The Thermal Elimination of Ketene from Alkyl Trimethylsilylacetates

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Alkyl trimethylsilylacetates readily undergo thermal elimination to give ketene and trimethylsilyl alkyl ethers; Arrhenius data have been obtained for this new unimolecular first-order reaction which involves a semi-concerted four-centre process.

The strength of the silicon–oxygen bond is the factor which provides the driving force for a number of reactions undergone by organosilicon compounds. For example *N*-substituted-2-(trialkylsilyl)acetamides undergo the rearrangement shown in reaction (1)[1] and the reaction of trimethylsilyl chloride with methyl lithioacetate gives mainly the *O*-silylated product [reaction (2)][2] produced almost certainly as a result of rearrangement of the *C*-silylated product in a process analogous to that in reaction (1). (The ratio of *C*- to *O*-silylated products found for other esters in this work appears to be a function of the size of the substituent in the alkyl and acyl portions.) Each of these reactions involves the silicon equivalent of tautomerism, *i.e.*, a four-centre rearrangement is involved.

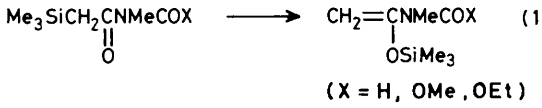
As far as we are aware there have been only two reports of thermally induced migration of silicon from carbon to oxygen. Brook *et al.* found that alkyl trialkylsilylcarboxylates (and the germanium analogues) underwent the three-centre process shown in reaction (3),[3] whilst β-ketosilanes rearranged to silyl enol ethers [reaction (4)],[4] a reaction closely related to reaction (2).

In a study of the thermal decomposition of t-butyl esters of substituted acetic acids [reaction (5)] we found the rates of elimination to be well correlated with σ_I-values for R except when R was $SiMe_3$.[5] The latter reaction was abnormally fast and this could not be satisfactorily explained in terms of either electronic or steric effects of the trimethylsilyl group. Further investigation has now revealed that an accompanying reaction, the four-centre elimination (6) takes place, and this is attributable to the strong silicon–oxygen bond that is formed.

In order to study this new reaction free of the possibility of intervention by reaction (5) the gas-phase pyrolysis of the methyl and ethyl esters has been studied. For the former the alternative reaction is impossible whilst for the ethyl ester the rate of reaction may be estimated (from the known rate difference of 3315 at 600 K for ethyl and t-butyl acetates)[6] to be *ca.* 7.5×10^{-6} s^{-1} at 600 K, *i.e.* insignificant. Both esters gave excellent first-order kinetics (greater than 95% of reaction), independent of a 5-fold variation in the initial concentration of ester, the stoicheiometry of the reaction was 2.00 ± 0.02, and separate product runs showed that only ketene and the silyl alkyl ethers were produced. At the highest temperatures employed some very slight polymerisation of ketene occurred but this did not interfere with determination of P_∞ values which were then obtained by back extrapolation. Rate data are given in Table 1. The log *A* values are towards the lower end of the range typical of semi-concerted four- and six-centre processes (10.0—14.0) which may reasonably be attributed to some steric hindrance to approach of the oxygen to the trimethylsilyl group. The activation energy is also towards the lower end of the spectrum of values obtained for gas-phase eliminations, and this most probably reflects the strength of the forming oxygen–silicon bond; lower activation energies were similarly obtained in the intramolecular thermal four-centre rearrangement (4).[4] As expected the ethyl ester is slightly the more reactive (by a factor of 1.32 at 600 K) consistent with the greater nucleophilicity of OEt compared to OMe. From our previous data on pyrolysis of t-butyl trimethylsilylacetate[5] we may estimate the rate of elimination according to reaction (5) by assuming that the correlation with σ_I-values holds exactly. This predicts *k* (600 K) 25×10^{-3} s^{-1}

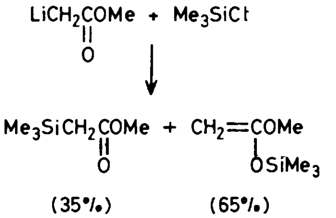
Table 1. Kinetic data for pyrolysis of esters $Me_3SiCH_2CO_2R$.

R	*T*/K	10^3 *k*/s^{-1}	log (*A*/s^{-1})	*E*/kJ mol^{-1}	10^3 *k*/s^{-1} at 600 K	Corr. coeff.
Me	628.2	56.0	10.098	136.55	16.2	0.99995
	681.3	36.2				
	605.4	20.3				
	581.0	6.61				
	571.1	4.07				
Et	628.2	68.2	9.777	138.68	20.6	0.99995
	618.3	44.5				
	605.4	20.3				
	581.0	8.80				
	571.1	5.56				

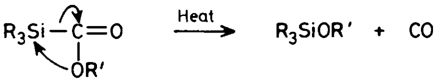

(1)

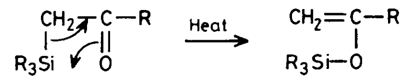
$$Me_3SiCH_2\underset{\underset{O}{\|}}{C}NMeCOX \longrightarrow CH_2{=}\underset{OSiMe_3}{C}NMeCOX \quad (1)$$

(X = H, OMe, OEt)


(2)

$$LiCH_2\underset{\underset{O}{\|}}{C}OMe + Me_3SiCl \longrightarrow \underset{(35\%)}{Me_3SiCH_2\underset{\underset{O}{\|}}{C}OMe} + \underset{(65\%)}{CH_2{=}\underset{OSiMe_3}{C}OMe} \quad (2)$$


(3)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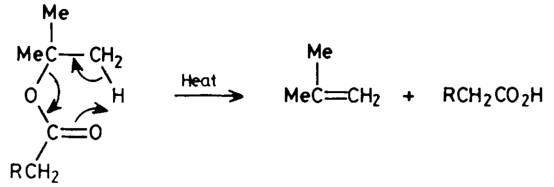
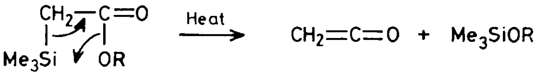

(5)


(6)

compared to the observed value of $73 \times 10^{-3}\ s^{-1}$; hence the rate coefficient for elimination by reaction (6) may be calculated to be $48 \times 10^{-3}\ s^{-1}$. This is thus higher than the values for the ethyl and methyl esters and accords with the expected greater nucleophilicity of the OBu^t group.

We hope in due course to investigate this reaction in further detail. Apart from its mechanistic interest the reaction may be a useful route for the generation of ketene as it is very clean and the byproduct is inert.

The general kinetic method has been described previously.[7]

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