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HAMMETT CORRELATIONS FOR THE SOLVOLYSIS OF SILYLPYRROLES

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Summary

The silicon—nitrogen bond in $(X{-}C_6H_4)Me_2SiNC_4H_4$ (X = *p*-MeO, *p*-Me, *m*-Me, H, *p*-F, *p*-Cl) is cleaved in absolute ethanol containing sulphuric acid or amine buffers. The logarithms of the rate constants correlate with σ^0-constants, the ρ-values being −0.97 for the acid-catalysed reaction, and +1.8 and +2.6 for the reactions catalysed by amine and ethoxide anion, respectively. Mechanisms involving pentacoordinate silicon are suggested.

Introduction

Compounds containing a silicon—nitrogen bond are known to be reactive, and silyl-amines and -amides are widely used in silylation reactions to replace active hydrogens [1]. The stability of the silicon—nitrogen bond in stationary phases for high pressure liquid chromatography was recently studied [2], and the mechanism of nucleophilic substitution at silicon has been studied in solvolytic reactions with oxygen as the leaving atom [3,4]; this study has now been extended to include nitrogen as the leaving atom. Trimethylsilylpyrrole is known to react in ethanol containing acid or base [5]. In the present study, the kinetics of silylpyrroles in ethanol have been studied under acidic and basic conditions. By attaching a substituted phenyl group to silicon it was possible to study the charge variations at silicon during the reactions.

Results and discussion

N-silylated pyrroles react in absolute ethanol containing acid or base according to eqn. 1. The reaction is first-order with respect to the organosilicon compound and is more susceptible to base catalysis than to acid catalysis (see below).

$$(X{-}C_6H_4)Me_2SiNC_4H_4 + EtOH \rightarrow (X{-}C_6H_4)Me_2SiOEt + HNC_4H_4 \quad (1)$$

TABLE 1

SOLVOLYSIS OF $(X{-}C_6H_4)Me_2SiNC_4H_4$ IN ABSOLUTE ETHANOL CONTAINING SULPHURIC ACID AT 25.0°, AND IN PARENTHESES AT 40.0°[a,b]

X	$[H_2SO_4] \times 10^3$ [mol/l]	$k \times 10^4$ $[s^{-1}]$	$k/[H_2SO_4]$ $(= k_A)$ $[l\ s^{-1}\ mol^{-1}]$	$\bar{k}_A$
p-MeO	2	4.20	0.210	
	4	9.65	0.241	
	8	18.4	0.230	
	16	34.6	0.216	0.224
p-Me	2	4.08	0.204	
	4	9.18	0.228	
	8	16.7	0.208	
	16	33.6	0.210	0.212
m-Me	2	3.42	0.171	
	4	6.75 (35.0)[c]	0.169	
	8	13.3	0.166	
	16	27.3	0.171	0.170
H	2	2.86	0.144	
	4	5.75 (29.5)[d]	0.144	
	8	11.7	0.146	
	16	22.6	0.141	0.144
p-F	2	2.16	0.108	
	4	4.14	0.104	
	8	8.34	0.104	
	16	16.9	0.106	0.105
p-Cl	2	1.71	0.0855	
	4	3.29	0.0822	
	8	6.75	0.0844	
	16	12.7	0.0794	0.0829

[a] $\rho = -0.97$, standard deviation 0.04, correlation coefficient −0.9965. [b] $\mu = 0.058$ by addition of $LiClO_4$. [c] $E_a = 20.2$ kcal mol^{-1}, $\Delta S = -7.3$ cal mol^{-1} K^{-1}. [d] $E_a = 20.2$ kcal mol^{-1}, $\Delta S = -7.7$ cal mol^{-1} K^{-1}.

A. Acid-catalysed solvolysis

This reaction has the following characteristics (see Table 1):

(1) it is first-order in catalyst ($2-16 \times 10^{-3}$ *N* sulphuric acid);

(2) The Hammett relationship (eqn. 2) is followed:

$$\lg k = \lg k^0 - 0.97 \cdot \sigma^0 \tag{2}$$

(3) activation parameters are: Activation energy $E_a = 20$ kcal mol^{-1} and activation entropy $\Delta S = -7.5$ cal mol^{-1} K^{-1}.

