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LEWIS ACIDITY OF ORGANOSILICON CHLORIDES

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Summary

In dry acetonitrile solution organosilicon chlorides, R_nSiCl_{4-n} ($0 \leqslant n \leqslant 3$) react with $4 - n$ equivalents of Lewis bases, B. The products are non-electrolytes of very high stability. Enthalpy data are reported for R = Me, Ph; B = PBu_3, pyridine *N*-oxide, $PhNMe_2$, NBu_3, pyridine, 4-methylpyridine, 2-methylpyridine, 2,4,6-trimethylpyridine, 2,2'-bipyridine and 1,10-phenanthroline; the data show no evidence for steric effect of 2-substitution in pyridine; bipy and phen apparently behave as unidentate bases. Infra-red spectra show that py and py-NO are coordinated. The evidence suggests that the bases are coordinated to Cl rather than Si.

Introduction

Addition compounds of bases with silicon halides, SiX_4, have long been known and are mostly of the type SiX_4B_2, in which the silicon atom is presumably 6-coordinate. A 6-coordinate, *cis*-octahedral structure has been confirmed by X-ray analysis for SiF_4(2,2'-bipyridine) [1] and *trans*-octahedral structures have been confirmed in the same way for SiF_4py_2 [2] and $SiCl_4(PMe_3)_2$ [3]. Infrared studies support *trans*-octahedral structures for $SiCl_4py_2$ [4] and also $SiF_4(NMe_3)_2$, $SiF_4(PMe_3)_2$, $SiCl_4(PMe_3)_2$ and $SiBr_4(PMe_3)_2$ [5]. Adducts of the type SiX_4B_4 are also known; they are mostly white solids, which decompose with the loss of base at about 200°C [6]. The adducts $SiBr_4(PPh_3)_4$, $SiBr_4(OPR_3)_4$ and $SiX_4(ONMe_3)_4$ have been shown to be non-electrolytes [7]. Adducts with four molecules of base have also been obtained from SiH_2Br_2, SiH_2I_2, $SiHBr_3$, $SiHI_3$ and SiI_4 but their structures remain unknown [8].

Pressure-composition isotherms for the system SiF_4/NMe_3 reveal the formation of both 1 : 1 and 1 : 2 adducts [9] and the 1 : 1 adducts SiF_4NMe_3, $SiCl_4NMe_3$ and SiF_4PMe_3 have been isolated; their infra-red spectra are consistent with C_{3v} symmetry, implying trigonal-bipyramidal, 5-coordinate structures with apical base molecules [5]. 5-Coordinate structures have also been proposed for the anion SiF_5^- and the complex organosilicon fluoride ions

$RSiF_4^-$ and $R_2SiF_3^-$ in solution in solvents of low polarity [10]. These appear to be the only reported examples of adduct formation by organosilicon halides. However, in a previous paper [11] we showed that organosilicon acetates, $R_nSi(OCOMe)_{4-n}$ $(0 \leqslant n \leqslant 3)$, react with Lewis bases in solution in non-donor solvents, forming 1 : 1 adducts of moderate stability.

Calcrimetric studies of the reaction of $SiCl_4$ with bases in hexane solution [12,13] gave enthalpies of formation of about —120 kJ mol^{-1} for crystalline $SiCl_4B_2$, but as these include an unknown contribution from the enthalpies of crystallisation, they are of limited value for comparative purposes. Enthalpy data have also been obtained from vapour pressure measurements for the dissociation of crystalline adducts of SiF_4 with various bases; the values range from about 115 kJ mol^{-1} for $SiF_4(NEt_3)_2$ to about 210 kJ mol^{-1} for SiF_4py_2 [14], but these also include an unknown contribution from the lattice energy of the solid.

In the present paper we report thermodynamic data for the formation of adducts of a variety of Lewis bases with organosilicon chlorides, R_nSiCl_{4-n} $(0 \leqslant n \leqslant 3)$. The data have been obtained calorimetrically in acetonitrile solution at concentrations in the range 10^{-3}—10^{-2} M, under which conditions all the species present remain in solution, so that enthalpies or crystallisation are not included.

Experimental

Organosilicon chlorides and silicon tetrachloride were obtained from Research Organic/Inorganic Chemical Corp., Sun Valley, California and purified by distillation or crystallisation. Liquid bases were purified by distillation and stored over anhydrous potassium carbonate. Pyridine *N*-oxide was sublimed in vacuo. 2,2'-Bipyridine (bipy) and 1,10-phenanthroline (phen) were crystallised from ethanol; phen was dehydrated by azeotropic distillation of benzene before making up solutions. Acetonitrile for use as solvent was dried over anhydrous sodium sulphate, distilled and stored over molecular sieve.

