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REACTIONS OF CHLORINE MONOFLUORIDE WITH TETRASULPHUR TETRANITRIDE, THIAZYL CHLORIDE AND THIAZYL FLUORIDE

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SUMMARY

Chlorine monofluoride reacts with tetrasulphur tetranitride to give thiazyl chloride (monomer and trimer) and thiazyl fluoride; with further ClF, NSCl reacts to form NSF then $ClNSF_2$, and finally N_2, Cl_2 and SF_4. The reaction NSCl/ClF to give NSF/Cl_2 reverses in SO_2 solvent due to removal of ClF as SO_2ClF. NSF was prepared, in a new method, by passing NSCl through a column of CsF at 110°.

INTRODUCTION

While studying the reaction between S_4N_4 and ClF, as a possible new route to NSF, we found that intermediate NSCl reacted with ClF as follows

$$NSCl + ClF \longrightarrow NSF + Cl_2 \qquad (1)$$

This is the reverse of a reaction described earlier [1], and so to find the cause of this discrepancy, we studied reactions of ClF with NSCl, $(NSCl)_3$ and NSF, and of Cl_2 with NSF (without and with SO_2 solvent).

EXPERIMENTAL

Techniques and reagents, unless specified, have been described in ref. 2. Tetrasulphur tetranitride [3] and trichlorocyclotrithiatriazene [4]

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were prepared by literature methods. Gaseous thiazyl chloride, in a mixture containing N_2 and Cl_2, was prepared by heating $(NSCl)_3$ at 70°C *in vacuo* [5], and expanded into an infrared cell prior to reaction with ClF.

Reactions were carried out in Monel metal vessels, of volume about 60 cm^3, equipped with removable tops. Gases (SF_4, SOF_2, SO_2Cl_2, $SClF_5$, SF_6, NCl_3 [6], $ClNSF_2$ [7,8] and SO_2ClF [9]) were identified by their i.r. spectra, liquid chlorine by Raman spectroscopy; S_3N_2Cl [10], $S_3N_2Cl_2$ [11], $(NSCl)_3$ [5], $(NSF)_3$ [12], S_4N_3Cl [13], S_4N_4 [14], and $S_4N_4Cl_2$ [15,16] by i.r. spectra of Nujol or fluorolube mulls and KBr discs.

Trichlorocyclotrithiatriazene, $(NSCl)_3$, was also characterised from its Raman spectrum (706 vw, 692 vw, 620 w(br), 485 w, 441 vw(sh), 434 w, 376 s, 336 vs, 319 m, 193 vs, 180 s, 109 s, 77 vs, 44 w) obtained using a Cary 82 spectrometer equipped with a Spectra Physics 125 laser (632.8 nm exciting line).

S_4N_4 and ClF

In a typical [ca. 1:1] reaction ClF (0.12 g, 2.20 mmole) was condensed on S_4N_4 (0.37 g, 2.01 mmole). The reaction vessel was held at -78°C for 4 h and at room temperature for 10 h. The products were N_2, SF_4, OSF_2 and NSF (0.1 g), and a solid (0.38 g) which gave an i.r. spectrum containing peaks attributable to S_4N_4 and probably $S_4N_4Cl_2$. A ^{19}F n.m.r. spectrum of the solid in fluorobenzene indicated the absence of fluorine.

In a 1:5 reaction of S_4N_4 (0.11 g, 0.60 mmole) with ClF (0.16 g, 2.94 mmole) the same gaseous products were formed and the i.r. spectrum of the solid product (0.15 g) indicated the presence of $(NSCl)_3$. Further absorptions at 1050 s(sh), 970 s, 800 w, 590 m, 555 w, 465 m, 420 m and 410 m cm^{-1}, clearly not $S_3N_2Cl_2$, S_3N_2Cl, S_4N_3Cl or S_4N_4, were assigned to $S_4N_4Cl_2$.

