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REACTION OF THE BIS-TRIFLUOROMETHYL NITROXIDE RADICAL WITH TETRASULPHUR TETRANITRIDE AND SOME OF ITS DERIVATIVES

H. J. EMELÉUS AND R. J. POULET

University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (Gt. Britain)

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SUMMARY

Liquid bis-trifluoromethyl nitroxide radical reacts quantitatively at room temperature with tetrasulphur tetranitride to form tetrathiazyl tetra(bis-trifluoromethyl nitroxide), $N_4S_4[ON(CF_3)_2]_4$ (nc). This material is a white crystalline solid which is unattacked at room temperature by water or hydrogen chloride. The same compound is formed in the reaction of the radical with $N_4S_4H_4$ or $N_3S_3Cl_3$ or in the reaction of $Hg[ON(CF_3)_2]_2$ with $N_3S_3Cl_3$. Reaction of $Hg[ON(CF_3)_2]_2$ with thiazyl fluoride, NSF, gives thiazyl bis-trifluoromethyl nitroxide (nc), a moisture-sensitive yellow oil, which polymerizes at room temperature to trithiazyl tri(bis-trifluoromethyl nitroxide), $N_3S_3[ON(CF_3)_2]_3$ (nc). Preliminary experiments show that the gaseous bis-trifluoromethyl nitroxide radical reacts with trisulphur dinitrogen dioxide, $S_3N_2O_2$, to form sulphanuric bis-trifluoromethyl nitroxide (nc).

INTRODUCTION

The highly electronegative bis-trifluoromethyl nitroxide radical behaves as a free halogen in many of its reactions. Thus, it converts tin[1], mercury[2], arsenic[3], selenium and tellurium[4], for example, to their respective bis-trifluoromethyl nitroxide derivatives at room temperature. In reactions with phosphorus[5], bismuth[6] and sulphur[7], oxidation by the radical takes place, with phosphorus, for example, giving $OP[ON(CF_3)_2]_3$ and $(CF_3)_4N_2$.

RESULTS AND DISCUSSION

The reaction of the radical with tetrasulphur tetranitride has been examined in order to determine whether in this case also the products resemble those formed by fluorination or chlorination. Fluorination of S_4N_4 by a suspension of silver(II) fluoride in carbon tetrachloride gave white needles of $S_4N_4F_4$[8], while chlorination by gaseous chlorine in carbon tetrachloride solution gave $N_3S_3Cl_3$[9]. We have found that the same product results from the reaction of liquid chlorine and tetrasulphur tetranitride at —78°. An earlier report of the formation of the tetramer $N_4S_4Cl_4$ by chlorination of N_4S_4 in refluxing SO_2Cl_2[10] was found to be erroneous, the product being $N_3S_3Cl_3$.

Reaction of the liquid radical with N_4S_4 at room temperature converted the latter quantitatively to tetrathiazyl tetra(bis-trifluoromethyl nitroxide), $N_4S_4[ON(CF_3)_2]_4$, the molar reaction ratio of 4:1 being completely reproducible. The product was not wetted by water and qualitative tests showed it to be insoluble, or only slightly soluble, in typical polar and non-polar solvents. In contrast to $N_4S_4F_4$, it was unchanged after prolonged contact with liquid water at room temperature, although decomposition by 10% aqueous sodium hydroxide was rapid at 60°. There was no reaction with gaseous hydrogen chloride at room temperature, though this reagent attacks many non-metal bis-trifluoromethyl nitroxides (*e.g.* $As[ON(CF_3)_2]_3$)[11] to give a quantitative yield of $(CF_3)_2NOH$. The product was also unaffected by concentrated hydrochloric and nitric acids. When the solid was heated *in vacuo* at 70°, a complex mixture of products was formed. Pure $(CF_3)_2NO\bullet$ recovered from this mixture corresponded to about 25% of the radical combined in the original specimen. Other products were not identified.