Calorimetric measurements were made on a LKB 8700-2 titration calorimeter, using previously described techniques [15]. Briefly, a solution of the base in acetonitrile was titrated into 100 ml of a solution of the silicon compound in the same solvent and the heat change measured after each incremental addition of titrant. Control titrations were carried out to determine heats of dilution. Enthalpograms were then obtained by plotting the total concentration of added base against the cumulative heat of reaction, corrected for dilution effects. Overall enthalpies of reaction were calculated from the total heat change when further addition of base produced no further heat change. Intermediate enthalpies of reaction were calculated from the slopes of the enthalpogram in appropriate regions. Enthalpy data in the tables are the mean of at least three determinations over a range of concentrations of the silicon compound; uncertainties are mean deviations. Silicon chlorides and their solutions were handled under dry nitrogen throughout.

Conductimetric titrations were carried out using a Philips model PW 9504 conductivity bridge at 30.0 ± 0.2°C with a conductivity cell specially adapted to exclude atmospheric moisture. Infra-red spectra were recorded on a Unicam SP 1000 infra-red spectrometer using rock-salt cells of 0.1 mm path, purged with dry nitrogen.

Results and discussion

The enthalpograms constructed from calorimetric titration data show almost quantitative reactions of the organosilicon halides with bases, according to eq. 1,

$$R_nSiCl_{4-n} + (4-n)B = R_nSiCl_{4-n}B_{4-n} \quad (1)$$

the number of molecules required to complete the reaction being equal to the number of chlorine atoms (Fig. 1)

Titration of bases into solutions of R_3SiCl (R = Me, Ph) showed the formation of 1 : 1 addition compounds. In nearly all cases the reaction was effectively quantitative ($K > 10^6$ l mol^{-1}), but with the two bases pyridine *N*-oxide and 2,2'-bipyridine the reaction was not quite quantitative, but formation constants were still too large to measure ($K > 10^4$). Enthalpies of adduct formation are shown in Table 1.

Comparison with corresponding organosilicon acetates [11] shows that the chlorides are much stronger Lewis acids. Reaction with the acetates could only be observed with the strongest bases. Thus, even with Et_3N, $Me_3Si(OCOMe)$ gave a 1 : 1 adduct of only moderate stability with a much smaller enthalpy of ad-

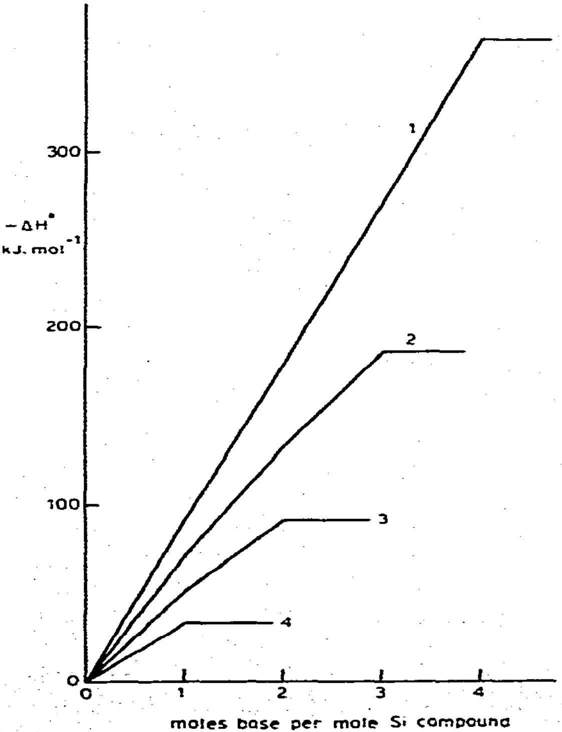

Fig. 1. Calorimetric titration of Lewis bases with organosilicon chlorides: NBu_3 with $SiCl_4$ (1), 4-methylpyridine with $PhSiCl_3$ (2), 2,2'-bipyridine with Me_2SiCl_2 (3) and pyridine-*N*-oxide with Ph_3SiCl (4). Acetonitrile solution at 30°C.

