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RELATIONSHIP BETWEEN ELECTRONIC CHARGES AT NITROGEN ATOMS OF NITRO GROUPS AND THERMAL REACTIVITY OF NITRAMINES

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Abstract

Thermal reactivity of eleven nitramines has been examined by means of non-isothermal differential thermal analysis, and the data were analyzed according to the Kissinger method. The reactivity was expressed as the E_aR^{-1} slopes of the Kissinger relationship. Electronic charges, q^N, at nitrogen atoms of the nitramine molecules were calculated by means of *ab initio* DFT B3LYP/6-31G** method. The relationships were confirmed between the slopes E_aR^{-1} and the q values for the nitro groups that are primarily split off. Conclusions are made in relation to the mechanism of initiation of polynitro compounds in general.

Keywords: DTA, initiation, nitramines, thermal decomposition

Introduction

It is well known that nitro groups are centres of reactivity in organic polynitro compounds [1–6]. Therefore, it is logical that there exist relationships between the ^{15}N NMR chemical shifts δ_N of nitrogen atoms in nitro groups of nitramines and the Arrhenius parameters of their thermolysis [7, 8], impact sensitivity [7, 9], electric spark sensitivity [10] and their detonation characteristics [11].

It is also known that the chemical shifts δ_N are connected with electron configurations at the respective nitrogen atoms and with steric conditions of the atom vicinage. The electronic configuration and steric conditions play decisive roles within the reaction centre of the molecule during its primary fission. From what has been said it follows, for instance, that the thermal decomposition characteristics from different thermal decomposition (DTA) of polynitro compounds should correlate with electronic charges at nitrogen atoms of nitro groups primarily reacting in the initiation of the process. This is the problem that we focus our attention on the present paper. For this purpose we have chosen some nitramines as models of polynitro compounds.

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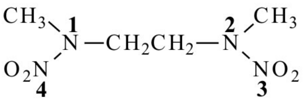
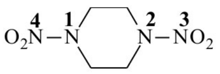
Table 1 Survey of the nitramines studied, their code designation, Mulliken B3LYP charges, q^N, at nitrogen atoms, and slopes E_aR^{-1} of the Kissinger relationship (where r is a correlation coefficient)

DMEDNA
2,5-Dinitro-2,5-diazahexane



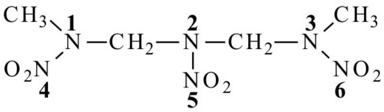
N	q^N(electron)	
1	–0293115	
2	–0.288564	E_aR^{-1} = 46530 K
3	0.659040	r^2 = 0.9658
4	0.642097	

DNDC
1,4-dinitropiperazine



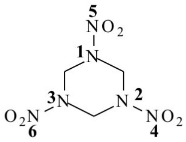
N	q^N(electron)	
1	–0.339494	
2	–0.339494	E_aR^{-1} = 23500 K
3	0.658983	r^2 = 0.9979
4	0.658983	

ORDX
2,4,6-Trinitro-2,4,6-triazaheptane



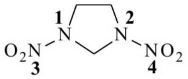
N	q^N(electron)	
1	–0.287247	
2	–0.288951	E_aR^{-1} = 24730 K
3	–0.273951	r^2 = 0.9845
4	0.667299	
5	0.659753	
6	0.662801	

RDX
1,3,5-Trinitro-1,3,5-triazinane



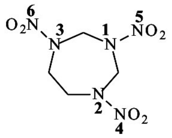
N	q^N(electron)	
1	–0.343516	
2	–0.343516	E_aR^{-1} = 36629 K
3	–0.343516	r^2 = 0.9767
4	0.677118	
5	0.677118	
6	0.677118	

CPX
1,3-Dinitroimidazolidine



N	q^N(electron)	
1	–0.356977	
2	–0.356977	E_aR^{-1} = 14273 K
3	0.654013	r^2 = 0.9630
4	0.654013	

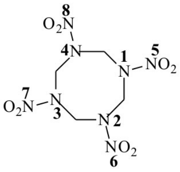
HOMO
1,3,5-Trinitro-1,3,5-triazepane



N	q^N(electron)	
1	–0.322158	
2	–0.324684	E_aR^{-1} = 20521 K
3	–0.320578	r^2 = 0.9941
4	0.674280	
5	0.668468	
6	0.655847	

