Mechanism of Thermal Eliminations. Part 29.[1] The Effect of Different Silyl Groups upon Thermal Elimination of Ketene from Ethyl Silylacetates

Sara E. Chapman and Roger Taylor *
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex, UK

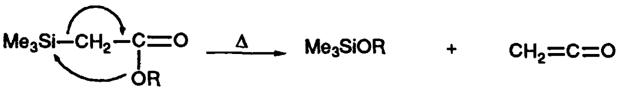
A series of ethyl silylacetates, $R_3SiCH_2CO_2Et$ where R_3 = Me_3, Me_2Ph, $MePh_2$, Ph_3, have been prepared and their rates of gas-phase thermal elimination to ketene and the corresponding ethyl silyl ether measured, each over a 50 °C temperature range. Activation energies are in the range 136–144 kJ mol^{-1}, and log(A/s^{-1}) values 10.1–10.8. Increase in the electrophilicity of silicon through replacement of one methyl group by phenyl produces a minor increase in reactivity, but further similar replacements eventually produce a rate decrease, which is attributed to steric hindrance. Overall the kinetic data indicate that the strength of the silicon–oxygen bond formed is sufficiently important that alteration in the ester structure is incapable of producing substantial variation in the rate of ketene formation.

In a preliminary communication one of us reported rate data for a new reaction, the thermal elimination of ketene from ethyl and methyl trimethylsilylacetates, eqn. (1).[2] At 600 K, the rate of elimination from the ethyl ester was 1.27 times faster than from the methyl ester, consistent with the greater nucleophilicity of the ethoxy group compared with methoxy. This reaction is somewhat similar to the Brook reaction[3] of esters R_3SiCO_2R' which eliminate carbon monoxide to give R_3SiOR' in a process which must be a three-centre reaction.

In view of these results it was anticipated that an increase in the electrophilicity of the silyl group would produce a corresponding increase in the rate of elimination. In this way it might be possible to optimise the structure of an ester such that it would give the maximum rate of ketene generation, and this might be advantageous for certain applications, since the by-product silyl ethers are inert. Accordingly a series of ethyl esters was synthesised; in these the methyl groups attached to silicon were successively replaced by phenyl groups, which, being less strongly electron-supplying, should increase the electrophilicity of the silyl group.

Results and Discussion

Each compound was pyrolysed at five different temperatures over a 50 °C range and gave excellent first-order kinetics reproducible to ±2% at a given temperature (independent of



(1)

(R = OEt, OMe)

Table 1 Kinetic data for pyrolysis of $R_3SiCH_2CO_2Et$

R_3	T/K	k/10^{-3} s^{-1}	log(A/s^{-1})	E_{act}/kJ mol^{-1}	Correlation coefficient	k/10^{-3} s^{-1} at 600 K
Me_3	633.1	81.3	10.112	135.70	0.999 94	19.8
	623.1	54.3				
	613.0	35.8				
	598.2	18.1				
	583.3	9.06				
Me_2Ph	633.1	86.6	10.048	134.62	0.999 65	21.2
	623.1	56.5				
	613.0	39.0				
	598.0	19.6				
	583.3	9.66				
$MePh_2$	643.2	130	10.842	144.39	0.999 87	18.6
	633.3	86.0				
	623.1	55.3				
	613.0	33.3				
	598.3	17.2				
	583.3	8.19				
Ph_3	633.5	67.3	10.613	143.10	0.999 05	14.2
	623.1	41.0				
	613.4	25.7				
	598.1	13.0				
	583.3	5.92				
	578.5	5.24				

Table 2 Relative rates for pyrolysis of esters $R_3SiCH_2CO_2Et$ at 600 K

R_3	k_{rel}
Me_3	1.00
Me_2Ph	1.07
$MePh_2$	0.94
Ph_3	0.72

the standard tests for heterogeneity), and a stoichiometry of 2.0 ± 0.05. The kinetic data are given in Table 1, and the relative elimination rates at 600 K are given in Table 2

For ethyl trimethylsilylacetate, the activation energy, $\log(A/s^{-1})$ value and rate coefficient agree within experimental error with those obtained previously (138.7 kJ mol^{-1}, 10.1 and 20.6×10^{-3} s^{-1}).[1] Small differences were expected because the present work was carried out with a different furnace, and recalibrated thermocouples.

The relative rates show that replacing one methyl group by phenyl produces a modest rate increase as had been anticipated. However, replacement of a further methyl group by phenyl causes no further rate increase. Indeed, at the majority of temperatures the rate is reduced, as shown by the data calculated at 600 K. This can best be attributed to steric hindrance at silicon to attack of the ethoxy group. This interpretation of the results is supported by the reactivity of the triphenyl compound which is further and significantly reduced from that of the diphenylmethyl compound. Overall, however, the relative rates are small, indicating that the driving force for the reaction, formation of the silicon–oxygen bond, is sufficiently strong that the groups attached to silicon have only a small electronic effect. The magnitude of the latter is such that it is easily overcome by the bulk effect of the groups attached to silicon.

Experimental

Each ester was made by means of the Reformatsky reaction between ethyl bromoacetate and the appropriate silyl chloride, R_3SiCl.[4] After normal work up, the trimethyl, phenyldimethyl and methyldiphenyl compounds were each purified by fractional distillation. The triphenyl compound was partially purified on a Buchi rotary still into three fractions. The first two were indicated by mass spectrometry to the Ph_3SiOEt (m/z = 304), and Ph_3SiOH (m/z = 276) the third fraction being the desired ester which was further purified (removal of a small amount of the thermal decomposition product) by recrystallisation from ethanol. The properties of the esters $R_3SiCH_2CO_2Et$ were, for R_3: Me_3, b.p. 124–126 °C at 200 mmHg (lit.,[4] 156–159 °C at 760 mmHg); Me_2Ph, b.p. 96 °C at 3 mmHg (lit.,[4] 92–93 °C at 3 mmHg); $MePh_2$, b.p. 135 °C at 0.15 mmHg (lit.,[4] 184–185 °C at 1.7 mmHg), Ph_3, m.p. 69–71 °C (lit.,[4] 72–73 °C).

The signals in the NMR spectra due to the CH_2 group appeared at (for R_3): 1.605 ppm (Me_3), 2.135 ppm (Me_2Ph), 2.409 ppm ($MePh_2$) and 2.750 ppm (Ph_3). A plot of these shifts against the number of phenyl groups attached to silicon is a smooth curve.

Kinetic studies were carried out in the static stainless-steel reactor system that has been described previously.[5] Kinetic runs were always duplicated until minimum rate coefficients agreeing to within ±2% were obtained, and which produced linear Arrhenius plots with no significant deviations. As we have repeatedly emphasized this is a much better indicator of the lack of surface catalysis than the generally accepted method of varying volume to surface ratios, which we find to be insufficiently sensitive.

References

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