TABLE 1

ENTHALPIES OF FORMATION (kJ mol^{-1}) OF 1 : 1 ADDUCTS OF LEWIS BASES WITH R_3SiCl IN ACETONITRILE SOLUTION AT 30°C

Base	Me_3SiCl	Ph_3SiCl
PBu_3	67.0 ± 0.9	73.8 ± 1.9
py-NO	37.3 ± 1.3	33.0 ± 2.1
$PhNMe_2$	52.2 ± 2.4	53.3 ± 1.8
NBu_3	90.3 ± 2.4	89.2 ± 2.9
pyridine	55.6 ± 0.7	61.2 ± 2.0
4-mepy	61.0 ± 0.7	70.6 ± 1.5
2-mepy	61.2 ± 0.2	63.1 ± 3.5
2,4,6-Me_3py	65.5 ± 0.2	
bipy	43.4 ± 1.1	41.8 ± 0.6
phen	50.5 ± 1.1	49.3 ± 0.7

duct formation (K 146, ΔH^0 -35.4) than is now observed for addition of Bu_3N to Me_3SiCl. In view of the general assumption that short period elements, including silicon, should form "hard" Lewis acid centres [16], it is interesting to note that with R_3SiCl the lowest enthalpy of adduct formation is given by the O-donor, py-NO, that enthalpies of addition of $PhNMe_2$, pyridine and PBu_3 are comparable and only the aliphatic amine, NBu_3, forms an adduct with considerably higher enthalpy of formation.

Comparison of the enthalpy data for the four heterocyclic bases reveals the usual increase due to the effect of methyl substitution, but it is surprising that steric effects do not lead to lower enthalpies with 2-methylpyridine or even 2,4,6-trimethylpyridine. The data for 2,2′-bipyridine and 1,10-phenanthroline show clearly that these are either not behaving as bidentate bases or, if they are, the two bonds formed are each only half as strong as those formed by pyridien.

A similar pattern of behaviour is revealed by the dihalides, Me_2SiCl_2 and Ph Ph_2SiCl_2, except that these compounds form adducts with two molecules of base. The adduct $Ph_2SiCl_2py_2$ is of particularly low solubility and readily crystallises from solution; this compound was isolated and its formula confirmed by analysis. Although the addition of two molecules of base is virtually quantitative, there is a slight change of slope of the enthalpogram after addition of the first and enthalpies of each step in the addition can be obtained from the slopes of the graph. These data are included in Table 2.

Comparison of the data for addition of the first molecule of base with data for the acetates, $R_2Si(OCOMe)_2$, again shows that the chlorides are much stronger acids. As with R_3SiCl enthalpies of adduct formation increase in the order py-NO $<$ py $\sim$ PBu_3 $<$ NR_3. In these systems also there is apparently no steric effect due to 2-substitution in pyridine. The enthalpies of adduct formation with bipy and phen are again slightly less than for pyridine, implying that these two bases behave as unidentate donors.

The same pattern of results is repeated for $RSiCl_3$ and $SiCl_4$, with the remarkable feature that three and four molecules of base respectively are added. Data for these systems are given in Tables 3 and 4.

Though adducts of the stoichiometry SiX_4B_4 have long been known, their structures are uncertain and the possibility has existed that they might be sol-

TABLE 2

ENTHALPIES OF ADDITION (kJ mol^{-1}) OF SUCCESSIVE MOLECULES OF LEWIS BASE TO R_2SiCl_2 IN ACETONITRILE SOLUTION AT 30°C

Base	Me_2SiCl_2			Ph_2SiCl_2		
	$-\Delta H_1^o$	$-\Delta H_2^o$	$-\Delta H_{1+2}^o$	$-\Delta H_1^o$	$-\Delta H_2^o$	$-\Delta H_{1+2}^o$
PBu_3	64 ± 1	60 ± 1	124 ± 2	73 ± 2	60 ± 1	133 ± 2
py-NO	40 ± 2	35 ± 1	75 ± 2	47 ± 2	39 ± 2	86 ± 3
$PhNMe_2$	62 ± 2	51 ± 2	114 ± 2	71 ± 1	60 ± 2	131 ± 2
NBu_3	91 ± 1	90 ± 1	181 ± 1	94 ± 1	90 ± 1	184 ± 1
pyridine	61 ± 3	57 ± 1	118 ± 5	59 ± 3	56 ± 2	116 ± 4
4-mepy	67 ± 3	58 ± 2	125 ± 3	75 ± 1	63 ± 2	138 ± 2
2-mepy	62 ± 1	56 ± 2	118 ± 2	75 ± 2	61 ± 2	135 ± 2
2,4,6-Me_3py	79 ± 2	69 ± 2	148 ± 1			
bipy	51 ± 3	40 ± 2	91 ± 3	61 ± 2	44 ± 2	105 ± 3
phen	53 ± 1	52 ± 2	105 ± 2	61 ± 3	53 ± 1	114 ± 2