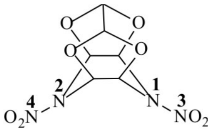
Table 1 Continued

HMX
1,3,5,7-Tetranitro-1,3,5,7-tetrazocane



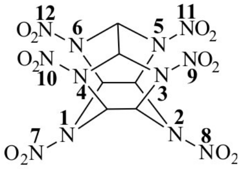
N	q^N(electron)	
1	–0.302285	
2	–0.301501	E_aR^{-1} = 40786 K
3	–0.302285	r^2 = 0.9872
4	–0.301501	
5	0.685032	
6	0.682944	
7	0.685032	
8	0.682944	

TEX
4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane



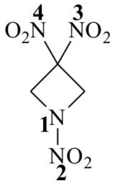
N	q^N(electron)	
1	–0.321327	
2	–0.321327	E_aR^{-1} = 67947 K
3	0.680084	r^2 = 0.9980
4	0.680084	

HNIW
2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane



N	q^N(electron)	
1	–0.289588	
2	–0.289588	α-HNIW:
3	–0.286772	E_aR^{-1} = 31186 K
4	–0.286720	r^2 = 0.9980
5	–0.286720	
6	–0.286772	ε-HNIW:
7	0.687099	E_aR^{-1} = 17747 K
8	0.687099	r^2 = 0.9897
9	0.665691	
10	0.665590	
11	0.665590	
12	0.665691	

TNAZ
1,3,3-Trinitroazetidine



N	q^N(electron)	
1	–0.313256	
2	0.626714	E_aR^{-1} = 12460 K
3	0.438054	r^2 = 0.9617
4	0.447578	

Experimental

Data and substances

The calculation of electronic charges, q^N, at nitrogen atoms of nitramino groups of the nitramines investigated was carried out by means of the Mulliken population analysis of electron densities obtained by DFT B3LYP/6-31G** method [12]. The method describes the equilibrium geometry (i. e. totally optimized B3LYP/6-31G** geometry) of an isolated molecule in the gas phase at 0 K. A survey of the compounds studied, their codes and the results obtained are presented in Table 1.

Non-isothermal differential thermal analysis

We used a DTA 550 Ex apparatus [14] specially developed at the Department of Theory and Technology of Explosives for thermal analysis of explosives. The measurements were carried out at atmospheric pressure, the tested sample being in direct contact with the air atmosphere. The sample tested (0.05 g) was placed in a test tube made of Simax glass, 5 mm in diameter and 50 mm in length. The reference standard was 0.05 g aluminum oxide. We used linear rates of temperature increase, *viz*. 5, 10, and 20 K min^{-1}. The results of these measurements were treated by means of the software delivered with the DTA apparatus [14]. This selected procedure was successfully verified in our previous research activity, e.g. in the study of the explosive mixtures initiation [13]. Examples of the corresponding DTA records are presented in Fig. 1 (α–HNIW). Notorius volatility of the TNAZ near ist melting point [15] was not observed under the applied conditions of measurements. The results obtained were treated using the Kissinger method [16] and are graphically presented in Fig. 2. The values E_aR^{-1} thus obtained (see in Table 1 where r is a correlation coefficient)

