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Solvolysis kinetics of trimethylsilyl esters of aromatic *N*-carboxylic acids

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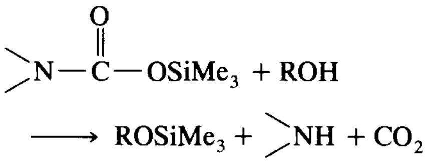
Abstract

Some new trimethylsilyl esters of cyclic and/or aromatic *N*-carboxylic acids were prepared. Their solvolysis reactions with isopropanol were studied by gas chromatography and by UV spectrophotometry respectively. The pseudo-first-order rate constants, the salt effects and the activation parameters were determined.

Keywords: Solvolysis; Kinetics; Trimethylsilyl; Carbamate; Silicon

1. Introduction

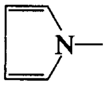
Many silylated carbamic acid derivatives have been prepared so far. They are versatile silylating agents of hydroxyl groups; thus it is of interest to study their alcoholysis:



$$>N-\overset{\overset{\displaystyle O}{\|}}{C}-OSiMe_3 + ROH \longrightarrow ROSiMe_3 + >NH + CO_2$$

Earlier we reported the study of reaction between the trimethylsilylated *N*,*N*-dimethyl-carbamate and *tert*-amyl alcohol [1]. The solvolysis kinetics of the *N*-aryl [2] and of the *N*-alkyl-*N*-phenyl [3] derivatives were also investigated in isopropanol.

Now we describe the comparative solvolysis study of the heteroaromatic trimethylsilyl *N*-carboxylic acid esters and relating compounds of type $RC(O)OSiMe_3$ (**1–7**), where R are the following groups:



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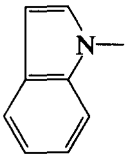

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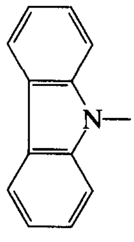

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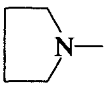

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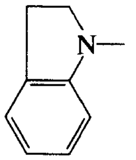

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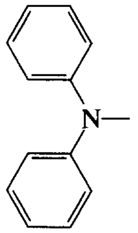

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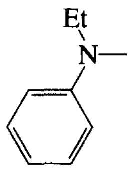

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2. Results

2.1. Preparation

All compounds were obtained in one-pot reactions; however, various preparative conditions were to be applied. Two main synthetic routes A [4] and B [3] described earlier were used with slight modifications. The general methods of syntheses are as shown in Scheme 1.

The yields, physical and spectroscopic data of products are listed in Table 1. The data for **7** were extracted from ref. [3]. In the literature there is an earlier report on the pyrrolidine derivative **4** prepared in a different way [5].

2.2. Kinetic studies

Kinetic measurements were carried out in isopropanol–dioxane mixtures containing the alcohol in

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Table 1.
Yields, physical and spectroscopic data of **1**–**7**

Compound	Method of preparation	Yield (%)	Boiling point (°C (mbar))	GC ret. index	Column temperature (°C)	Mass spectroscopy M^+ m/e	M^+ (%)	$M\text{-}15^+$ (%)	IR (CCl_4), $\nu(C{=}O)$ cm^{-1}	^1H NMR (tetramethylsilane–$CDCl_3$) $\delta(SiMe_3)$ ppm
1	B	77	65(2)	1110	80	183	33	13	1728	0.40
2	B	80	102(2)	1616	150	233	28	7	1721	0.50
3	B	75	Oil	2139	200	283	10	3	1710	0.53
4	A	80	62(3)	1209	80	187	31	100	1684	0.29
5	A	85	118(3)	1660	150	235	64	28	1682	0.38
6	B	83	Crystal	1837	200	285	16	7	1698	0.27
7	B	70	81(2)	1402	120	237	33	18	1681	0.25

large excess (> 100) relative to the concentration of the substrate. Preliminary experiments revealed that there are very large differences in the rates of the alcoholysis of compounds; so reaction media of different compositions needed to be used for better comparison of solvolytic properties. The reactions were monitored by gas chromatography (GC) (for **1**–**6**) and by UV spectrophotometry (for **5**–**7**). The pseudo-first-order rate constants were calculated from the plot of observed data vs. time fitting the curve of the appropriate integrated formula to it by non-linear regression.

