Trifluoromethyl Thionitrite

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Trifluoromethyl thionitrite, CF₃SNO, a red gas, has been made by the action of NOCI on Hg(SCF₃)₂, and also from CF₃SH with an alkyl nitrite or NOCI, all at low temperatures. It decomposes quickly at room temperature, but very slowly at -78° , to give the disulphide CF₃S·SCF₃ and NO.

The i.r. spectrum (4000-400 cm.-1) of the solid at -196°, and the gas at low pressure at room temperature, allows the assignment of 10 of the 15 fundamental vibrations. The u.v. and visible spectrum of the gas (at -116° to -20°) resembles that of NOCI.

TRIFLUOROMETHYL thionitrite, CF₃SNO, has been made in high yield by the reaction of NOCl with $Hg(SCF_3)_2$, and also by the reaction of CF₃SH with an alkyl nitrite, or NOCl, all at low temperatures. It is less stable even than the alkyl thionitrites, decomposing to give the disulphide and NO. The decomposition is slow enough at -78° for physical properties to be measurable, but fast above -30° or so; it is readily observed by the disappearance of the deep red thionitrite colour, and by the increase in pressure.

 CF_3SNO is readily prepared pure by the addition of NOCl to a slight excess of the thiomercurial at -196° . After brief warming to thaw, the product can be distilled out at about -100° . Treatment with a little more thiomercurial converts the last traces of NOCl, which is of similar volatility to CF₃SNO. The decomposition products, NO (b.p. -152°) and CF₃S·SCF₃ (b.p. 35°) have very different volatilities, and are easily separated from CF₃SNO, which boils at about -3° (extrapolated).

The reaction of CF_3SH with alkyl nitrites (ethyl, pentyl, etc.) gives the thionitrite, as does (in lower yield, since some NOCl is reduced by the thiol) the reaction of NOCl with CF_3SH . In these cases, however, separation of the CF₃SNO from traces of the reactants is less easy, and in any case the thiol is normally made from the thiomercurial, so that the first method is more direct.

It has been known since 1840 that thiols give a red colour with nitrous acid, but the lower alkyl thionitrites are still little known. The triphenylmethyl compound was made in 1919,¹ and the t-butyl² and ethyl³ compounds in 1926. The tertiary compounds are more stable than the secondary and primary, the decomposition to the disulphide being accelerated by the presence of air. Cases are known, *e.g.*, the primary alkyl nitroso-compounds, in which perfluorination of the alkyl group ⁴ has stabilised a labile functional group, but this is not true of the thionitrites RSNO in which stability appears to decrease with increasing (negative) inductive effect of R. In the nitroso-compounds a strong -I effect prevents the NN dimerisation, in the thionitrites it favours disulphide formation. The unfluorinated thionitrites are formed in lower yield by the reaction of NOCl with the mercurial, the better method here being the esterification of the thiol with an alkyl nitrite.^{3,5}

- ¹ D. Vorlander and E. Mittag, Ber., 1919, **52**, 413. ² H. Rheinboldt et al., Ber., 1926, **59**, 1311; J. prakt. Chem., 1931, (2), **130**, 133; 1932, **133**, 328; **134**, 257.
- H. Lecher and W. Siefken, Ber., 1926, 59, 1314, 2594.
 J. (Banus) Mason, Nature, 1953, 171, 173; J. Chem. Soc., 1953, 3755.

Kresze and Uhlich ⁵ have listed the main features of the u.v. and i.r. absorption, and report the dipole moment (which is similar for RSNO and RONO) for t-butyl and triphenylmethyl thionitrites.

The saturation vapour pressure of CF₃SNO at low temperatures was measured with a spiral gauge tensimeter designed so that the liquid and gas are completely immersed in the coolant. The uncertainties in the measurements are described in the Experimental section. In Table 1 the properties of CF₃SNO are compared with

