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# RATE STUDIES OF SILYLATION WITH SILYLAMIDES

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## Summary

The rates of silylation of *p*-nitrophenol with *N,O*-bis(trialkylsilyl)acetamides in dioxane have been measured, the reaction shown to be slowed down by replacing methyl by ethyl in the trialkylsilyl group. The rates of methanolysis of some *N,O*-bis(aryldimethylsilyl)acetamides (I) and *N*-aryldimethylsilylacetamides (II) have been measured. The reactions of compounds II were found to be acid catalyzed and accelerated by electron-withdrawing substituents in the benzene ring. At 30°C the methanolysis was shown to be entropy controlled. Compounds of series I were found to be aproximately 1000 times more reactive than those of series II. Introducing a methyl at nitrogen in the monosilylamides produced a similar rate enhancing effect as introduction of a second silyl group. Promotion of $(p\text{-}d)\pi$ coordination of silicon to oxygen or nitrogen in the ground state of the silylamide molecule is suggested as the factor responsible for this effect.

## Introduction

The structure and reactivity of silylamides depend on the groups making up the molecule. In most cases the disilylamides have the *N,O*-disilyliminoether structure and in silylation the silyl group is replaced by hydrogen from the silylated substrate [1]. However, bis(trimethylsilyl)formamide is an *N,N*-disilylamide [2], and we have recently found that bis(halomethyldimethylsilyl)-amides also have the *N,N*-disilylamide structure [3]. The latter compounds do not lose their silyl groups on solvolysis, the carbon—halogen bonds being cleaved instead.

Despite the wide use of *N,O*-bis(trimethylsilyl)acetamide (BSA) in silylation, little is known about the kinetics and mechanisms of this process. The reaction

of trimethylsilylacetanilides with ethanol and t-butanol was investigated by Klebe and Bush [4] who found that electron-withdrawing substituents in the benzene ring increased the rate of silylating within this series. BSA was found to have a superior silylating power to any of the silylanilides. A mechanism for the reaction involving formation of an octahedral transition state was suggested [5].

To gain more knowledge on the mechanism of silylation we have measured the rates of methanolysis of mono and bis silylated amides in which one of the substituents at silicon is aromatic.

## Results and discussion

Initially we measured the rates of the reaction of three bis(trialkylsilyl)acetamides with *p*-nitrophenol in dioxane (Table 1). In the presence of an excess of silylamide the reaction is irreversible and *p*-nitrophenoxysilane and trialkylsilylacetamide are the products. The progress of the reaction was followed by recording the changes in the UV spectrum.

First-order rate constants $k_1$ determined from the slope of the initial straight section of the log[*p*-$NO_2C_6H_4OH$] vs. time line changed with varying proportion of initial concentrations of the reagents, in spite of a 20 to 150 molar excess of silylamide used. However, the second-order rate constant $k_2$ obtained as $k_1$/(initial concentration of silylamide) was fairly constant. From its values the relative rates of reaction of the silylamides could be roughly evaluated, and showed bis(dimethylethylsilyl)acetamide and bis(triethylsilyl)acetamide to be 2.8 times (30°C) and 24.6 times (25°C), respectively, less reactive than BSA. Silylation with silylamides is thus subject to steric hindrance by substituents at silicon.

To determine the magnitude of the polar effects of substituents we measured the rates of methanolysis of two series of silylamides containing substituents in the benzene ring:

*N,O*-bis(dimethylarylsilyl)acetamides (I)

and *N*-dimethylarylsilylacetamides (II)

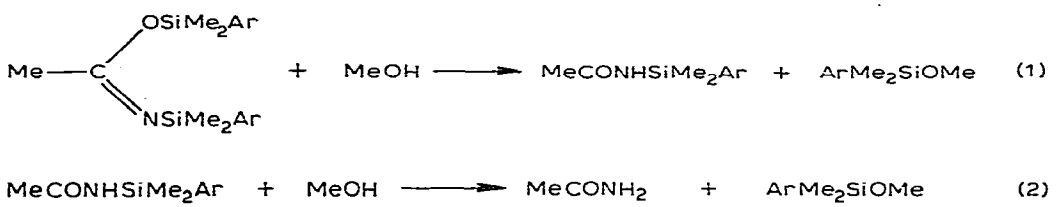
The iminoether structure of the compounds of series I was established previously [6]. These compounds react according to the equations:

