CATALYZED CLEAVAGES OF $C_6H_5COCH_2SiMe_3$ AT 24°C

Medium	10^3 [NaOH] (M)	10^4k (s^{-1})	r.i.e. [a]
H_2O	0.00	5.80	1.71
D_2O	0.00	3.40	
H_2O	1.18	58.4	1.65
D_2O	1.18	35.5	
H_2O	5.90	398	1.42
D_2O	5.90	280	

[a] Rate isotope effect.

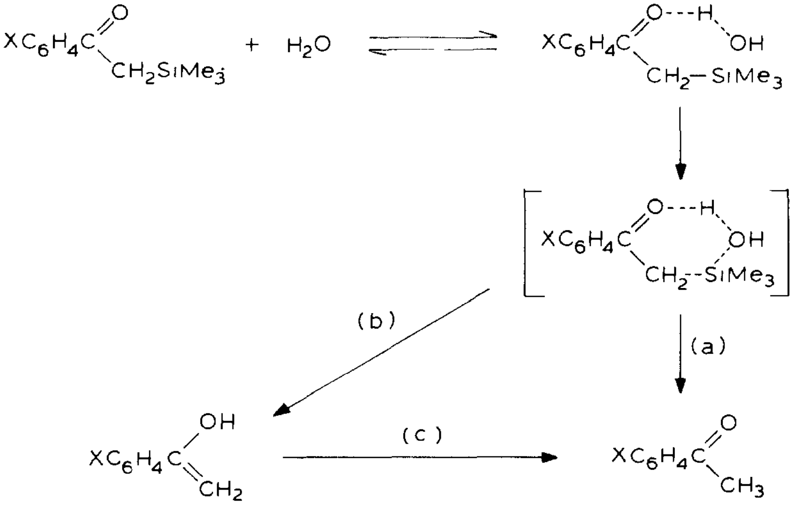
constants k_s, and k_{rel}, constants relative to that for the parent compound $C_6H_5COCH_2SiMe_3$. Rate constants at the various temperatures and the derived activation parameters are shown for some representative compounds in Table 3.

As shown in Tables 1 and 2, β-ketosilanes are very reactive, the Si–CH_2 bond being cleaved rapidly even in the absence of base, and ca. 50 times more reactive than the corresponding α-ketosilanes [1a]. For the limited range of substituents examined, the effects of varying the substituent X correlate well with their Hammett σ constants, and correspond to rough ρ values of 2.2 and 0.77 for the spontaneous and base-catalyzed reactions, respectively, indicating development of a negative charge in the transition state for both these reactions. However these smaller ρ values as compared with that (3.5) for $XC_6H_4COSiR_3$ [1e] and that (4.9) for $XC_6H_4CH_2SiR_3$ [3], reveal a smaller sensitivity of the cleavage to substituent effects.

Other significant features of the results are the effects of substitution at silicon, the activation parameters and the solvent isotope effect: as shown in Tables 1 and 2, the Me_3Si/Et_3Si ratio for the reactivity of $C_6H_5COCH_2SiR_3$ compounds has a value of 41 in the absence and 132 in the presence of base. Since it has been suggested that this ratio, which reflects mainly steric influences, increases with the reactivity of the substrates in those cases where the rate-determining step moves closer to a Si^V intermediate [4], we can conclude that the transition state for the cleavage of β-ketosilanes resembles a pentacoordinate Si species more closely that does that for α-ketosilanes, for which the Me_3Si/Et_3Si ratio is only 31 [1e]. On the other hand the activation entropies have large negative values, viz. −45.0 and −43.8 cal mol^{-1} deg^{-1} in the absence and in the presence of base respectively, which are consistent with a rather rigid cyclic transition state. Finally the rate isotope effects (r.i.e.) given by the rate constant in THF/H_2O to that in THF/D_2O are (Table 4) 1.71, 1.65 and 1.42, indicating that there is a varying degree of proton transfer from the solvent to the substrate in the rate-determining step as the base increases.

The mechanism which seems to fit the observed results most satisfactorily in the neutral medium is shown in Scheme 1.

In this there is a rapid formation of the hydrogen bonded species and the reaction then proceeds by nucleophilic attack by the oxygen of the solvent molecule on the silicon atom, through the 6-centred cyclic transition state pictured in Scheme 1. The subsequent fast step may involve intermediate formation of an highly unstable enol (route b) or simultaneous transfer of the hydrogen from the oxygen to the carbon

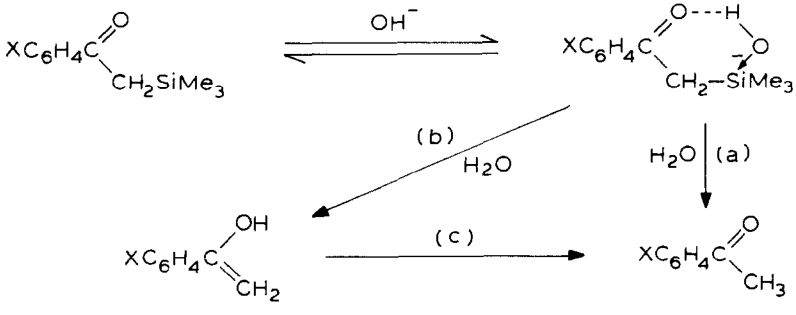


SCHEME 1

(route a). In this Scheme, for convenience, we have shown only a process involving synchronous C–Si breaking and Si–OH bond making but we cannot rule out the possibility that one of these two processes could be more advanced than the other.

