The Mechanism of Thermal Eliminations. Part 27.[1] Steric Acceleration in Pyrolysis of 3,3,3-Tris(trimethylsilyl)propyl Acetate

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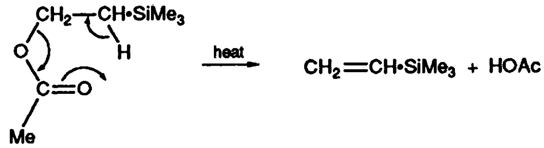
3,3,3-Tris(trimethylsilyl)propyl acetate has been prepared and its rate of unimolecular first-order decomposition measured between 633.1 and 687.8 K. The linear Arrhenius plot obtained from the rate data yields log $A = 12.485$ s^{-1} and $E_{act} = 189.60$ kJ mol^{-1}. At 650 K this ester undergoes elimination 14.0 times faster per β-hydrogen than does ethyl acetate, measured under the same conditions. This effect of the β-$C(SiMe_3)_3$ substituent is attributed to steric acceleration and is the largest such effect observed in a gas-phase elimination. The results confirm that the much larger effect (125-fold per β-hydrogen) previously found to be produced by the smaller $SiMe_3$ substituent is due principally to C–Si hyperconjugative stabilisation of the partial carbocation produced at the α-position in the transition state of this electrocyclic reaction. Hyperconjugation involving the electrons of the C–$C(SiMe_3)_3$ bond is an alternative but less probable explanation of the present results.

In a previous paper[2] in this series it was reported that at 600 K, 2-trimethylsilylethyl acetate (**1**) underwent *cis* β-elimination [equation (1)] some 125 times faster per β-hydrogen than ethyl acetate; the alternative elimination to give $AcOSiMe_3$ and ethene was insignificant under the reaction conditions. Three possible reasons were advanced to account for this rate acceleration, which is extremely large for a gas-phase reaction.

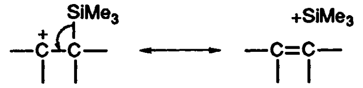


(1)

(1)

(i) *Increase in acidity of the* β-*hydrogen.* While the $SiMe_3$ substituent could be expected to stabilise the incipient carbanion produced at the β-carbon in the transition state, the charge produced is very small, and the acceleration produced is wholly out of line with the σ_p^- value for $SiMe_3$.

(ii) C–Si *Hyperconjugation.* Since a partial carbocation is produced at the α-position in the transition state, stabilisation by C–Si hyperconjugation known to be a major effect in solution chemistry,[3] could be expected. Support for this view was as follows.



(2)

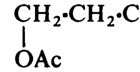
(*a*) The very high rate acceleration is consistent with the large corresponding effects observed in solution reactions.

(*b*) The acceleration by β-$SiMe_3$ of the elimination of acetic acid from 1-phenylethyl acetate (the transition state for which, being a secondary ester, has greater carbocationic character than for elimination from ethyl acetate) was likewise greater (160-fold per β-hydrogen).[2]

(*c*) The β-$SiEt_3$ group accelerated the elimination of acetic acid from ethyl acetate 179-fold per β-hydrogen, and thus more than the β-$SiMe_3$ group.[2]

(iii) *Steric acceleration.* This is known to be a significant factor governing the rates of *cis* β-elimination.[4–6] For example, a β-CMe_3 substituent increases the rate of elimination of ethyl acetate 2.38-fold per β-hydrogen at 675 K.[6] That this factor contributed to the high rate of elimination of 2-trimethylsilylethyl acetate was suggested by the fact that a β-$SiMe_2Ph$ group activated 216 times per β-hydrogen and thus more than the β-$SiMe_3$ group. (This could also arise from hyperconjugation, but the relative effects of these two groups in this mode of electron supply is not known.) Likewise the greater acceleration by β-$SiEt_3$ than by β-$SiMe_3$, attributed above to C–Si hyperconjugation, could equally well be attributed to steric acceleration, and the greater effect in 1-phenylethyl acetate could be similarly explained.

In order to resolve this question we have prepared and pyrolysed 3,3,3-tris(trimethylsilyl)propyl acetate (**3**). In this compound the bulk of the β-substituent is greater than any that has been examined in a thermal elimination. On the other hand the substituent is unable to stabilise the incipient α-carbocation by C–Si hyperconjugation.



$$\underset{\displaystyle OAc}{CH_2}\cdot CH_2\cdot C(SiMe_3)_3$$

(3)

Results and Discussion

The compound was pyrolysed using the static stainless steel reactor employed throughout this series of studies, the method involving measurement of the increase in pressure with time. On completion of reaction the final pressure is normally double that of the initial pressure *i.e.*, the stoicheiometry is 2.0. For primary acetates, the acetic acid byproduct of the elimination undergoes significant decomposition to methane and carbon dioxide during the time of the primary elimination, and this is indicated by a continuing pressure rise at P_∞. Back extrapolation of this secondary pressure increase to $t = 0$ then gives the true P_∞, and kinetic plots are then obtained in the normal way. For 3,3,3-tris(trimethylsilyl)propyl acetate, excellent first-order kinetic plots were obtained with linearity to >85% reaction. Rates were independent of variation in initial pressure (though we do not ascribe great significance to this traditional test for homo-

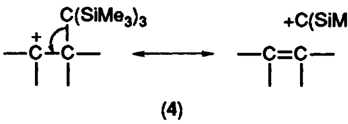
Table. Kinetic data for pyrolysis of $AcOCH_2CH_2X$.