TABLE 1							
Physical properties							
	CF ₃ SNO *	CF ₃ NSO †	NOCI				
$\log p$ (mm.) (liq.)	(7.88	(7.733 -	(7.992 -				
$\mathbf{D} = \langle 0 \rangle$	1350/T)	1413/T	1347/T)				
$\Delta T = \langle z \rangle$	-3 I	18 1	-5.8				
ΔH_g (cal. mole -)	6150	6470	6160				
(cal. deg. ⁻¹ mole ⁻¹)	22.8	$22 \cdot 2$	$23 \cdot 0$				
M.p. (°)	< -116		-59.6				
* Approx.	values. †	Ref. 6. ‡ Extrap					

those of NOCl, which it resembles, and of its isomer CF₃NSO.6

The i.r. spectrum of CF₃SNO was measured in the 4000-400 cm.⁻¹ region, for the solid at -196° and the gas at low pressure (about 1 mm.) at room temperature. The spectrum of the solid (Figure 1) shows that possible contaminants, such as CF₃SCl and NOCl, are absent, and that $CF_3S \cdot SCF_3$ is present only on warming, the patterns of the CF stretching bands being characteristic. The spectrum of the gas at room temperature showed traces of the decomposition products, but the strong bands of CF_aSNO were clearly distinguished. Unless otherwise indicated, the discussion refers to the spectrum of the solid.

The CF₃SNO spectrum is readily assigned (Table 2) since the CF₃SN frequencies closely match those in known CF₃SN and CF₃S compounds, and the NO frequencies are then obvious. Gas-phase spectra (or solid-phase, where mentioned), are available for CF₃SNH₂^{7,8} and its mono- and di-methyl derivatives,7 the bis- and tris-compounds 8 (CF3S)2NH and (CF₃S)₃N, solid (CF₃SNCO)₂,⁹ and CF₃SN.SF₂ and

⁵ G. Kresze and U. Uhlich, Chem. Ber., 1959, 92, 1048.

M. Lustig, Inorg. Chem., 1966, 5, 1317.
 H. J. Emeléus and S. N. Nabi, J. Chem. Soc., 1960, 1103.

⁸ A. J. Downs and A. Haas, unpublished work.
⁹ A. J. Downs and A. Haas, Spectrochim. Acta, 1967, 23A, 1023.

J. Chem. Soc. (A), 1969

CF₃SN:S:NSCF₃;¹⁰ and for the CF₃S compounds CF₃SCl,¹¹ CF₃S·SCF₃,¹¹ and solid Hg(SCF₃)₂,¹² although not all of these have been assigned. Downs's assignments include Raman evidence.

The CF_3SNO spectrum is that of a molecule of C_s symmetry, probably trans-bent, with ten A' and five A''fundamental vibrations all i.r.- and Raman-active. The question of rotational isomerism is discussed below. The spectrum clearly shows the three very strong CF stretching vibrations, those at 1140 (A'') and 1100 (A')derived from the E vibrations of CF_3 (cf. CF_3NO^{13}), and the totally symmetric vibration at 1083 cm.⁻¹, all in the appropriate region. The medium-strong (ms) symmetric band is a sharp singlet. If the CF₃ rocking modes absorb below 400 cm.⁻¹ in CF₃SNO, then very weak bands at 792 and 680 cm.⁻¹ may represent their first overtones (and there is some evidence for 396 and 342 as fundamental frequencies from combination bands), although they could be combination bands themselves. The rocking frequencies are 380 and 370mw for $(CF_3SNCO)_2$, and 385 and 345 for $(CF_3S)_3N$.

The SN and CS stretching vibrations are more sensitive to substitution than are the CF₃ modes, and are probably coupled together. The CS frequency does not vary by more than 30 cm.⁻¹ among the comparison compounds, however.



FIGURE 1 I.r. spectrum of solid CF₃SNO at -196° (the thickness increasing in numerical order). The movement of the NO and CF stretching bands on slow warming (3 to 2 to 1) is shown, and the NO stretching band of the gas at room temperature

bending vibration of the CF_3 group, at 754 cm.⁻¹, matches the frequencies (752-757 cm.-1) and intensities (ms to s) of this vibration in all the five trifluoromethyl sulphenylamines mentioned above.

The nearly degenerate CF₃ asymmetric bending vibrations at 541 and 538m in CF₃SNO correspond to 552 and 522s in CF₃SNHMe, 558s in CF₃SNMe₂, 547m in (CF₃S)₂NH, and 561 and 540mw in (CF₃S·NCO)₂.