First the rates of solvolysis of the heterocyclic derivatives **1**–**4** were determined in an isopropanol–dioxane mixture of 1/3 (v/v) ratio (Tables 2 and 3). The compounds **5** and **6** were found to react too slowly under similar conditions. For the pyrrolidine derivative **4** the concentration of substrate against time plot shows a typical S shape (Fig. 1) characteristic of autocatalysis which has been similarly observed by the alcoholysis on trimethylsilyl *N*,*N*-dimethyl-carbamate [1] (Table 3).

The effect of the ionic strength on the rate of solvolysis were determined in LiCl solutions under different conditions (Tables 2 and 4).

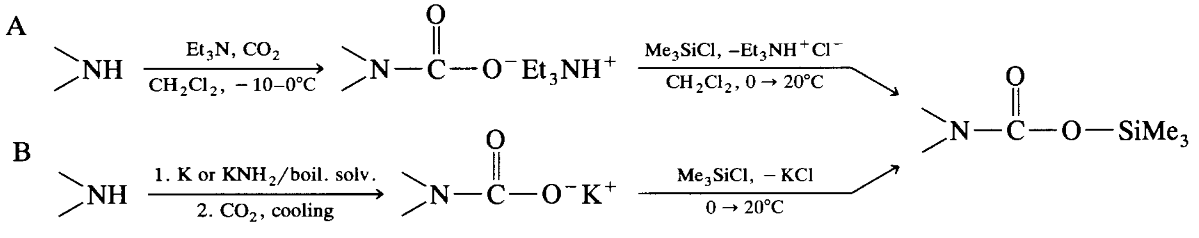
The solvolysis of compounds were also studied as a function of temperature (Tables 4 and 5).

3. Discussion

Although various sets of conditions depending on the nature of substrates were to be maintained during the measurements, the relations between structure and reactivity of compounds are well evidenced by the experimental data.

The general order in reactivity of substrates is the following: **1** > **2** > **3** > **6** > **5** > **7** > **4** (Tables 2–5).

A positive salt effect is observed in all cases; thus we can conclude that a polar intermediate is formed during the reactions (Tables 2 and 4). For the substrates the order of the increasing effect is the same as described



Scheme 1.

Table 2.
Rates of the solvolysis depending on the concentration of LiCl (in an isopropanol–dioxane mixture of 1/3 (v/v) ratio at 25°C)

c ($\times 10^4$ mol dm^{-3})	k ($\times 10^5$ s^{-1}) **1**	**2**	**3**	c ($\times 10^4$ mol dm^{-3})	k ($\times 10^5$ s^{-1}) **5**	**6**
0	116	77	47	125	10	35
2.4	210	95	57	250	18	67
4.8	330	147	68	500	31	120
9.5	550	200	84			
18.2	850	330	118			
$\Delta k \Delta c$ (dm^3 mol^{-1} s^{-1})	4.1	1.4	0.4		0.006	0.023

Table 3.
The substrate concentration vs reaction time data for the solvolysis of **4** in an isopropanol–dioxane mixture of 1/3 (v/v) ratio at 25°C, c(LiCl) = 0 M

t (min)	$c(\times10^2$ mol dm$^{-3})$ Experimental	$c(\times10^2$ mol dm$^{-3})$ Calculated	t (min)	$c(\times10^2$ mol dm$^{-3})$ Experimental	$c(\times10^2$ mol dm$^{-3})$ Calculated
0	2.67	2.59	29.4	1.01	1.02
3.2	2.48	2.57	31.0	0.88	0.86
5.2	2.67	2.55	32.5	0.74	0.71
7.9	2.48	2.51	34.1	0.57	0.58
10.0	2.39	2.47	35.7	0.46	0.47
13.8	2.24	2.35	37.6	0.35	0.36
16.6	2.37	2.22	39.2	0.26	0.28
18.6	2.03	2.09	40.8	0.21	0.22
20.3	1.90	1.95	42.4	0.16	0.17
22.8	1.77	1.73	44.0	0.13	0.13
24.5	1.56	1.56	45.7	0.09	0.10
26.1	1.43	1.38	47.3	0.07	0.08
27.9	1.17	1.19	50.6	0.04	0.05

