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## LETTERS TO THE EDITOR

# Thermal Decomposition of Some Eight-Membered Cyclic *N*-Nitramines

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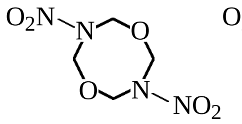
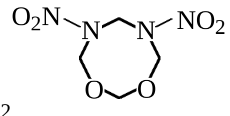
Thermal decomposition of eight-membered cyclic *N*-nitro amines, except for 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane [1], was almost not discussed in the literature, though these compounds attract specific interest as energy-rich substances [2].

We examined thermal decomposition of compounds **I**–**VII** with a view to elucidate the effect of functional groups and their position in the ring on the rate and activation parameters of the process.



**I**



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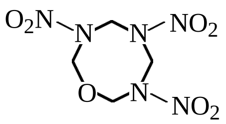

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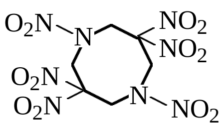
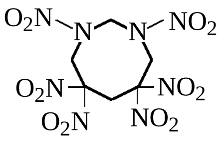
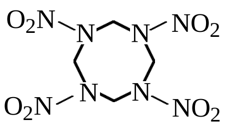


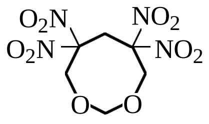
**IV**



**V**



**VI**



**VII**

Compounds **I**–**VII** were synthesized and purified by known methods [2, 3]. Experiments were performed with chromatographically pure samples. The kinetics of their thermal decomposition were studies by the manometric method [4] in melt and in solution in 1,3-dinitrobenzene and dibutyl phthalate. Compounds **I**–**VII** decomposed with acceleration which was stronger in melt than in solution. The solvent polarity and substrate concentration (in the range 1–5 wt%) did not affect the rate constant which was determined from the initial rate of thermal decomposition. The error in the determination of rate constants did not exceed 12% (from three parallel runs). The kinetic parameters of thermal decomposition of compounds **I**–**VII** (solutions in dibutyl phthalate, substrate concentration 1–2 wt%) are given below.

| Comp. no. | Temperature, °C | $k_{200°C} \times 10^5$, $s^{-1}$ | $E_a$, kJ $mol^{-1}$ | $\log A$ |
|---|---|---|---|---|
| **I** | 195–225 | 0.9 | 186.8 | 15.57 |
| **II**[a] | 180–225 | 1.5 | 186.7 | 15.80 |
| **II**[b] | 195–230 | 1.3 | 188.0 | 15.87 |
| **II** | 190–225 | 1.4 | 187.1 | 15.81 |
| **III** | 190–225 | 2.4 | 190.1 | 16.37 |
| **IV** | 175–205 | 33.9 | 164.1 | 14.65 |
| **V** | 160–180 | 335.9 | 153.0 | 14.42 |
| **VI** | 180–225 | 2.3 | 193.8 | 16.76 |
| **VII** | 175–195 | 136.4 | 151.2 | 13.83 |

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[a] In melt. [b] In 1,3-dinitrobenzene solution.

According to [1], the rate-determining stage in the thermolysis of compound **VI** is homolytic dissociation of the N–$NO_2$ bond. Replacement of one nitramino group in molecule **VI** by oxygen atom (compound **III**) does not change the rate of decomposition (cf. the corresponding rate constants). Replacement of one more N–$NO_2$ group by oxygen (compounds **I** and **II**) reduces the rate of thermolysis. Introduction into molecule **VI** of two reactive dinitromethylene groups instead of two nitramino groups leads to increase in the rate of decomposition by a factor of 15 and 59 for compounds **IV** and **V**, respectively. It is difficult to identify the reaction center in isomer **IV**, for the thermal stabilities of $C(NO_2)_2$ and N–$NO_2$ groups in the α-position are almost similar [5]. On the other hand, the reaction center in isomer **V** is the carbon atom attached to two nitro groups; this follows from comparison of the rates and activation parameters of thermal decomposition of compounds **V** and **VII**.

Presumably, higher rates of decomposition of nitro derivatives **V** and **VII** are determined by mutual steric influence of bulky dinitromethylene moieties in the α-position with respect to each other.

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