# Brief Communications

## Photoelectron spectral study of the thermolysis of benzofuroxan

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Photoelectron spectroscopy data have shown that thermolysis of benzofuroxan vapor *in vacuo* results in thermal abstraction of the exocyclic oxygen to afford a nonvolatile product, which decomposes to give nitrogen monoxide, carbon monoxide, and carbon dioxide.

**Key words:** thermolysis; benzofuroxan; photoelectron spectra.

Although the literature on the chemistry of benzofuroxan (BFO) is rather extensive,[1] the directions of benzofuroxan thermolysis are still not well understood. It is known that benzofurazan (BF) is formed at 800 °C.[2] The kinetics of the gas-phase thermolysis of BFO at 260—290 °C has been studied by manometric methods. However, the composition of the mixture of gases liberated has not been analyzed.[3] The only fact established was that isocyanates, which are typical products of the thermolysis of furoxans, were not present in the condensed thermolysis products.[3]

In this communication we present data on the thermolysis of BFO at 300 °C to 520 °C obtained by X-ray photoelectron spectroscopy.

### Experimental

Photoelectron spectra were recorded on an AS-3201 instrument with a hemispherical analyzer and a He(I) emitter. Spectra were calibrated against Ar and Kr emission. The set-up for thermolysis was made up of a heated quartz tube (18 mm diameter, 180 mm length), which was empty or filled with quartz pieces. One end of the tube was connected to the high-vacuum system of a spectrometer ionization chamber, and the other end was connected to an ampule containing BFO.

The pressure of BFO vapor was sufficient for recording the photoelectron spectra without heating the ampule. When it was necessary to separate the thermolysis products according to their volatility, a cooled trap was placed between the thermolysis tube and the ionization chamber.

### Results and Discussion

If the temperature of the thermolysis tube filled with quartz glass was below 300 °C, only the photoelectron spectrum of BFO was recorded. At 300—320 °C, additional bands corresponding to BF appeared. In the experiments using a trap cooled to −20 °C, the vapors of BFO were frozen out and only the spectrum of BF was

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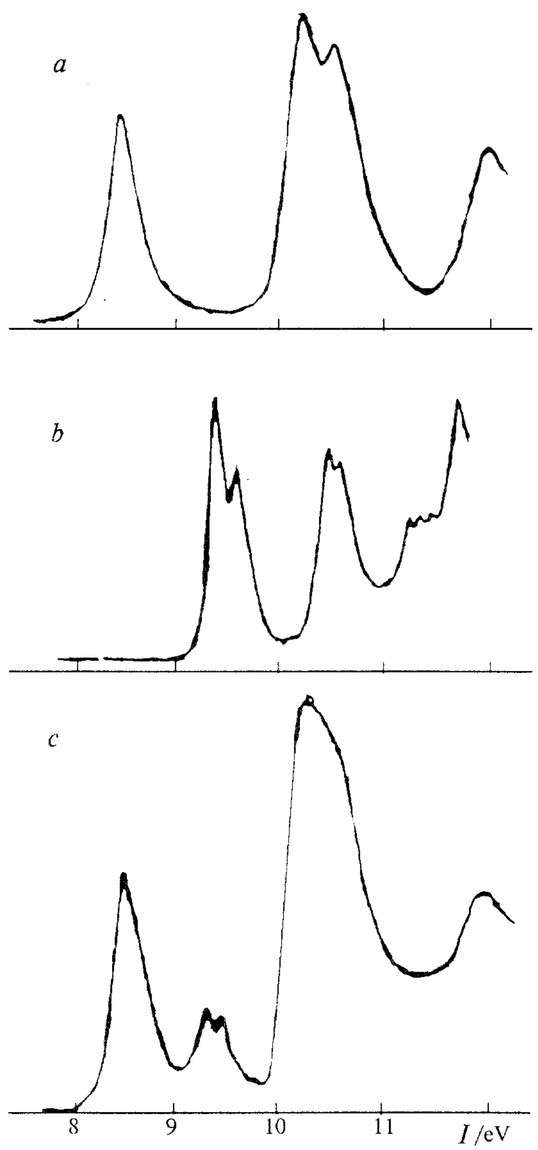



**Fig. 1.** Photoelectron spectra of benzofuroxan (*a*), benzofurazan (*b*) and the products of the initial step of benzofuroxan thermolysis at 320 °C (*c*).

