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TRIMETHYLSILYLATED *N*-ALKYL-SUBSTITUTED CARBAMATES

II *. ALCOHOLYSIS OF TRIMETHYLSILYL *N*,*N*-DIMETHYLCARBAMATE

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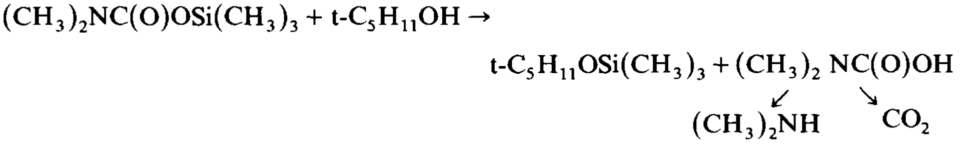
Summary

The reaction of trimethylsilyl *N*,*N*-dimethylcarbamate with the sterically hindered alcohol 2-methylbutan-2-ol has been studied kinetically. The reaction shows autocatalytic character, and an equation has been derived which satisfactorily describes the kinetic behaviour. A mechanism is suggested for the reaction.

Introduction

In an previous communication we described the preparation of trimethylsilyl derivatives of alcohols, phenols and carboxylic acids by use of trimethylsilyl *N*,*N*-dimethylcarbamates [1]. The mechanisms of silylation reactions have received relatively little attention; however, both acid [2–7] and base [8,9] catalysis has been observed in the alcoholysis of silylamines. Pentacovalent transition states and an S_N2 mechanism are generally assumed for these reactions [7, 9–11].

In the present communication we describe a kinetic study of the reaction of trimethylsilyl *N*,*N*-dimethylcarbamate and the sterically hindered alcohol 2-methylbutan-2-ol. With this alcohol several hours are required for completion of the silylation even at higher temperature (70°C). The overall reaction is represented as follows:



$$(CH_3)_2NC(O)OSi(CH_3)_3 + t\text{-}C_5H_{11}OH \rightarrow t\text{-}C_5H_{11}OSi(CH_3)_3 + (CH_3)_2NC(O)OH \rightarrow (CH_3)_2NH + CO_2$$

In the kinetic study the reactions were carried out in dibutyl ether, and the reaction mixtures were analysed by GLC.

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* For part I see ref. 1.

The percentage reaction against time plots exhibit a typical S shape, characteristic of autocatalysis. The rate was found to increase abruptly when dimethyl amine was added to the reaction mixture, indicating the autocatalysis is accosiated with the dimethyl amine formed during the reaction. The observed reaction appears to involve both the spontaneous reaction and the reaction catalyzed by dimethyl amine.

The spontaneous process can be represented by the reactions (1)–(3):

$$2\ \text{t-C}_5\text{H}_{11}\text{OH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\text{t-C}_5\text{H}_{11}\text{O}]^- + [\text{t-C}_5\text{H}_{11}\text{OH}_2]^+ \qquad (1)$$

$$(\text{CH}_3)_2\text{NC(O)OSi(CH}_3)_3 + [\text{t-C}_5\text{H}_{11}\text{O}]^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [(\text{CH}_3)_2\text{NC(O)OSi(CH}_3)_3 \cdot \text{t-C}_5\text{H}_{11}\text{O}]^- \qquad (2)$$

$$[(\text{CH}_3)_2\text{NC(O)OSi(CH}_3)_3 \cdot \text{t-C}_5\text{H}_{11}\text{O}]^- + [\text{t-C}_5\text{H}_{11}\text{OH}_2]^+ \xrightarrow{k_3} \text{t-C}_5\text{H}_{11}\text{OSi(CH}_3)_3 + \text{t-C}_5\text{H}_{11}\text{OH} + (\text{CH}_3)_2\text{NH} + \text{CO}_2 \qquad (3)$$