The function of the catalyst is to protonate the nitrogen atom and thus make a better leaving group. By analogy with the mechanism proposed by Eaborn and coworkers [6] for the acid-catalysed methanolysis of *N*-(trialkylsilyl)-anilines, the mechanism given in eqns. 3—5 for the alcoholysis of silylpyrroles is suggested. According to the electron-shift hypothesis, substituents on silicon which shift the bonding electron pair towards the nitrogen atom increase the rate of cleavage of the silicon—nitrogen bond, while the rate of formation of the silicon—oxygen bond will be decreased. From the sign of the reaction constant (eqn. 2) it is clear that electron donating substituents on silicon increase the rate, and that cleavage of the silicon—nitrogen bond determines the reactivity of the silyl-substituted pyrroles.

We may regard the ρ-value as an indicator of charge development at the transition state, and conclude that the silicon atom acquires a positive charge.

$$\mathrm{Si{-}N + ROH_2^+ \rightleftharpoons Si{-}NH^+ + ROH}\ \text{(fast)} \qquad (3)$$

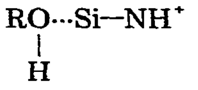
$$\mathrm{Si{-}NH^+ + ROH \rightarrow Si{-}ORH^+ + HN}\ \text{(slow)} \qquad (4)$$

$$\mathrm{Si{-}ORH^+ + ROH \rightarrow Si{-}OR + ROH_2^+} \qquad (5)$$

This charge could in principle result from the formation of a siliconium ion, as in eqn. 6, but such a mechanism is considered highly unlikely for solvolytic reactions in polar media [7]. If an $S_N1{-}Si$ mechanism were operating, we would expect the logarithms of the rates to be correlated with σ^+ constants [8], and not with σ^0 constants as observed (eqn. 2). Furthermore, positive or slightly negative activation entropies would be expected, contrary to the observed value. In conclusion, the available evidence seems to rule out an $S_N1{-}Si$ mechanism. The slow step, eqn. 4, is therefore of the bimolecular type. Electron-donating substituents on silicon increase the basicity of the nitrogen atom and so shift the protonation equilibrium 3 towards the right. At the same time, the rate-determining bond cleavage in step 4 will be facilitated by electron-donation, and it seems necessary to consider both these factors to explain the great difference in rates between the acid-catalysed ethanolysis of Si—N(pyrrole) and Si—N-(aniline) bonds [9]. The Si—N(aniline) bond is easily cleaved in ethanol without added catalyst, according to eqns. 3—5 above, even in moderately basic ethanol solution ($\rho = -1$). No base-catalysed cleavage was detected and *N*-protonation seems to be necessary for cleavage of silicon—nitrogen bonds where the cleaved group is as basic as *N*-methylaniline. For substrates having less basic nitrogen atoms, such as *N*-silyl-substituted pyrroles, acid-catalysed cleavage of the silicon—nitrogen bond becomes less facile, while base-catalysed cleavage becomes possible. In the absence of steric effects, the rates for the solvolytic cleavage of the silicon—nitrogen bond in acidic ethanol solution increase with the basicity of the nitrogen atom.

