

# The Comparative Analysis Of Energetic Materials Reactivity At Thermal, Radiation-chemical And Explosive Decomposition

Yu.A. Zakharov, V.Kh. Pak, S.M. Ryabykh, D.G. Yakubik

*Kemerovo State University, Ul. Krasnaya, 6, Kemerovo, 650043, Russia*

**Abstract – There has been carried out the comparative analysis of different models of energetic materials solid-phase decomposition.**

**The differences of radiolysis and thermolysis mechanisms are analyzed on the crystal surface and in its bulk.**

**The quality differences of energetic materials explosive decomposition from these reactions are discussed.**

The comparative analysis of different mechanisms of solid-phase decomposition is carried out rather rarely, and it is quite understandable. As a rule, some kinds of decomposition are studied on different classes of substances. From the whole set of solid matters only initiating explosives are capable to undergo all kinds of solid-phase decomposition that gives an opportunity to carry out the comparative analysis of their mechanisms on one class of objects, that is certainly mostly correct. The given report is devoted to the comparative analysis of mechanisms of thermal, radiation-chemical and explosive decomposition of energetic materials (EM). Mechanic-chemical and electro-field decomposition is not taken into consideration here.

The attempts of such comparison were earlier carried out on silver and lead azides, well known EM and convenient modeling objects. The simple chemical composition, famous crystal and band structures, the type of ionic deficiency, high reactivity facilitated such analysis. But simple composition of termination products like molecular nitrogen and corresponding metal has played original "a malicious joke". At any kind of decomposition the set of termination products is the same, and it causes a desire to put forward the general mechanism of decomposition, with distinction only in an initial stage character depending on a kind of the influencing on the power factor object. In the case of thermolysis, photolysis and radiolysis it is an adaptation of famous Gerney – Mott and Mitchell mechanisms, developed for the description of silver halides photolysis. Such approach is quite justified because the azides are pseudo-halogenides, and according to many properties, they are close to chlorides and bromides.

EM set expansion made reconsider the concept of the uniform mechanism of thermal and radiation-chemical decomposition. As it turned out, different products are formed and the different topography of decomposition is realized at a thermolysis and radio-

lysis of these. It is especially evident for nitroaromatic compounds – a lead styphnate and potassium picrate.

The thermolysis of these substances goes on an external surface and during it there is a tearing up of a benzene ring with gaseous products formation, major of which are carbon dioxide and nitrogen. So, in potassium picrate composition of evolving out gaseous products is the following: nitrogen – 20–30 %, carbon dioxide – 65–70 %, carbon monoxide – about 1 %, nitrous oxide – less than 1 %, water of 6–11 %. Traces of ammonia are registered, nitric oxide is not found. The total amount of gases allocated at a thermolysis is equal 3.7–4 mole / mole. Close indexes of lead styphnate: the total amount of gases is 3.5 mole / mole; the main products are carbon dioxide and nitrogen.

There is practically no gas evolution at the irradiation of these substances. So, from a styphnate of lead there has been evolved 0,04 ml of gas at scale irradiation by isotope of gold-198 from a shot with 2 grams weight on the 10th day and after the irradiation termination the gas has been precipitated out. For comparison: at the same conditions there has been evolved 2.22 ml of gas from lead azide and in 30 days after the irradiation termination there have been more 5.58 ml. The same data are received for potassium picrate while using of the high-vacuum installation working in the gas flow measurement mode: gas evolution at a background level, composition of evolving gases is not differed from air composition of laboratory. The radiation-stimulated adsorption of air may only take place.

At the same time the analysis on the basic anion decreasing has shown that radiolysis goes with a constant radiation-chemical yield which at room temperature is equal 0.8 molecule/100 eV for potassium picrate and 0.7 molecule/100 eV for a lead styphnate, i.e. rather reasonable sizes.

The generalization of a large set of experimental data gives the bases for the following conclusions.