X	T/K	$k/10^{-3}$ s^{-1}	log(A/s^{-1})	E_{act}/kJ mol^{-1}	Correlation coefficient	k/s^{-1} at 650 K
$C(SiMe_3)_3$	633.1	0.696	12.285	189.60	0.998 78	1.76×10^{-3}
	643.4	1.26				
	653.3	1.96				
	662.8	3.75				
	672.9	5.60				
	687.8	12.3				
H	648.4	0.176	12.320	199.62	0.999 57	1.89×10^{-4}
	662.9	0.401				
	687.8	1.38				
	697.7	2.42				

geneity since it is in fact not very sensitive). More importantly, the rates obtained fitted on a linear Arrhenius plot with no scatter, this being a much more reliable indicator of the absence of surface-catalysis. For comparative purposes rate data were also obtained again for ethyl acetate, because the present reactor, furnace and thermocouples (NPL calibrated) were different from those used for our earlier study of this compound;[7] the data are given in the Table.

The Arrhenius parameters obtained for the tris(trimethylsilyl)-substituted ester are wholly consistent with those which apply for 6-centred eliminations, and pyrolysis of primary acetates in particular.[7] The parameters for ethyl acetate agree within experimental error with those (12.50 s^{-1}, 200.00 kJ mol^{-1}) obtained previously.[7] From the two sets of Arrhenius data the rate coefficients for elimination at 650 K may be calculated for the tris(trimethylsilyl)-substituted ester and ethyl acetate as 1.76×10^{-3} and 1.89×10^{-4} s^{-1}, respectively. The substituted ester is therefore 14.0 times more reactive, per β-hydrogen, than ethyl acetate. This is a very substantial effect, but though the $C(SiMe_3)_3$ group is larger than $SiMe_3$, it produces a much smaller activation. We may therefore with confidence attribute the much larger effect of the latter group to C–Si hyperconjugative stabilisation of the incipient carbocation produced at the α-position. The activating effect of the very bulky β-$C(SiMe_3)_3$ group seems most probably to be derived from steric acceleration, and is the largest such effect that has been observed in a gas-phase elimination.

It is not possible at this stage entirely to rule out the possibility that hyperconjugative stabilisation of the incipient α-carbocation by the β-$C(SiMe_3)_3$ occurs, as shown in (**4**). This has to be deemed rather unlikely since the $SiMe_3$ group is generally regarded as destabilising towards an adjacent carbocation. As far as we are aware there is no information regarding the electronic effect of the $C(SiMe_3)_3$ group. This could for example be determined from rates of acid-catalysed hydrogen exchange of toluene and benzyltris(trimethylsilyl)methane; higher reactivity of the latter would indicate that this type of hyperconjugation is feasible.



(**4**)

Experimental

The kinetic apparatus and general kinetic technique have been described.[8] The apparatus was modified in two ways but these do not however have any direct bearing on the overall method: the AEI temperature controller was replaced by a Eurotherm type 820 device, and a new furnace was constructed out of pure aluminium rather than the aluminium alloy of its predecessor; this has a higher m.p. and will facilitate kinetic studies at higher temperatures. The chromel–alumel thermocouples were recalibrated against a Pt/PtRh NPL standard.

Product studies showed the formation only of acetic acid and 3,3,3-tris(trimethylsilyl)propene.

3,3,3-*Tris(trimethylsilyl)propyl Acetate*.—3,3,3-Tris(trimethylsilyl)propanol, δ($CDCl_3$) 3.81 (2 H, m, CH_2O), 1.93 (2 H, m, CH_2), 1.34 (1 H, s, OH), and 0.14 [27 H, s, $(SiMe_3)_3$] was prepared in 60% yield by the literature method,[9] modified in that the product was partially purified using a rotary still and then recrystallised from methanol.

This alcohol (4 g) was acetylated by being warmed with acetic anhydride (30 cm^3) and pyridine (60 cm^3). Normal work-up followed by fractional distillation using a Vigreux column of *ca.* 10 theoretical plates yielded colourless plates of 3,3,3-tris(trimethylsilyl)propyl acetate, 95%, b.p. 97 °C/0.1 mmHg, m.p. 31–32 °C, δ($CDCl_3$) 4.23 (2 H, m, CH_2O), 2.06 (3 H, s, CH_3CO), 1.93 (2 H, m, CH_2), and 0.15 [27 H, s, $(SiMe_3)_3$].

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