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LEWIS ACIDITY OF ORGANOSILICON ISOCYANATES AND ISOTHIOCYANATES

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Summary

Organosilicon isocyanates show no evidence of Lewis acidity. The isothiocyanates, $R_nSi(NCS)_{4-n}$ ($0 \leqslant n \leqslant 3$), react with $4 - n$ molecules of Lewis bases giving adducts of high stability. Enthalpy data are reported for the formation of adducts of various bases with Me_3SiNCS, $Me_2Si(NCS)_2$ and $Si(NCS)_4$ in acetonitrile solution. The data suggest that the sulphur atoms behave as the Lewis acid centres. $Si(NCS)_4$ forms an adduct in solution with five molecules of pyridine-*N*-oxide; the first four molecules of base are probably coordinated to the four S atoms and the fifth to the Si atom.

Introduction

The behaviour of silicon tetrahalides as Lewis acids is well known and addition compounds of various stoichiometries have been isolated with a wide range of bases, but corresponding reactions of other silicon compounds have received little attention. There appear to be no previous reports of Lewis acidity of organosilicon isothiocyanates, $R_nSi(NCS)_{4-n}$, or isocyanates, $R_nSi(NCO)_{4-n}$. The crystal structure of triphenylsiliconisothiocyanate shows that the thiocyanate group is N-bonded to silicon [1]. In the corresponding tin compound, Ph_3SnNCS, intermolecular association occurs by coordination of the S atom of one molecule to the Sn of another, making the tin 5-coordinate [2], but in the silicon compound there is no such interaction between neighbouring Ph_3SiNCS molecules. In this respect the silicon atom fails to behave as a Lewis acid where the tin atom does so. Spectroscopic studies of $Si(NCS)_4$ [3] and $Si(NCO)_4$ [4] support truly tetrahedral molecular structures with linear Si—N—C groups. This too is in contrast to the corresponding tin or germanium compounds, in which there is bending at the N atoms.

In previous papers we have shown that in acetonitrile solution the organosilicon chlorides, R_nSiCl_{4-n} ($0 \leqslant n \leqslant 3$), form very stable addition compounds with Lewis bases; the number of molecules of base in these adducts is the same as the number of chlorine atoms [5]. In contrast to this the organosilicon acetates, $R_nSi(OCOMe)_{4-n}$ ($0 \leqslant n \leqslant 3$), form only 1 : 1 adducts of moderate stability with Lewis bases, whatever the number of acetate groups [6]. Our studies of these systems have led us to propose that while the base molecules are presumably coordinated to the silicon atom in the adducts of the acetates, they are probably coordinated to the chlorine atoms in the chlorides. We are now making a study of other types of silicon compound in an attempt to assess factors which may account for the surprising differences between these two groups of compounds.

The present paper reports calorimetric studies of the reactions of Lewis bases with selected organosilicon isocyanates and isothiocyanates.

Experimental

$Si(NCO)_4$ and $Me_2Si(NCO)_2$ were prepared from $SiCl_4$ and Me_2SiCl_2 by reaction with silver cyanate suspended in benzene [7]. After filtration of silver chloride and evaporation of solvent the products were isolated by distillation in vacuo and purified by redistillation at atmospheric pressure: $Me_2Si(NCO)_2$ b.p.139—140° C, $Si(NCO)_4$ b.p.185—189° C. $Si(NCS)_4$, $Me_2Si(NCS)_2$ and Me_3SiNCS were prepared from corresponding chlorides by reaction with ammonium thiocyanate suspended in benzene [8]. After filtration of ammonium chloride and evaporation of solvent $Si(NCS)_4$ remained as white crystals, $Me_2Si(NCS)_2$ and Me_3SiNCS were recovered by distillation in vacuo. The purity of all silicon compounds was checked by C, H and N analyses.

The methods of purification of bases and solvent and details of calorimetric titration procedures have been previously reported [5].

Results and discussion

The two isocyanate compounds, $Me_2Si(NCO)_2$ and $Si(NCO)_4$, gave no evidence of reaction with tertiary amines or heterocyclic bases in solution in benzene or acetonitrile, showing that they do not form addition compounds. With secondary and primary amines a small amount of heat was liberated, but this may arise from formation of ureas by reaction of the amino groups with the isocyanate and cannot be taken as evidence of Lewis acidity of the silicon compounds. In view of the failure of these silicon compounds to give evidence of Lewis acidity no further studies were made of organosilicon isocyanates.

The three isothiocyanate compounds, Me_3SiNCS, $Me_2Si(NCS)_2$ and $Si(NCS)_4$, all reacted instantly with a wide range of bases in benzene or acetonitrile solution. In most cases the reactions were quantitative or nearly so ($K > 10^6$ l mol^{-1}) and the number of base molecules needed to complete the reaction was the same as the number of isothiocyanate groups (Fig. 1). In a few systems the reactions were not quite quantitative, but in these cases the adduct formation constants were very large. When more than one molecule of base was added, successive enthalpies of reaction could be obtained from the slopes of the enthalpograms. Details are given in Table 1 for addition of bases to Me_3SiNCS and $Me_2Si(NCS)_2$.

