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Low-temperature ionization of neutral hexacoordinate to ionic pentacoordinate silicon complexes. Unusual temperature, solvent and substituent effects[†]

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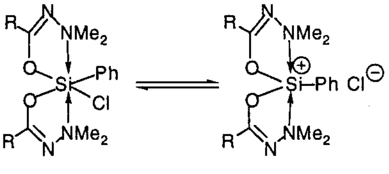
ABSTRACT: Neutral hexacoordinate complexes of silicon (**1**) ionize to pentacoordinate siliconium chloride salts (**2**) in CH_2Cl_2, $CHCl_3$ or $CHFCl_2$ solutions. ^{29}Si NMR measurements prove that the extent of ionization increases as the temperature of the solution is lowered. The ionizations are slightly exothermic, and have negative entropies. It is shown that increased solvent polarity drives the reaction to the ionic side, i.e. that ion solvation is responsible for the ionization. The lack of a common-ion effect on addition of tetrabutylammonium chloride indicates the formation of unseparated ion pairs. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: silicon complexes; ionization; common ion; ^{29}Si NMR

INTRODUCTION

Neutral octahedral silicon bis-chelate complexes (**1**)[1–3] have been shown to undergo ionization at low temperature to give siliconium ion salts[4] in polar non-aqueous solvents, as outlined in Eqn. (1):



(1)

1a-d **2a-d**

a, R = *t*-Bu
b, R = Me
c, R = CH_2Ph
d, R = Ph

The evidence for ionization is found in the huge dependence of the ^{29}Si NMR chemical shifts upon temperature (Table 1, Fig. 1), with eventual emergence of two signals at low temperatures, assigned to the hexa- and pentacoordinate species (**1** and **2**, respectively)[5] (the characterization of ionic **2** follows from a crystal structure of an analog of **2b** in which the chloride counterion was replaced by a triflate group;[5] the triflate and chloride salts had identical ^{29}Si chemical shifts in solution). The unusual temperature dependence, in which a single molecule splits into two ions preferentially at low temperature, led to the examination of the enthalpies and entropies of the reaction.

RESULTS AND DISCUSSION

The ionization is fully reversible, and the equilibrium constants have been evaluated at various temperatures: below the coalescence temperature simply by comparison of the signal areas, and above the coalescence temperature by calculating the contributions of the two individual signals to the weighted average chemical shift. The equilibrium constants were used for a ln*K* against reciprocal temperature plot (Fig. 2), from which the reaction enthalpy and entropy were calculated. In the same manner, the equilibrium constants and the resulting enthalpies and entropies were evaluated for the other complexes $\mathbf{1} \rightleftharpoons \mathbf{2}$, for which the remote substituents R are different. The data are presented in Table 1, along with the number of temperatures used for each correlation and the quality of the linear correlation expressed by its correlation coefficient.

The compounds are listed in Table 1 in order of decreasing electron-releasing power of the substituent group R. It is evident from Table 1 that the more electron-releasing the substituent, the more exothermic is the ionization reaction (as expressed in greater negative

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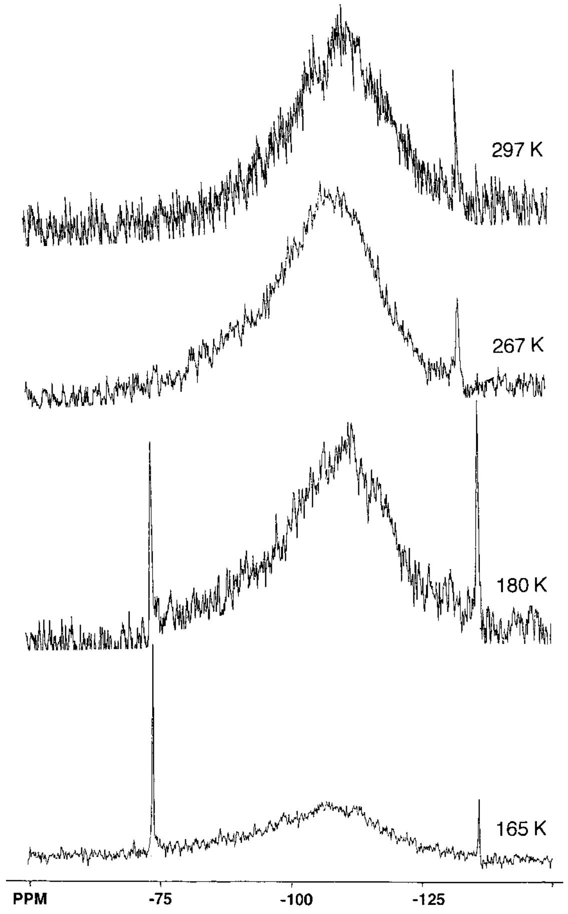

