1327. *Perfluoroalkyl Derivatives of Nitrogen. Part XX.*[1] *Thermal Decomposition of Trifluoronitrosomethane*

By R. E. Banks, M. G. Barlow, R. N. Haszeldine, M. K. McCreath, and H. Sutcliffe

Trifluoronitrosomethane decomposes slowly in glass at 100°, to give, as major products, trifluoronitromethane, hexafluoroazomethane, perfluoro(methylenemethylamine), and nitrogen.

Trifluoronitrosomethane was reported earlier [2] to decompose at 100° during 14 days in glass according to the equation

$$4CF_3{\cdot}NO \longrightarrow 2CF_3{\cdot}NO_2 + N_2 + 2CF_3{\cdot}\ (\xrightarrow{SiO_2} CO_2 + SiF_4)$$

Further investigation has now shown that more rigorously purified trifluoronitrosomethane is destroyed under similar conditions only after 6 months. The yield of trifluoronitromethane (50%) is then close to that (48%) reported earlier, but hexafluoroazomethane and perfluoro(methylenemethylamine) are also present as major products. Decomposition of the nitroso-compound in glass at 160° is almost complete (97%) after 24 hours, and the products formed are again $CF_3{\cdot}NO_2$, $CF_3{\cdot}N{:}N{\cdot}CF_3$, $CF_3{\cdot}N{:}CF_2$, N_2, CO_2, and SiF_4 (molar ratio 53 : 9 : 12 : 9 : 2 : 4), together with traces of carbonyl fluoride, hexafluoroethane, and

---

[1] Part XIX, R. E. Banks, M. G. Barlow, R. N. Haszeldine, and M. K. McCreath, preceding Paper.

[2] D. A. Barr, R. N. Haszeldine, and C. J. Willis, *J.*, 1961, 1351.

nitrous oxide. The addition of a small amount of trifluoroiodomethane, from which the nitroso-compound is prepared, and a possible impurity in the earlier sample of the nitroso-compound,[2] does not inhibit the formation of the azo-compound or of the perfluoro(methylenemethylamine).

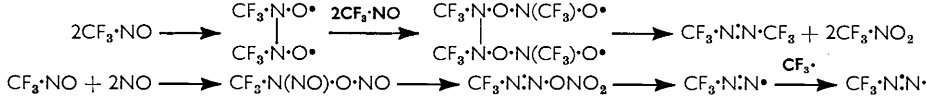
The formation of nitrogen suggests that decomposition occurs partly through formation of the diazonium nitrate $CF_3{\cdot}N_2{\cdot}ONO_2$, as postulated earlier; [2] it is now suggested that this reaction path is accompanied by dimer formation [3] and by reactions of the type proposed [4] for the thermal decomposition of pentafluoronitrosoethane and of heptafluoro-2-nitrosopropane:

$$2CF_3{\cdot}NO \longrightarrow (CF_3)_2N{\cdot}ONO \longrightarrow CF_3{\cdot}N{:}CF_2 + NO_2F$$

$$NO_2F \xrightarrow{SiO_2} NO_2,\ SiF_4$$

$$2CF_3{\bullet} + 2NO_2 \longrightarrow CF_3{\cdot}NO_2 + CF_3{\cdot}O{\cdot}NO \longrightarrow COF_2 + NOF \xrightarrow{SiO_2} CO_2,\ NO,\ NO_2,\ SiF_4$$

The unexpected formation of hexafluoroazomethane can be accounted for by reactions of the type:



$$2CF_3{\cdot}NO \longrightarrow \begin{array}{c} CF_3{\cdot}N{\cdot}O{\bullet} \\ | \\ CF_3{\cdot}N{\cdot}O{\bullet} \end{array} \xrightarrow{2CF_3{\cdot}NO} \begin{array}{c} CF_3{\cdot}N{\cdot}O{\cdot}N(CF_3){\cdot}O{\bullet} \\ | \\ CF_3{\cdot}N{\cdot}O{\cdot}N(CF_3){\cdot}O{\bullet} \end{array} \longrightarrow CF_3{\cdot}N{:}N{\cdot}CF_3 + 2CF_3{\cdot}NO_2$$

$$CF_3{\cdot}NO + 2NO \longrightarrow CF_3{\cdot}N(NO){\cdot}O{\cdot}NO \longrightarrow CF_3{\cdot}N{:}N{\cdot}ONO_2 \longrightarrow CF_3{\cdot}N{:}N{\bullet} \xrightarrow{CF_3{\cdot}} CF_3{\cdot}N{:}N{\cdot}CF_3$$