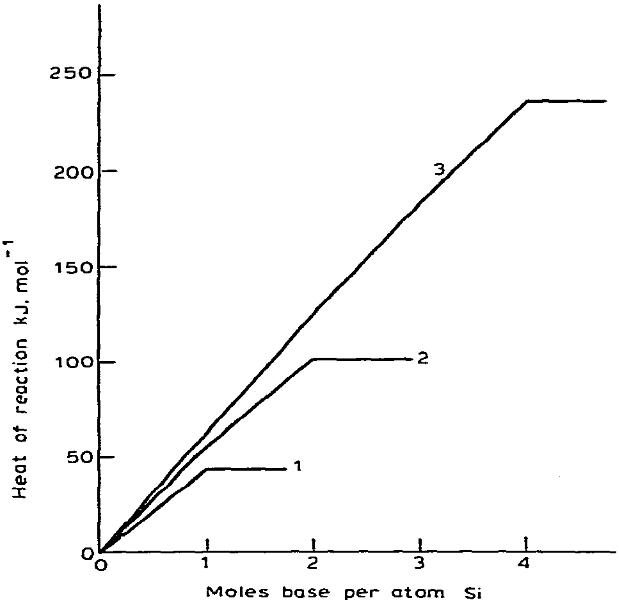


Fig. 1. Calorimetric titration in acetonitrile solution of Me_3SiNCS with phenanthroline (1), $Me_2Si(NCS)_2$ with pyridine (2) and $Si(NCS)_4$ with PBu_3 (3).

The pattern of these results follows very closely that shown by the corresponding chlorides, though enthalpies of adduct formation with the isothiocyanates are a little smaller (the difference between Me_3SiCl and Me_3SiNCS is 8 kJ mol^{-1} on average). The stabilities of the adducts with pyridine-*N*-oxide are low enough for measurements of the formation constants to be possible and adduct formation with $PhNMe_2$ and bipyridine was also observably not quantitative. As with the organosilicon chlorides PBu_3 is a comparable base to heterocyclic nitrogen compounds, 2-substitution in pyridine produces no observable steric

TABLE 1

ENTHALPIES OF REACTION (kJ mol^{-1}) OF LEWIS BASES WITH Me_3SiNCS AND $Me_2Si(NCS)_2$ IN ACETONITRILE SOLUTION AT 30°C

Base	Me_3SiNCS	$Me_2Si(NCS)_2$		
		$-\Delta H_1^0$	$-\Delta H_2^0$	$-\Delta H_{1+2}^0$
PBu_3	58.3 ± 0.7	62.3 ± 0.8	54.2 ± 0.9	116.6 ± 1.6
Py-*N*-O	32.2 ± 7 [a]	41 [b]	36 [b]	77.3 ± 0.9
$PhNMe_2$	40.9 ± 1.4 [c]	47.3 ± 0.9	39.7 ± 0.5	85.3 ± 1.0
NBu_3	78.5 ± 0.2	82.6 ± 1.0	81.1 ± 1.5	163.6 ± 2.0
Pyridine	49.4 ± 0.8	54.9 ± 0.2	45.8 ± 1.4	100.8 ± 1.6
4-Mepy	53.2 ± 0.7	59.8 ± 0.3	55.1 ± 0.6	114.2 ± 0.8
2-Mepy	52.6 ± 0.4	57.5 ± 1.0	53.6 ± 1.7	110.0 ± 1.4
2,4,6-Me_3py	55.2 ± 0.7	63.8 ± 0.5	60.3 ± 2.1	124.1 ± 2.1
Bipy	36.3 ± 0.8 [c]	44.0 ± 0.5	34.1 ± 2.2 [c]	78.1 ± 2.2
Phen	43.2 ± 0.2	50.0 ± 0.4	43.6 ± 1.0	93.6 ± 1.3

[a] K 2070 ± 240 l mol^{-1}. [b] $K_1 \simeq 1000$, $K_2 \simeq 500$ l mol^{-1}. [c] $10^4 < K < 10^6$ l mol^{-1}.

TABLE 2

ENTHALPIES OF REACTION (kJ mol^{-1}) OF LEWIS BASES WITH $Si(NCS)_4$ 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	64.1 ± 1.0	62.0 ± 0.5	58.2 ± 2.2	51.4 ± 1.1	235.6 ± 1.8
Py-*N*-O	31.8 ± 0.7	31.8 ± 0.7	31.9 ± 1.1	29.0 ± 1.0	121.6 ± 2.4 [a]
$PhNMe_2$	48.6 ± 0.2	48.8 ± 0.0	44.5 ± 1.7	38.8 ± 0.3	180.8 ± 1.3
NBu_3	87.9 ± 0.6	87.0 ± 0.4	86.4 ± 0.3	85.9 ± 2.0	347.2 ± 2.3
Pyridine	56.9 ± 0.8	55.0 ± 0.8	49.8 ± 1.3	39.7 ± 1.9	201.4 ± 1.2
4-Mepy	57.6 ± 0.9	56.6 ± 0.5	52.1 ± 0.4	48.4 ± 1.7	214.7 ± 1.2
Bipy	44.2 ± 1.3	44.5 ± 1.4	35.2 ± 0.6	29.7 ± 0.3 [b]	153.6 ± 3.0
Phen	50.1 ± 0.5	50.2 ± 0.9	47.6 ± 2.9	40.4 ± 0.9	188.4 ± 2.5