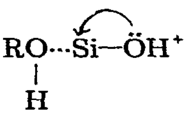
$$\mathrm{Si{-}NH^+ + ROH \rightarrow Si^+ + HN + ROH} \qquad (6)$$

The ρ-value of -1 in the acid-catalysed alcoholysis of the silylpyrroles (and silylanilines [9]) indicates more positive transition-state silicon than for the cleavage of silicon—oxygen bonds in similar media [3,4]. A possible explanation for this may be the different possibilities for back-donation in structures I and II.



$$\underset{\substack{|\\ \mathrm{H}}}{\mathrm{RO}}\cdots\mathrm{Si{-}NH^+}$$

(I)



$$\underset{\substack{|\\ \mathrm{H}}}{\mathrm{RO}}\cdots\mathrm{Si{-}\ddot{O}H^+}$$

(II)

While back-donation is not possible in I, the oxygen lone pair electrons in II may participate in π-orbital overlap with the empty $3d$ orbitals on the silicon atom and thus reduce the positive charge on silicon. It must be remembered, however, that $(d{-}p)\pi$ dative bonding between silicon and the hetero atom is weak in the ground states of both trimethylsilylpyrrole [10], and trimethylphenoxysilane [11,12].

The activation energy is 20 kcal mol^{-1}, and is considerably higher than the value of about 2 kcal mol^{-1}, measured for the acid-catalysed solvolysis of

TABLE 2

SOLVOLYSIS OF $(X{-}C_6H_4)Me_2SiNC_4H_4$ IN ABSOLUTE ETHANOL CONTAINING BUTYLAMINE BUFFERS AT 25.0°, EXCEPT WHEN GIVEN IN PARENTHESES (40.0°)[a,b]

X	$k \times 10^4$ (s^{-1}), $[BuNH_2]$[c] (M)				$k_{amine} \times 10^3$	$k_{EtO} \times 10^{-2}$
	0.20	0.15	0.10	0.05	($l\ s^{-1}\ mol^{-1}$)	($l\ s^{-1}\ mol^{-1}$)
p-MeO	6.65	4.56	4.31	2.70	2.70	3.0
p-Me	7.63	6.28	4.54	3.18	2.57	6.0
m-Me	8.62	7.85	5.59 (10.7)[d]	4.58 (9.90)[d]	3.14	7.0
H	14.0	11.3	9.40 (17.5)[e]	7.22 (13.4)[e]	4.43	13
p-F	29.6	22.4	20.8	14.7	9.85	24
p-Cl	57.5	48.1	41.4	31.9	16.2	62

[a] ρ(amine) = 1.8, standard deviation 0.1, correlation coefficient 0.9943, ρ(EtO) = 2.6, standard deviation 0.3, correlation coefficient 0.9741. [b] $\mu = 0.050$ by addition of $LiClO_4$. [c] The concentration of $BuNH_3^+Cl^-$ was one tenth of the base concentration in each case. [d] $E_a = 8.0$ and 9.5 kcal mol^{-1}, $\Delta S = -46$ cal mol^{-1} K^{-1}. [e] $E_a = 7.7$ and 7.6 kcal mol^{-1}, $\Delta S = -49$ cal mol^{-1} K^{-1}.

silylanilines [9]. The activation entropy of -7.5 cal mol^{-1} K^{-1} is much less negative than the figure of about -62 cal mol^{-1} K^{-1} found for the silylanilines [9]. Since the electronic situation at the silicon atom is the same in the two reaction series (identical ρ-values) we may reasonably assume that the transition state energy associated with the leaving group is different in the two cases. Protonation of the pyrrolic nitrogen involves loss of aromatic character while the anilinic nitrogen is protonated without any loss of aromaticity. The higher activation energy is thus expected for the silylpyrroles. Solvation of the nitrogen atom by hydrogen bonding probably also plays a part.

B. Base-catalysed solvolysis

The kinetics follow eqn. 7 and rate constants calculated on basis of this

$$k_{obs} = k_{EtO} \cdot [EtO^-] + k_{amine} \cdot [amine] = -d[S]/[S]dt \qquad (7)$$

(S = organosilicon substrate)

equation are given in Table 2. The base constant for butylamine in ethanol is known [13]. This reaction has the following characteristics:

(1) it is general base-catalysed;

(2) Hammett equations 8 and 9 are followed;

$$\lg k_{amine} = \lg k^0_{amine} + 1.8\,\sigma^0 \qquad (8)$$

$$\lg k_{EtO} = \lg k^0_{EtO} + 2.6\,\sigma^0 \qquad (9)$$

(3) the activation parameters are, activation energy $E_a = 8$ kcal mol^{-1} and activation entropy $\Delta S = -48$ cal mol^{-1} K^{-1}.