The presence of an eight- rather than a six-membered ring was proved by the mass spectrum, in which the highest peak was at *m/e* 688 (corresponding to the $N_4S_4[ON(CF_3)_2]_3^+$ ion). Peaks corresponding to the successive stripping of $ON(CF_3)_2$ units were also observed, together with those for the ions $N_4S_4^+$, $N_3S_3^+$, $N_2S_2^+$ and NS^+. The latter are also the main features of the mass spectrum of N_4S_4 where, with a source temperature of 110° and a beam energy of 70 eV, the corresponding intensities were: $N_4S_4^+$, 18.5%; $N_3S_3^+$, 93%; $N_2S_2^+$, 100%; NS^+, 59%. Conclusive confirmation of the tetrameric nature of this product has been obtained from an X-ray analysis of its structure[12,13], which has shown that the ring configuration present is very similar to that of $N_4S_4F_4$, with two alternating N–S bond distances and with the $(CF_3)_2NO$ groups bonded to the sulphur atoms.

Liquid bis-trifluoromethyl nitroxide radical also reacted quantitatively at room temperature with tetrasulphur tetraimide forming $N_4S_4[ON(CF_3)_2]_4$ and $(CF_3)_2NOH$. The former was contaminated with a very small amount of a water-sensitive yellow solid, which was probably the monomer, $NSON(CF_3)_2$, or the trimer, both of which are described below. The tetramer, $N_4S_4[ON(CF_3)_2]_4$, was also the major product of the reaction of the radical with trithiazyl trichloride, although it was again contaminated by traces of yellow material. This result is in agreement with the observation[14] that the radical displaces chlorine from both S_2Cl_2 and SCl_2, although some oxidation occurs and $O_2S[ON(CF_3)_2]_2$ is amongst the products. Reaction of the mercurial $Hg[ON(CF_3)_2]_2$ with $N_3S_3Cl_3$ also gave the tetramer, although fluorination of the chloro compound is known to give $N_3S_3F_3$[15].

The failure to obtain the trimer, $N_3S_3[ON(CF_3)_2]_3$, from the above reactions suggests that the monomer, $NSON(CF_3)_2$, if it could be isolated, might trimerize as NSF and NSCl are known to do. Reaction of thiazyl fluoride and chlorine in the gas phase has been reported to give thiazyl chloride[15], but there was no evidence of a reaction at room temperature between NSF and $\cdot ON(CF_3)_2$. Mercury(II) bis-trifluoromethyl nitroxide, however, gave the desired product, thiazyl bis-fluoromethyl nitroxide, as a yellow oil. The mass spectrum of this compound indicated the presence of the parent ion $NSON(CF_3)_2^+$, and its reaction with gaseous HCl gave an almost quantitative yield of $(CF_3)_2NOH$ together with $N_3S_3Cl_3$. A second product from this reaction, which was formed in very small yield, was tentatively identified from its mass spectrum as $NSF[ON(CF_3)_2]_2$.

Thiazyl bis-trifluoromethyl nitroxide was volatile in vacuum and was hydrolyzed by water with the liberation of $(CF_3)_2NOH$. On standing *in vacuo* for several days crystals of trithiazyl tri(bis-trifluoromethyl nitroxide) were deposited. These could be isolated from the monomer by volatilizing the latter *in vacuo* and were identified by the mass spectrum, the highest peak in which corresponded to the ion $N_3S_3[ON(CF_3)_2]_2^+$. The trimer was readily hydrolyzed by water, in contrast to $N_4S_4[ON(CF_3)_2]_4$, and gave an almost quantitative yield of $(CF_3)_2NOH$ on treatment with gaseous HCl.