Figure 1. ^{29}Si NMR spectra of **1a** in CD_2Cl_2 solution at various temperatures. At intermediate temperatures (~267–180 K) the signal completely merges into the baseline owing to exchange and coalescence. The broad signal is due to the glass sample tube

reaction enthalpies). This can be rationalized as follows: an electron-releasing R makes the Me_2N group a stronger electron donor, through the C=N double bond. As a result, the electron density on silicon is greater and therefore it more readily allows the separation of a negatively charged ion. This is reflected in a greater negative enthalpy.

However, examination of Table 1 reveals that in addition to the trend found for the enthalpies, a similar trend is found for the reaction entropies: they are all negative, and their absolute values are greater for the more exothermic reactions, i.e. for the more electron-releasing substituents.

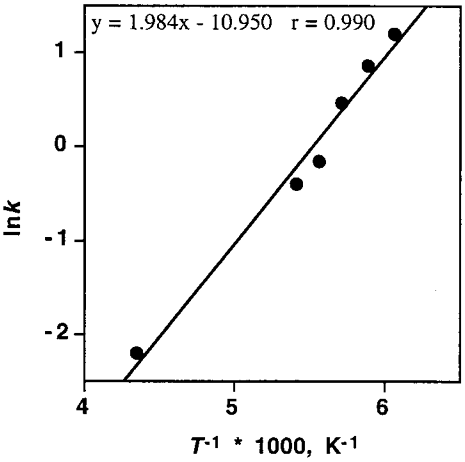

Figure 2. Thermodynamic plot of ln*K* vs T^{-1} for the equilibrium reaction **1a** ⇌ **2a**

The negative entropies suggest that there is more organization and fewer degrees of freedom in the ionic state (**2**), despite the increase in number of particles, relative to the neutral hexacoordinate precursors (**1**). The only way to accommodate this conclusion is by invoking a solvent effect: presumably, the ions are stabilized by solvent organization, which constitutes higher order and hence negative entropy (a similar phenomenon was reported[6] in the ionization of diarylmethyl chlorides in BCl_3–CH_2Cl_2 solution).

To account for the observed trend in negative entropies, one may assume that in the more exothermic reactions ionization is complete and leads to separate ions which are well solvated, whereas in the nearly thermoneutral case (**1d**) ionization results in a contact ion pair, in which solvation is less effective. In the present study we have sought evidence for this effect by measuring the effect of added common ion (chloride). Should there be dissociation of **1** to free ions, then the addition of chloride (as tetrabutylammonium chloride) should suppress dissociation and decrease the observed population ratio [**2**]:[**1**]. However, in cases were ionization leads to contact ion pairs and not to dissociation, the addition of

Table 1. ^{29}Si NMR chemical shifts for **1a–d** at two temperatures and the reaction enthalpies and entropies for **1** → **2** in CD_2Cl_2 solution

		$\delta(^{29}Si)$ (ppm)					
Compound	R	300 K	165 K	$\Delta H°$ (kcal mol^{-1})	$\Delta S°$ (cal mol^{-1} K^{-1})	Correlation coefficient	No. of points[a]
1a	*t*-Bu	−132.9	−73.6; −135.9	−3.9	−21.8	0.990	6
1b	Me	−131.3	−73.1; −135.7	−2.8	−15.0	0.992	9
1c	CH_2Ph	−131.3	−73.4; −135.9	−1.9	−9.4	0.996	5
1d	Ph	−133.7	−73.2; −136.9	−0.8	−8.6	0.996	3

[a] Number of points included in the correlation.