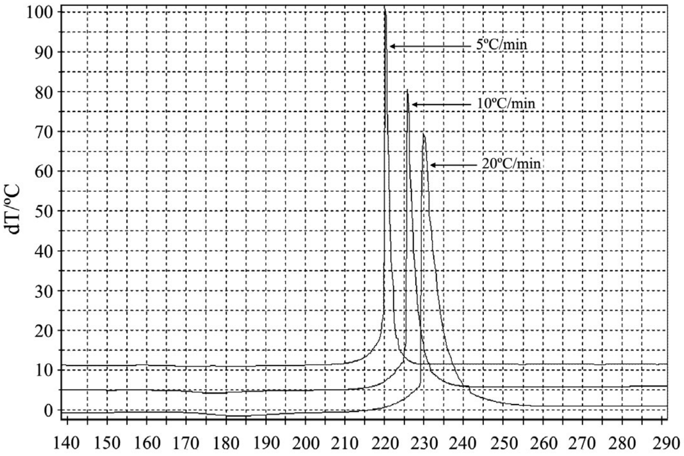


Fig. 1 DTA-records of α–HNIW

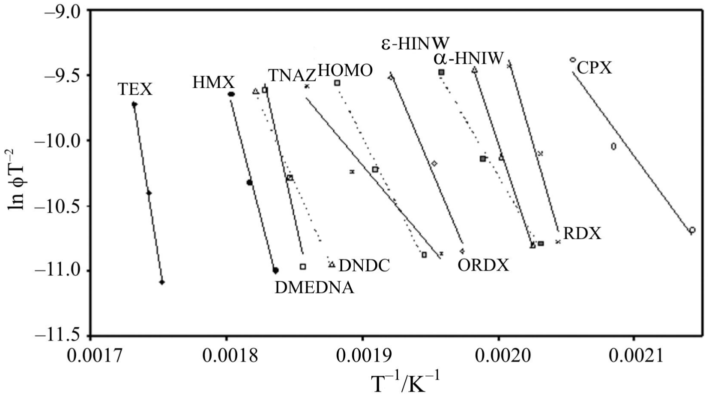


Fig. 2 DTA results treated using the Kissinger method [15], here ϕ is the rate of temperature increase and T is the peak teperature

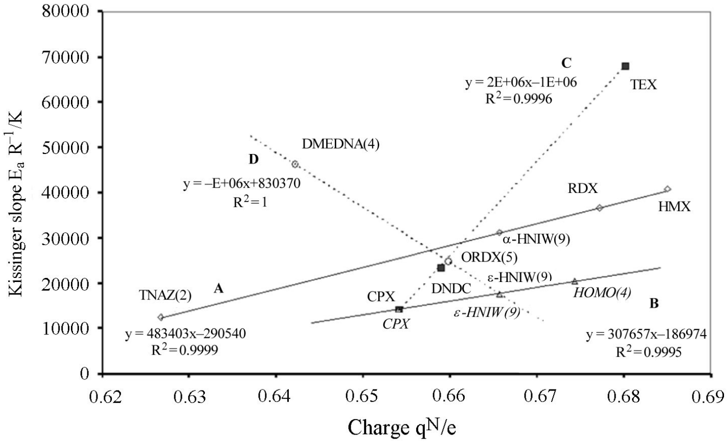


Fig. 3 Graphic representation of Eq. (1) – numbers in parenthesis correspond to the nitrogen atoms in molecule according to the Table 1

were then plotted *vs*. the charges, q^N, at the nitrogen atoms of the primarily split off nitro groups – see Fig. 3.

Discussion

A simple comparison of Mulliken B3LYP/6-31G** charges, q^N, at the nitrogen atoms of the primarily split off nitro groups with the detonation characteristics of *m*-dinitrobenzopolyazaarenes was used in a study of chemical micro-mechanism of initiation of these compounds by shock [17]. A similar treatment was adopted in the study of micro-mechanism of initiation of polynitro arenes by impact [18]. The same procedure in the case of sensitivity of nitramines to heat provided the dependence in the general form (as depicted in Fig. 3):

$$E_\mathrm{a}R^{-1}=aq^\mathrm{N}+b \tag{1}$$

The sensitivity (thermal reactivity) is expressed here in the form of slope, $E_\mathrm{a}R^{-1}$, of the Kissinger relationship (Fig. 2).

The meaning of relationship (1) can be interpreted as follows: a linear relationship between the q^N values at the nitrogen atom of the primarily split off nitro group in molecule and explosion heat, Q, of polynitro arenes was found and interpreted [17]. This means that the relationship (1) can be expressed as

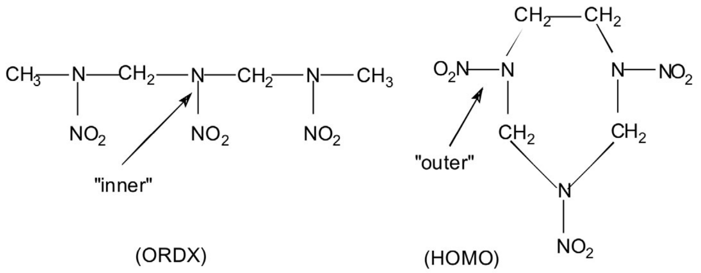
$$E_\mathrm{a}R^{-1}=C\pm\alpha Q \tag{2}$$

which is another form of the modified Evans–Polanyi–Semenov equation [11, 13, 17, 23], originally derived for radical substitution reactions [11, 23 and references herein]. This equation is valid for narrow sets of substance structures and it documents that the strength of bond being split is a decisive factor in the given reaction [11, 13, 23], i. e. in the splitting by shock or impact in the case of relationship (2) [11, 23, 24].