The fairly small slope (0.77) of the $\log k_{\mathrm{rel}}$–σ plot in the basic medium means that the Si–CH_2 bond must be broken only to small extent in the rate-determining step, with negligible carbanionic character being developed in the transition state; moreover, the r.i.e. values, falling in the range 1.65–1.42, are consistent with an electrophilically assisted mechanism. Rate-determining formation of a cyclic Si^V intermediate, as shown in Scheme 2, might account for these results. The breakdown of the complex, with participation of a solvent molecule, then takes place in a subsequent fast step, through either route b or route a.

These mechanisms, which resemble to some extent those proposed by Webster and his colleagues for the neutral cleavages of the 2-trimethylsilyl pyridine [5a,b] and by Eaborn and Seconi [6] for the cleavages of 1-methyl-2-trimethylsilylbenzimidazole, readily account for all the experimental features of the reactions. Thus:



SCHEME 2

(i) The combination of low $\Delta H^\ddagger$ and large $\Delta S^\ddagger$ values in both the spontaneous or base-catalyzed reactions strongly favours mechanisms involving a cyclic activated complex.

(ii) The magnitudes of the ρ values derived by the effects of substituents are consistent with mechanisms in which the reaction center is remote from the benzene ring.

(iii) The higher Me_3Si/Et_3Si ratio in the base-catalyzed reactions suggests that the structure of the transition state is much closer in this case than it is in the neutral medium to a Si^V intermediate in which, according to previous findings [5b] steric crowding at Si is fairly marked.

(iv) The substantial electrophilic assistance by the solvent suggested by the rate isotope effect (r.i.e.) is clearly in line with mechanisms in Schemes 1 and 2.

In both cases the reaction appears to be a nucleophilic substitution by oxygen at silicon with electrophilic assistance by hydrogen at the carbonyl oxygen.

Experimental

THF was purified by distillation from lithium aluminium hydride. The commercial materials used for the synthesis were carefully purified before use. The β-ketosilanes were prepared according by the methods described by Lutsenko [2a] and by Kuivila [7]. The new compounds were purified by distillation, and showed satisfactory IR, NMR and mass spectral data (see Table 5).

Infrared spectra were recorded on a Perkin–Elmer 283, NMR spectra on a Perkin–Elmer R-32 and mass spectra on a Hewlett-Packard 5970 A.

TABLE 5

PHYSICAL AND SPECTROSCOPIC DATA OF $XC_6H_4COCH_2SiR_3$ COMPOUNDS

R	X	B.p. (°C (mmHg))	ν(C=O) (cm^{-1})	^1H NMR $\delta(CCl_4)$	MS *m/e* (*I* (%))
CH_3	H	83–85 [a] (0.15)	1670	0.30 (9H,s,$Si(CH_3)_3$); 2.63 (2H, s,CH_2); 7.60 (5H,m,Ar).	192(43); 177 (74); 75(100)
	m-CH_3	84–86 (0.15)	1665	0.30 (9H,s,$Si(CH_3)_3$); 2.35 (3H, s,CH_3); 2.60 (2H,s,CH_2); 7.45 (4H,m,Ar).	206 (27); 191 (100).
	p-CH_3	99–102 (0.22)	1665	0.30 (9H,s,$Si(CH_3)_3$); 2.35 (3H, s,CH_3); 2.60 (2H,s,CH_2); 7.50 (4H,m,Ar).	206 (8);191 (100).
	p-OCH_3	84–87 (0.19)	1655	0.30 (9H,s,$Si(CH_3)_3$); 2.55 (2H, s,CH_2); 3.80 (3H,s,OCH_3); 7.30 (4H,m,Ar).	222 (34); 207 (100).
	m-Cl	64–65 (0.5)	1670	0.30 (9H,s,$Si(CH_3)_3$); 2.60 (2H, s,CH_2); 7.50 (4H,m,Ar).	226 (24);211 (63); 75(100)
	p-Cl	68–70 (0.075)	1665	0.30 (9H,s,$Si(CH_3)_3$); 2.60 (2H, s,CH_2); 7.60 (4H,m,Ar).	226 (7); 211 (56); 75(100)
C_2H_5	H	106–107 [b] (1.5)	1665	0.70 (15H,m,$Si(C_2H_5)_3$); 2.70 (2H,s,CH_2); 7.75 (5H,m,Ar).	234 (17); 205 (100).

[a] Lit. 2a b.p. 78–79 (1). [b] Lit. 2a b.p. 106–107 (1.5).

Rate studies

The cleavages were monitored by observing the changes of the optical density at 315–345 nm with a Pye-Unicam SP-8-100 spectrophotometer. The β-ketosilane (2 μl) was added to a mixture of 2 ml of THF and 1 ml of water or aqueous NaOH solution in 1 cm quartz cell thermostatted at the required temperature, and the spectrum was recorded at intervals. The final spectrum exactly matched that of the corresponding acetophenone, confirming that the reaction was quantitative. For the most reactive compounds, fixed-wavelength or stopped-flow techniques were used. Pseudo-first order rate constants were evaluated in the usual way. Kinetic runs were usually carried out in triplicate, and rate constants were reproducible to within 2%.

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