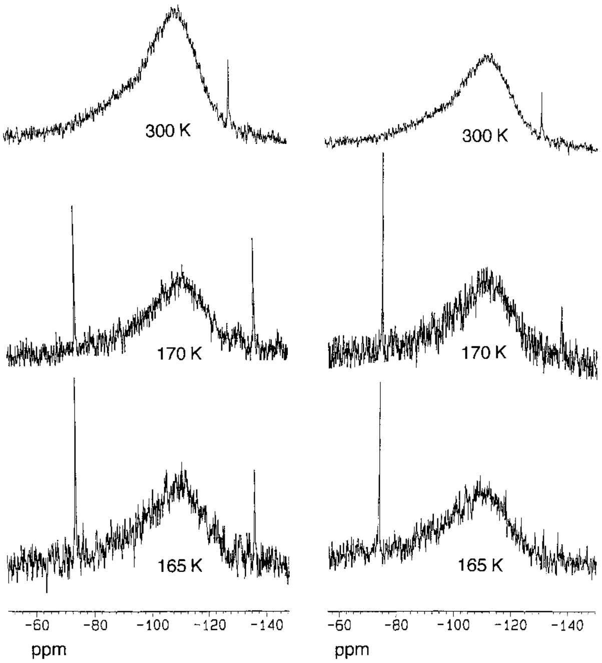

Figure 3. ^{29}Si NMR spectra of **1b** in CD_2Cl_2 with (right) and without (left) an added stoichiometric amount of $(CH_3CH_2CH_2CH_2)_4NCl$ at equal concentrations and temperatures

external chloride would have a marginal effect on the relative populations of **1** and **2**.

A solution of **1b** in CD_2Cl_2 was divided in to two equal portions. To one of these portions was added an equimolar amount of dry tetrabutylammonium chloride, and the ^{29}Si NMR spectra of both samples were measured at several low temperatures. The resulting NMR spectra are depicted in Fig. 3. It is evident from Fig. 3 that at room temperature there is no significant effect of the added salt on the spectrum: the average ^{29}Si chemical shifts are essentially equal in the salt-treated and the reference samples. However, when the temperature is lowered, a surprising result is observed: the equilibrium population in the salt-treated sample has shifted toward the ionic side (**2b**): the low-field (ionic) to high-field (neutral) signal ratio is *greater* in the treated vs the untreated sample. This clearly demonstrates the *absence* of a common ion effect, which would have shifted the population ratio toward **1b**, and constitutes evidence that no free ions are present in solution.

The different reaction entropies measured for the series **1a–d** may still be interpreted as a reflection of varying degrees of solvation of the ion pairs: these appear to be looser and more solvated in the exothermic case (**1a**) and tighter in the less exothermic case (**1d**), resulting in greater solvent organization in the former (greater negative entropy) and weaker solvent organization in the latter, without dissociation to free ions. The unexpected ionizing effect of the added salt may be due to the increase in ionic strength, which facilitates ionization.

Table 2. Solvent effect on the enthalpies and entropies of the ionization reaction for **1b**

Solvent	$\Delta H°$ (kcal mol^{-1})	$\Delta S°$ (cal mol^{-1} K^{-1})	Correlation coefficient	No. of points
CD_2Cl_2	−2.8	−15.0	0.992	9
$CDCl_3$	−3.6	−18.9	0.988	6
$CHFCl_2$	−6.8	−22.9	0.996	6

Since the entire phenomenon of ionization of **1** and the substantial temperature dependence of the ^{29}Si chemical shift is attributed to the solvent, it seemed appropriate to study the solvent effect directly. To this end the equilibrium constants for **1b** were evaluated in three different solvents at different temperatures, and the corresponding enthalpies and entropies of the ionization reaction were determined. The results are presented in Table 2. It is evident from Table 2 that the solvent indeed plays a major role in controlling the state of equilibrium. The three solvents are listed in Table 2 in order of increasing hydrogen-bond donor ability. Clearly, the reaction is more exothermic as the solvent is more effective in stabilizing the ions, i.e. the ionization reaction is essentially driven by the solvent polarity.

