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THE REACTIVITY OF $Me_3Si—NMe_2$ TOWARDS AsF_5 AND BF_3

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Abstract—Trimethylsilyldimethylamine, $Me_3Si—NMe_2$ (**1**), reacts with AsF_5 to yield Me_3SiF, Me_2NF and AsF_3. The reaction of **1** in liquid sulphur dioxide with BF_3 afforded Me_3SiF, $(Me_2N—BF_2)_n$ [$n = 1$ (**2**), 2 (**3**)] and the SO_2 adduct ($Me_2N—BF_2 \cdot SO_2$) (**4**), the latter of which is stable in solution only. The equilibrium between **2**, **3** and **4** has been studied by means of temperature-dependent proton NMR spectroscopy.

Recently we studied the coordination behaviour of the Lewis acid AsF_5 towards nitriles and aminonitriles.[1–4] Therefore, we also became interested in the reactivity of AsF_5 towards substituted amines and we chose $Me_3Si—NMe_2$ (**1**) to investigate the reaction behaviour. Since we could show that **1** is readily oxidized by AsF_5, it was thought worthwhile to undertake a re-investigation of the reaction of **1** with BF_3[5–7] as, in contrast to AsF_5, BF_3 does not represent a strong oxidizing agent. The present paper reports on the reaction of **1** and BF_3 in SO_2 solution and the formation of $(Me_2N—BF_2)_n$ [$n = 1$ (**2**), 2 (**3**)] and ($Me_2N—BF_2 \cdot SO_2$) (**4**), the latter of which is stable only in solution.

EXPERIMENTAL

All techniques have been described previously.[8] $Me_3Si—NMe_2$ (Aldrich) was purified by distillation, SO_2 (Messer-Griesheim) dried over CaH_2 and BF_3 (T. J. Baker) used as supplied. AsF_5 was prepared in our own laboratory from As and excess F_2.

^1H NMR data were obtained in SO_2 solution (c^0, $AsF_5 = c^0$, $BF_3 = 0.6$ mol dm^{-3}) using a Bruker WP 80 (80 MHz) or a Varian EM-360 (60 MHz) instrument and are referred to external TMS in SO_2 solution. The ^{19}F NMR spectra have been obtained in SO_2 solution using a Bruker SXP4-100 instrument (84.7 MHz) and are (unlocked) referred to external $CFCl_3$. For all NMR measurements, 5 mm NMR tubes with rotationally symmetrical PTFE J. Young valves were used.

Reaction of 1 *with* AsF_5

Onto a frozen solution of **1** (0.70 g, 6.00 mmol) in SO_2 (10 cm^3) in an NMR tube, AsF_5 (1.02 g, 6.00 mmol) was condensed at −196°C. The reaction mixture was allowed to warm to room temperature. ^1H NMR (SO_2, 20°C, δ in ppm): 0.20 d, $J = 9$ Hz (Me_3SiF), 4.03 s, br (Me_2NF). ^{19}F NMR (SO_2, 20°C, δ in ppm): −22.0 s (Me_2NF); cf. ref. 16, −35 to −41 s, br (AsF_3), −155.5 s (Me_3SiF); cf. ref. 17. When the experiment was finished the solvent and all volatile products were pumped off at 0°C and AsF_3 was identified by mass spectroscopy. MS (E.I., 70 eV, 25°C), m/z: 132 (AsF_3), 113 (AsF_2), 94 (AsF), 75 (As).

Reaction of 1 *with* BF_3

Onto a frozen solution of **1** (0.70 g, 6.00 mmol) in SO_2 (10 cm^3) in an NMR tube, BF_3 (0.41 g, 6.00 mmol) was condensed at −196°C. The reaction mixture was allowed to warm to room temperature. ^1H NMR (SO_2, 20°C, δ in ppm): 0.20 d, $J = 9$ Hz (Me_3SiF), 2.36 m, br (**3**), 2.70 m, br (**2**), 3.95 m, br (**4**). Temperature-dependent ^1H NMR spectra have been recorded between +60°C and −50°C and are shown in Fig. 1.

The reaction of **1** with BF_3 in $CFCl_3$ as the solvent was done on the same scale. ^1H NMR ($CFCl_3$, 20°C, δ in ppm): 0.18 d, $J = 12$ Hz (Me_3SiF), 2.42