The reaction is general base-catalysed with ethoxide ion being about 10^5 times more efficient a catalyst than butylamine. The ρ(amine) value of +1.8 is significantly higher than ρ-values for S_N2 substitutions of benzyl derivatives (0.5—0.8) [14] and may be taken to indicate the participation of *d*-orbitals of silicon in forming bonds to the nucleophile in the transition state III. A slight weakening of the silicon—nitrogen bond seems reasonable in view of the fact that for the solvolysis of *N*-(trialkylsilyl)anilines in methanolic potassium hydroxide solution the nitrogen atom was shown to be negatively charged in the transition state [15]. Increased nucleophilicity of X in III favours Si^V intermediates and increases the ρ-value. If the reaction is subject to nucleophilic catalysis (X = B) and if we assume that nucleophilic order follows base order (R_3Si is classified as a hard electrophile) [16], we would expect ethoxide to form a stronger dative bond to silicon than does butylamine. The higher ρ-value for the ethoxide-catalysed process is thus explained. In a general base-catalysed reaction the base serves to remove the hydroxylic proton from the solvent ethanol. From the ρ-values we conclude that ethanol/ethoxide is a stronger nucleophile than is ethanol/butylamine.

$$B + EtOH + Si{-}NC_4H_4 \longrightarrow X{\cdots}Si{-}NC_4H_4$$
$$(X = EtO\cdot\cdot HB \text{ or } B,\ B = \text{base}) \qquad \text{(III)}$$

Leaving-group ability is another factor which determines the extent of π-bond interaction in the transition state. It is expected that poor leaving groups will favour Si^V intermediates [14]. In this connection it is interesting to note the ρ-value 2.7 found in the methoxide-catalysed methanolysis of trialkylmenthoxysilanes [7]. ρ-Values of this magnitude have been taken as evidence for π-orbital participation in reactions of organosilicon compounds, the main reason for this being the much smaller ρ-values observed in analogous carbon and sulfur compounds [14].

Conjugative stabilisation of the negative charge in the leaving group decreases the extent of π-bond formation between the silicon and the incoming nucleophile and lowers the ρ-value. For the ethanolysis of phenoxysilanes a much smaller ρ-value (viz. 0.2) was found in the base-catalysed cleavage, and this was taken to indicate synchronous bond making an breaking [4]. This difference in mechanism may be due to the fact that phenoxide anion is a better leaving group than is the pyrryl anion (and menthoxide anion).

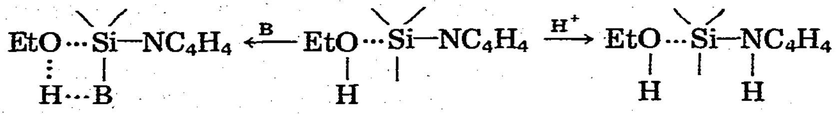
The activation entropy of about -48 cal mol^{-1} K^{-1} is consistent with a process in which five groups are ordered around the silicon atom in the transition state.

C. Comparison of the acid- and base-catalysed solvolysis

The kinetics of the unsubstituted compound follow eqn. 10. It is seen that the ethoxide anion is a more efficient catalyst than the proton by a factor of about 10^4.

$$k_{obs}\,(s^{-1}) = k_0 + 0.144\,[H^+] + 1260\,[EtO^-] + 4.43 \times 10^{-3}\,[BuNH_2] \qquad (10)$$
$$(k_0 \ll 3 \times 10^{-4})$$

It has been suggested that solvent coordination by dative π-bonding to silicon is important in both the ground and exited states [17]. Following this suggestion we take as our substrate the species IV. The role of the catalyst is to modify the substrate in such a way that the product state is reached. In the acid-catalysed process protonation of the nitrogen atom allows the leaving group to come off as a neutral molecule, thereby increasing the leaving-group ability. In the base-catalysed process the nucleophilicity of the coordinated solvent is increased by the attacking base, and therefore the $(p{-}d)\pi$ dative bond to silicon is strengthened.