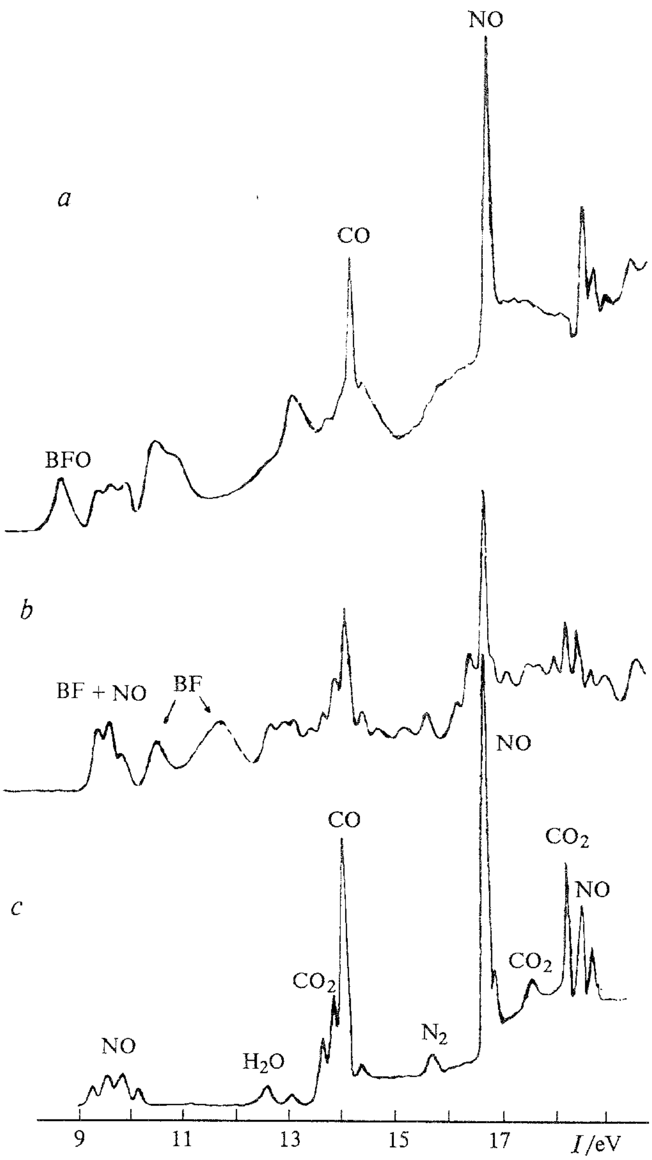



**Fig. 2.** Photoelectron spectra of the products of the initial step of benzofuroxan thermolysis at 400 °C: *a*, without a trap; *b*, at the temperature of the trap, −20 °C; and *c*, −50 °C.

**Table 1.** Vertical ionization potentials of benzofurazan and benzofuroxan and energies of the molecular orbitals calculated using the MNDO method (eV)

| BF | | BFO | |
|---|---|---|---|
| *I* | −*E* | *I* | −*E* |
| 9.38 | 9.64 | 8.56 | 9.04 |
| 10.51 | 10.74 | 10.31 | 10.69 |
| 11.50 | 12.27 | 10.31 | 11.36 |
| 11.80 | 12.93 | 10.69 | 11.89 |
| 12.10 | 13.20 | 12.15 | 13.20 |

observed (Fig. 1). When the temperature of the reactor was increased, the content of BF increased, and at 400 °C more than half of the BFO was transformed into BF, judging by the intensity of the well-resolved bands.

The experimental vertical ionization potentials of BF and BFO and the energies of the molecular orbitals calculated using the MNDO method, which are in good correlation with the experimental data, are given in Table 1.

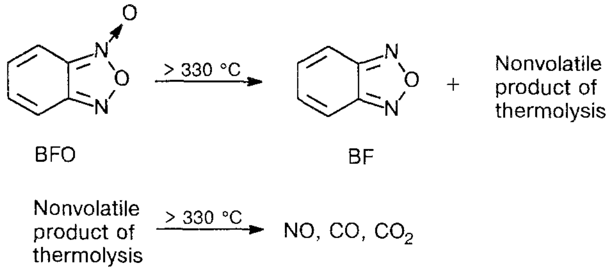
In addition to BF, a dark non-volatile substance was formed during thermolysis, which precipitated on the tube walls and on the glass packing.

At temperatures above 330 °C, in addition to the bands corresponding to BFO and BF, sharp peaks of low-atomic gases, namely, NO, CO, and $CO_2$, were recorded. These peaks were easily identified after the vapors of BFO and BF were frozen (Fig. 2).[4] Along with the peaks of the above gases, present in the products of thermolysis at 400 °C in the ratio of 6 : 3 : 2, peaks with low intensities corresponding to $H_2O$ and $N_2$ were also observed. The spectrum also contained peaks of unidentified products.

As was established in a special experiment, NO, CO, and $CO_2$ were probably formed not from BFO and BF, but from a nonvolatile thermolysis product. Thermolysis of BFO was first carried out at 310 °C, then the volatile BFO and BF were evacuated. The remaining nonvolatile product was subjected to thermolysis at 400 °C. In this case, the photoelectron spectrum obtained was identical to that shown in Fig. 2, *c*. Thus, the vacuum thermolysis of BFO vapor in a filled tube proceeds in accordance with Scheme 1.

When the thermolysis was carried out in an empty tube, the bands corresponding to BF appeared in the photoelectron spectrum only at temperatures above 330 °C, and at 400 °C the intensity of the first band of BF amounted to only ~10 % of the corresponding value for BFO. Hence, thermolysis in the empty tube proceeds considerably more slowly, which indicates that reactions on a solid surface contribute substantially to this process.

**Scheme 1**

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