[a] $K_5 = 53 \pm 2$, $\Delta H_5^0 = -48.6 \pm 0.6$. [b] $10^4 < K < 10^6$ l mol^{-1}.

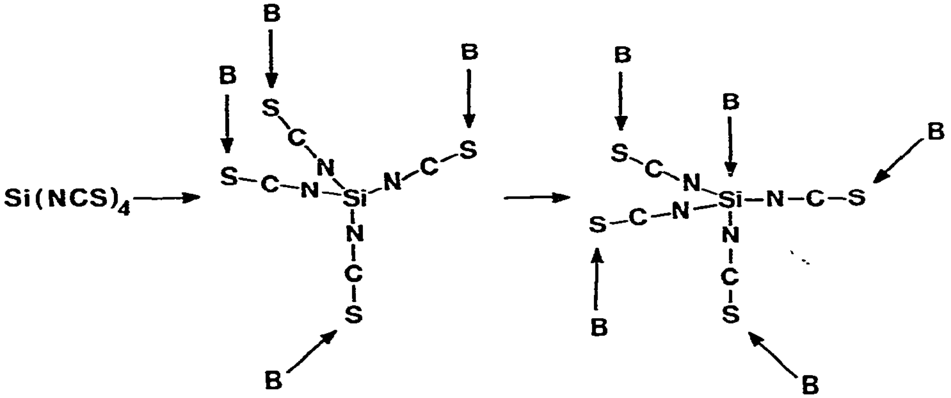
effect and there is no evidence of chelation with bipyridine or phenanthroline, which form adducts with rather smaller enthalpies of formation than those of pyridine.

Details are given in Table 2 of enthalpies of formation of adducts with $Si(NCS)_4$. Here too the pattern of behaviour is similar to that of the chlorides. Enthalpies of formation of adducts with bipyridine and phenanthroline are noticably smaller than with pyridine and the addition of the fourth molecule of bipyridine is not quantitative. The reaction of $Si(NCS)_4$ with pyridine-*N*-oxide is particularly remarkable: after virtually quantitative addition of four molecules of base, heat continued to be evolved and the additional heat could be interpreted as arising from addition of a fifth molecule of base. The addition of this fifth molecule of base, however, is accompanied by a larger enthalpy of adduct formation, though the adduct is of only moderate stability.

The reactions of the silicon isothiocyanates with bases, like those of the silicon chlorides, are consistent with addition of the base to the thiocyanate group rather than the silicon atom. The failure of the isocyanates to behave in the same way suggests that addition of base to the thiocyanate group occurs at the sulphur atom. This is consistent with the requirement that the acceptor atom should have available suitable vacant orbitals and should be sufficiently polarisable for the Lewis acidity to be transferred from the inaccessible central silicon atom. The remarkable reaction of pyridine-*N*-oxide with $Si(NCS)_4$ suggests that after addition of one base molecule to each sulphur atom the fifth one adds to the silicon. The enthalpy of addition of this fifth base and the stability of the adduct are comparable to those for addition of the only molecule of pyridine-*N*-oxide to $Si(OCOMe)_4$ (ΔH^0 — 57 kJ mol^{-1}, K 12 l mol^{-1}). Addition of the base to the silicon atom apparently occurs only with pyridine-*N*-oxide among the bases studied; this is the weakest of these bases but one in which the isolated O-donor atom must lead to minimal steric interference. It appears that both the isolated O-donor and the linear —NCS groups are necessary before base addition occurs at the silicon atom and even then it occurs preferentially at the peripheral sulphur atoms (Scheme 1).

By comparison with these silicon compounds the corresponding tin compounds are quite normal Lewis acids. The isocyanate, $Bu_2Sn(NCO)_2$, forms

SCHEME I



1 : 1 adducts of moderate stability with pyridine [9]. The organotin isothiocyanates, $R_nSn(NCS)_{4-n}$ $(1 \leqslant n \leqslant 3)$ add one or two molecules of base with $K_1 > K_2$; bipyridine is bidentate [10,11]. The tin atom is the Lewis acid centre and apparently steric interference limits the coordination number to six. It is thus not surprising that addition to the smaller silicon atom is more difficult. What is more unexpected is that addition of base should take place, but in a different part of the molecule and, because this part of the molecule is not subject to steric effects, with much greater adduct formation constants.

Acknowledgments

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