In another reaction, S_4N_4 (0.20 g, 1.08 mmole) was reacted with four aliquots of ClF (total 0.96 g, 17.63 mmole) in a highly exothermic reaction. The volatile products were mainly N_2, SF_4 and Cl_2 with some $SClF_5$ and SF_6. No solid residue remained.

S_4N_4 was also reacted with ClF in a slurry of CCl_3F or CCl_4. In a typical reaction CCl_3F (4.4 g) was condensed on to finely powdered S_4N_4 (0.47 g, 2.55 mmole) in a Teflon vessel. ClF (0.3 g, 5.25 mmole) was added in aliquots. After each addition the mixture was held at -50°C for 15 min. with shaking. The volatile products above the mixture held at -50° were mainly $CFCl_3$, SOF_2, (hydrolysis product of SF_4) and possibly NSF. The solid product (0.52 g) was a mixture of $S_4N_4Cl_2$ and S_4N_4. In another experiment, crystals of $S_4N_4Cl_2$ were mechanically separated from the reaction product mixture and identified by their infrared spectrum. In other experiments $(NSCl)_3$ was formed, and in one case the solid product contained a few small colourless crystals. The infrared spectrum of this mixture showed the presence of S_4N_4, and weak peaks in the 1000-1100 cm^{-1} region, including peaks attributable to $(NSF)_3$.

$(NSCl)_3$ and ClF

In a typical reaction ClF (0.09 g, 1.65 mmole) was condensed in three aliquots on to $(NSCl)_3$ (0.13 g, 1.60 mmole NSCl). The vessel was held at -78°C for 1 h between additions and then was warmed to room temperature for 18 h. The volatile products were identified as N_2, SF_4, SOF_2 and Cl_2 (main products); there were also small quantities of NSF and $SClF_5$. The residue (0.09 g) was identified as $(NSCl)_3$.

In a higher temperature reaction, chlorine monofluoride (0.97 g, 17.80 mmole) was also reacted with $(NSCl)_3$ (1.33 g, 16.32 mmole NSCl) at 60°C for 35 h; the same volatile and solid products were obtained, and in addition, a small quantity of SF_6.

NSF and ClF

NSF (10 torr, 0.033 mmoles) was expanded into an i.r. cell, its spectrum recorded and then condensed into an isolatable side arm (15 cm x ¼" O.D.). Chlorine monofluoride (30 torr, 9.9×10^{-2} mmole) was added to the cell; an i.r. spectrum was taken and the valve, separating the side arm and cell, was opened. The spectrum was obtained immediately and showed the presence of SF_4 only.

$NSCl_{(g)}$ and ClF

$NSCl_{(g)}$ (18 torr, 0.06 mmole) was expanded into an i.r. gas cell and aliquots of ClF were added. An i.r. spectrum was obtained after each addition of ClF and products were identified as shown in Table 1.

TABLE 1.

Gas phase reaction of NSCl with ClF

Pressure ClF	Species present (from i.r.)		
0		NSCl(s)	
20 torr	NSCl(w)	$ClNSF_2$(m)	NSF(m)
40 torr		$ClNSF_2$(s)	NSF(w)
65 torr	NCl_3(m)	$ClNSF_2$(m)	SF_4(s)
90 torr	NCl_3(s)	SF_4(vs)	
165 torr	NCl_3(s)	SF_4(vs)	