TABLE 1

KINETIC DATA FOR THE REACTION OF BIS(TRIALKYLSILYL)ACETAMIDES $MeCON(SiR^1R^2R^3)_2$ WITH *p*-NITROPHENOL IN DIOXANE

| | Temp.(°C) | $10^4\ a_0$ [a] | SA/N [b] | $k_1$ ($min^{-1}$) | $k_2$ (l $mol^{-1}$ $min^{-1}$) |
|---|---|---|---|---|---|
| $R^1 = R^2 = R^3 = Me$ | 26 | 1.19 | 80 | 0.172 | 18.1 |
| | | 1.83 | 26 | 0.089 | 18.7 |
| | 30 | 1.17 | 80 | 0.167 | 17.8 |
| | | 1.77 | 26 | 0.087 | 18.9 |
| $R^1 = R^2 = Me$; $R^3 = Et$ | 30 | 1.22 | 140 | 0.108 | 6.3 |
| | | 1.83 | 47 | 0.068 | 7.9 |
| $R^1 = R^2 = R^3 = Et$ | 25 | 1.41 | 150 | 0.016 | 0.76 |

[a] Initial concentration of *p*-nitrophenol (mol $l^{-1}$). [b] Initial ratio of concentration of silylamide and *p*-nitrophenol.




Reaction (1) was too fast to follow in methanol, and a dioxane/methanol (9/1, v/v) medium had to be used. In this solution the monosilylamides reacted ca. 1000 times slower than the disilylamides (Table 2). Only two compounds of series I were investigated kinetically. Due to low volatility and limited thermal

TABLE 2

SOLVOLYSIS OF SILYLACETAMIDES IN DIOXANE-METHANOL MIXTURE (9 : 1 v/v)

| Compound | Temp.(°C) | $10^3k$ ($min^{-1}$) | $E_a$ (kcal $mole^{-1}$) |
|---|---|---|---|
| $MeCON(SiMe_2Ph)_2$ | 20 | 186 | 4.1 |
| | 25 | 213 | |
| | 30 | 248 | |
| | 35 | 260 | |
| | 40 | 293 | |
| $MeCON[SiMe_2(pMeC_6H_4)]_2$ | 30 | 166 | 10.3 |
| | 40 | 272 | |
| | 45 | 359 | |
| $MeCON(Me)SiMe_2Ph$ | 40 | 301 | |
| $MeCONHSiMe_2Ph$ | 40 | ca. 0.45 | |

TABLE 3

SOLVOLYSIS OF $MeCONHSiMe_2C_6H_4X$ COMPOUNDS IN A METHANOLIC SOLUTION OF ACETIC ACID (0.05 *M*), SODIUM ACETATE (0.005 *M*) AND LITHIUM CHLORIDE (0.02 *M*)

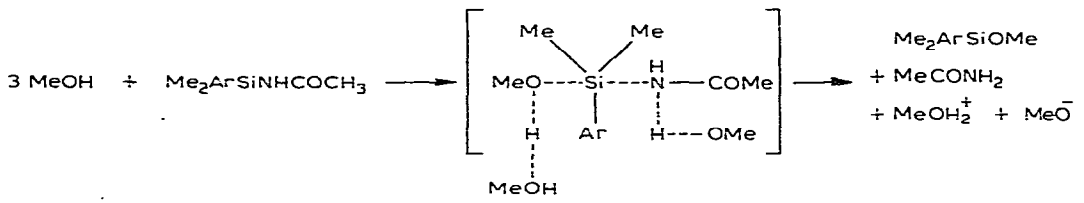
| X | Temp. (°C) | $10^3k$ ($min^{-1}$) | $k_{rel}$ | $E_a$ (kcal $mole^{-1}$) | log *A* (30°) |
|---|---|---|---|---|---|
| H | 30 | 91.2[a] | | | |
| | | 91.0[b] | | | |
| | | 94.4[c] | | | |
| | | 93.3[d] | | | |
| | 30 | 96.6 | 1.000 | 18.1 | 12.0 |
| | 40 | 252.3 | | | |
| | 30 | 91.0[e] | | | |
| *p*-$CH_3$ | 30 | 66.0 | 0.68 | 17.6 | 11.5 |
| | 40 | 167.8 | | | |
| *p*-Br | 30 | 204.4 | 2.11 | | |
| *m*-Cl | 30 | 275.3 | 2.85 | 18.3 | 12.6 |
| | 40 | 700.3 | | | |
| *m*-$CF_3$ | 30 | 323.2 | 3.35 | 21.1 | 14.7 |
| | 40 | 988.0 | | | |

