



Accounts of the New Aspects of Nitromethane Initiation Reactivity

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Abstract. A well-known effect of amines, and also of water, on detonation characteristics of nitromethane (NM) is discussed from the point of view of the published knowledge about the study of initiation reactivity of this nitro paraffin. It is documented that bimolecular and higher interactions during the initiation of NM are impossible. The most widespread concepts of the primary steps of this initiation, i.e. formation of *aci*-NM anion $[\text{CH}_2=\text{NO}_2]^-$ by intermolecular hydrogen transfer in the neat NM submitted to shock and formation of this anion by action of an amine, have been scrutinized by the DFT B3LYP/cc-pVTZ+ method and evaluated as thermodynamically disadvantageous. Also the 1,3-intramolecular hydrogen shift in the NM molecule was characterized as a higher-barrier process. Two favorable primary mechanisms of fission in the NM initiation and development

of its detonation were investigated by DFT B3LYP/cc-pVTZ+ calculations: homolysis of C–NO₂ bond in the neat NM and homolysis of N–OH bond in its *aci*-form. The second mentioned pathway was found to be thermodynamically the most preferable mechanism of fission. Consequently, a detonation wave of NM with admixture of amine or water has a considerably reduced reaction zone length in comparison with the detonation of neat NM. The B3LYP/6-311++G(d,p) calculations of transition states revealed that an admixture of methylamine and/or water influences the conversion of nitromethane to its *aci*-form, and this effect is more feasible in the case of methylamine rather than water.

Keywords: DFT B3LYP methods, detonation, initiation, nitromethane

Introduction

It is well known that nitromethane is more easily initiated when various amines are added to it [1-7]. Walker studied this effect [1] using nitromethane sensitized with *N*-(2-aminoethyl)ethane-1,2-diamine (diethylenetriamine, DETA) in the concentration range of 0-5%. The amount of 0.05% by wt. of DETA raised the detonation velocity from the original value of 6.32 km s⁻¹ to 6.70-6.76 km s⁻¹ (this is the maximum increase) [1]. This amount of DETA resulted in formation of a shorter reaction zone and a higher pressure within the zone [1, 7] as compared with those observed in pure nitromethane. In this case the increase in the detonation pressure was 7 GPa (from about 13 GPa to 20 GPa [1]), which is very interesting. Walker explained this phenomenon by acceleration of the decomposition of nitromethane owing to the action of DETA [1].

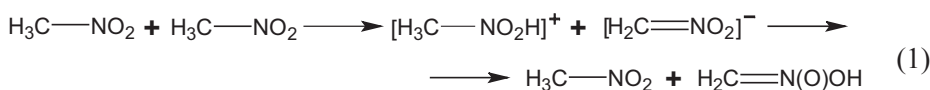
As compared with the above-mentioned enhancement of detonation parameters, the influence of amines on failure diameter of nitromethane has been better known and studied [2, 4-7]. Also this effect is connected with an increase in reaction rate in the reaction zone of detonation (i.e., with reduction of the zone length) due to the influence of amines on nitromethan [7]. It needs to be mentioned here that also water and acids have a similar (but weaker) influence on this diameter [2, 8] – the water content of 2% by wt. in nitromethane decreases it from 13.5 mm to 8 mm [8].

In the present paper we will try to explain Walker's finding [1] scrutinizing the published data on initiation reactivity of nitromethane with theoretical calculations by-DFT B3LYP/cc-pVTZ+ and DFT B3LYP/6-311++G (d,p) methods [9, 10].

Problem of nitromethane initiation

The monitoring of the shock exposure of nitromethane by means of Raman spectroscopy [11] and detonation of nitromethane by means of the MS spectroscopy [11] led to the conclusion that condensation reactions of two or more nitromethane molecules take place in its initiation (see Schemes, for example, in Ref. [11]). However, the arrangement of both experiments had to detect extinguishing detonation (in the first case explosive decomposition in a very thin layer – from 0.20 to 0.35 mm [11], in the second case an expansion of the explosive decomposition of a very small sample into high vacuum [5]). The critical diameter of NM is in the range of 10-20 mm [13, 14], which also supports the idea of extinguishing detonation at the conditions used in the two experiments, which means that the secondary termination reactions should be detected in both cases [35].

