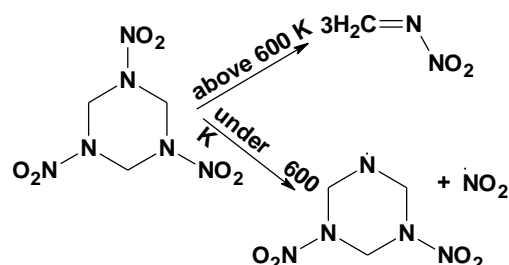


Interesting paper dealing with a study of the RDX decomposition by means of energetic electrons.

A fission of RDX molecule by electron beams is different from a well-studied its thermal decomposition. Also realization of the RDX splitting by electrons in a high vacuum practically eliminates secondary consequential mutual reactions of primary fragments, therefore, comparison with thermal decomposition is not there on the spot. I briefly present very important findings from the study of thermal decomposition of RDX:

Increasing filling of the reaction volume inhibits the thermal decomposition of RDX - this finding of Cosgrove and Owen [1] has been confirmed by Maksimov [2]. Rauch and Fanelli [3] found that change in the degree of filling of the reaction volume is accompanied by change in the NO₂ content of the products of RDX pyrolysis. The NO₂ content is directly proportional to the increase in the degree of filling of the mentioned volume. Though the NO₂ content of the products of thermolysis of RDX rapidly decreases to zero as the pyrolysis proceeds [3]. The NO₂ content is most probably the factor influencing the degree of filling and is manifested in the heat effect of unit mass in the RDX thermolysis. Batten [4] confirmed that both NO₂ and oxygen inhibit the thermal decomposition of RDX because they remove catalysts of its thermal decomposition, which being hydroxymethyl formamide [5, 6] (it is one of the RDX thermolysis product) and formaldehyde [4, 7]; the resulting variability of the partial reaction mechanism of RDX pyrolysis makes itself felt in the overall enthalpy change of the reaction. That means that a part of RDX thermolysis should go through solution-melt of RDX in hydroxymethyl formamide, and that the degree of reaction volume filling (in practice filled volume in ammunition - for example) should have a relatively big significance here: at least the distribution of the RDX decomposition into two steps in real terms can be related to the above mentioned effects on this thermolysis.

We also made molecular-dynamic simulation of thermal decomposition of some individual energetic materials, including RDX, at extremely high temperatures (over 600 K). It turned out that the primary fragmentation mechanism at these conditions is entirely different from the low-temperature variant. In the case of the RDX unimolecular decomposition, it can be mentioned that elimination of NO₂ group by homolysis of one N–N bond is observed for all reaction conditions whereas triazinane ring fission (depolymerization to 1-nitro-1-azaethylene) occurs predominantly in the gas phase thermal decomposition of this nitramine, i.e. at higher temperatures (see Ref. [8] and quotations herein).



We found that another primary step of this monomer fission consists in the C-H bond homolysis, which may be reason of the OH radical appearing in products.

The N-NO₂ bond primary homolysis and depolymeration should appaeare in decomposition at all temperatures used, only at the lower temperatures this homolysis is dominating, and above 600 K depolymerization is a main fission. Authors of the reviewed paper reflect this depolymerization, but without elimination of hydrogen from monomer, but it is a matter of opinion.

Nevertheless, the reviewed paper good dovetails into the studies of this type in a nowadays time (as it was already stated), the above-mentioned is presented here as information for the other activities of authors in the reviewed area.

The paper is written clearly and comprehensible. Its conclusions are adequately supported by data (including illustrations and tables) given in its text. A topic of the manuscript is is compatible with thematic priorities of the Journal of Physical Chemistry.

References.

- [1] J.D. Cosgrove, A.J. Owens, Chem. Commun. 1967, p. 286.

- [2] Yu.Ya. Maksimov, Teorya vyryvchatykh veshchestv (Theory of Explosives), Trudy MCHT, 1967, 53, p. 73
- [3] F.C. Rauch, A.J. Fanelli, J. Phys. Chem. 1969, 73, p.1604.
- [4] J.J. Batten, Austral. J. Chem. 1971, 24, p. 945.
- [5] J.D. Cosgrove, A.J. Owen, Combust. Flame. 1974, 22, p. 13.
- [6] J.D. Cosgrove, A.J. Owen, Combust. Flame. 1974, 22, p. 19
- [7] J.J. Batten, Austral. J. Chem. 1971, 24, p. 2025.
- [8] D. V. Shalashilin and D. L. Thompson, J. Phys. Chem., A 101 (1997) 961.