Decomposition of Isomeric *N*-Nitro-*N*-fluorobutylamines

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The major decomposition products of *N*-nitro-*N*-fluoro-*t*-butylamine in refluxing carbon tetrachloride have been described in an earlier report. Data are reported here for the decomposition products of the primary and secondary isomers in the same solvent.

A PREVIOUS paper (*2*) of the same title described the major decomposition products of the tertiary isomer in refluxing carbon tetrachloride. This paper presents additional data on the major decomposition products of the primary and secondary isomers in the same solvent. The nonvolatile products from the decomposition of the primary and secondary isomers in carbon tetrachloride at 76° C. are summarized in Tables I and II, along with their gas chromatographic retention times and per cent relative areas. For comparison purposes, the same data for the tertiary isomer are given in Table III.

The major nonvolatile decomposition products were isolated by preparative gas chromatography and identified by matching their infrared spectra and gas chromatographic retention times with authentic samples. The volatile decomposition products were trapped in carbon tetrachloride and were identified by matching their infrared spectra and gas chromatographic retention times with authentic samples. The identity of these products is listed in Table IV.

Table I. Gas Chromatographic Data of the Decomposition Products of *N*-Nitro-*N*-fluoro-*n*-butylamine

Component	Identity	Retention Time, Min.	Relative Area, %
1	Nitrous oxide	0.5	0.5
2	Unknown	2.5	0.5
3	Unknown	3.0	1.0
4	Unknown	3.5	1.7
5	*n*-Butyl nitrate	5.0	10.3
6	Unknown	6.0	3.5
7	1-Nitrobutane[a]	9.6	16.5
8	*n*-Butyl butyrate	9.6	50.0
9	Unknown	18.5	7.0
10	Butyric Acid	26.0	5.9
11	1,1-Dinitrobutane	32.0	3.0

[a] The relative amounts of 1-nitrobutane and *n*-butyl butyrate were determined on a column 4-ft. × 0.25-inch packed with 15% Silicone 550 on Chromosorb W.

Table II. Gas Chromatographic Data of the Decomposition Products of *N*-Nitro-*N*-fluoro-sec-butylamine

Component	Identity	Retention Time, Min.	Relative Area, %
1	Nitrous oxide	0.5	2.3
2	Butene-1	0.6	1.3
3	Unknown	0.8	1.5
4	Methyl ethyl ketone	2.0	2.3
5	Unknown	3.2	8.4
6	*sec*-Butyl nitrate	4.0	2.0
7	Unknown	4.3	0.9
8	Unknown	5.0	1.3
9	2-Nitrobutane	5.5	37.0
10	Unknown	6.0	1.7
11	Unknown	9.5	2.1
12	1-Nitrobutene-1	10.8	9.8
13	Unknown	17.5	0.9
14	2,2-Dinitrobutane	22.0	28.5

Table III. Gas Chromatographic Data of the Decomposition Products of *N*-Nitro-*N*-fluoro-*t*-butylamine

Component	Identity	Retention Time, Min.	Relative Area, %
1	Nitrous oxide	0.4	5.5
2	Isobutylene	0.6	1.6
3	Acetone	0.8	5.7
4	Carbon tetrachloride	2.0	
5	2-Methyl-2-nitropropane	4.0	17.5
6	2-Fluoro-2-methyl-1-nitropropane	7.1	19.5
7	2-Methyl-1-nitroprop-1-ene	12.6	5.6
8	Unknown	16.0	7.4
9	Unknown	18.6	13.0
10	2-Hydroxy-2-methyl-1-nitropropane	23.6	24.2

Table IV. Volatile Decomposition Products of the Isomers of *N*-Nitro-*N*-fluorobutylamines

Primary	Secondary	Tertiary
Nitrous oxide	Nitrous oxide	Nitrous oxide
Hydrogen fluoride	Hydrogen fluoride	Hydrogen fluoride
Butyraldehyde	Butene-1	Isobutylene
	Methyl ethyl ketone	Acetone

The primary isomer yielded only monosubstituted derivatives of the butane chain, in contrast to both mono- and disubstituted butane derivatives from the secondary and tertiary isomers. In the preceding paper (*2*), the authors proposed that one pathway for the decomposition of the tertiary isomer involved a cyclic activated complex which could dissociate to isobutylene, the precursor of the disubstituted butane products. It is likely that a similar mechanism applies to the secondary isomer, but not the primary isomer.

EXPERIMENTAL SECTION

Materials and Reference Compounds. The *N*-nitro-*N*-fluorobutylamines were prepared as described in the previous paper (*2*). Butyric acid, *n*-butyl butyrate, 1-nitrobutane, 2-nitrobutane, *n*-butyraldehyde, *n*-butyl nitrate, methyl ethyl ketone, butene-1, and nitrous oxide were all commercial products. 1-Nitrobutene-1 was prepared by the method of Bahner and Kite (*1*). *sec*-Butyl nitrate was prepared by the method of Urbanski and Witanowski (*4*). 1,1-Dinitrobutane and 2,2-dinitrobutane were prepared by the method of Shechter and Kaplan (*3*).

Instrumentation. Infrared spectra were determined on a Beckman IR-8 spectrophotometer. NMR spectra were obtained on a Varian A-60 instrument. Carbon tetrachloride solutions with tetramethyl silane as an internal standard were used. All analytical g.l.p.c. were run on a Perkin-Elmer Model 154-D chromatograph, using a thermal conductivity cell. The columns used included a 2-foot × 0.25-inch column, packed with 20% Paraplex G-25 on Chromosorb W for the primary isomer, and a 4-foot × 0.25-inch column, packed with 15% UCON LB-550-X on Chromosorb W for the secondary isomer. The g.l.p.c. data on the relative amounts of the various components were obtained from the areas under the curves and then calculating percentage contribution. Preparative gas chromatography was carried out on a F&M Prepmaster Jr. Model 776 with a 0.75-inch column of 80-inch length, with 20% UCON-W98 on chromosorb at 150° C.

Characterization of Decomposition Products. The procedure for the decomposition of the isomeric *N*-nitro-*N*-fluorobutylamines was the same as described in the previous publication (*2*). The components in the nonvolatile residue (Tables I and II) were separated by preparative g.l.p.c. The spectral data and the g.l.p.c. retention times matched those of authentic samples. The volatile decomposition products (Table IV) were collected in a trap containing carbon tetrachloride cooled to 20° C. The identity of the volatile components were revealed by matching their infrared spectra and g.l.p.c. retention times with authentic samples.

ACKNOWLEDGMENT

NMR spectra were determined by Elton Price, Standards Laboratory, Naval Ordnance Research, Naval Ordnance Station, Indian Head, Md.

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RECEIVED for review April 30, 1969. Accepted August 2, 1969. This work was performed under the Independent Research Program of the Director of Naval Laboratories, Code DNL-4; additional funding was obtained from Task Assignment ORD-033 101/067-1/F009-06-01. The opinions or assertions made in this paper are those of the authors and are not to be construed as official or reflecting the views of the Department of the Navy or the naval service at large.