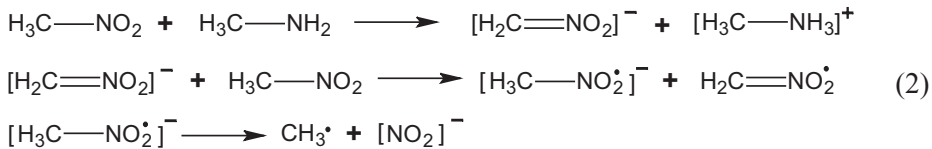
Studies of electronic excitations in shocked crystals of NM showed [15] that dynamic actions have a more significant effect on the band gap than static actions, but relative molecular velocities in excess of 6 km s⁻¹ are required to produce a significant population of thermally excited states. Some authors [16, 17-19] consider the hydrogen transfer in the sense of Scheme (1) to be the primary process in shocked NM.



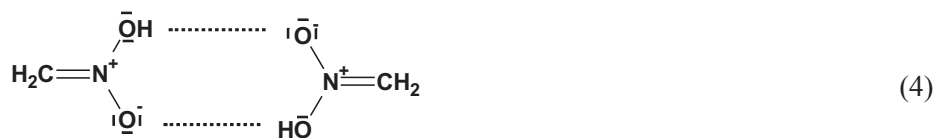
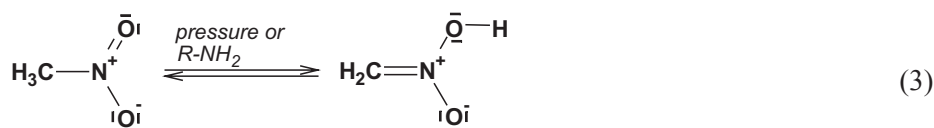
Applying DFT-binding method to crystalline NM at 0 K [20], the authors came to the conclusion (surprising – in their opinion) that uniaxial compression of about 25-40 GPa along the *b* lattice vector causes the C–H bond to be highly stretched, which leads to proton dissociation.

In primary and secondary nitro paraffins, hydrogen transfer reactions take place involving a 1,3-H shift [21, 22], according to the paper [22] through a four-membered transition state. This process produces *aci*-forms of these compounds, which are also called nitronic acids. According to Manelis [21], the existence of *aci*-form of NM represents a more probable cause of lowering of the activation energy of thermal decomposition of liquid NM as compared with the gas-phase thermolysis (i.e. in relation to the theories of bimolecular mechanism of this decomposition [21]). Paper [22] discusses both possible ways and intermolecular mechanisms of formation of the said acids. However, the 1,3-intramolecular hydrogen shift is a high-barrier process (see in Figure 2) [22, 23]. The acid

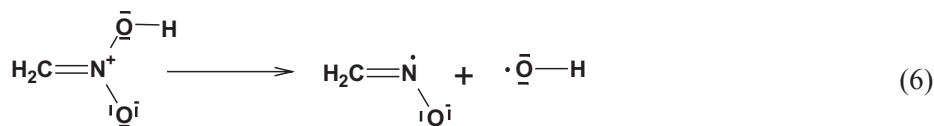
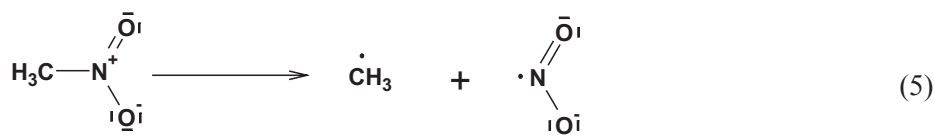
dissociation of NM is highly endothermic and little dissociation occurs at the equilibrium [23]. The mentioned transfer of hydrogen atom can also be evoked by amines [22], whose presence sensitizes both primary and secondary nitro paraffins to stimuli [14, 24]. For this case, Gruzdkov and Gupta [25] suggested the following mechanism of initiation (Scheme 2):