1) There are two mechanisms of radiolysis of EM: surface and bulk, where the surface one is not realized in all EM, it can not be found in nitroaromatic compounds

2) The bulk mechanism of radiolysis essentially differs from the mechanism of thermolysis. At a thermolysis formation processes of termination products of decomposition are only on the surface. Probably, their passing demands the free volume presence. For example, in azides for nitrogen formation it is necessary to create an intermediate promoted complex from 6-atoms of nitrogen. It does not depend on a configuration

(there are some of them) and such complex is not packed in a ideal crystal lattice of azides and consequently the process of nitrogen formation due to such mechanism in the crystal volume does not exist. The bulk mechanism of radiolysis is connected with excitons decay on ionic defects or with dissociates recombination generated by radiation of electrons and holes (it is likely the same thing). In azides the process of the anionic exciton decay is the eliminating of trailer atom of nitrogen with the diatomic ion-radical formation. In nitroaromatic compounds there is the eliminating of nitro-group as partly as wholly.

3) The analogies can be searched between the thermolysis mechanisms and the surface radiolysis. In both cases there is a localization of holes on splays with next formation of an active complex and then on the terminate gaseous products. The difference is in holes formation: at radiolysis it is practically the homogeneous by volume generation of electron-hole pairs, at thermolysis it is the local electron stimulation from a valence zone to the acceptor level (usually it is to extrinsic cation). These processes are well expressed for azides, fulminates and they practically do not exist in picrates and styphnates.

Convenient model objects for the comparative analysis of thermal, radiation-chemical and explosive decomposition mechanisms are nitroaromatic substances, in particular, lead styphnate and potassium picrate firstly because of different composition of products of each kind of decomposition.

The total amount of the gases formed at explosion 1 mole lead styphnate – 5–8 moles, at a thermolysis – 3.5 moles. They are close meanings to potassium picrate. The composition of gaseous products at lead styphnate thermolysis is basically carbonic gas and molecular nitrogen. The detailed data were mentioned above. At explosion 2 mole of lead styphnate, 4 moles of carbon dioxide, 8 moles of carbon monoxide, 1 mole of hydrogen, 2 moles of lead, 3 moles of nitrogen are formed, also precipitates out 335 kcal energy. Probably, the similar scheme is realized at explosion of picrate potassium. The final solid product of lead styphnate thermolysis presents black amorphous polymer which does not detonate and has the following element composition: nitrogen – 6.2 %, hydrogen – 0.4 %, carbon – 12.2 %, lead – 69 %, oxygen – 12.1 %.

The distinction in composition of termination products decomposition at explosion and a thermolysis is obvious: a solid product of explosive decomposition is a metal, and thermolysis's is amorphous polymer with complex structure and the presence of expected substances of lead oxide for lead styphnate and potassium carbonate for potassium picrate in it can be discussed. In gas products of explosive decomposition there is the oxide carbon in great amounts but at thermolysis it practically does not exist.

The presence of different decomposition mechanisms initial explosives at various by the nature energetic influences is the immutable experimental fact.

For development of approaches to the discussion in the work there is the analysis of features processes initial explosives electronic subsystem stimulation and initial simple steps at different factors influence.

In particular it is marked that at explosive decomposition in the front of a detonation wave all atoms making a crystal have gone to excited condition and consequently the efficient temperature in it is thousand degrees, and the efficient pressure is more then 100000 atmospheres. There is a resonant power transmission from the excited atoms to unexcited ones. Thus the electronic shells of components should be blocked. Probably, it is achieved due to crystal deformation in front of a detonation wave because of high pressure. There is a direct experimental acknowledge of this assumption. In the experiments carried out on Bridgman's anvil with thermite compositions under Enikolopov's supervision it is established that under collateral high-pressure influence (ten thousand atmospheres) and the shift, the thermite compositions are destroyed in the detonation mode without essential warming-up. The important parameter is the speed of detonation wave spreading. It makes about 5 km/s that correspond to one constant crystal lattice passing about 5 angstrom for  $10^{-13}$  second, i.e. for the normal mode period. In other words, one fluctuation means one transferring.