$$\mathrm{EtO\cdots Si{-}NC_4H_4} \xleftarrow{B} \mathrm{EtO\cdots Si{-}NC_4H_4} \xrightarrow{H^+} \mathrm{EtO\cdots Si{-}NC_4H_4}$$

(B = base) (IV)

To exercise its basic property the aryldimethylsilylpyrrole has to lose its aromatic character and stability. No such loss of aromaticity occurs in the base-catalysed solvolysis, and therefore the activation energy is higher in the acid-catalysed process. Both increased nucleophilicity of the solvent and decreased leaving group-ability increase the importance of Si^V intermediates in the base-catalysed reaction compared to the acid-catalysed reaction. In basic ethanol bond formation is kinetically most important, while acid catalysis involves bond breaking as the rate-determining process, as shown by the electronic situation at the silicon atom measured by the ρ-values. Thus five organic groups are closer to silicon in the base-catalysed reaction, resulting in a higher activation entropy.

The applicability of σ^0 constants in the Hammett equations rules out the possibility of extra π-bonding stabilisation between the reaction centre and the phenyl group in the transition state.

Experimental

Materials

The silylpyrroles $(X{-}C_6H_4)Me_2SiNC_4H_4$ were synthesised by the method used for the preparation of *N*-(trimethylsilyl)pyrrole [5], with modifications. The lithium salt of pyrrole, employed instead of the potassium salt, was made by treating an etheral solution of pyrrole with phenyllithium in benzene/ether solution under nitrogen. To the resulting solution was added the aryldimethylchlorosilane prepared by the method given in ref. 18. The ether was removed and replaced by benzene, and the product worked up after reflux.

The silylpyrroles were purified by fractional distillation and small samples were further purified by GLC for elemental analyses and for kinetics studies. All the compounds show a characteristic band at 1190 cm^{-1} in the infrared and no band at 3400 cm^{-1} demonstrating the absence of the N—H bond. The compounds, all of which are new, had the following properties: X = *p*-Cl: b.p. 143°/8 mm (Found: C, 61.31; H, 5.90; N, 5.83. $C_{12}H_{14}ClNSi$ calcd.: C, 61.13; H, 5.99; N, 5.94%.) X = *p*-F: b.p. 123°/8 mm (Found: C, 65.89; H, 6.40; N, 6.49. $C_{12}H_{14}FNSi$ calcd.: C, 65.71; H, 6.43; N, 6.39%.) X = *m*-Me: b.p. 130°/10 mm (Found: C, 72.64; H, 8.00; N, 6.54. $C_{13}H_{17}NSi$ calcd.: C, 72.50; H, 7.96; N, 6.50%.) X = *p*-MeO: b.p. 153—158°/10 mm (Found: C, 67.32; H, 7.60, N, 5.98. $C_{13}H_{17}NOSi$ calcd.: C, 67.49; H, 7.41; N, 6.05%.) X = *p*-Me: b.p. 130—133°/10 mm (Found: C, 72.47; H, 7.79; N, 6.48. $C_{13}H_{17}NSi$ calcd.: C, 72.50; H, 7.96; N, 6.50%.) X = H, 118—124°/10 mm (Found: C, 71.62; H, 7.44; N, 6.80. $C_{12}H_{15}NSi$ calcd.: C, 71.58; H, 7.51; N, 6.96%.)