Not surprisingly, the entropies show a similar trend to that of enthalpies (Table 2): in the more polar solvents, in which the ionization is more exothermic, also the entropies have greater negative values. This is readily understood in terms of the stronger solvation of the ion pair in the more exothermic case: stabilization of the ions by the more effective solvents requires better organization of solvent molecules around the solute ions, which is manifested in greater negative reaction entropy.

EXPERIMENTAL

General. All the reactions were carried out under dry nitrogen or argon, using solvents dried and purified by standard methods. NMR spectra were recorded on a Bruker Avance DMX-500 spectrometer operating at 500.13 and 99.36 MHz for ^{1}H and ^{29}Si spectra, respectively, and are reported in δ (ppm) relative to tetramethylsilane (TMS). The variable-temperature ^{29}Si NMR spectra for the determination of population ratios were run using 45° pulses, without ^{1}H decoupling, and with 5–10 s delay times between pulses. NMR measurements in $CHFCl_2$ solutions were carried out below 9 °C, and the solvent was condensed directly into pre-evacuated sample tubes.

Synthesis of ***1b–d***. These were prepared as described previously.[3a]

Compound **1a** was prepared from *O*-trimethylsilylated 1,1-dimethyl-2-pivaloylhydrazine.

O-Trimethylsilylated 1,1-dimethyl-2-pivaloylhydrazine. A solution of 4.81 g (0.080 mol) of 1,1-dimethylhydrazine and 16.90 g (0.166 mol) of triethylamine in 80 ml of dry Et_2O was cooled to −20 °C. A pivaloyl chloride (9.65 g, 0.080 mol) solution in 50 ml of dry Et_2O was added dropwise with stirring. The mixture was stirred for 1 h at ambient temperature and then refluxed for 2 h. Trimethylchlorosilane (8.69 g, 0.080 mol) was added dropwise, followed by 8 h of reflux. The mixture was cooled and filtered under argon, and the filtrate was distilled under reduced pressure. The product was collected at 61–62 °C (11 mmHg) (12.6 g; 73% yield). ^{1}H NMR ($CDCl_3$, 300 K): δ 0.16 (s, 9H, $SiMe_3$), 1.06 (s, 9H, CMe_3), 2.25 (s, 6H, NMe_2). ^{13}C NMR ($CDCl_3$, 300 K): δ 0.85 ($SiMe_3$), 27.51 [$C(CH_3)_3$], 36.42 (CMe_3), 46.52 (NMe_2), 165.86 (C=N). ^{29}Si NMR ($CDCl_3$, 300 K): δ 14.92. Anal. Calcd for $C_{10}H_{24}N_2OSi$: C, 55.50; H, 11.18; N, 12.95. Found: C, 55.72; H, 10.99; N, 13.05%.

*Bis[N-(dimethylamino)pivaloimidato-N,O]chloro(phenyl)silicon(IV) (**1a**).* To a stirred solution of *O*-trimethylsilylated 1,1-dimethyl-2-pivaloylhydrazine (0.584 g, 2.70 mmol) in 10 ml of dry $CHCl_3$ was added $PhSiCl_3$ (0.274 g, 1.29 mmol) at room temperature under dry argon. The mixture was stirred for 1 h. Removal of the volatiles under vacuum (0.05 mmHg) resulted in a colorless crystalline solid (0.534 g; 97% yield), m.p. 119–120.5 °C. ^{1}H NMR ($CDCl_3$, 300 K): δ 1.17 (s, 18H, *t*-Bu), 2.32 (s, 6H, NMe_2), 2.86 (s, 6H, NMe_2), 7.23–8.08 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 300 K): δ 27.19 [$C(CH_3)_3$], 35.36 (CMe_3), 51.36 (NMe_2), 127.36, 128.29, 137.08, 144.15 (Ph), 173.19 (C=N). ^{29}Si NMR ($CDCl_3$, 300 K): $\delta - 131.20$. Anal. Calcd for $C_{20}H_{35}ClN_4O_2Si$: C, 56.25; H, 8.26; N, 13.12. Found: C, 55.99; H, 8.33; N, 12.96%.

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