In sense of Eq. (1), the set of the nitramines studied falls into four logical groups (Fig. 3). Equation (1) in groups *A* and *B* in Fig. 3 is fulfilled with the charge value at nitrogen atom **9** in the molecules of α-HNIW and ε-HNIW (for numbering see the Table). This atom corresponds to 2-nitro group in HNIW molecule, whose bond to the respective aza atom is the longest (143.5 pm) [19] from among the nitramine groups in ε-HNIW molecule: hence it is the most reactive one [20]. This nitro group primarily leaves on shock initiation of HNIW [11]. The thermal decomposition of both polymorphous modifications of HNIW practically proceeds only after their transition to γ-HNIW [21]. The difference between mechanisms of these transitions of α-HNIW and ε-HNIW will probably cause a difference in arrangement of defects in crystal lattice in particular (i.e., a difference in intermolecular forces) in the resulting γ=moddifications [21]. The different concentrations of crystal defects in the γ-modifications of HNIW, which have different histories, should make themselves felt in their different reactivity (in general).

If the N–N bond length exceeds 141.0 pm, Arrhenius parameters of the given nitramine thermal decomposition in the solid-state correspond to those obtained from decomposition of this kind of substances in the liquid-state [20]. Therefore, the $E_\mathrm{a}R^{-1}$ values of HNIW (thermal decompn. in the solid-state) correlate well with those of nitramines of the groups *A* and *B* (decompn. in the liquid-state). From the point of view of the group *B* composition it may be added that 1,3-imidazolidine skeleton of CPX and 1,3,5-triazepane skeleton of HOMO form parts of the 'caged' skeleton of HNIW globular molecule. Equation (1) for group *B* is fulfilled by nitramine HOMO when using the charge q^N at nitrogen atom **4**. This nitrogen atom corresponds to 1-nitro group in the HOMO molecule and this nitro group also primarily leaves after shock initiation of the said nitramine [11, 24].

The composition of group *C* nitramines (TEX, DNDC and CPX) needs no comment. Within the group *D* nitramines, the data of DMEDNA and ORDX correlate with those of ε-HNIW. The molecular skeletons of these two nitramines can be considered as fragments of the molecular skeleton of HNIW (e.g., ORDX can be considered as an 'open' HOMO molecule). The nitramine ORDX correlates with the data of group *D* by its q^N value of nitrogen atom **5**. This nitrogen atom corresponds to 4-nitro group of the nitramine mentioned: this nitro group also primarily leaves after shock initiation of ORDX [11, 22]. The similar mechanism was also confirmed by molecular-dynamics simulation of action of shock and impact on linear nitramines [22] and by analysis of action of these stimuli on linear and cyclic nitramines by means of the ^{15}N NMR chemical shifts [9, 11, 24]. All the above-mentioned can be illustrated by Scheme 1, which is taken from [9, 11, 24]:



Scheme 1 Primary splitting 'inner' N-N bond in ORDX molecule, confirmed by molecular dynamics simulation [22] and by means of the ^{15}N NMR chemical shifts [9, 11, 24] for shock and impact and by this paper for thermal decomposition. Primary splitting 'outer' N-N bond in HOMO molecule, confirmed by means of the ^{15}N NMR chemical shifts [8, 11, 24] for shock and impact and by this paper for thermal decomposi-

The way of correlation of the data of HNIW, HOMO, and ORDX in sense of Eq. (1) signalizes again the identity of the primary chemical micro-mechanism of low-temperature thermal decomposition with those of impact and shock initiations of energetic materials (e.g. [7, 9, 11, 13, 23, 24]).

Conclusions

There exists a linear relationship between the characteristics of thermal decomposition of nitramines, expressed as the slope E_aR^{-1} of Kissinger relationship [16], and Mulliken B3LYP/6-31G** charges, q^N, of the primarily split off nitro groups in their molecules. The relationship is valid for closely molecular-structurally related molecules. The primarily split off nitro groups in the low-temperature thermal decomposition of nitramines should be identical with those in the impact and shock initiations. This statement perfectly agrees with the findings [7, 9, 11, 13, 23, 24] concerning thermal, shock and impact reactivity of polynitro compounds.

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