Azo-compounds are apparently not formed during the pyrolysis of other polyfluoronitroso-compounds.[4,5]

Trifluoronitrosomethane is recovered almost quantitatively (93—98%) after passage at 3 mm. pressure through a platinum tube at 250 or 300° with a contact time of *ca.* 3 seconds, and the only product is the dimer $(CF_3)_2N{\cdot}O{\cdot}NO$; pyrolysis at 400°/3 mm. converted 86% of the nitroso-compound into a mixture of tristrifluoromethylhydroxylamine (66% yield), perfluoro(methylenemethylamine), hexafluoroethane, nitric oxide, dinitrogen tetroxide, and carbonyl fluoride. The high yield of tristrifluoromethylhydroxylamine is noteworthy; reaction schemes of the type postulated earlier for the formation of tristrifluoromethylhydroxylamine by photolysis of trifluoronitrosomethane with trifluoroiodomethane,[6] and for the formation of trisheptafluoro-n-propylhydroxylamine by pyrolysis of heptafluoro-1-nitrosopropane [1] satisfactorily account for these products.

EXPERIMENTAL

Products were identified by molecular weight determination, infrared spectroscopy, and gas–liquid chromatography (Perkin-Elmer Vapor Fraktometer, model 116). Molar % compositions of mixtures were calculated from gas-chromatographic peak areas by triangulation, and the column used (8 m. × 4 mm. i.d. packed with 30% Kel-F No. 1 oil on Celite, and operated at room temperature) was calibrated with known mixtures.

Trifluoronitrosomethane, prepared by photochemical reaction of trifluoroiodomethane with nitric oxide,[7] was purified by precise distillation in a semi-automatic low-temperature still.[8]

Static Pyrolysis of Trifluoronitrosomethane.—(a) *At* 100°. Trifluoronitrosomethane (12·21 g., 123·4 mmoles), sealed in a 420-ml. Dreadnought ampoule and heated at 100° for 6 months, gave trifluoronitromethane (62·1 mmoles; 50% based on $CF_3{\cdot}NO$ taken), hexafluoroazomethane (17·2 mmoles; 28%), perfluoro(methylenemethylamine) (6·0 mmoles; 10%), trifluoromethyl isocyanate (0·5 mmole; 1%), bistrifluoromethylamine (0·1 mmole) (the last two compounds arise from reaction of $CF_3{\cdot}N{:}CF_2$ with traces of water), nitrogen (9·5 mmoles), carbon dioxide (7·0 mmoles; 6%), silicon tetrafluoride (7·6 mmoles), and traces of hexafluoroethane and nitrous

---

[3] R. N. Haszeldine and B. J. Mattinson, *J.*, 1957, 1741.

[4] S. Andreades, *J. Org. Chem.*, 1962, **27**, 4163.

[5] V. A. Ginsburg, N. F. Privezentseva, V. A. Shpanskii, N. P. Rodionova, S. S. Dubov, A. M. Khokhlova, S. P. Makarov, and A. Ya. Yakubovich, *J. Gen. Chem.* (*U.S.S.R.*), 1960, **30**, 2391; A. Ya. Yakubovich, S. P. Makarov, V. A. Ginsburg, N. F. Privezentseva, and L. L. Martynova, *Doklady Akad. Nauk S.S.S.R.*, 1961, **141**, 125; D. E. O'Connor and P. Tarrant, *J. Org. Chem.*, 1964, **29**, 1793; J. M. Birchall, A. J. Bloom, R. N. Haszeldine, and C. J. Willis, *J.*, 1962, 3021.

[6] A. H. Dinwoodie and R. N. Haszeldine, *J.*, 1965, 1681.

[7] A. H. Dinwoodie and R. N. Haszeldine, *J.*, 1965, 1675.

