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Abstract

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CHEMISTRY

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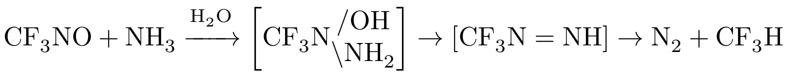
Synthesis of Hexafluorodimethylhydroxylamine and Hexafluorodimethylazomethane Oxide

(Presented by Academician Ya. K. Syrkin on 8 XII 1964)

In our work devoted to the study of the transformations of polyfluoronitrosoalkanes upon interaction with amines (1), the reactions of trifluoronitrosomethane with aqueous and alcoholic solutions of ammonia were described. When trifluoronitrosomethane reacts with ammonia in an aqueous medium, fluoroform is formed in quantitative yield, whereas with ammonia in methanol solution at −70°, trifluoromethylazohydride is formed. The study of these processes, together with the investigation of a large number of condensations of perfluorinated nitroso compounds with primary amines, in which the corresponding azo compounds are formed, allowed us to conclude that all these reactions proceed by the same mechanism. This mechanism consists in the amine molecule adding to the nitroso compound molecule in the manner of an aldol condensation, with formation of an unstable aminoreduction derivative, which readily loses water and is converted into the azo compound. In this way trifluoromethylazohydride arises.

Unlike other azo compounds, trifluoromethylazohydride is a rather unstable compound possessing acidic properties. As was described earlier (1), it gives derivatives with many reagents. When trifluoronitrosomethane reacts with an excess of aqueous ammonia solution, the trifluoromethylazohydride formed apparently cannot exist and decomposes into nitrogen and fluoroform according to the scheme:



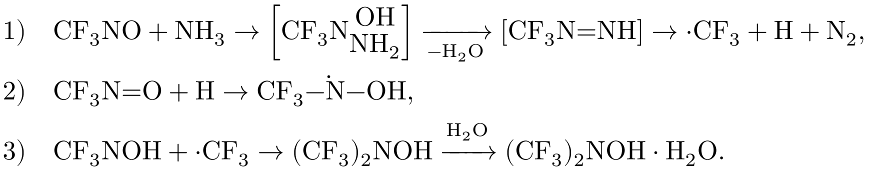
$$CF_3NO + NH_3 \xrightarrow{H_2O} \left[CF_3N\begin{matrix}/OH\\ \backslash NH_2\end{matrix}\right] \rightarrow [CF_3N = NH] \rightarrow N_2 + CF_3H$$

In methanol solution (or ether), the trifluoromethylazohydride formed in the reaction is stabilized, since with these solvents it gives stable compounds of the type $CF_3N{=}NH \cdot O(C_2H_5)_2$, which, with an excess of solvent, are even capable of being distilled.

Below we describe the interaction of trifluoronitrosomethane with ammonia in the gas phase. The reaction was carried out by mixing equal volumes of the reagents at atmospheric pressure and ordinary temperature. A slight heating was observed, along with the appearance of a mist, gradual decolorization of the gas mixture, and a decrease in pressure to 360 mm Hg. The reaction is completed after 3-4 hours. Under these conditions a new substance is formed—hexafluorodimethylhydroxylamine hydrate—in a yield of ~ 70% of theory, and in small amounts fluoropicrin, hexafluoroazoxymethane, urea, and ammonium fluoride.

The formation of hexafluorodimethylhydroxylamine upon the interaction of trifluoronitrosomethane with ammonia in the gas phase apparently occurs as a result of a radical reaction, which begins with attack on the trifluoronitrosomethane molecule by the radicals $\cdot CF_3$ and $\cdot H$, arising from the decomposition of trifluoromethylazohydride, unstable under these conditions and evidently also an intermediate product in this reaction.

The reaction may be represented by the following scheme:



$$
\begin{aligned}
&1)\quad CF_3NO + NH_3 \rightarrow \left[CF_3N\begin{smallmatrix}OH\\ NH_2\end{smallmatrix}\right] \xrightarrow[-H_2O]{} [CF_3N{=}NH] \rightarrow \cdot CF_3 + H + N_2,\\
&2)\quad CF_3N{=}O + H \rightarrow CF_3{-}\dot{N}{-}OH,\\
&3)\quad CF_3NOH + \cdot CF_3 \rightarrow (CF_3)_2NOH \xrightarrow{H_2O} (CF_3)_2NOH \cdot H_2O.
\end{aligned}
$$

The addition of radicals $\cdot CF_3$ and others to trifluoronitrosomethane in the gas phase was studied previously in the course of its pyrolysis and photolysis (^{2}).

The by-products—fluoropicrin and hexafluoroazomethane—are formed, probably, as a result of the disproportionation reaction of trifluoronitrosomethane in an ammonia-water medium, while hydrogen fluoride and carbonyl fluoride are formed during decomposition of trifluoronitrosomethane.

Table 1

Compound	B.p., °C	d_4^4	n_D^4	Found, % C	Found, % H	Found, % N	Found, % F	Calculated, % C	Calculated, % H	Calculated, % N	Calculated, % F
$(CF_3)_2NOH$	36	1.6060	1.2600	14.59 13.99	0.70 0.68 **[0.59]	8.10 8.17 [7.76]	67.11 67.48	14.20	0.6	8.28	67.45
$(CF_3)_2NOH \cdot H_2O$	73	1.5805*	–	13.69 13.55	1.57 1.67	7.05 6.98	59.45 59.12	12.83	1.60	7.48	60.96
$(CF_3)_2NO$	−20	–	–	14.75 14.40	–	8.28 7.96	67.45 68.12	14.28	–	8.33	67.84

$*$ d_{20}^{20}.
$**$ Mobile hydrogen.