Alternatively, a hydrogen-bridged dimer of the alcohol could be involved:

$$\text{t-C}_5\text{H}_{11}\text{OH} + \text{t-C}_5\text{H}_{11}\text{OH} \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} [\text{t-C}_5\text{H}_{11}\text{OH}]_2 \qquad (1')$$

$$[\text{t-C}_5\text{H}_{11}\text{OH}]_2 + (\text{CH}_3)_2\text{NC(O)OSi(CH}_3)_3 \xrightarrow{k'_2} \text{t-C}_5\text{H}_{11}\text{OSi(CH}_3)_3 + \text{t-C}_5\text{H}_{11}\text{OH} + (\text{CH}_3)_2\text{NH} + \text{CO}_2 \qquad (2')$$

The steps in the process catalyzed by the amine may be represented as follows:

$$\text{t-C}_5\text{H}_{11}\text{OH} + (\text{CH}_3)_2\text{NH} \underset{k^\star_{-1}}{\overset{k^\star_1}{\rightleftharpoons}} [\text{t-C}_5\text{H}_{11}\text{O}]^-[(\text{CH}_3)_2\text{NH}_2]^+ \qquad (1^\star)$$

$$(\text{CH}_3)_2\text{NC(O)OSi(CH}_3)_3 + [\text{t-C}_5\text{H}_{11}\text{O}]^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [(\text{CH}_3)_2\text{NC(O)OSi(CH}_3)_3 \cdot \text{t-C}_5\text{H}_{11}\text{O}]^- \qquad (2^\star)$$

$$[(\text{CH}_3)_2\text{NC(O)OSi(CH}_3)_3 \cdot \text{t-C}_5\text{H}_{11}\text{O}]^- + [(\text{CH}_3)_2\text{NH}_2]^+ \xrightarrow{k^\star_3} \text{t-C}_5\text{H}_{11}\text{OSi(CH}_3)_3 + 2\ (\text{CH}_3)_2\text{NH} + \text{CO}_2 \qquad (3^\star)$$

or taking account of the possible involvement of a hydrogen-bridged dimer:

$$\text{t-C}_5\text{H}_{11}\text{OH} + (\text{CH}_3)_2\text{NH} \underset{k^{\star\prime}_{-1}}{\overset{k^{\star\prime}_1}{\rightleftharpoons}} [\text{t-C}_5\text{H}_{11}\text{OH} \cdot (\text{CH}_3)_2\text{NH}] \qquad (1^{\star\prime})$$

$$[\text{t-C}_5\text{H}_{11}\text{OH} \cdot (\text{CH}_3)_2\text{NH}] + (\text{CH}_3)_2\text{NC(O)OSi(CH}_3)_3 \xrightarrow{k^{\star\prime}_2} \text{t-C}_5\text{H}_{11}\text{OSi(CH}_3)_3 + 2(\text{CH}_3)_2\text{NH} + \text{CO}_2 \qquad (2^{\star\prime})$$

The overall rate of the reaction is given by the following equation:

$$\frac{dx}{dt} = \bar{k}_1[a-x]^2[b-x] + \bar{k}_2[a-x][b-x]x \tag{4}$$

where

x = the concentration of the product.

$a = [\text{t-C}_5\text{H}_{11}\text{OH}]$

$b = [(\text{CH}_3)_2\text{NC(O)OSi(CH}_3)_3]$

$$\bar{k}_1 = \frac{k_1 k_2 k_3}{k_{-1} k_{-2}} \text{ or } \bar{k}_1 = \frac{k_1' k_2'}{k_{-1}'}$$

$$\bar{k}_2 = \frac{k_1^{\star} k_2 k_3^{\star}}{k_{-1}^{\star} k_{-2}} \text{ or } \bar{k}_2 = \frac{k_1^{\star\prime} k_2^{\star\prime}}{k_{-1}^{\star\prime}}$$

By integration of eq. 4 we obtain:

$$t = -\frac{1}{\bar{k}_2 a(b-a)} \ln\left(1 - \frac{x}{a}\right) + \frac{1}{\left[\bar{k}_1(a-b) + \bar{k}_2 b\right](b-a)} \ln\left(1 - \frac{x}{b}\right) + \frac{\bar{k}_2 - \bar{k}_1}{\bar{k}_2 a\left[\bar{k}_1(a-b) + \bar{k}_2 b\right]} \ln\left[\frac{(\bar{k}_2 - \bar{k}_1)x}{\bar{k}_1 a} + 1\right] \tag{5}$$

The observed data were analysed both by curve fitting of spline functions [12,13] on the basis of the original differential equation (eq. 4) and by iteration of the integrated formula (eq. 5) using curve fitting by the method of least-squares. The results of both calculation methods are presented for one typical example in Table 1, and it will be seen that essentially identical results were obtained in both cases.