[8] R. E. Banks and H. Sutcliffe, *Chem. and Ind.*, 1962, 979.

oxide. Sodium silicofluoride (0·18 g.) and an unidentified yellow solid (0·10 g.) were recovered from the slightly-etched reaction vessel.

(b) *At* 160°. Trifluoronitrosomethane (0·792 g., 8·00 mmoles), sealed in a 30-ml. Dreadnought ampoule and heated at 160° for 24 hr., gave unchanged nitroso-compound (0·22 mmole; 3% recovery), and the compounds (% yields based on $CF_3{\cdot}NO$ consumed) $CF_3{\cdot}NO_2$ (4·09 mmoles; 53%), $CF_3{\cdot}N{:}N{\cdot}CF_3$ (0·69 mmole; 18%), $CF_3{\cdot}N{:}CF_2$ [+$CF_3{\cdot}NCO$ and $(CF_3)_2NH$] (total 0·93 mmole; 24%), N_2 (0·70 mmole), CO_2 (0·17 mmole; 2%), COF_2 (0·09 mmole; 1%), SiF_4 (0·34 mmole), and a trace of C_2F_6.

(c) *At* 100° *in the presence of trifluoroiodomethane*. A mixture of trifluoronitrosomethane (12·01 g., 121·3 mmoles) and trifluoroiodomethane (1·24 g., 6·34 mmoles), sealed in a 445-ml. Dreadnought tube and heated at 100° for 4 months, gave unchanged iodo-compound (6·4 mmoles; 100% recovery), the nitroso-compound (0·4 mmole; 0·3% recovery), and the compounds $CF_3{\cdot}NO_2$ (62·2 mmoles; 51%), $CF_3{\cdot}N{:}N{\cdot}CF_3$ (21·4 mmole; 35%), $CF_3{\cdot}N{:}CF_2$ [+$CF_3{\cdot}NCO$ and $(CF_3)_2NH$] (6·6 mmoles; 11%), CO_2 and SiF_4 (total 4·7 mmoles), nitrogen (7·5 mmoles), and traces of hexafluoroethane and nitrous oxide.

Flow Pyrolysis of Trifluoronitrosomethane.—Samples of trifluoronitrosomethane were passed at 3 mm. pressure through a 100 × 1·0 cm. platinum tube heated over 56 cm. of its length, and the product was condensed in two Pyrex traps at −196°. Pyrolysis at 250 or 300° gave 98 and 93%, respectively, of recovered nitroso-compound, together with *O*-nitrosobistrifluoromethylhydroxylamine.

Trifluoronitrosomethane (0·835 g., 8·43 mmoles), pyrolysed at 400°/3 mm. with a contact time of *ca.* 3 sec., gave recovered nitroso-compound (1·15 mmoles; 14% recovery), tristrifluoromethylhydroxylamine (1·60 mmoles; 66% yield based on $CF_3{\cdot}NO$ consumed), perfluoro(methylenemethylamine) (0·35 mmole; 9%), hexafluoroethane (0·64 mmole; 18%), nitric oxide (2·23 mmoles; 61%), dinitrogen tetroxide (0·41 mmole; 11%), carbonyl fluoride and silicon tetrafluoride (total 0·2 mmole), and traces of trifluoromethyl isocyanate and nitrous oxide. The tristrifluoromethylhydroxylamine (0·379 g.) (Found: *M*, 235. Calc. for C_3F_9NO: *M*, 237), spectroscopically (i.r.) identical with a sample prepared by photolysis of a mixture of trifluoroiodomethane and trifluoronitrosomethane,[6] was isolated by fractionation of the product to yield impure material contaminated with dinitrogen tetroxide, perfluoro(methylenemethylamine), and trifluoromethyl isocyanate, followed by removal of the first impurity with mercury and the last two with 2N-sodium hydroxide.

One of us (M. K. M.) is indebted to the Bowen Scholarship Committee of the British Plastics Federation for the award of a research scholarship for the period 1958—1961.

FACULTY OF TECHNOLOGY, THE UNIVERSITY, MANCHESTER. [*Received, June 28th,* 1965.]