[a,b] At constant concentrations of LiCl (0.04 *M*) and MeCOONa (0.005 *M*) and varying concentrations of MeCOOH: 0.02 *M* for *a* and 0.07 *M* for *b*. [c,d] At constant concentrations of MeCOOH (0.05 *M*) and MeCOONa (0.005 *M*) and varying concentrations of LiCl: 0.01 *M* for *c* and 0.1 *M* for *d*. [e] In methanol and deuterated acetic acid (MeOD and $CH_3COOD$).

stability, the other compounds of this series could not be obtained sufficiently pure for rate measurements [6].

Solvolysis of the *N*-dimethylarylsilylacetamides was carried out in anhydrous methanol containing fixed amounts of acetic acid, sodium acetate, and lithium chloride, to maintain a constant acidity and ionic strength. However, it should be noted that for dimethylphenylsilylacetamide the rate was independent of acid concentration (at constant concentration of salts) and of salt concentration (at constant acidity) within 0.01 to 0.1 *M* of either acid or salt (Table 3). Neither was the rate affected (within experimental error) by using the deuterium-containing compounds MeOD and MeCOOD in place of methanol and acetic acid.

These results show that initial protonation of the silylamide does not seem to be indispensable for the attack by a methanol molecule on silylamide to take place. Proton transfers from and to methanol would be clearly necessary as represented in the hypothetical form of the transition state for the reaction:




but they could occur in fast consecutive steps.

However, addition of 1 $\mu$l of methanol saturated with hydrogen chloride to 2 ml of the solution caused an instantaneous complete conversion. The reaction is thus acid catalysed but at low methoxonium ion concentrations the "spontaneous" reaction prevails. Catalysis by undissociated acetic acid is undetectable, presumably because of the small Bronsted coefficient for the reaction. In methanolysis of a series of trimethylsilylbenzamides a similar apparent lack of dependence of rate on acid concentration at low acidities and a very small deuterium isotope effect was also found [7]. On the other hand, solvolysis of trialkylsilylanilines in aqueous methanol was shown to be subject to powerful oxonium ion catalysis which precluded detection of any general acid catalysis [8]. This difference in behaviour between silylamines and silylamides is probably due to the lower basicity of the latter.

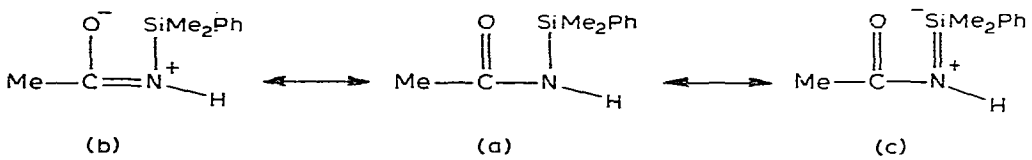
The effects of substituents in the benzene ring are reflected in the values of the relative rates ($k_{rel}$), activation energies ($E_a$) and log $A$ factors in Table 3. Electron-withdrawing substituents accelerate the reaction and from a plot of log $k_{rel}$ vs. Hammett $\sigma$ constans a $\rho = 1.4$ can be calculated. However, the changes in activation energies do not follow the expected trend and, indeed, the highest rate corresponds to the highest energy of activation for the reaction of the trifluoromethyl substituted amide. The remaining compounds all have activation energies lying within 0.5 kcal/mole of 18 kcal/mole, which is the estimated experimental error. The reaction is thus entropy controlled at 30°C, which is also reflected in the variations of the log $A$ factor.