Rate Measurements

All reactions were carried out in absolute ethanol containing acid or base. Acidic solutions were made up by adding 2.5—20 μl of 3.95% sulphuric acid in ethanol to 1 ml absolute ethanol in the reaction vessel. The ionic strength was kept constant at μ 0.058 by the appropriate addition of lithium perchlorate. Basic solutions consisted of a buffer system using 0.05—0.20 *M* butylamine and its hydrochloride (c_{base}/c_{salt} 10). The ionic strength was kept at μ 0.050. The reaction vessel was kept in a thermostat at 25 or 40 ± 0.1°. The silylpyrrole compound was added to give a concentration of about 0.05 *M*. Samples of 15 μl were withdrawn at regular intervals during a period of two half-lives, and the reaction was stopped by injecting into 150 μl ethanol containing 0.0025 *M* sodium acetate for the acid-catalysed reaction, or 0.01 *M* ammonium acetate for the base-catalysed reaction. The samples were analysed by GLC on a 2 m × 1/8″ column packed with 15% Apiezon L on Celite 545. Analyses were carried out using a Varian Aerograph model 1740 gas chromatograph with flame ionisation detector and nitrogen carrier gas. The decrease in concentration of the silylpyrroles was followed by measuring peak heights relative to solvent. Reaction mixtures after ten half-lives showed no peaks corresponding to the starting silylpyrroles. Rate constants were obtained graphically. The analytical method was checked by measuring the concentrations of the product ethoxysilanes $(X—C_6H_4)Me_2SiOEt$ in the following instances: (X =) *p*-Me and H in the acid-catalysed reaction and *p*-Me and *p*-Cl in the base-catalysed reaction. The rate constants thus obtained were identical with those based on the concentrations of the silylpyrroles.

Reaction products

The reaction of dimethylphenylsilylpyrrole in ethanol containing acid or base gave two products with retention times identical to those of pyrrole and dimethylphenylethoxysilane [19]. The $(X—C_6H_4)Me_2SiNC_4H_4$ compounds gave pyrrole and another product having retention times as expected for $(X—C_6H_4)$-Me_2SiOEt.

References

1 A.E. Pierce, Silylation of Organic Compounds, Pierce Chemical Company, Rockford, Illinois, 1968.
2 O.E. Brust, I. Sebestian and I. Halasz, J. Chromatogr., 83 (1973) 15.
3 B. Bøe, J. Organometal. Chem., 43 (1972) 275.
4 B. Bøe, J. Organometal. Chem., 57 (1973) 255.
5 R.J. Fessenden and D.F. Crowe, J. Org. Chem., 25 (1960) 598.
6 A.R. Bassindale, C. Eaborn and D.R.M. Walton, J. Organometal. Chem., 25 (1970) 57.
7 L.H. Sommer, Stereochemistry, Mechanism and Silicon, McGraw-Hill, New York, 1965.
8 J. Vencl, J. Hetflejs, P. Kucera and V. Chvalovsky, Collect. Czech. Chem. Commun., 38 (1973) 1248.
9 B. Bøe and C. Eaborn, J. Organometal. Chem., to be published.
10 J. Nagy, P. Hengsei and E. Gergö, Z. Anorg. Allg. Chem., 367 (1969) 293.
11 J. Nagy and P. Hengsei, J. Organometal. Chem., 9 (1967) 57.
12 J.R. Chipperfield, D.F. Ewing and G.E. Gould, J. Organometal. Chem., 46 (1972) 263.
13 L.D. Goodhue and R.M. Hixon, J. Amer. Chem. Soc., 57 (1935) 1688.
14 J.L. Kice, in A. Senning (Ed.), Sulfur in Organic and Inorganic Chemistry, Marcel Dekker, New York, 1971, pp. 180—181.
15 A.R. Bassindale, C. Eaborn and D.R.M. Walton, J. Organometal. Chem., 43 (1972) 265.
16 R.G. Pearson, in N.B. Chapman and J. Shorter (Eds.), Advances in Linear Free Energy Relationships, Plenum Press, London and New York, 1972, p. 287.
17 R. Corriu and J. Masse, Tetrahedron, 26 (1970) 5123.
18 G. Schott and V. Bondybey, Chem. Ber., 100 (1967) 1773.
19 H. Freiser, M.V. Eagle and J. Speier, J. Amer. Chem. Soc., 75 (1953) 2824.