The second transformation is determined by the initial particles set formed by the energetic factor.

The surface branch of decomposition is usually a binary reaction of two holes with formation of a promoted complex that requires the free volume being on a surface. As the hole has an efficient positive charge, this process requires preliminary localization of the first hole on the negative-charged defect and only then the connection with the second hole of next formation of a promoted complex and termination products. Usually these are the gases precipitating out in the atmosphere.

Basically such process is possible without of the intermediate negative-charged defect presence as a variant of a self-compensation by Vinetsky and it is energetically more possible on a surface.

The bright example of everything mentioned is the decomposition of azides where the hexatomic complex is formed of the located holes like azides-radicals and then three molecules of nitrogen more. The localization of the first hole is likely occurred on cationic vacancy and the silver azide is defective by Frenkel in the cationic sublattice. In the case of self-indemnification, the hole supersedes a cation on a surface and is turned to the electron that is a poor center attaching the second hole.

This mechanism can be realized at the thermolysis and radiolysis. A difference between them is in the

solid product formation. At radiolysis we have free electrons in a conducting band, trapped by a growing particle, at a thermolysis there is a local thermal stimulation of an electron immediately on a growing metal cluster.

The bulk mechanism includes an excitons decay on a pair of defects. In EM as a result of its passing there is an eliminating from anions of easy fragments: atoms of nitrogen from an azide-ion, nitrate group or its parts from picrate and styphnates-ions, etc. On a surface this process, probably, does not go because of the excitons surface relaxation which has an advantage at a decomposition reaction of excitons. This process is specific only for radiolysis.

The general phenomenon at radiolysis of EM is the formation in the crystals volume of the areas with gaseous products or their predecessors. We are inclined to consider that vicinities of growing area because of straining voltages are more preferable to localization with the following excitons decay. However, to believe this area to be a primitive cavity with gas is impossible because too much cations should be removed. We suggest that this area is a complex radiating defect where the anionic sublattice highly turned into the gaseous products formation or their predecessors, and in cationic cations it turned into atoms but have not changed their coordinates, i.e. have not still formed a metal particle with a necessary crystal lattice and preserve interatomic distances specific for a parent crystal.

The particle of a solid product is formed at dissolution of the irradiated crystal. They have the unique properties which are distinct from physical and chemical properties of massive analogue.

An explosion within the framework of abbreviated representations is considered as two-stage one: the center formation of initiation with the detonation wave forming and the explosive decomposition itself in a detonation wave front.

The question, whether this process is the radiation unique by the mechanism at pulse initiation or it is led to the habitual thermal mechanisms, has been discussed till now.

We believe, that the explosion initiated by pulse radiation, basically is similar to explosive decomposition at other methods of initiation, i.e. goes in front of a detonation wave. A difference is in the creation mechanism of the center of initiation. At the thermal mechanism the center is created by coagulation to the critical sizes of the electronic stimulations generated by the phonons, i.e. the nuclear subsystem is also stimulated. At the pulse radiation stimulation it itself creates these stimulations. And consequently their coagulation process does not require the nuclear subsystem stimulation. It is especially understandable if to take into account that even in adiabatic approach the warming-up due to the stimulating pulse influence of radiation does not exceed 10 degrees.

The thermolysis and explosion are threshold processes. There is a temperature of the thermolysis start and it is quite correct determined on curves of the differential thermal analysis. The explosion has quite fixed parameters of influence stimulating explosion: minimum temperature, minimum height of falling of a cargo at initiation by impact or a pinholes, minimum energy of a stimulating pulse radiation, etc. For parameters of stimulating influence there is a fixed range in which explosion initiation is possible: at parameter of the lowest limit explosion does not occur at parameters explosion is higher than the upper bound occurs always with probability 1. As there is such a limit, so a critical parameter for the center of initiation formation takes place. It can be, as an example, a critical concentration of electronic excitations in the center of their concentrating, at which the detonation wave and the center of concentrating is formed, turns to the initiation center.