$k_1 = 3.011\times10^{-5}$ s^{-1}; $k_2 = 1.079\times10^{-1}$ dm^3 mol^{-1} s^{-1}; $c_0 = 2.586\times10^{-2}$ mol dm^{-3};
$\bar{k}_1 = 2.82\times10^{-6}$ dm^6 mol^{-2} s^{-1}; $\bar{k}_2 = 3.31\times10^{-2}$ dm^6 mol^{-2} s^{-1}; $\Delta G^\ddagger(25°\mathrm{C}) = 98.8$ kJ mol^{-1}.

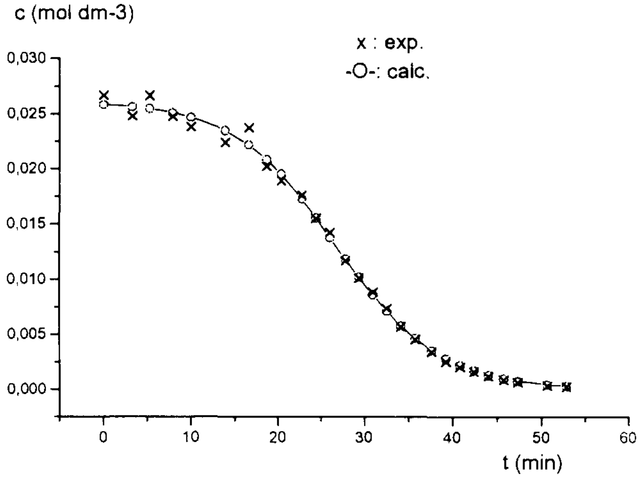


Fig. 1. Typical S shape of the concentration of substrate vs. time plot.

above. In the heteroaromatic series **1**–**3** the values are much higher than those of the other compounds. For **5**–**7** the salt effect increases with increasing temperature (Table 4).

For the heteroaromatic derivatives **1**–**3** the activation enthalpy $\Delta H^\ddagger$ values are rather small and decrease with increasing reactivity (Table 5).

The kinetic character of solvolysis for the pyrrolidine derivative **4** was sharply different from that of the other compounds. The experimental data were interpreted on the basis of the mechanism suggested in [1]; however, under solvolytic conditions the corresponding differential equation is simpler:

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = k_1 c + k_2 c(c_0 - c) \qquad (1)$$

where c is the concentration of the substrate, c_0 is the initial concentration of the substrate, $c_0 - c$ is the concentration of pyrrolidine formed during the solvolysis, $k_1 = \bar{k}_1 a^2$ and $k_2 = \bar{k}_2 a$, where a is the constant concentration of isopropanol, and $\bar{k}_1$ and $\bar{k}_2$ are the same as in [1]. By integration of Eq. (1) we obtain

$$c = \frac{\left(k_1 c_0 + k_2 c_0^2\right)}{k_1 \exp\left[\left(k_1 + k_2 c_0\right)t\right] + k_2 c_0} \qquad (2)$$

where k_1, k_2 and c_0 were considered as parameters in the regression analysis.

The measured and calculated concentration values of substrate depending on the reaction time and the rate constants obtained from the evaluation of Eq. (2) are summarized in Table 3. Fig. 1 shows the excellent agreement between the experimental and the calculated data.

4. Experimental details [3,4]

4.1. Preparation of the trimethylsilyl ester of pyrrole-N-carboxylic acid (method B)

All operations were carried out under moisture-free conditions.