It was shown in the course of this research that thiotrithiazyl chloride, N_3S_4Cl, remains completely unchanged even after prolonged contact with liquid $(CF_3)_2NO\cdot$ at room temperature. Trisulphur dinitrogen dioxide, $S_3N_2O_2$, however, reacts readily at room temperature with either the gaseous or the liquid radical. Two moles of gaseous radical were used per mole of $S_3N_2O_2$, very little volatile material was formed, and the yellow involatile oil crystallized to a yellow solid. The mass spectra of both oil and solid exhibited a peak corresponding to the parent ion of sulphanuric bis-trifluoromethyl nitroxide, $S_3N_3O_3[ON(CF_3)_2]_3^+$. The stoichiometry of the reaction suggests that the $O{=}S{=}N{-}S{-}N{=}S{=}O$ molecule is cleaved to form free sulphur and $(CF_3)_2NOS(O){\equiv}N$, which trimerizes to the sulphanuric compound. This material was not fully characterized. Reaction with gaseous HCl at room temperature gave approximately 25% of the radical as $(CF_3)_2NOH$, although such a reaction is less likely to occur readily for a sulphur (VI) derivative than when the element is in a lower oxidation state. The yellow solid left after this reaction showed peaks in its mass spectrum corresponding to the ions $S_3N_3O_3Cl_2^+$ and $S_3N_3O_3Cl^+$: other peaks were also present, including one due to the $(CF_3)_2NO^+$ ion. This shows that the reaction was incomplete, although, clearly, a sulphanuric derivative was present in the mixture of products.

In two experiments with liquid $(CF_3)_2NO\bullet$ and $S_3N_2O_2$ the reaction was more complicated. When approximately 4 moles of radical were used per mole of $S_3N_2O_2$ a mixture of volatile products was formed, the infrared spectrum of which showed an $S{-}ON(CF_3)_2$ derivative to be present. If free sulphur is formed in the reaction with gaseous radical, the volatile material could result from the further reaction of this sulphur with liquid radical, which is known to be a slow process. An involatile product which was also formed was a yellow oil which decomposed slowly, and from which a small amount of a yellow solid was deposited. This involatile component was, however, most probably a mixture, and identification of the components proved impossible with the small quantities available. The corresponding reaction between liquid chlorine and $S_3N_2O_2$ has been shown[16] to give the ring compound $N_3S_3OCl_3$, derived from sulphanuric chloride by the loss of two oxygen atoms. The other products formed included sulphur oxychlorides.

An attempt was made to transfer the solid from the reaction of gaseous radical and $S_3N_2O_2$ into an NMR tube in a dry box. This proved impossible and it was therefore necessary to prepare the product from a crystal of $S_3N_2O_2$ and a small excess of the radical in the NMR tube using a minimal contact time (*ca.* 6 h) to avoid side reactions as far as possible. After removal of the excess radical and other volatiles, CCl_3F was distilled in and the tube sealed. Surprisingly, the spectrum was a strong singlet at 69.3 ppm. This is in the range expected for bis-trifluoromethyl nitroxide derivatives. The NMR spectrum was recorded again after three, six and nine days, and at the end of this period of time the original peak had completely decayed and had been replaced by peaks at 69.5 and 68.1 ppm, the area of which were in the ratio of 2:1. It was shown that the mass spectrum of a sample made by an identical method was the same as that for $N_3S_3O_3R_3$, and did not change significantly during the nine day period. This observation, which was reproducible, suggests that the compound can exist in two forms similar to those reported for the sulphanuric halides. The initial product, which gives a singlet would then correspond to the *cis* form of $N_3S_3O_3[ON(CF_3)_2]_3$ which slowly isomerises to the *trans* form in which one of the $-ON(CF_3)_2$ groups has a different orientation.

EXPERIMENTAL

Pure samples of S_4N_4 and $S_3N_2O_2$ were provided by Dr. J. Mason to whom we wish to express our thanks. Bis-trifluoromethyl nitroxide radical was prepared by the reaction of CF_3NO with ammonia[17], followed by the oxidation of the resulting $(CF_3)_2NOH$ with Ag(II)O[18]. Mercury bis-(iminosulphur difluoride), $Hg(NSF_2)_2$, was prepared by reaction of $FCON{=}SF_2$ with HgF_2[19]. Infrared spectra were recorded on a Perkin–Elmer 457 spectrophotometer, mass spectra on an A.E.I. MS9 spectrometer and ^{19}F NMR spectra on a Perkin–Elmer R.10 instrument using CCl_3F as an internal standard. Known compounds formed as reaction products were identified by their infrared spectra and molecular weights unless otherwise stated.