The strong band at 442 cm.⁻¹ may be due to a CF₃ rocking vibration, although in related compounds these modes absorb below 400 cm.⁻¹, and with somewhat lower intensity; for example in CF_3SNH_2 , $(CF_3SNCO)_2$, $Hg(SCF_3)_2$, $CF_3S\cdot SCF_3$, and CF_3SCl . They extend above 400 cm.⁻¹ in the bis-sulphenylamine, perhaps because split over a wider range, but are at 438 cm.⁻¹ in CF₃NO.¹³ The CS stretching frequency, however, should be in this region, as explained below. It is unlikely that the CS stretching frequency and a CF₃ rocking frequency are coincident at 442 cm.⁻¹, since the

¹⁰ A. Haas and P. Schott, Angew. Chem. Internat. Edn., 1967, 6; 370. ¹¹ S. N. Nabi and N. Sheppard, J. Chem. Soc., 1959, 3439.

With two electronegative groups attached to sulphur, these bands should be quite strong. The SN stretching frequencies are 880m for CF₃SNH₂, 880s and 795m for the bis-compound, 844s for the tris-compound, 847 and 797m in CF₃SNHMe, but 770s, 711w (Raman) for (CF₃SNCO)₂, and possibly 672m for CF₃SNMe₂. In the CF₂SNO spectrum the band at 880 cm.⁻¹ is too weak for this vibration (and the doublet at 614, 610 too strong, and appropriate for the NO deformation). We are left with only the sharp 759s, 754ms doublet in the appropriate region. This doublet presumably arises from both the SN stretching and the CF₃ symmetric bending vibrations, exchanging intensity.

Similarly the band at 472 cm.⁻¹ seems too weak for the CS stretching mode. If this can be identified with the strong band at 442 cm.⁻¹, it corresponds to 469ms for CF₃SNH₂, 472m and 462s for the N-methylamines, 473m for the bis-compound, and 479m for the tris-

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¹² A. J. Downs, E. A. V. Ebsworth, and H. J. Emeléus, J. Chem. Soc., 1961, 3187.

¹³ J. (Banus) Mason and J. Dunderdale, J. Chem. Soc., 1956, 754.

compound, 493vw and 466ms for (CF₃SNCO)₂, and 477ms for CF₃S·SCF₃. If, however, the 442 cm.⁻¹ band is due to a CF_3 rocking vibration, then the CS stretching frequency is below 400 cm.⁻¹, possibly at 396 cm.⁻¹, but this seems low compared with the related compounds.

TABLE 2

The i.r. absorption frequencies (cm.⁻¹) of solid CF₃SNO at -196° (values in parentheses are of the gas at room temperature)

= inflection, sh = sharp,	\mathbf{br}	= broa	d, $w = weak$, $m = medium$,
s ==	stro	ong, v =	= very
3378 (3260)		w	2 imes 1700
2480	\mathbf{br}	vw	1700 + 759
2240		w	$2 \times 1100; 1083 + 1140;$
			1700 + 538
2140		vvw	2 imes 1071; 1700 + 442
2035	\mathbf{br}	vvw	1700 + 342
(1950	i		1200 + 754
$\{1937$		w	1700 + 236
(1915	1		1300 + 614
1880	1		1140 + 754
< 1850		W	1100 + 754, 759
(1843	1		1083 + 754, 759
1755	1		1140 + 612
A'_{1} 1700 (1660)		vs	
1665	1		1140 + 540
1540	1		1140 + 442
1040	br	VVW	1100 + 442 1140 + 996 + 750 + 619
1370	DI	VVW	1140 + 230; 759 + 012
1300 (1315)	1. m	111	109, 104 + 041, 000
1200	br	VVW	1700 - 442
1230	DI	vvw	2×014 750 1 449, 9 × 610
1102	ch	5	$759 + 442; 2 \times 010$
1192	SII	w	754 + 442
A = 1140(1108) A' = 1100(1194)		VS VS	
A' = 100 (1124) A' = 1082 (1000)		v 5	$CF \nu_8$
1071	ch	v 5 c	2×528
1065	i	5	614 ± 449
082	br		540 ± 442
955	br	vw	612 + 342
880	D1	w	2×442 : 540 + 342
867		vw	472 + 396
850		vw	612 + 236; 442 + 396
792	br	vvw	$2 \times 396: 442 + 342$
776	br	vvw	540 + 236
A' = 759 (757)	sh	s	SN v
A' 754 (753)	sh	ms	CF ₂ δ ₂
685	br	vvw	$442 + 236; 2 \times 342$
(614 (635)			
A' (629)		vs	ΝΟδ
610 (625)			
580	i		342 + 236
(541 (536)		ms	
A' + A''			$CF_3 \delta_{as}$
538 (524)		ms	
472		w	2 imes236
442 (43 0)		s	$CS \nu$ (or CF_3 rock)
Conjectural:			
396			
A' + A''		CF_3 ro	ock? (or CS ν ?)
342			
236		CSN 8	57 · · ·
Also A''		CS to	rsion
$A^{\prime\prime}$		SN to	rsion