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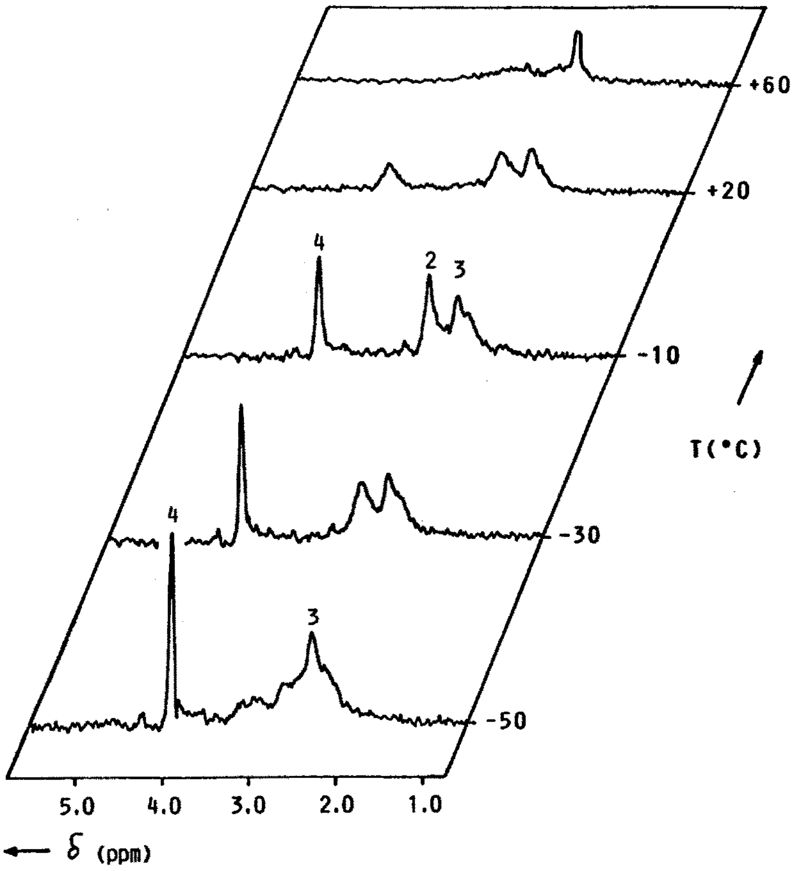


Fig. 1. Temperature-dependent ^{1}H NMR spectrum of a mixture of **2**, **3** and **4** in SO$_2$ solution.

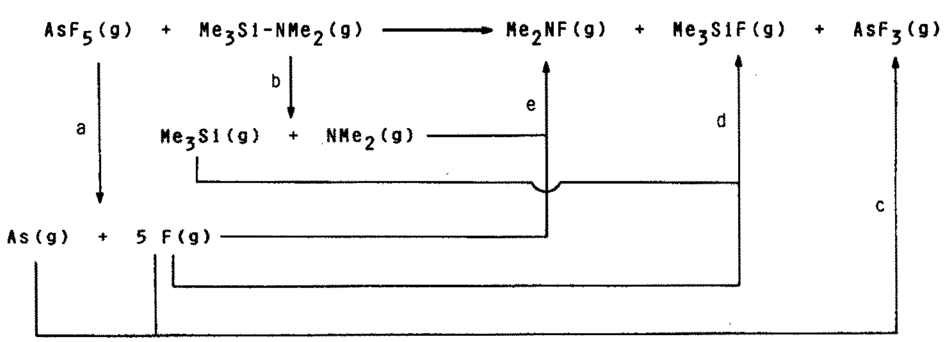
m, br (**3**). The temperature-dependent NMR spectrum of the CFCl$_3$ sample did not show any change in the range −50 to +60°C.

RESULTS AND DISCUSSION

Although the adduct formation between **1** and AsF$_5$ should be exothermic,[3] the oxidation of **1** by AsF$_5$ [eq. (1)] seems to be even more thermodynamically favourable ($\Delta H = -1.3$ kcal mol^{-1}, Scheme 1) and AsF$_3$, Me$_2$NF and Me$_3$SiF are the only products which have been identified.

$$1 + AsF_5 \longrightarrow Me_3SiF + Me_2NF + AsF_3 \quad (1)$$

In contrast to AsF$_5$, BF$_3$ does not represent a strong oxidizing agent and therefore we investigated



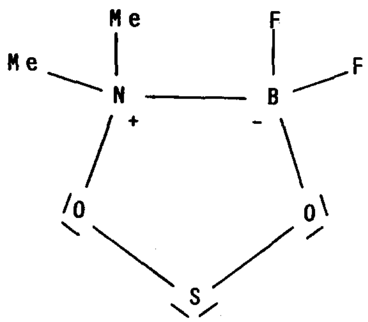
Scheme 1. Energy cycle to estimate the heat of reaction (1). (a) B.E.(As^{V}—F) = 97.1,[9] (b) B.E.(Si—N) = 79.7,[10] (c) B.E.(As^{III}—F) = 116.5,[10] (d) B.E.(Si—F) = 142.8,[10] (e) B.E.(*N*—F) ≥ 74.2, calibrated on B.E.(*N*—F, *N*F$_3$) = 66.5[10] and B.E.(*N*—F, *N*F$_2$) = 70.3[10] (all values in kcal mol^{-1}; cal = 4.184 J).

its reaction behaviour in polar (SO_2) and non-polar ($CFCl_3$, Freon-11) solvents towards **1**. Previously it has been reported[6,7] that the neat reaction of **1** with BF_3 led to the formation of the four-membered planar heterocycle $(Me_2N—BF_2)_2$ (**3**). We found that in $CFCl_3$, **3** is the only boron–nitrogen species which had been formed according to eq. (2).