TABLE 1

MEASURED AND CALCULATED PRODUCT CONCENTRATIONS (T 343.1 K; a 1.56 mol dm^{-3}; b 3.53 mol dm^{-3})

Reaction time, t (min)	Product concentration (mol dm^{-3})		
	Measured	Calculated	
		by spline functions	on the basis of the integral equation
15	0.033	0.032	0.035
30	0.086	0.069	0.074
90	0.237	0.245	0.254
105	0.289	0.294	0.305
150	0.450	0.453	0.465
156	0.487	0.474	0.487
168	0.546	0.534	0.531
210	0.706	0.678	0.681
240	0.780	0.778	0.782
270	0.891	0.875	0.877
480	1.289	1.308	1.314

TABLE 2

RATE CONSTANTS AT VARIOUS TEMPERATURES

Temperature, T (K)	Concentration, a (mol dm^3)	Molar ratio (b/a)	$\bar{k}_1 \times 10^6$ ($dm^3\ mol^{-2}\ s^{-1}$)	$\bar{k}_2 \times 10^5$ ($dm^3\ mol^{-2}\ s^{-1}$)
343.1	1.78	1.80	4.80 ±0.63	2.22 ±0.56
343.1	2.12	1.28	4.19 ±0.81	2.05 ±0.48
323.1	2.16	1.22	2.06 ±0.27	1.18 ±0.25
313.1	1.87	1.85	1.56 ±0.21	0.964 ±0.169
305.6	1.82	1.72	0.873 ±0.149	0.776 ±0.146
303.1	1.67	2.00	0.727 ±0.087	0.650 ±0.162

The rate constants obtained at various temperatures are summarized in Table 2. The rates vary by a fairly small amount with temperature, or, in other words the apparent activation energies are small:

$E_{a_1} = 38.0 \pm 5$ kJ, $E_{a_2} = 24.5 \pm 4$ kJ

Log A values are also rather small; this reflect the effect of a polar transition state and the operation of pre-equilibria in the reaction.

Experimental

Materials

2-Methylbutan-2-ol (BDH) and di-n-butyl ether (BDH) were dried by refluxing with calcium hydride and distilled in vacuum from calcium hydride. Anhydrous dimethyl amine was prepared by adding a 40% solution of dimethyl amine (BDH) dropwise to solid KOH, then percolating it through a column of solid KOH. It was then frozen in dry ice-acetone mixture and distilled as required.

Trimethylsilyl *N,N*-dimethylcarbaminate was prepared from the reaction of trimethylchlorosilane with the dimethylammonium salt of *N,N*-dimethylcarbaminate [1]. The product was purified by repeated vacuum distillation. The material used in the experiments was > 99.5% pure, and the only impurity detected by GLC was 0.1% of hexamethyldisiloxane. The purified substance was stored in sealed glass ampoules.

2-Methyl-2-trimethylsiloxybutane. A 2/1 molar mixture of trimethylsilyl *N,N*-dimethylcarbaminate and 2-methylbutan-2-ol was heated at 100°C for 15 h until 2-methylbutan-2-ol reacted quantitatively. The product was subsequently purified by repeated vacuum distillation.

Reactions and sampling

The reactions were carried out in a 5 cm^3 reaction vessel equipped with a tap and a rubber septum. Samples were withdrawn by microsyringe through the septum then injected into the GLC apparatus.

For the GLC analysis a JEOL GC 1100 instrument was used. Carrier gas: high purity nitrogen, 50 cm^3 min^{-1}. Column: double column system. A glass spiral of 3 m length and 3 mm inner diameter, filled with 5% OV-1 on Gas-Chrom Q (60–80 mesh). Column temperature: programmed to 4 min at 70°C, then heated to 130°C at a rate of 15° min^{-1}.

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