The effect of electron-withdrawing substituents may be to disperse the nega-

tive charge and thus reduce the solvation requirements of the transition state. This would result in increased entropy of activation but also contribute to lowering the energy of the activated complex. To account for the observed increase in activation energy (at least in the case of the *m*-trifluoromethyl group) another explanation must be offered. It seems plausible that *m*-trifluoromethyl will strengthen the $(p\text{-}d)\pi$ interaction between silicon and nitrogen in the ground state of the silylamide, thus heightening the energy barrier to reach the transition state where the Si—N bond is partly broken. If this effect is stronger than the other, that of reduction of the charge density in the transition state, the net result will be a rise in the energy of activation.

Introducing a methyl or a second aryldimethylsilyl group in place of hydrogen at nitrogen produces a substantial increase in the reactivity of a silylamide in methanolysis (Table 2). In dioxane-methanol (9/1, v/v) the rate constant is increased by three orders of magnitude. The energies of activation are decidedly lower than in solvolysis of series II in methanol. This suggests that substantial changes in the structure of the molecule are now involved which give rise to reaction paths which are inaccessible for silylamides unsubstituted at nitrogen. Bis-silylamides were long known to be more reactive than mono-silylamides in silylation, but no comparative data have been reported and no explanation for this fact has been advanced.

It is possible that a silyl group at nitrogen hinders the resonance (a) ⟷ (b) in the amide system due to participation of structure (c):




(b) (a) (c)

On substitution of an alkyl group for hydrogen, the positive inductive effect may again facilitate this resonance and raise the energy barrier to rotation around the C—N bond and stabilization of the rotamer in which a partial $(p\text{-}d)\pi$ bond between silicon and oxygen can be formed. With silicon assuming a tetragonal pyramid (or trigonal bipyramid) structure, as suggested by Klebe [5], the molecule may become highly reactive because of the slight change of geometry which is necessary to assume the tetragonal bipyramidal structure of the transition state in nucleophilic substitution.

*N*-aryl substituted silylacetamides (silylacetanilides) are known to occur in solution as tautomeric mixtures of the amide and iminoether forms [4,9] and hindered rotation around C—N in the amide tautomers has been recently established [10]. Restricted rotation was also observed in *N*-methyl-*N*-trimethylsilylacetamide [11].

In the bis(aryldimethylsilyl)acetamides the silyl groups are in a state of constant mutual exchange between nitrogen and oxygen. One of the silicon atoms is always attached to nitrogen in the ground state of the molecule thus fulfilling the previously mentioned requirements for high reactivity in nucleophilic substitution.

TABLE 4

PHYSICAL AND NMR DATA FOR $MeCONRSiMe_2C_6H_4X$

| R | X | Yield (%) | B.p. (°C/mmHg) | M.p. (°C) | Analysis found (calcd.) (%) | | | δ values[a] (ppm) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Si | C | H | MeSi | MeC | NH | $C_6H_4$ [b] | X |
| H | H | 85 | 125—7/3 | 56 | 14.30 (14.52) | | | 0.45 | 1.80 | 6.02 | 7.4m | |
| H | *p*-$CH_3$ | 80 | 120—2/0.2 | 63 | 13.45 (13.55) | | | 0.41 | 1.85 | 6.05 | 7.3k | 2.30 |
| H | *p*-$CH_3O$ | 70 | | 54 | 12.68 (12.75) | | | 0.40 | 1.80 | 6.02 | 7.2k | 3.73 |
| H | *m*-Cl | 54 | 85—7/$10^{-3}$ | 45 | 12.29 (12.33) | 53.04 (52.73) | 6.31 (6.14) | 0.45 | 1.86 | 6.43 | 7.5m | |
| H | *m*-$CF_3$ | 55 | 82—5/$10^{-2}$ | 55 | | 50.72 (50.56) | 5.47 (5.40) | 0.42[c] | 1.68 | 6.89 | 7.6m | |
| H | *p*-Br | 50 | | 73—5 | 10.63 (10.32) | | | 0.38[c] | 1.80 | 6.35 | 7.4k | |
| H | *p*-$Me_2N$ | 27 | | 72—3 | 11.42 (11.88) | | | 0.51[d] | 1.64 | | | 2.56 |
| Me | H | 44 | 93—4/2 | | 13.19 (13.54) | | | 0.49 | 1.80 | 2.70[e] | 7.4m | |