Reactions of the bis-trifluoromethyl nitroxide radical

(a) with tetrasulphur tetranitride

In a typical experiment, N_4S_4 (0.105 g, 0.571 mmole) was treated in a 20 ml ampoule fitted with a "Rotaflow" tap with $(CF_3)_2NO\bullet$ (1.09 g, 6.48 mmoles) at room temperature (16 h) using a mechanical shaker. Excess radical (0.708 g, 4.22 mmoles) was recovered. The residual colourless crystalline solid was tetrathiazyl tetra(bis-trifluoromethyl nitroxide), $N_4S_4[ON(CF_3)_2]_4$. (Found: C, 11.1; N, 13.2; S, 14.6%. $C_8F_{24}N_8O_4S_4$ requires: C, 11.2; N, 13.1; S, 14.9%). The highest peak in the mass spectrum (source temperature 45°, beam energy 70 eV) was at *m/e* 688 ($N_4S_4[ON(CF_3)_2]_3{}^+$). The chief infrared bands were at 1355 sh, 1335 vs, 1267 vs, 1215 vs, 1200 vs, 1100 s, 1026 vs, 979 vs, 955 w, 810 m, 770 ms, 755 ms, 732 sh, 720 s, 560 w, 535 w, 520 w, 470 s, 400 w, 350 w cm^{-1}.

The compound was not wetted by water and was recovered quantitatively after treatment at 20° with H_2O (30 days), HCl gas (24 h), conc. HNO_3 (3 h) and conc. HCl (3 h). Sulphur was precipitated quantitatively as $BaSO_4$ after alkaline hydrolysis at 60° and treatment of the hydrolysate with H_2O_2. Qualitative tests showed the compound to be insoluble, or only slightly soluble, in acetone, ether, carbon tetrachloride, alcohol, benzene, acetonitrile and dimethylsulphoxide. When a sample was heated at 60–80° with continuous pumping, a small amount of white solid sublimed. Discoloration became rapid at 65°, and a yellow oil began to condense on the cooler parts of the ampoule. At 80°, orange-yellow crystals had sublimed on to the walls of the ampoule. The solid residue was dark green-brown in colour. From the material which passed over into a cooled trap in the vacuum line $(CF_3)_2NO\bullet$ (0.082 g, 0.048 mmole) was recovered.

The preparation was repeated at 20° in CCl_4 solution using N_4S_4 (0.131 g, 0.714 mmole), CCl_4 (0.430 g, 2.79 mmoles) and $(CF_3)_2NO\bullet$ (0.852 g, 5.06 mmoles), the ampoule being shaken for 24 h. Excess radical (0.404 g, 2.42 mmoles) was recovered. The solid residue (0.581 g) was a white crystalline solid containing a small amount of a yellow, moisture-sensitive solid. A trace of yellow material also passed into the vacuum line. The mass spectrum and infrared spectrum were identical with those of a specimen from the first preparation.

(b) with tetrasulphur tetraimide

$S_4N_4H_4$, (0.112 g, 0.608 mmole) was shaken at room temperature with $(CF_3)_2NO\bullet$ (0.976 g, 5.81 mmoles) for 24 h. $(CF_3)_2NOH$ (0.411 g, 2.43 mmoles) was separated from the volatile product by fractionation, together with excess radical. The solid residue (0.474 g, 5.54 mmoles) had an infrared and mass spectrum identical with that of $N_4S_4[ON(CF_3)_2]_4$. It was again contaminated by a trace of yellow material.