NSF and Cl_2

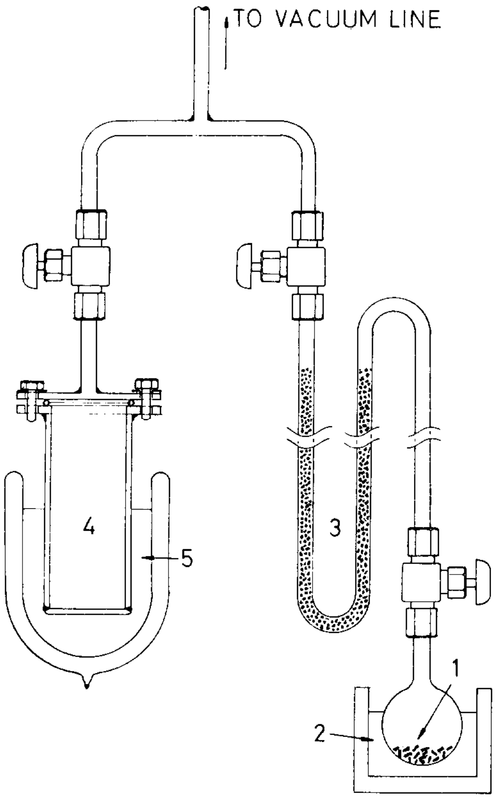
NSF (10 torr, 0.033 mmole) was expanded into an i.r. gas cell and Cl_2 added in three aliquots, giving total pressures of chlorine of 20, 100 and 300 torr. An i.r. spectrum was run after each addition. The spectra showed only NSF and the final mixture did not change over a period of 10 h.

NSF with Cl_2 and SO_2

NSF (5 torr, 0.0165 mmole), SO_2 (50 torr, 0.0105 mmole) and Cl_2 (100 torr, 0.34 mmole) were added to an i.r. gas cell. The i.r. spectrum was run eight times over a period of 65 h. Bands were observed which corresponded to NSF, SO_2, SO_2Cl_2, SO_2ClF and NSCl. The NSF and SO_2 intensities decreased whilst those of SO_2ClF, NSCl, and SO_2Cl_2 steadily increased as a function of time.

Preparation of small quantities of thiazyl fluoride by the reaction of thiazyl chloride with caesium fluoride at 110°C

In a typical reaction good quality recrystallised $(NSCl)_3$ (2.436 g, 9.96 mmole) was placed in a dry pyrex vessel connected to a Monel column (¼" diam. and 25 cm in length) packed with powdered anhydrous CsF (8.10 g, 53.29 mmole), see Figure 1.



1. Pyrex flask with $(NSCl)_3$
2. Oil bath at 70°C
3. Monel column (¼ in. O.D.) packed with CsF at 110°C
4. Monel collection can
5. Dewar with liquid nitrogen

Fig. 1. Apparatus for the synthesis of NSF

The column was heated to 160° in a dynamic vacuum and then cooled to 110°C. The system was then isolated and $(NSCl)_3$ was slowly heated to 70°C and the volatiles passed through the column with the collection vessel held at -196°C. The volatiles were monitored from their gas phase infrared spectra. Initially the main products were SF_4 and NSF but after ca. 10 min. the concentration of SF_4 was negligible. After sublimation of ca. 75% of the $(NSCl)_3$ (visual estimate) NSCl was detected in the volatiles, and so the NSF used in the above reactions was taken from the column in the middle of the run. The volatile products in the collection vessel were identified by infrared spectra as NSF and smaller amounts of SOF_2 and SO_2ClF.

It is important to use good quality $(NSCl)_3$ in this preparation, otherwise the trimer melts (below 70°) resulting in a low surface area of the melt, and much decreased NSCl concentration and NSF formation.

DISCUSSION

The reactions indicated that S_4N_4 and $(NSCl)_3$ reacted with excess ClF according to the equations:

$$S_4N_4 + 16ClF \rightarrow 4SF_4 + 2N_2 + 8Cl_2 \quad \Delta H = -2776 \text{ kJ mol}^{-1} \tag{2}$$

$$(NSCl)_3 + 12ClF \rightarrow 3SF_4 + {}^3/2N_2 + {}^{15}/2Cl_2 \tag{3}$$

Heats of reaction were calculated from published enthalpies of formation of S_4N_4 (110.0 k.cal mol^{-1}) [17], ClF (-13.02 k.cal mol^{-1}) [18], SF_4 (-185.2 k.cal mol^{-1}) [18], and $\Delta H^{20.9}_{sub.}$ S_4N_4 = 21.2 k.cal mol^{-1} [19].

