BRIEF COMMUNICATIONS

THERMAL DECOMPOSITION OF BENZOTRIFUROXANE

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The thermal decomposition of benzotrifuroxane proceeds through cleavage of the C-C and O-N(O) bonds of the furoxane ring with formation of dinitriloxodifuroxanyl.

Data on the kinetics of the thermal decomposition of benzotrifuroxane (BTF) have only been given by Maksimov and Kogut [1], who carried out manometric measurements of the rate of the decomposition of BTF in the melt and in the solid state and determined the gaseous decomposition products, namely, NO, CO₂, N₂O, CO, and N₂; $k_{dec} = 10^{14.2} \exp(-41,200/\text{RT}) \sec^{-1}$. The decomposition mechanism for BTF was not examined by Maksimov and Kogut [1]. The decomposition of related bicyclic furoxanes has been interpreted as proceeding through cleavage of the O-N(O) and C-C bonds of the furoxane ring and formation of the corresponding dinitrile oxide [2]. On the other hand, there have been reports of the thermal loss of the extracyclic oxygen atom from imidazobenzofuroxane with the formation of furazane in 70% yield [3] and the formation of benzofurazane upon the pyrolysis of benzofuroxane [4]. In the present work, we obtained the most complete information on the primary step in the thermolysis of BTF.

The thermal decomposition of BTF was carried out at 200°C over 1-4 h in evacuated glass ampuls. The reaction was stopped and the products formed were analyzed. In order to trap nitrile oxides, benzonitrile was used as the dipolarophile. In this case, the reaction was carried out in the presence of excess benzonitrile. The products of the decomposition of BTF were analyzed by thin-layer chromatography and subsequent mass spectrometry. Thus, we found that dinitriloxodifuroxanyl identified as its adduct with benzonitrile (1), bis(isocyanato)difuroxanyl (II), dicyanogen, polymer of undetermined structure, and, possibly, cyanodifuroxane isocyanate are formed in addition to the gaseous products reported by Maksimov and Kogut [1]. Hence, the following scheme is proposed for this thermolysis:



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5,5-Diphenylbis(1,2,4-oxadiazole), which is the product of the decomposition of (II) at the furoxane rings, is formed in small amounts in addition to adduct (II). Bis(isocyanato)difuroxanyl, unfortunately, could not be separated as a pure sample; this compound decomposes at a rate comparable to the rate of decomposition of BTF. At 180°C and 0.1 mm Hg, (II) sublimes along with BTF, while a polymer, most likely, the product of further transformations of (III) is found in the residue.

EXPERIMENTAL

The products of the thermal decomposition of BTF in the presence of benzonitrile was separated by thin-layer chromatography on silica gel and analyzed on an MKh-1310 high-resolution mass spectrometer. The metastable transitions were determined by the defocusing method. Since the thin-layer chromatographic separation was not very good, only the major mass spectral peaks are given.

<u>Adduct (I) of Dinitriloxodifuroxanyl with Benzonitrile.</u> Thin-layer chromatography: R_f 0.35 (R_{fBTF} 0.26). Mass spectrum (m/z): [M] 458, [M - NO] 428, [M - 2NO] 398, [M - 3NO] 368. Metastable transitions, m/z: 458 + 428 + NO, 428 + 398 + NO, 398 + 368 + NO.

<u>Bis(isocyanato)difuroxanyl (II)</u> may be directly detected relative to the quantitative change in the mass spectrum of a thermally decomposed sample of BTF. The relative intensity of the following ions is strongly enhanced, m/z: [M - O], [M - CO], [M - 2O], and [M - 2CO] and the corresponding metastable peaks arise.

<u>Difuroxane-bismethylcarbamate (III)</u> was obtained by dissolving a thermally decomposed BTF sample in methanol at 40°C. Thin-layer chromatograph: $R_f 0.4$. Mass spectrum, m/z: [M] 316.

<u>5.5-Diphenylbis(1.2.4-oxadiazole)</u> was separated by vacuum sublimation at 120°C and 0.1 mm Hg from the BTF decomposition products in benzonitrile solution and purified by recrystallization from acetone, mp 210°C. Mass spectrum, m/z: [M] 290, 187, 171, 157, 103.

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