(c) with trithiazyl trichloride

Trithiazyl trichloride was made by the reaction of N_4S_4 with excess liquid chlorine in the ampoule used for subsequent reactions. The stoichiometry was checked by weighing the excess chlorine. In a typical experiment N_4S_4 (0.121 g, 0.658 mmole) was treated at −78° with Cl_2 (0.568 g, 8.26 mmoles) of which 0.494 g (6.96 mmoles) was recovered. The product was a yellow crystalline material, readily hydrolyzable in the atmosphere. The highest peak in the mass spectrum was at *m/e* 208 ($N_3S_3Cl_2^+$) and there was no evidence of the formation of $N_4S_4Cl_4$. Analysis gave: N, 17.2; Cl, 43.5; S, 39.4%. (Calc. for $N_3S_3Cl_3$: N, 17.17; Cl, 43.55; S, 39.2%). The reaction of N_4S_4 with SO_2Cl_2 is reported to give $N_4S_4Cl_4$. N_4S_4 (0.082 g, 0.446 mmole) was refluxed with SO_2Cl_2 for 12 h. The mass spectrum of the product was identical with that for $N_3S_3Cl_3$.

N_4S_4 (0.083 g, 0.451 mmoles) was treated at −78° with Cl_2 (0.082 g, 1.16 mmoles), of which 0.0169 g (0.231 mmole) was recovered. $(CF_3)_2NO\bullet$ (0.461 g, 2.75 mmoles) in a liquid form was distilled on to the $N_3S_3Cl_3$ produced. The volatile products (0.311 g) were shaken with excess Hg, which reacted with Cl_2 and excess radical, forming $HgCl_2$ and $Hg[ON(CF_3)_2]_2$ respectively. The latter was then decomposed with HCl (0.108 g, 2.95 mmoles) and $(CF_3)_2NOH$ (0.197 g, 1.16 mmoles) was recovered. The residue in the reaction ampoule (0.324g, 0.378 mmole), which was $N_4S_4[ON(CF_3)_2]_4$, was a colourless crystalline solid. (Found: C, 11.3; N, 13.0%: $C_8F_{24}N_8O_4S_4$ requires C, 11.2; N, 13.1%), the infrared and mass spectra of which were identical with that previously recorded for $N_4S_4[ON(CF_3)_2]_4$.

$N_3S_3Cl_3$ (0.086 g, 0.351 mmole), iodine (0.069 g, 0.272 mmole) and $(CF_3)_2NO\bullet$ (2.60 g, 15.50 mmoles) were shaken together at room temperature for 12 h. Excess radical (2.43 g, 14.47 mmoles) was recovered. Iodine halides were pumped off from the solid residue *in vacuo* leaving a yellow product (0.210 g) which was hydrolyzed by water (1 ml). The volatile hydrolysis product was dried with P_2O_5 to yield $(CF_3)_2NOH$ (0.021 g, 0.012 mmole). The remaining white solid had a mass spectrum identical to that of $N_4S_4[ON(CF_3)_2]_4$.

$N_3S_3Cl_3$ (0.077 g, 0.314 mmole), prepared as above, was shaken with a suspension of $Hg[ON(CF_3)_2]_2$ (3.42 g, 6.40 mmoles) in dry CCl_3F (5 ml). Excess mercurial compound was removed in a specially designed evacuated apparatus by extraction with CCl_3F, in which it has a small solubility, and filtration. The white solid product (0.192 g), which contained $HgCl_2$, exhibited a mass spectrum identical with that of $N_4S_4[ON(CF_3)_2]_4$.

(d) with thiazyl fluoride

Thiazyl fluoride was prepared by heating $Hg(NSF_2)_2$ *in vacuo* at 80°. A sample (0.710 g, 10.92 mmoles) was treated with $(CF_3)_2NO\bullet$ (2.45 g, 14.60 mmoles) for 3 weeks. No reaction apparently occurred since the colour of the radical was unchanged and no residue was left on removing the volatile material, all of which passed through a trap cooled to −96° but condensed at −116°. Both reactants behaved in this way and could not be separated by fractionation. Any $NSON(CF_3)_2$ would either polymerize, or condense at a temperature higher than −96°.