Freshly cut potassium (13.0 g, 332 mmol) was added into a 500 ml three-necked flask equipped with a

Table 4.
Rates of the solvolysis depending on the concentration of LiCl (in an isopropanol–dioxane mixture of 1/1 (v/v) ratio at 25 and 35°C)

c (mol dm^{-3})	$k(\times10^5$ s$^{-1})$					
	5		**6**		**7**	
	25°C	35°C	25°C	35°C	25°C	35°C
1×10^{-2}	7.0	18.1	29	66	5.0	9.5
2×10^{-2}	33	64	101	172	13.3	22
$\Delta k/\Delta c$ (dm^3 mol^{-1} s^{-1})	0.026	0.046	0.072	0.106	0.008	0.012
$\Delta(\Delta k/\Delta c)/\Delta T$ (K dm^3 mol^{-1} s^{-1})	0.0020		0.0034		0.0004	

Table 5.
The temperature dependence of the rate constants

Temperature (°C)	$k(\times 10^5\ s^{-1})$					
	In an isopropanol–dioxane mixture of 1/3 (v/v) ratio, $c(LiCl) = 0$ M			In an isopropanol–dioxane mixture of 1/1 (v/v) ratio, $c(LiCl) = 10^{-2}$ M		
	1	**2**	**3**	**5**	**6**	**7**
25	116	77	47	7.0	29	5.0
35	125	85	55	18.1	66	9.5
45	133	100	68	57	220	21.3
$\Delta H^\ddagger$ (kJ mol^{-1})	3	8	12	80	77	54
$\Delta S^\ddagger$ (J mol^{-1} K^{-1})	−292	−279	−269	−56	−54	−145
$\Delta G^\ddagger$ (25°C) (kJ mol^{-1})	89.8	90.8	92.0	96.8	93.4	97.7

stirrer, a condenser, a dropping funnel and gas inlets. Then 150 ml of abs. dioxane was transferred and the content of the flask was heated to melt potassium under stirring. After the heat source had been removed, 22.3 g (332 mmol) of abs. pyrrole in 40 ml of dioxane were added dropwise while vigorously stirring. After the complete disappearance of the small pieces of potassium, dried carbon dioxide was introduced under ice cooling for 2 h. A solution of 42.2 ml (332 mmol) of trimethylchlorosilane in 100 ml of dioxane was added dropwise; the mixture was allowed to warm to room temperature and then stirred for a further 1 h. After filtration, the solvent was evaporated at reduced pressure and the product was purified by vacuum distillation.

The other compounds were prepared by the general procedure A or B (Table 1).

4.2. Rate measurements

For the solvolysis reactions followed by UV spectrophotometry, materials and experimental conditions were the same as described in [3].

In the kinetic measurements carried out using GC, the reaction media were isopropanol–dioxane mixtures of 1/3 (v/v) ratio containing the substrate at the initial concentration of approximately 2×10^{-2} mol dm^{-3}. The GC parameters and the *n*-alkane internal standard were selected so that the peak of the standard was well separated from those of the other components on the chromatogram. The initial oven temperatures and the internal standards were the following for the substrates: **1** and **4**, 110°C, *n*-dodecane and *n*-undecane, respectively; **2** and **5**, 180°C, *n*-octadecane; **3** and **6**, 220°C, *n*-eicosane.

The rate of temperature increase was 10°C min^{-1}; the concentration of the internal standard was approximately 1×10^{-2} mol dm^{-3}. The linearity of the relative molar response of detector was checked for **4** the silicon content of which is the highest of all compounds.

Screw-capped vials containing samples were equipped with a Mininert valve and thermostated within ±0.1°C. In each run 1 μl of sample was transferred on the GC column as quickly as possible. The concentration of substrate relative to that of the internal standard was determined sufficiently frequently so as to obtain at least 13–15 data points within the 20–90% conversion range in most runs.

4.3. Instrumentation

For details of the mass spectroscopy, NMR, IR and UV measurements see [3].

The GC retention indices were determined under the same parameters as described there [3] except for the oven temperature (Table 1).

Acknowledgement

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