[a] Chemical shifts recorded on JEOL C-60HL spectrometer on 10% solutions in $CCl_4$ at room temperature with TMS as internal standard. [b] k denotes quartet, m denotes centre of multiplet. [c] Dioxane as internal standard. [d] Benzene as solvent; it masks signals of NH and $C_6H_4$ groups. [e] Value for Me—N group.

## Experimental

Syntheses of *N,O*-bis(aryldimethylsilyl)acetamides and *N,O*-bis-(trialkylsilyl)-acetamides were described previously [6].

*N-aryldimethylsilylacetamides*

The appropriate aryldimethylchlorosilane (0.11 mol) was added dropwise to a solution of acetamide (or *N*-methylacetamide) (0.1 mol) in triethylamine (100 ml) and subsequently refluxed for 4 h. After filtering, the triethylamine hydrochloride was extracted with boiling cyclohexane (15 ml) or, alternatively, cyclohexane (20 ml) was added to the reaction mixture which was then filtered hot, since the solubility of monosilylacetamides in $Et_3N$ is limited. The filtrates were combined, the solvents were evaporated, and the residue was distilled or recrystallized from cyclohexane or n-heptane. The physical constants and NMR data are listed in Table 4.

*Reaction of bis(trialkylsilyl)acetamides with p-nitrophenol*

The appropriate bis(trialkylsilyl)acetamide (0.06 mol) was added dropwise to a suspension of *p*-nitrophenol (0.05 mol) in n-hexane (30 ml). The progress of the reaction was followed by observing the gradual dissolution of p-nitrophenol which is insoluble in n-hexane. The clear solution obtained was fractionally distilled to give trialkylsilylacetamides and trialkyl(*p*-nitrophenoxy)silane. Physical constants and analyses of new compounds: $MeCONHSiMe_2Et$, b.p. 107—9°C/20 mmHg, $n_D^{25}$ 1.4400, Si found 19.20 (calcd. 19.33): $p$-$NO_2C_6H_4OSiMe_2Et$, b.p. 116°C/2 mmHg, $n_D^{25}$ 1.5248, Si found 12.50 (calcd. 12.46); $p$-$NO_2C_6H_4OSiEt_3$ (cited in [12], but no data were given), b.p. 143—4°C/2.5 mmHg, $n_D^{25}$ 1.5250, Si found 11.10 (calcd. 11.08).

*Kinetic studies*

A Specord UV-VIS spectrophotometer was used for all kinetic runs.

*Silylation of p-nitrophenol*

Thermostatted solutions of *p*-nitrophenol and bis(trialkylsilyl)acetamide in dioxane were mixed in appropriate proportions and a sample was transfered to a thermostatted cell. The reaction was followed by recording the changes in absorption at 320 mμ.

*Methanolysis of aryldimethylsilylacetamides I and II*

*I.* A dioxane-methanol mixture (9 : 1 v/v) was thermostatted in the spectrophotometer cell and the calculated amount of bis(aryldimethylsilyl)acetamide was added. Changes in the UV absorption at 238 mμ were recorded to 90% conversion.

*II.* Samples of stock solutions of acetic acid, sodium acetate and lithium chloride in anhydrous methanol were mixed in a volumetric flask in calculated proportions and diluted to obtain the desired concentration. The solution was transfered to the spectrophotometer cell, the aryldimethylsilylacetamide was added and rate measurements were carried out as for I.

Rate constants of methanolysis of aryldimethylsilylacetamides were calculated by Guggenheim method and values given are averages from a minimum of 3 determinations.

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