

Solvolysis of trimethylsilyl-*N*-aryl carbamates

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Abstract

The kinetics of the solvolysis reaction of various trimethylsilyl esters of *N*-aryl carbamic acid with isopropanol was studied.

UV spectrophotometry was used to monitor the reaction and the pseudo first order rate constants were determined. The experiments were carried out in dioxane solutions containing lithium chloride. A reaction mechanism is suggested on the basis of the dependence of the reaction rate on ionic strength, the parameters of activation, the reaction constant (ρ) and the isotope effect.

Introduction

Silylated carbamic acid derivatives are efficient for the silylation of various compounds containing protic hydrogen (alcohols, phenols, acids, aromatic amines) [1–4]. In a previous study the alcoholysis of trimethylsilyl *N,N*-dimethylcarbamate has been reported [5]. Here we describe the kinetic study of the solvolysis of trimethylsilyl-*N*-aryl carbamates.

The hydrolysis reactions of *N*-aryl-*N*-trimethylsilyl urethanes were thoroughly studied by Rühlmann et al. [6–8]. In general the base- and acid-catalyzed solvolysis of these compounds was found to follow an S_N2 -Si mechanism.

Experimental

Materials

Dioxane (Fluka, UV grade) was refluxed in the presence of sodium metal and freshly distilled over sodium before use. Isopropanol (Fluka, UV grade) was refluxed in the presence of calcium hydride and then distilled, sodium (8 g/l) was added, and it was redistilled before use [9]. *O*-Deuteroisopropanol was prepared by

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Table 1

Physical constants and yields of XPhNHCOOSiMe₃ compounds

X	Reaction time (h)	Yield (%)	Melting point (°C)	GC ret. indices
1 H	6	45	129–131	1485 ± 2
2 <i>o</i> -Me	16	19	66–67	1506 ± 3
3 <i>p</i> -Me	8	43	82–84	1587 ± 2
4 <i>m</i> -Me	14	63	73–74	1536 ± 2
5 <i>m</i> -MeO	17	41	56–58	1708 ± 3
6 <i>p</i> -MeO	15	61	63–65	1723 ± 3
7 <i>p</i> -Cl	8	51	105–107	1683 ± 3
8 <i>m</i> -Cl	8	64	54–55	1663 ± 3
9 <i>m</i> -Br	15	43	68–69	1742 ± 3

basic hydrolysis of diisopropyl ester of oxalic acid in heavy water, and its water content was removed as for isopropanol. The deuterium content of the product was deduced from its IR spectrum. The lithium chloride (Fluka, puriss. p.a.) which was used to adjust the ionic strength was desiccated by heating at 400°C, and then stored in an exsiccator containing phosphorous pentoxide. Trimethylsilyl *N*-aryl carbamates were prepared by allowing the corresponding aryl amine, carbon dioxide and hexamethyldisilazane to react [10] and were recrystallized several times from hexane. The purified materials were stored in sealed glass ampoules. The physical constants and yields are listed in Table 1 and Table 2 contains the MS, IR and ¹H NMR data.

Dioxane solutions containing 2×10^{-3} mol dm⁻³ of the given compound were prepared. The concentration of the isopropanolic solution of the lithium chloride was 2.0×10^{-2} mol dm⁻³.

Kinetic measurements

The reaction was followed by measurement of the extinction of the aryl amine formed during solvolysis. The wavelength was selected so as to avoid interference by the extinction of carbamate (Table 3).