Of the three remaining fundamental vibrations of the CSN chain, the CSN bending vibration is at 204 cm.⁻¹ in CF₃SNH₂, about 240 in (CF₃S)₂NH, and 209 in

 $(CF_3SNCO)_2$. The weak band at 472 cm.⁻¹ is perhaps the first overtone of this vibration in CF₂SNO, and some of the very weak bands observed could represent its combinations with other frequencies, as shown conjecturally in Table 2. There is no evidence for the remaining two fundamentals, the CS and SN torsions, which are probably at lower frequencies.

The NO stretching frequency, 1700 cm.⁻¹ for solid CF_3SNO , 1660 for the gas, is compared with those for related molecules in Table 3. In NOCl it is much lower

Table	3
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Stretching	and	bending	frequencies	of	the	nitroso-group
			(orm -1)			

	(cm)		
	ν (N O)	δ(NO)	Refs.
NOCl (s)	1946br	245	15
(g)	1799	332	
$CF_3SNO(s)$	1700br	614, 610sh	
(g)	1660	629	
EtSNO (g)	$1530\mathrm{br}$	620br	16
ButSNO (1)	1490-1530br	670, 662	5
MeONO (g) cis	1625	617	17
trans	1680	565	
CF_3NO (g)	1595	405	13
Bu ^t NO	1574		a
a D Tente D	17 Constitut tota	1054 00 505	

^a P. Tarte, Bull. Soc. chim. belges, 1954, 63, 525.

for the gas than for the solid. Bellamy and Williams¹⁴ have remarked that the N:O stretching vibration, like that of C:O, is mass-insensitive for masses of 12 and above of the attached atom(s), but that dipolar effects may be important. These can explain the lower stretching frequencies for N:O in cis-MeONO, and in the unfluorinated thionitrites that have been examined. Kresze and Uhlich⁵ report a broad structured band at 1480-1530 cm.⁻¹ for this mode in (liquid) t-butyl and triphenylmethyl thionitrites, overlapped by the asymmetric CH₃ deformation in the former and by ring vibrations in the latter. The band is somewhat structured also for CF₃SNO, less so for NOCl.

The NO stretching band is broad for solid CF₃SNO or NOCl, deposited from the gas phase on a silver chloride window at -196° . The breadth of the band may demonstrate the varying polarity of the environment of the N:O group, since the band for the gas is less broad. The sensitivity of the NO stretching frequency in NOCl to the nature of the matrix has been remarked.¹⁵ The band for pure NOCl moved 20 cm.-1 to lower frequencies for a mixture of NOCl and CF₃SNO, although the presence of NOCl did not cause any frequency shift for CF₃SNO. For both compounds the band moved to lower frequencies on slow warming of the sample.

The NO bending frequencies are compared in Table 3. Bu^tSNO was measured in the NaCl region only,⁵ and there is no further information on the triphenylmethyl thionitrite spectrum. In the spectrum of CF₃SNO at room temperature, the NO and CF stretching bands are less broad than at low temperature, but the other bands

L. J. Bellamy and R. L. Williams, J. Chem. Soc., 1957, 863.
 I. C. Hisatsune and P. Miller, jun., J. Chem. Phys., 1963, 38, 49.

J. Mason, unpublished work.

¹⁷ P. Tarte, J. Chem. Phys., 1952, 20, 1570.

are broadened. The singularity of the skeletal stretching bands, and of the NO deformation band, in the CF₃SNO spectrum, suggests that the rotational isomerism found in the primary alkyl nitrites is absent here, as does the relative simplicity of the u.v. spectrum described below. The single ¹⁹F n.m.r. line points to a single isomer, or fast (enough) rotation at -60° . Tertiary alkyl nitrites are almost wholly trans, secondary are mainly trans, and primary are a mixture of cis and trans.¹⁷ On steric grounds CF₃SNO may then resemble the tertiary alkyl nitrites. The t-butyl and triphenylmethyl thionitrites would be expected to be all trans. Kresze and Uhlich considered that the structure of their NO stretching bands, and the doublet observed for the NO deformation in ButSNO, were due to rotational isomerism, but this structure is not very pronounced



FIGURE 2 U.V. and visible spectrum of CF₃SNO gas at low temperatures, with that of NOCl at room temperature

(and the splittings relatively small) and can be explained otherwise.