As shown, the first step should be, according to the authors' opinion, an acid-base equilibrium. This conclusion was drawn on the basis of application of time-resolved optical spectroscopic techniques and action of shock (12-17 GP) upon an NM layer of 0.2 mm thickness (conditions for extinguishing of detonation should be in this adjustment). Similar conclusion was obtained by Woods [26] on the basis of laser-initiated decomposition of single aerosol particles of NM and NM-diethyl amine. In comparison to the above-mentioned increase in the detonation parameters, the influence of amines on failure diameter of nitromethane [14] is better known and has been more studied [2, 5, 7, 8, 14]. Also this effect is connected with the increase in reaction rate in the reaction zone of detonation (i.e. with reduction of the zone length) due to the influence of amines on nitromethane [7]. This fact might indicate that the primary fragments entering the reaction zone of detonation wave in the case of neat NM are different from those in the case of NM sensitized by addition of amines [35]. It has been known for quite a long time that the concentration of *aci*-NM anion $[\text{CH}_2\text{NO}_2]^-$ in the NM should increase not only with the addition of bases [22] but also by application of static high pressure [27] (see also [21]). However, evidence for an increase in concentration of the anion in neat nitromethane under shock conditions (dynamic high pressure) has been found lacking [28]. The facts mentioned so far about the influence of pressure and amines might be simply illustrated by Scheme (3) [37]. Taking molecular dynamic simulation of liquid NM shocked to 143 kbar at 600 K, Seminario *et al.* [29] found that the most of pair of NM molecules were linked by two hydrogen bonds, which means that *aci*-form of NM exists as a dimer similar to the dimers of carboxylic acids (see Scheme 4). At the standard atmospheric pressure, however, an electron density analysis did not indicate the presence of any hydrogen bonding between the *aci*-nitro hydrogen and the NO unit, although the H...O distance of 2.13 Å is rather short (see [22] and references herein).



Another particularity of nitromethane initiation reactivity must be mentioned here: depending upon pressure, its low-temperature thermolysis in the condensed state can follow two reaction mechanisms [30] which have not yet been specified. One mechanism changes into the other [31] at 5 GPa pressure or of at 4 GPa pressure at a temperature higher than 130 °C (the latter mechanism has a negative activation volume [32, 33]). It is known that relationships exist between the kinetic parameters of non-autocatalyzed low-temperature thermolysis of energetic materials and characteristics of their detonation [34, 35]. Therefore, the existence of these two ways of NM thermal decomposition signalizes a possibility that there also exist two different pathways of fission of its molecule during its detonation (i.e., it should have two detonation velocities) – see Schemes (5) and (6). This is in accordance with the mentioned Walker's observation [1].

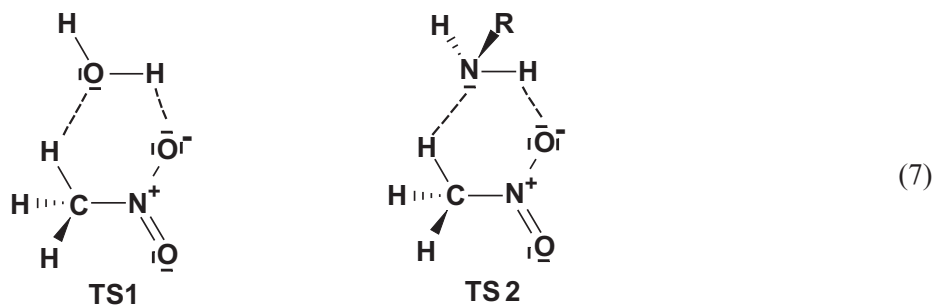


From what has been said so far and from the published papers it is clear that two basic mechanisms of primary fission of NM seem to be acceptable: homolysis of C–NO₂ bond of the neat NM [12, 21, 36] according to Scheme (5) and homolysis of N–OH bond in molecule of *aci*-NM [37] in the sense of Scheme (6). The third, frequently mentioned, type of fission – a unimolecular isomerization and dissociation of NM, was examined theoretically by means of different MO calculations in two papers [38, 39]. In both cases, the isomerization