Table 2

MS, IR and ¹H NMR data of XPhNHCOOSiMe₃ compounds

X	MS			IR (in CCl ₄)		¹ H NMR (δ) (in CDCl ₃) (standard TMS)	
	<i>M</i> ⁺	<i>M</i> - 15 ⁺ Int. (%)	<i>M</i> - 15 ⁺ Int. (%)	<i>ν</i> (N-H) (cm ⁻¹)	<i>ν</i> (C=O) (cm ⁻¹)	<i>δ</i> (NH) (ppm)	<i>δ</i> (OSiMe ₃) (ppm)
	<i>m/e</i>						
1 H	209	34	17	3440	1719	6.76	0.34
2 <i>o</i> -Me	223	45	21	3455	1719	6.45	0.34
3 <i>p</i> -Me	223	42	14	3445	1717	7.11	0.31
4 <i>m</i> -Me	223	31	12	3448	1718	6.65	0.34
5 <i>m</i> -MeO	239	51	18	3440	1719	7.25	0.33
6 <i>p</i> -MeO	239	85	21	3445	1715	7.25	0.33
7 <i>p</i> -Cl	243	43	26	3435	1720	6.75	0.33
8 <i>m</i> -Cl	243	40	23	3445	1722	6.75	0.33
9 <i>m</i> -Br	287	38	20	3444	1721	6.90	0.35

Table 3

Wavenumbers used in the measurement of solvolysis reactions

X	ν (cm ⁻¹)
<i>p</i> -MeO	31500
<i>p</i> -Me	33500
<i>m</i> -Me	34000
H	33500
<i>m</i> -MeO	33500
<i>p</i> -Cl	33000
<i>m</i> -Cl	33500
<i>m</i> -Br	33500
<i>o</i> -Me	34000

The measurements were carried out with a Specord M40 UV/VIS spectrophotometer using thermostated 0.5 cm stoppered cells. The blank was a 1/1 mixture of isopropanol containing lithium chloride and pure dioxane. The measuring cell contained a 1/1 mixture of the solution of the compound to be measured and the isopropanol containing lithium chloride. The solutions were thermostated to the temperature of measurement before mixing. The rate constant of the pseudo first order reaction was calculated from the slope of the $\ln\{E_\infty - E(t)\}$ vs. t plot.

Results

Preliminary experiments revealed that the hydrolysis of the trimethylsilyl esters of *N*-aryl carbamic acid is so rapid that it cannot be followed by photometry, however, the rate of the reaction with isopropanol can be conveniently and so it was used in the experiments.

Firstly, the effect of ionic strength on the rate of solvolysis was studied for trimethylsilyl *N*-phenylcarbamate in LiCl solutions of various concentrations. The results are listed in Table 4.

It is apparent that the reaction rate was increased by increasing LiCl concentration, thus we can conclude that a polar intermediate was formed during the reaction.

The solvolysis of various $\text{XC}_6\text{H}_4\text{NHCOOSiMe}_3$ compounds was studied as a function of temperature. The experimental results are shown in Table 5. Since the relationship between the rate constants and the Hammett σ -values [11] shown in Fig. 1 was found to be linear we presumed that the reaction mechanism of the compounds under study must be identical. The positive values of the reaction

Table 4

The dependence of the rate of solvolysis of trimethylsilyl *N*-phenyl carbamate on the concentration of LiCl

LiCl concentration (mol dm ⁻³)	$k \times 10^5$ (s ⁻¹)
0.0	4.9
2.0×10^{-2}	11.3
4.0×10^{-2}	19.8

Table 5

The pseudo first order rate constants of the solvolysis of $XPhNHCOOSiMe_3$ compounds with isopropanol

X	25 °C	35 °C	45 °C
	$k \times 10^5 (s^{-1})$	$k \times 10^5 (s^{-1})$	$k \times 10^5 (s^{-1})$
<i>p</i> -MeO	3.8	7.6	15.1
<i>p</i> -Me	4.5	8.8	16.9
<i>m</i> -Me	5.0	9.5	18.6
H	6.0	11.3	22.1
H ^a	5.5	10.8	21.5
<i>m</i> -MeO	7.9	14.3	25.5
<i>p</i> -Cl	9.0	16.1	29.4
<i>m</i> -Cl	12.9	22.3	39.3
<i>m</i> -Br	14.1	22.1	34.8
<i>o</i> -Me	9.0	19.4	38.8

^a The solvolysis was carried out with *O*-deuteroisopropanol.

constants (ρ) point to the fact that the rate-determining step of the reaction is a nucleophilic attack on the silicon atom. The relatively small value of the reaction constants due to the separation of the reaction center (Si) from the aromatic ring by several atoms and consequently the effect of the substituent of the aromatic ring, is weakly extended to the silicon atom through the conjugated bond system of the compound [12–17].