The ¹⁹F chemical shift for CF₃SNO, +37.7 p.p.m. from CFCl₃, is in the expected range for CF₃S compounds (cf. 38.6 for CF₃SCF₃,¹⁸ 38.8 for CF₃SCN,¹⁹ and 49.8 for CF_3SCl^{19}). The n.m.r. spectrum measured at -60° shows the CF₃S·SCF₃ line ¹⁸ at 46.9 p.p.m. increasing with time at the expense of the CF₃SNO line, with the disulphide as the only fluorine-containing product.

The u.v. and visible spectrum of CF₃SNO gas at low temperatures is shown, together with that of NOCl at room temperature,²¹ in Figure 2, and the extinction coefficients compared in Table 4 with preliminary values for EtSNO,¹⁶ and with those reported for Bu^tSNO.⁵ The very intense A band at 2255 Å in the CF_aSNO spectrum was measured at -80° to -116° , and the extinction coefficient is approximate because of the uncertainty in estimating the very low pressure required

		Та	BLE 4				
	Electron	ic abso	orption	ι (λ _{max.}	in Å)		
	A		Ĺ	В	(5	
	emax.	λ _{max.}	ε_{\max}	λ _{max.}	ε _{max.}	λmax.	Refs.
CF ₃ SNO (g)	$\sim 20,000$	2250	112	3730	~ 6	5700	
EtSNO (g) †			650	3425	21	5500	16
Bu ^t SNO (in	10,500	2290	980	3390	15	5988	5
heptane)							
NOCl (g)	2550	1970	$32 \cdot 5$	3350	0.9	6017	21
† Minimum values.							

for a measurable optical density. The extinction coefficients are more accurate for the B band, measured at -60° to -78° .

The long-wavelength bands, however, are very weak indeed at the saturation pressure of CF_3SNO at -60° and below; and at the higher temperatures (-60° to -20°) which give measurable optical densities the decomposition is very fast so that the pressure of CF₃SNO is unknown. This was therefore estimated from the intensity of the B band, since the decomposition products do not absorb above 3000 Å. The extinction coefficients of the long-wavelength bands are approximate, then, because they are weak, and also because at the higher temperatures there is some broadening of the B band.

There is a marked similarity between the electronic spectra of RSNO, where R includes perfluoroalkyl, and of NOCl and NOBr.¹⁶ It seems possible that corresponding bands have corresponding assignments, that is, that the strong A bands are $\pi \rightarrow \pi^*$ transitions, and that the B and C (etc.) bands are due to $n \to \pi^*$ transitions from nitrogen, sulphur, halogen, or oxygen. Orgel²⁰ has ascribed the 3350 Å NOCl band to a singlet-singlet $n_{\rm N} \rightarrow \pi^*$ transition, with the weak C band at 6017 Å as its triplet counterpart (cf. ref. 21). His expectation that the latter band in NOBr would be similarly placed, but several times stronger, is now confirmed,¹⁶ and a similar argument may hold for CF₃SNO.

The assignment of the 3350 Å NOCl band as singlet $n_N \rightarrow \pi^*$ has been criticised ²² as giving too large a singlet-triplet separation. This seems to point to the 4750 Å band as the $n_N \rightarrow \pi^*$ singlet. There is a band near this position in the NOBr spectrum, but for CF₃SNO and EtSNO, only slight inflections resembling vibrational structure. (No curve is given for ButSNO, for which the C band is labelled $n_N \rightarrow \pi^*$, and the B band as -SNO group or $n_0 \rightarrow \pi^*$ absorption; ⁵ but nitroso $n_0 \rightarrow \pi^*$ bands usually have higher energies and lower intensities than this.²³) Thus if corresponding bands have corresponding assignments, the comparison suggests that the *B* bands may be due to the $n_{\rm N} \rightarrow \pi^*$ transition. These interpretations will be discussed further in conjunction with the nitrosyl halide spectra,

 ¹⁸ H. J. Emeléus and A. Haas, J. Chem. Soc., 1963, 1272.
 ¹⁹ R. K. Harris, J. Mol. Spectroscopy, 1963, 10, 309.
 ²⁰ L. E. Orgel, J. Chem. Soc., 1953, 1276.