$Hg[ON(CF_3)_2]_2$ (0.906 g, 1.69 mmoles) was prepared from mercury (0.338 g, 1.69 mmoles) and excess radical and allowed to react at room temperature with NSF (0.170 g, 2.62 mmoles). On fractionation, thiazyl bis-trifluoromethyl nitroxide (0.060 g, 0.028 mmole) was collected at −78°. (Found: mol. wt., 214; C_2F_6NSO requires mol. wt., 214). The parent ion at *m/e* 214 was observed in the mass spectrum. Analysis was by reaction with HCl. A sample (0.0512 g, 0.024 mmole) reacted in a 40 ml ampoule with HCl (0.073 g, 2.00 mmole) to give $(CF_3)_2NOH$ (0.038 g, 0.023 mmole). The solid yellow residue (0.210 g, 0.086 mmoles) was identified as $N_3S_3Cl_3$ by its mass spectrum. The chief infrared bands were at 1400 w, 1350 m, 1312 vs, 1269 vs, 1227 vs, 1035 m, 978 s, 802 w, 712 m, 661 w, 583 m, 536 m cm^{-1}. The ^{19}F NMR spectrum was a singlet at 69.4 ppm.

When the residue in the ampoule used in the above preparation from $Hg[ON(CF_3)_2]_2$ was warmed to 60°, and the volatile material fractionated, a very small amount of a pale yellow oil condensed at −78°. An approximate molecular weight by Regnault's method at a pressure of 2.7 cm Hg gave a value of 405 ($NSF[ON(CF_3)_2]_2$ requires a mol. wt. of 401). The highest peak in the mass spectrum was at *m/e* 382, corresponding to the $NS[ON(CF_3)_2]_2^+$ ion. The infrared spectrum showed a strong band at 1500 cm^{-1}, attributable to the $N{\equiv}S$ bond.

Yields of $NSON(CF_3)_2$ in excess of 80% were subsequently obtained by preparing the mercurial *in situ*. In a typical experiment NSF (0.139 g, 2.14 mmoles) was condensed on to mercury (3.0 g). There was no reaction at room temperature. Excess of radical was distilled in. The strongly exothermic reaction was moderated by cooling to −78°. The only volatile product was $NSON(CF_3)_2$ (0.39 g, 1.8 mmoles), the molecular weight, infrared spectrum and mass spectrum of which were identical with those of the sample previously prepared.

(e) with trisulphur dinitrogen dioxide

$S_3N_2O_2$ (0.097 g, 0.623 mmole) and liquid $(CF_3)_2NO\bullet$ (1.259 g, 7.50 mmoles) were allowed to react in a 20 ml ampoule for 12 h. The volatile product was separated by vacuum fractionation into unreacted $(CF_3)_2NO\bullet$ (0.998 g, 5.95 mmoles) and a colourless liquid (0.021 g). The infrared spectrum corresponded to a sulphur-radical compound[5]. No $N_2(CF_3)_4$ was found. The yellow oil remaining in the ampoule did not distil in vacuum and was very moisture-sensitive. It decomposed on warming, or with prolonged pumping, to a dark green-brown solid, and gave very small amounts of volatile material which were not identified. Some yellow crystalline material was also deposited.

A prolonged experiment, using $S_3N_2O_2$ (0.130 g, 0.836 mmole) and liquid $(CF_3)_2NO\bullet$ (0.706 g, 4.21 mmoles) which was left for four days, gave a larger quantity of the colourless oil (0.117 g, 0.318 mmole as $S[ON(CF_3)_2]_2$) mol. wt., 362 ($S[ON(CF_3)_2]_2$: mol. wt., 368). The infrared spectrum again corresponded to a sulphur-radical compound and, as no $(CF_3)_4N_2$ was found, (mol. wt., 304) no oxidation to $OS[ON(CF_3)_2]_2$ or $O_2S[ON(CF_3)_2]_2$ had occurred.