$$1 + BF_3 \xrightarrow{\text{Freon-11}} \underset{\mathbf{3}}{1/2(Me_2N—BF_2)_2} + Me_3SiF \quad (2)$$

In the variable-temperature proton NMR spectrum ($CFCl_3$ solution) there was no evidence up to 60°C for the formation of significant amounts of the monomeric species $Me_2N—BF_2$ (**2**). This is in agreement with earlier thermodynamic studies which report the appearance of **2** (from **3**) in the liquid state at a temperature of 160°C.[11]

However, in SO_2 solution from the reaction of **1** with equimolar amounts of BF_3, besides Me_3SiF, three species had been formed. Two of these species have undoubtedly been identified as the monomer $(Me_2N—BF_2)$ (**2**) and the dimer $(Me_2N—BF_2)_2$ (**3**).[12] The width of the band, which is attributed to **3** (2.36 ppm), and the absence of fine structure suggests that in addition to B—H coupling, further broadening occurs due to the F nuclei (Fig. 1).[12] The sharper peak at lower field (2.70 ppm) can be assigned to the monomer **2**.[12] The rather low field resonance at 3.95 ppm has been assigned to the adduct species $(Me_2N—BF_2 \cdot SO_2)$ (**4**) (cf. NMR data of AsF_5 adduct complexes).[3] As according to the HSAB principle[13,14] both N and B on the one hand and O on the other hand are hard, compared with the relatively soft S, the heterocyclic structure A might represent a likely resonance structure for species **4**. Moreover, usually SO_2 coordinates via oxygen.[15]

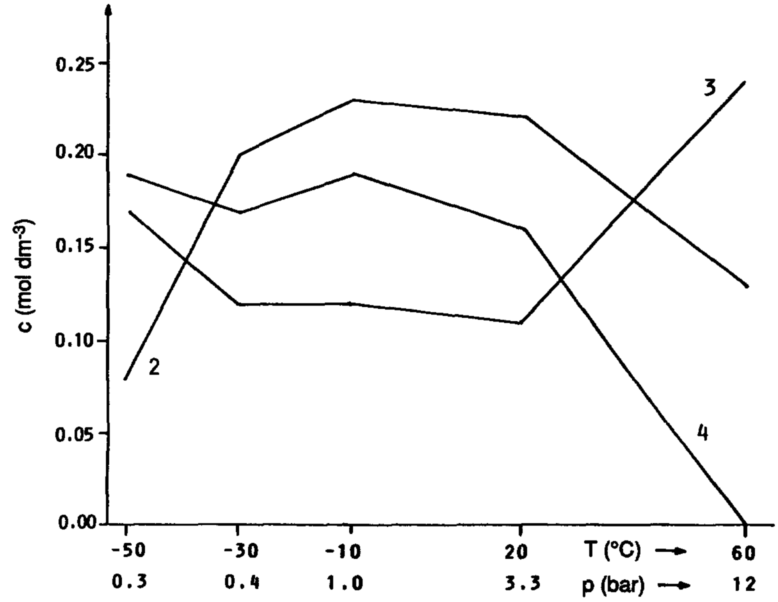


Structure A. Proposed structure for **4**.

However, despite several attempts so far we have been unable to isolate **4** in the solid state and **3** was the only product crystallizing from an evaporating SO_2 solution containing **2**, **3** and **4**.

The temperature-dependent ^1H NMR spectrum of an SO_2 solution containing **2**, **3** and **4** revealed that these three species are in equilibrium with each other (Fig. 1, Table 1, Scheme 2).

Expectedly, increasing the temperature from −50 to −10°C increases the concentration of the monomer **2**, whereas the concentrations of the dimer **3** and the adduct **4** decrease. At higher temperatures (above 20°C), however, the dimer seems to be far more favourable again and at 60°C **3**



Scheme 2. Concentrations of **2**, **3** and **4** in a sealed NMR tube in SO_2 solution at various temperatures and pressures, starting from an equimolar mixture of **1** (0.6 mmol) and BF_3.

Table 1. Concentrations of **2**, **3** and **4** in a sealed NMR tube in SO_2 solution at various temperatures and pressures, starting from an equimolar mixture of **1** (0.6 mmol) and BF_3

		c (mol dm^{-3})		
T (°C)	p/bar (psi)	**2**	**3**	**4**
+60	12.0 (168)	0.13	0.24	0.00
+20	3.3 (46)	0.22	0.11	0.16
−10	1.0 (14)	0.23	0.12	0.15
−30	0.4 (5.6)	0.20	0.12	0.17
−50	0.3 (4.2)	0.08	0.17	0.19

represents the major product, while the concentration of **4** decreased to almost zero. This behaviour can be explained by the exothermic dimerization of **2** yielding **3**[11] and the weak but still exothermic adduct formation between **2** and SO_2 (yielding **4**). Therefore, at high temperatures **2** should be favoured rather than **3**. However, the SO_2-containing NMR tube was sealed and the increasing pressure (cf. Fig. 1) strongly favours the formation of the dimer.

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