²¹ C. F. Goodeve and S. Katz, Proc. Roy. Soc., 1938, A, 172, 432.

²² A. D. Walsh, Ann. Rev. Phys. Chem., 1954, 5, 169; J. Chem. Soc., 1953, 2286. ²³ J. Mason, J. Chem. Soc., 1957, 3904.

and with the ¹⁴N n.m.r. shifts ²⁴ of these compounds, since they correlate with $n_{\rm N} \rightarrow \pi^*$ transitions.

The inflection at about 2750 Å is possibly due to a transition from sulphur; $\text{CF}_3\text{S}\text{-}\text{SCF}_3$ has $\epsilon_{\text{max.}}$ 290 at 2350 Å, CF₃SCl 25 at 3330 Å, and CF₃SCF₃ 6.8 at 2100 Å.²⁵

The N:O stretching vibration is usually excited in $n_{\rm N} \rightarrow \pi^*$ transitions of the nitroso-group, for example in the nitrosyl halides, and in R_2NNO , RONO, HONO, and CF₃NO.²⁰ This frequency in the (somewhat antibonded) upper state is 200-500 cm.⁻¹ less than in the ground state, for these compounds. In the CF₃SNO (and also the EtSNO) spectrum there are intervals corresponding to such a frequency among the longwavelength bands and some inflections on the longwavelength flank of the *B* band. No hot band is evident. Unlike NOCl, CF₃SNO is still very strongly coloured (red-black) at -196° .

The oxidation of CF₃SNO to the thionitrate was attempted, since ButSNO can be oxidised to the thionitrate by fuming nitric acid in glacial acetic acid.²⁶ The oxidising agent must be fluid at low enough temperatures for the CF₃SNO to survive to react. Fuming nitric acid was tried at its m.p. (-42°) , and CrO_5 in ether, but no fluorine-containing product other than some residual CF_3SNO could be distilled out at -45° , at which temperature CF_3SNO_2 should be volatile.

The reaction of CF₃SCl with AgNO₂, which gave ²⁷ the disulphide and $NO_2 - N_2O_4$ at above -60° , was attempted at low temperatures, but no CF3SNO2 product was obtained. Variation of the conditions might lead to a more fruitful result: a longer contact time at low temperature may be required.

As described in the Experimental section, there were some indications of the formation of CF_3SNO_2 , as well as a little CF_3SNO , in the reaction of $Hg(SCF_3)_2$ with $NO_2-N_2O_4$, under the conditions used for the reaction with NOCI. This reaction will be investigated further.

EXPERIMENTAL

The compounds were handled in a glass vacuum system, with greaseless (Teflon) taps and Kel-F-greased joints where necessary. Light was excluded from NOCI and thionitrite or thionitrates.

 $\rm Hg(SCF_3)_2$ was made 28 from $\rm CS_2$ and $\rm HgF_2$ at 250°, in a Hastelloy-C-lined autoclave, kindly lent by Professor H. J. Emeléus. CF₃SH was made from the thiomercurial with HCl gas.²⁵ EtONO was made from EtOH and HONO.²⁹ Isopentyl nitrite was the commercial product. NOCl was made 30 from NaCl and NOHSO₄ (made by the action of SO₂ on fuming nitric-glacial acetic acid mixture), and purified from HCl. NO2-N2O4 was made by oxidation of NO (from the reduction of HONO by iodide), and also by heating $Pb(NO_3)_2$.

CF₃SCl was made by photochlorination of CF₃S·SCF₃,²⁵ and the excess of chlorine removed with iodine.⁷ Even after distillation, the CF₃SCl gave several ¹⁹F n.m.r. lines

- ²⁷ A. Haas and M. E. Peach, Z. anorg. Chem., 1965, 338, 299.

in the CF₃S region, as well as those of CF₃SCl and residual CF_3S ·SCF₃, so after the reaction with excess of dry AgNO₂, the spectra of the product were compared with those of the starting material, as below. CrO_5 solution in ether was made by Wiede's method.