The ρ -values determined at various temperatures are listed in Table 5.

The temperature dependence of the reaction constant (Table 7) indicates that the reactivity of the compounds is increased by increasing temperature and that the specific effect of the substituents is manifested less at higher temperatures.

Table 6

Activation parameters of the reaction of $XPhNHCOOSiMe_3$ compounds with isopropanol

X	ΔH (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J K mol ⁻¹)	$\Delta G^\ddagger$ (kJ mol ⁻¹)
<i>p</i> -MeO	50	-162	100
<i>p</i> -Me	48	-166	100
<i>m</i> -Me	47	-169	99
H	47	-167	98
H ^a	50	-160	99
<i>m</i> -MeO	42	-183	98
<i>p</i> -Cl	42	-180	98
<i>m</i> -Cl	40	-187	97
<i>m</i> -Br	32	-212	97
<i>o</i> -Me	50	-160	99

^a The solvolysis was carried out with *O*-deuteroisopropanol.

Table 7

The reaction constant (ρ) at various temperatures

	25 °C	35 °C	45 °C
Reaction constant	0.85	0.73	0.61

Table 8

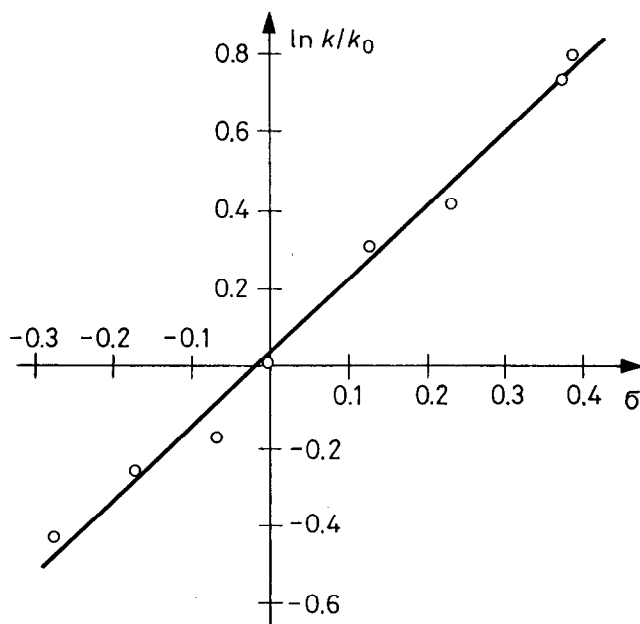
Wavenumbers of $\nu(\text{N-H})$ band of some XPhNHCOOSiMe_3 compounds in hexane and dioxane (cm^{-1})

X	Dioxane	Hexane	$\Delta \nu(\text{N-H})$
<i>p</i> -MeO	3318	3455	137
<i>m</i> -Me	3312	3452	140
H	3307	3452	140
<i>m</i> -MeO	3305	3455	150
<i>m</i> -Br	3291	3451	160
<i>o</i> -Me	3312	3467	155

Comparison of the data of the 4th and 5th rows of Tables 5, 6 indicates that the isotope effect is very weak ($k(\text{i-PrOH})/k(\text{i-PrOD}) = 1.09$, 25°C). Protonation does not take place in the rate-determining step and it cannot be the first step of the reaction either i.e. protonation takes place during the rapid process after nucleophilic attack.

The activation parameters calculated on the basis of the temperature dependence of the rate constants are listed in Table 6.

It is clear that the activation enthalpies and activation entropies decrease because of increased electron attracting ability of the substituents. This can be explained by the fact that the charge separation in the molecule is larger under the effect of the electron-attracting substituent and consequently a more polar transition state which is more solvated is formed. The transition state is stabilized by an increase in solvation and corresponds to increased order in the structure which results in a more negative activation entropy. It is noteworthy, from the data of Table 5, that

Fig. 1. The Hammett relationship (at 25°C).