vates, better formulated as $SiX_4B_2 \cdot 2B$, or salts $SiX_2B_4{}^{2+}2X^-$. The present observation of species SiX_4B_4 and $RSiX_3B_3$ as species of high stability in solution cannot be explained in terms of solvates and raises again the problem of possible structures. Even with unidentate bases coordination numbers of seven and eight are implied and these rise to ten and twelve if phen behaves in the usual manner as a bidentate ligand.

Conductimetric titrations of Me_3SiCl, Me_2SiCl_2 and $MeSiCl_3$ with pyridine and of Ph_3SiCl, Ph_2SiCl_2, $PhSiCl_3$ and $SiCl_4$ with 4-methylpyridine in acetonitrile solution in the concentration range 10^{-3}—10^{-2} M gave molar conductances $\Lambda_M < 1$ ohm^{-1} cm^2 mol^{-1} before addition of base, rising slightly until the equivalence of one molecule of base per chlorine atom, but always remaining with $\Lambda_M < 1$. For solutions of $SiCl_4$, $\Lambda_M < 1$ before adding base rose to $\Lambda_M \sim 6$ on addition of base. Since molar conductances of 1 : 1 electrolytes in acetonitrile at concentrations of about 10^{-3} M are in the range $120 < \Lambda_M < 160$ ohm^{-1} cm^2 mol^{-1} [17], these results show conclusively that no significant amounts of ionic species are formed when these organosilicon chlorides react with bases.

TABLE 3

ENTHALPIES OF ADDITION (kJ mol^{-1}) OF SUCCESSIVE MOLECULES OF LEWIS BASE TO $RSiCl_3$ IN ACETONITRILE SOLUTION AT 30°C

Base	$MeSiCl_3$				$PhSiCl_3$			
	$-\Delta H_1^o$	$-\Delta H_2^o$	$-\Delta H_3^o$	$-\Delta H_{1+2+3}^o$	$-\Delta H_1^o$	$-\Delta H_2^o$	$-\Delta H_3^o$	$-\Delta H_{1+2+3}^o$
PBu_3	67 ± 1	66 ± 1	60 ± 2	193 ± 2	69 ± 3	64 ± 3	62 ± 2	193 ± 4
py-NO	47 ± 1	45 ± 1	36 ± 3	128 ± 2	41 ± 2	36 ± 2	32 ± 1	109 ± 3
$PhNMe_2$	65 ± 1	61 ± 2	56 ± 2	182 ± 3	67 ± 1	62 ± 1	56 ± 2	184 ± 3
NBu_3	93 ± 1	92 ± 2	94 ± 1	280 ± 2	86 ± 1	87 ± 2	86 ± 2	259 ± 4
pyridine	69 ± 1	61 ± 3	54 ± 1	184 ± 3	69 ± 2	57 ± 1	56 ± 0	181 ± 1
4-mepy	69 ± 1	62 ± 2	56 ± 1	187 ± 2	71 ± 2	63 ± 1	52 ± 2	186 ± 2
2-mepy	67 ± 2	63 ± 1	58 ± 2	187 ± 2	66 ± 1	61 ± 1	58 ± 1	185 ± 2
bipy	60 ± 3	50 ± 1	42 ± 1	153 ± 3	58 ± 4	48 ± 3	42 ± 4	152 ± 5
phen	62 ± 2	61 ± 1	60 ± 3	182 ± 4	55 ± 1	55 ± 2	54 ± 2	164 ± 3