 CF_3SNO .—In a typical preparation, slightly less than the stoicheiometric amount of NOCl was condensed on 2-3 g. of $Hg(SCF_3)_2$ in vacuo in a reaction tube cooled in liquid nitrogen. The tube was warmed briefly to melt the NOCI and re-cooled, once or twice, then the small amount of NO that had formed was pumped from the tube held at -170° or so. Then the tube was warmed to $ca. -100^{\circ}$ and the CF_3SNO distilled out through a very short connecting tube (cooled to -78° if great purity was required) into another reaction tube containing about 300 mg. of $Hg(SCF_3)_2$ to convert any residual NOCI. The trifluoromethyl thionitrite was distilled from this tube as before, as required, any disulphide being left behind. The yield of CF₃SNO is 80-90%. The excess of thiomercurial was recovered from the mercuric chloride product by extraction with dry ether, and (or) vacuum sublimation at 60° . CF₃SNO can be stored indefinitely at -196° , but only for short periods at – 78°.

For the reaction of CF₃SH with EtONO, C₅H₁₁ONO, or NOCl, a stoicheiometric mixture at -196° was gently warmed, to thaw the reagents, and watched for changes in colour, but kept cold. Where possible, and necessary, the products were distilled through a Fenske-packed column at -80° , but this tended to decompose the thionitrite. The preparation of CF₃SNO from CF₃SH was not studied in detail when the preparation from $Hg(SCF_3)_2$ was found to be easy.

The material balance in the preparation and decomposition of CF₃SNO was examined. The chloride in the solid product was estimated by standard methods, and the by-product NO collected. The CF₃SNO was then left to decompose, and the products collected. CF₃S·SCF₃, total NO, and chloride in the solid, corresponded almost quantitatively with the NOCl taken.

In the reaction of $NO_2-N_2O_4$ with $Hg(SCF_3)_2$, and of CF₃SCl with AgNO₂, an excess of the solid was taken to convert all the gaseous reagent. The reaction with NO2- N_2O_4 gave some disulphide and NO, a little CF₃SNO, and a product with i.r. absorption at room temperature which suggests the presence of thionitrate CF₃SNO₂, that is, at 1595, 1625 as for the asymmetric stretching frequency of the nitro-group, at 1416 as for the symmetric stretching frequency, and at 610 cm.⁻¹ as for the symmetric deformation. Only CF₃S·SCF₃ was obtained (as fluorine-containing product) in a single experiment with CF₃SCl and AgNO₂. This reaction is rather slow at low temperature.

The saturation vapour pressure of CF₃SNO was measured in a spiral gauge tensimeter, designed so that the liquid and gas were completely immersed in a tall Dewar vessel of cold ether. Decomposition was shown by an increase in pressure at constant temperature. After the CF₃SNO was distilled from a tube at -105° into the tensimeter at -196° , it was put in melting ether at -116° , at which temperature CF₃SNO has a very small vapour pressure, and the absence of NO checked.

in Gas Reactions,' Macmillan, London, 1964, p. 203.

²⁴ J. Mason and W. van Bronswijk, unpublished work.
²⁵ R. N. Haszeldine and J. M. Kidd, J. Chem. Soc., 1953, 3219.
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The s.v.p. could be measured directly up to about 10 mm., at about -77° , above which correction for the decomposition was necessary (by measurement of the pressure of NO after cooling to freeze out the CF₃SNO). By the time the vapour pressure had reached 40 mm., the decomposition was too fast for this correction to be possible. The observed saturation pressures were 10 mm. at $-76 \cdot 7^{\circ}$ and 40 mm. (corrected) at -58° . Extrapolation to a hypothetical b.p. at atmospheric pressure thus involves an error of a few degrees, but the limitation of the Trouton coefficient to a reasonable value, *e.g.*, by comparison with that of the isomeric CF₃NSO, reduces the uncertainty. CF₃SNO is not associated or dissociated, according to the spectroscopic and other properties. The u.v. spectrum of CF_3SNO gas was measured with a Cary 14 spectrophotometer in an all-quartz Dewar cell, the low temperatures being obtained with slush baths, *etc.*

The i.r. spectrum of solid CF_3SNO was measured with a Perkin-Elmer 125 spectrophotomer, in a low-temperature cell designed by Dr. D. M. Adams, in which the gas was condensed on a silver chloride window in a copper frame that was cooled with liquid nitrogen, or heated electrically, monitored by a thermocouple.

The ¹⁹F n.m.r. spectra were measured with an HA 100 Varian spectrometer.

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