With insufficient ClF for complete reaction, the weights of residues corresponded to all fluorine being present in the volatiles [as NSF and/or SF_4 (or SOF_2)] and all chlorine in the solid [as $(NSCl)_3$ and suspected $S_4N_4Cl_2$]. The steps in these reactions are shown in Figure 2, the experimental evidence being drawn mainly from Table 1.

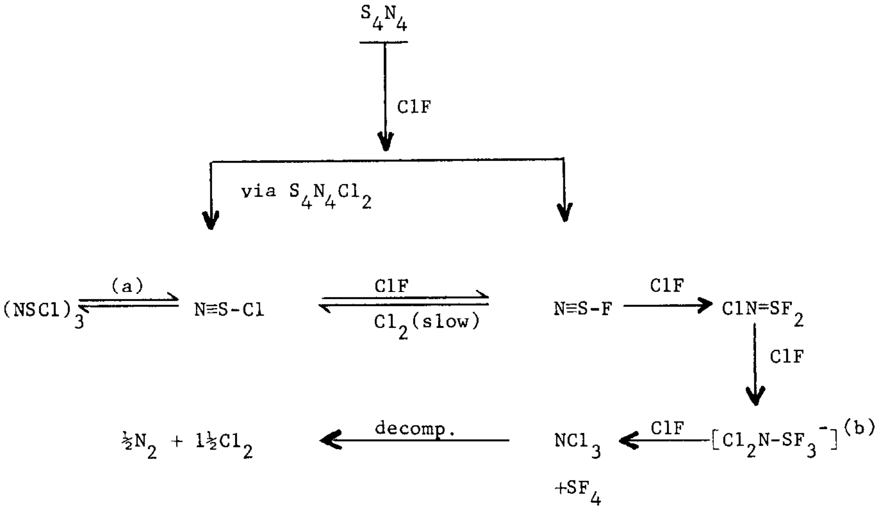


Fig. 2. Proposed steps in the reaction of ClF with S_4N_4

(a) R.L. Patton and W.L. Jolly, Inorg. Chem., 9 (1970) 1079.
(b) Proposed reaction intermediate.

Chlorine monofluoride is known [20] to add to unsaturated centres. In this case it adds to sulphur-nitrogen multiple bonds and, as expected, with fluorine becoming attached to sulphur, and chlorine to nitrogen; thus chlorine monofluoride and thiazyl fluoride react to give $Cl\text{-}N{=}SF_2$ (usually prepared from $Hg(NSF_2)$ and Cl_2 [8]). The addition of ClF to NSCl does not yield $Cl\text{-}N{=}SClF$, or by rearrangement $N{\equiv}SCl_2F$, but gives NSF, presumably by elimination of chlorine:

$$NSCl + ClF \rightarrow NSF + Cl_2 \quad \Delta H \approx -49 \text{ kJ mol}^{-1} \tag{4}$$

Since ΔH_{NSCl} is not known, an upper limit to the enthalpy of reaction can be estimated by taking similar NS bond energies for NSF and NSCl (though it is expected to be larger for NSF) and assuming that the S-Hal bond strengths differ as for SOF_2 and $SOCl_2$ (calc. 76.9-63.3 k.cal mol^{-1} per S-Hal bond = 56.9 kJ mol^{-1} stronger in SOF_2) [21]. The bond energies of ClF and Cl_2 differ by 8.0 kJ mol^{-1} [22].

Glemser et al. [1] have reported a reaction [of NSF and Cl_2 in a glass vessel at room temperature for 10 days to give $(NSCl)_3$] which appears to be the thermodynamically unfavourable reverse of reaction (4). We detected no reaction between NSF and excess Cl_2. However, on adding SO_2, we found that NSCl is formed. Thus reaction (4) is displaced to the left by SO_2 (which removes ClF as SO_2ClF). The results of Glemser et al show that it is also disturbed by the presence of SiO_2; reaction occurs with formation of SiF_4, SOF_2 and $SOCl_2$ as well as $(NSCl)_3$ [1].

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