In a repeat experiment designed to minimize the production of $S[ON(CF_3)_2]_2$, $S_3N_2O_2$ (0.124 g, 0.795 mmole) reacted with gaseous $(CF_3)_2NO\bullet$ (0.907 g, 5.40 mmoles) in a 100 ml flask at room temperature (12 h) to give unreacted radical (0.637 g, 3.80 mmoles) which condensed at −116°, but only a trace amount of $S[ON(CF_3)_2]_2$ condensed at −84°. No other volatile product was detected. A yellow oil (0.371 g) remained in the flask. After 2 h a trace of volatile material was pumped off and the oil then crystallized rapidly to a yellow solid.

The mass spectrum of the solid showed peaks at *m/e*: 690, $N_3S_3O_3[ON(CF_3)_2]_3^+$ 1%; 522, $N_3S_3O_3[ON(CF_3)_2]_2^+$, 2.25%; 506, $N_3S_3O_2[ON(CF_3)_2]_2^+$ 1%; 490, $N_3S_3O[ON(CF_3)_2]_2^+$ 1%; 474, $N_3S_3[ON(CF_3)_2]_2^+$ 1.1%; 322, $N_3S_3O[ON(CF_3)_2]^+$ 100%; 306, $N_3S_3ON(CF_3)_2^+$ 40.6%; 168, $ON(CF_3)_2^+$ 19.5%; 138, $N_3S_3^+$ 16.7%; 133, $C_2F_5N^+$ 25%; 92, $S_2N_2^+$, 22.2%; 69, CF_3^+, out of scale; 64, CF_2N 35.6%; 46, NS^+, 83.5%. This indicates that the compound sulphanuric bis-trifluoromethyl nitroxide, $N_3S_3O_3[ON(CF_3)_2]_3$ was present in the solid. A sample (0.332 g, 0.482 mmole) was treated at room temperature in a 100 ml flask with HCl (0.0912 g, 250 mmoles) (2 days). Excess HCl (0.076 g, 2.08 mmoles) was recovered together with $(CF_3)_2NOH$ (0.057 g, 0.337 mmole). A repeat experiment under the same conditions gave an almost identical percentage yield of $(CF_3)_2NOH$. The mass spectrum of the solid residue after the reaction with HCl showed peaks at *m/e* 256 (12.9%), and 205 (37%), attributed to $S_3N_3O_3Cl_2^+$ and $S_3N_3O_3Cl^+$ respectively. There were further peaks at *m/e* 168, $ON(CF_3)_2^+$, 3.7%; 138, $S_3N_3^+$, 16.2%; 92, $S_2N_2^+$, 100%; 81, $NSCl^+$, 55% and 69, CF_3^+, 12.9% (and unidentifiable ones at *m/e* 278, 16.2% and 223, 54.9%).

Reactions of thiazyl bis-trifluoromethyl nitroxide

The compound was volatile in vacuum. A sample (0.032 g, 0.149 mmoles) was treated with H_2O (0.0399 g, 22.2 mmoles). The yellow colour disappeared rapidly and, after a few minutes, white crystals formed. The volatile product after drying with P_2O_5 was $(CF_3)_2NOH$ (0.226 g. 0.134 mmole). The solid which was not identified was probably a polymer of $[-N(H)S(O)-]_x$.

When liquid $NSON(CF_3)_2$ was allowed to stand for several days at room temperature yellow crystals separated, but no new volatile product was formed. A small amount of yellow oil remained after one month. When this was distilled off in vacuum a sample of the residual yellow solid (0.0719 g, 0.112 mmole as $NSON(CF_3)_2$) on treatment with gaseous HCl (*ca.* 2 mmoles) gave $(CF_3)_2NOH$ (0.0559 g, 0.330 mmole) and the residual yellow solid (0.027 g, 0.110 mmole) was identified as $N_3S_3Cl_3$ by its mass spectrum. The highest peak at *m/e* 208 corresponded to the $N_3S_3Cl_2^+$ ion. The mass spectrum of the polymerized material, identified as trithiazyl tri(bis-trifluoromethyl nitroxide), showed the following ions: *m/e*, 474, $S_3N_3[ON(CF_3)_2]_2^+$ 4.8%; 306, $S_3N_3ON(CF_3)_2^+$ 31.8%; 168, $ON(CF_3)_2^+$ 100%.

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