TABLE 4

ENTHALPIES OF ADDITION (kJ mol^{-1}) OF SUCCESSIVE MOLECULES OF LEWIS BASE TO $SiCl_4$ IN ACETONITRILE SOLUTION AT 30°C

Base	$-\Delta H_1^0$	$-\Delta H_2^0$	$-\Delta H_3^0$	$-\Delta H_4^0$	$-\Delta H_{1+2+3+4}^0$
PBu_3	78 ± 4	77 ± 1	67 ± 8	63 ± 4	285 ± 5
py-NO	52 ± 1	47 ± 2	44 ± 1	37 ± 1	180 ± 3
$PhNMe_2$	68 ± 2	66 ± 1	60 ± 2	56 ± 2	250 ± 4
NBu_3	92 ± 0	89 ± 2	91 ± 1	91 ± 1	363 ± 1
pyridine	70 ± 1	66 ± 1	65 ± 2	64 ± 2	265 ± 1
4-mepy	71 ± 2	68 ± 2	64 ± 2	64 ± 2	268 ± 4
2-mepy	67 ± 1	63 ± 3	58 ± 1	56 ± 3	243 ± 5
2,4,6-Me_3py	84 ± 1	81 ± 2	72 ± 1	69 ± 1	306 ± 2
bipy	62 ± 4	58 ± 2	50 ± 1	41 ± 1	211 ± 5
phen	61 ± 1	58 ± 2	61 ± 3	55 ± 2	236 ± 5

Infra-red studies of acetonitrile solutions of pyridine and mixtures of pyridine and Me_nSiCl_{4-n} in the proportion of one molecule of pyridine per atom of chlorine revealed shifts of the pyridine absorption bands at 705, 750, 993, 1040, 1152 and 1220 cm^{-1} to approximately 688, 755, 1004, 1045, 1204 and 1265 cm^{-1}. Corresponding shifts of these bands have been observed [18] when pyridine is coordinated to metal atoms. In the same way, infra-red spectra of acetonitrile solutions of py-NO and mixtures of py-NO with the appropriate amount of organosilicon chloride showed the shift of the N—O stretching mode at 1265 cm^{-1} [19] to about 1201 cm^{-1}, which is characteristic of coordination through the O atom. These infra-red results show conclusively that the bases are behaving as donor molecules in the formation of coordination compounds.

Detailed analysis of the calorimetric titration data reveals that when successive additions of base occur the enthalpy of the last step is similar to that for addition of base to R_3SiCl; the enthalpy of the penultimate step is simialr to that for addition of the first molecule of base to R_2SiCl_2 and so on. This is particularly clear for the data for 2,2′-bipyridine, which is collected in Table 5.

The effect of addition of one equivalent of base on the enthalpy of addition of the next is thus the same as the effect of replacing chloride by an alkyl group.

Considering this last observation together with the absence of observable steric effect of 2-substitution in pyridine, the extremely high stabilities of all the adducts, implying minimal steric interference, and the improbability of coordination numbers greater than six for an atom so small as silicon, it seems likely that these addition compounds are formed by coordination of the base to the chlorine atoms rather than the central silicon atom. In proposing the formation of such addition compounds it is necessary to discuss circumstances which might favour coordination of base to a peripheral atom rather than the central atom of a Lewis acid.

For the Lewis acidity of the central atom to be transferred to the peripheral atoms it is necessary firstly that these atoms should have reasonable polarisability and it is essential that they have available orbitals for acceptance of electron pairs. These conditions are met by larger atoms better than smaller and not by atoms in the first row (Li—F). Thus, in principle such adducts could be formed by chlorides or bromides, but not by fluorides or ethers. We have shown previ-

TABLE 5

ENTHALPIES OF ADDITION (kJ mol^{-1}) OF SUCCESSIVE MOLECULES OF 2,2'-BIPYRIDINE TO ORGANOSILICON HALIDES IN ACETONITRILE SOLUTION AT 30°C

R_nSiCl_{4-n}	n	$-\Delta H^o_{4-n}$	$-\Delta H^o_{3-n}$	$-\Delta H^o_{2-n}$	$-\Delta H^o_{1-n}$
$SiCl_4$	0	41	50	58	62
$PhSiCl_3$	1	42	48	58	
Ph_2SiCl_2	2	44	61		
Ph_3SiCl	3	42			
$MeSiCl_3$	1	42	50	60	
Me_2SiCl_2	2	40	51		
Me_3SiCl	3	43			

ously that acetates form only 1 : 1 adducts with bases, presumably with the silicon atom becoming 5-coordinate [11]. We should also expect that formation of adducts by coordination to the peripheral chlorine would only occur if access to the more acidic silicon atom were restricted. Thus, although this apparently occurs with the organo-silicon chlorides, the organotin chlorides, in which the larger tin atom is readily accessible, form only normal addition compounds of moderate stability in which the coordination number of the tin atom is five or six [20].

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