Directly from the reaction mixture, hexafluorodimethylhydroxylamine is isolated in the form of a hydrate, which is a colorless liquid with a characteristic odor resembling the odor of trichloroethyl alcohol. When treated with phosphorus anhydride it loses water and is converted into hexafluorodimethylhydroxylamine—also a mobile colorless liquid with the same odor.

In the IR spectrum of the substance, a band at 2.7 μ, characteristic of an O—H bond, was found.

Hexafluorodimethylhydroxylamine was also obtained from its nitrous ester, which is a product of the photolysis of trifluoronitrosomethane ([2,3]), by saponifying it with aqueous alkali or by reaction with aniline. In the first case the hydrate is isolated, and in the reaction with aniline—anhydrous hexafluorodimethylhydroxylamine. The reactions may be represented by the following schemes:

$$1)\quad (CF_3)_2NONO \xrightarrow[20^\circ]{10\%NaOH} (CF_3)_2NOH \cdot H_2O + NaNO_2,$$

$$2)\quad (CF_3)_2NONO + 2C_6H_5NH_2 \rightarrow (CF_3)_2NOH + C_6H_5N{=}N{-}NHC_6H_5.$$

Hexafluorodimethylhydroxylamine is a reactive compound entering into various reactions. Its most interesting transformation is the oxidation reaction, in which hexafluorodimethylazote oxide ([8]) is formed, which under ordinary conditions is a stable free radical (Fig. 1*a*). This same reaction confirms the structure of the substance as hexafluorodimethylhydroxylamine.

Upon oxidation of hexafluorodimethylhydroxylamine with potassium permanganate in a solution of glacial acetic acid at 60—70°, a new substance—hexafluorodimethyl-

nitrogen. The reaction proceeds according to the scheme:

$$(CF_3)_2NOH \xrightarrow[CH_3COOH]{KMnO_4} (CF_3)_2NO.$$

Hexafluorodimethylnitrogen oxide is a violet-pink gas with a boiling point of −20°. Below this temperature the gas condenses to a dark-violet liquid. On further cooling, the liquid gradually changes color and at −55° crystallizes in the form of

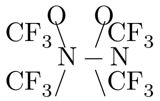
Fig. 1. EPR spectra of hexafluorodimethylnitrogen oxide: *a*—gas, $t = 25^\circ$, $g = 2.0046$; the arrow indicates the DPPH signal; *b*—condensed state of the

Figure 1

Figure 1: Figure 1

substance, $t = 0^\circ \div -90^\circ$, $g = 2.0040$; v—solution in CCl_4, $g = 2.0040$; $\Delta H_F = \Delta H_N$, 1 : 7.3 : 23 : 44 : 52 : 44 : 22 : 7 : 2

light-yellow crystals. The compound formed is apparently a dimer



and is diamagnetic (Fig. 1b). The substance is stable on storage for many months. Its high stability may be indicated by the considerable content of molecular ions, 1.66% of the total ionization.

Elemental analysis and molecular weight correspond to the empirical formula C_2NOF_6. In the mass spectrum of the substance an ion is found (4.01%) corresponding to the NO group; at the same time, the IR spectrum contains no band characteristic of an N=O double bond. In the EPR spectrum of a solution of the radical in CCl_4, h.f.s. is observed (Fig. 1c). The dipole moment of $(CF_3)_2N-\overline{O}$ is 1.8 D, and that of $(CF_3)_2NOH$ is 2.3 D. The substance is soluble in water. Aqueous solutions are colored violet-pink.

On interaction with an acidified solution of potassium iodide, hexafluorodimethylnitrogen oxide liberates one equivalent of iodine, being converted into the starting hexafluorodimethylhydroxylamine according to the scheme:

$$2(CF_3)_2NO + 2HJ \rightarrow J_2 + 2(CF_3)_2NOH.$$

When equal volumes of hexafluorodimethylnitrogen oxide and NO are mixed at room temperature, a reaction occurs instantaneously and hexafluorodimethylhydroxylamine nitrite is formed in quantitative yield according to the scheme:

$$(CF_3)_2NO + NO \rightarrow (CF_3)_2NONO.$$

The same substance is formed on interaction at room temperature of hexafluorodimethylnitrogen oxide with trifluoronitrosomethane. The reaction proceeds more slowly than with NO. The reaction product is hexafluorodimethylhydroxylamine nitrite, and its yield is somewhat greater than

could be expected from the amount of oxide taken. In this case, apparently, a radical reaction takes place, in which, upon interaction of hexafluorodimethylamine oxide with trifluoronitrosomethane, $\cdot CF_3$ radicals arise, which then attack trifluoronitrosomethane molecules with formation of the radical $(CF_3)_2NO$, etc.

The reaction may be represented by the scheme:

$$(CF_3)_2NO\cdot + CF_3NO \rightarrow (CF_3)_2NONO + \cdot CF_3,$$

$$CF_3NO\cdot + \cdot CF_3 \rightarrow (CF_3)_2NO.$$

It should be noted that compounds constructed analogously to hexafluorodimethylazote oxide were known from the work of Wieland ([5,6]), who, on oxidizing colorless diphenylhydroxylamine with moist silver oxide, obtained a crystalline substance colored bright red and assigned to it the structure of diphenylazote oxide $(C_6H_5)_2NO$. Subsequent special studies showed that this substance is a stable free radical ([7]).

In addition to hexafluorodimethylazote oxide, we have also investigated certain other fluorinated analogs—free radicals ([9]).

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Note: Figure translations are in progress. See original paper for figures.