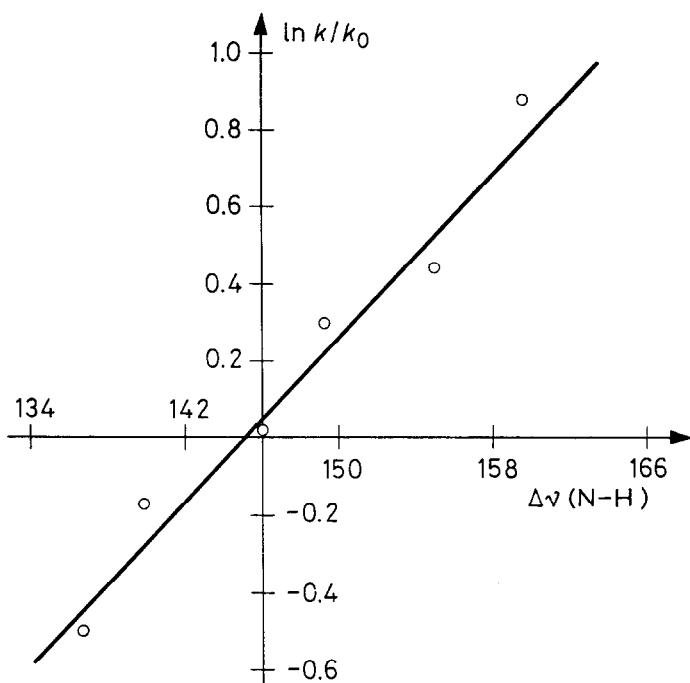
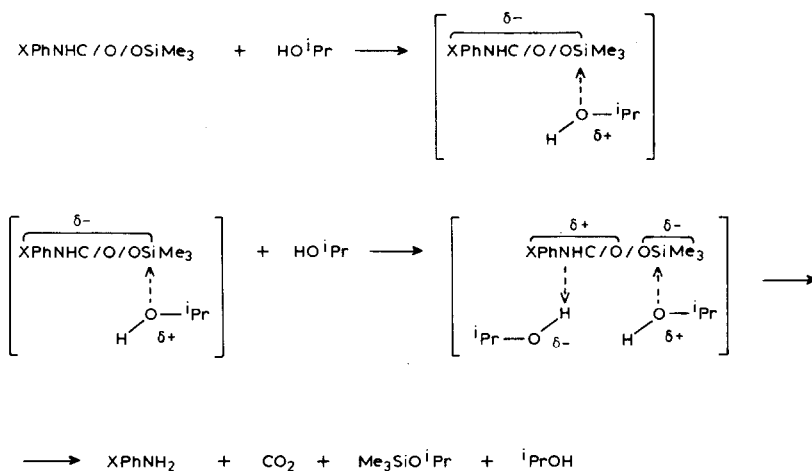


Fig. 2. $\ln k/k_0$ plotted vs. $\Delta\nu(\text{N-H})$.

the rate of solvolysis of *ortho*-tolyl derivatives is greater than that of the corresponding *para* or *meta* isomers, which is contrary to expectation.

In order to elucidate this phenomenon, $\nu(\text{N-H})$ vibration frequencies of the above compounds were determined in an apolar solvent (hexane) and in dioxane, which was also used as the medium for the kinetic measurements. Table 8 lists the



Scheme 1

data obtained at 0.5 mol dm^{-3} concentration. The difference in the vibration frequencies of the two solvents is linearly correlated with the logarithm of the relative rate constants of the compounds including the *o*-tolyl derivative (Fig. 2). These $\Delta\nu$ values correspond to solvation encountered in kinetics measurements. Thus the mechanism of the solvolysis of the *o*-tolyl derivative is identical to that of the other compounds. The steric hindrance of the *o*-methyl substituent was not evident. The larger activation enthalpy and entropy values indicate that *o*-tolyl compound is less solvated and has a less polar structure in the transition state.

Thus from the foregoing, the solvolysis of the compounds under study can best be described by reaction Scheme 1. Nucleophilic attack of isopropanol on the silicon atom of the trimethylsilyl ester of *N*-aryl carbamic acid follows the $S_N2\text{-Si}$ mechanism, and is both the first and rate-determining step. This step is followed by rapid protonation of the intermediate which converts into the product.

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