to methyl nitrite seems to be improbable, the homolysis of C–NO₂ bond being dominant. Also photolytic decomposition of NM starts by homolysis of C–NO₂ bond [12, 40]. Often discussed bimolecular and higher reactions in the initiation of NM are not probable – see the above-mentioned reasons and also the following ones: the IR spectra of gaseous, liquid or solid NM are identical [30]. This experimental finding agrees with a conclusion drawn by Alper *et al.* [41] from the molecular dynamic simulation of NM, *viz.* that the intermolecular interactions in its liquid state are not highly directional and site-specific, as would be expected if strong hydrogen bonding was involved. Li *et al.* [42] found that the hydrogen bond is not preset in the optimized structure of NM dimer. The charge-transfer interaction between NM subsystems is weak and the correlation interaction energy makes a small contribution to the intermolecular interaction energy of the dimer [42].

Analysis of possibility of primary fission pathways

What was a strategy of our approach. We considered the processes in the sense of Schemes (1), (2), (5) and (6) to analyze the likelihood of their occurrence. However, in the case of Scheme (5) we also had to analyze the pathways of formation of *aci*-NM. For this purpose we assumed a conception of very effective catalytic influence of water on the *aci*-NM formation by Kiselev and Gritsan [36] (it should have an experimental ground [8]) and the same influence of amines [43] (see Schemes (7) of corresponding transition states TS1 [36] and TS2);



Also already mentioned, monomolecular formation of the *aci*-NM through four-membered transition state [16] was included in our observation (the corresponding calculation was performed by authors of Ref. [16]).

The calculations of bond dissociation energies $BDE(\text{C-NO}_2)$ and $BDE(\text{N-OH})$

were performed by DFT B3LYP/cc-pVTZ+ method [9, 10]. The calculations by total optimization gave equilibrium geometries of the studied molecules in the gas phase at 0 K. The optimized structures were verified by normal mode frequency analysis to exclude imaginary frequencies for the remaining 3N-6 vibrational degrees of freedom. The respective data are given in Table 1.

The data given in Table 1 allow to scrutinize the fission Schemes (1), (2), (5) and (6). In Scheme (1) the final energy change is 54.98 kJ mol⁻¹ but the ionic dissociation of NM in the first step is characterized by an improbable energy difference of 740.70 kJ mol⁻¹. Similarly, in Scheme (2) the ionic dissociation of NM and methyl amine is again an improbable step due to the energy difference of 579.64 kJ mol⁻¹. Even the second step in Scheme (2), the creation of an anion radical [CH₃-NO₂•]⁻, is a quite endothermic reaction (420.99 kJ mol⁻¹).

The direct homolytic dissociation of NM is described by Scheme (5), and the calculated bond dissociation energy *BDE*(C-NO₂) is 259.19 kJ mol⁻¹. On the other hand, the homolytic dissociation of N-OH bond in *aci*-form of NM, which is given in Scheme (6), is characterized by *BDE*(N-OH) of 203.05 kJ mol⁻¹.

Table 1. DFT calculated total energies of nitromethane dissociation intermediates

Structure	Total energy (a.u.)	Method ^a
Nitromethane	-245.10602	A
	-245.09166	B
Nitromethane <i>aci</i> -form	-245.08508	A
	-245.06918	B
Methylamine	-96.25569	A
	-95.89389	B
Water	-76.45852	B
TS 1	-321.49002	B
TS 2	-340.94648	B
CH ₃ •	-39.85701	A
NO ₂ •	-205.15028	A
HO•	-75.76556	A
CH ₂ =N(O)•	-169.24218	A
[CH ₃ -NO ₂ •] ⁻	-245.11496	A
CH ₂ =NO ₂ •	-244.36097	A
[CH ₃ -NH ₃] ⁺	-96.25569	A
[NO ₂] ⁻	-205.23505	A

^a) Method A: B3LYP/cc-pVTZ+ ; ^a)Method B: B3LYP/6-311++G(d,p)

On the basis of the previous homolytic bond dissociation energy calculations and also findings of Kiselev and Gritsan [36], we have investigated the mechanism of *aci*-form of NM formation again by DFT B3LYP methods. It is obvious from Schemes (7) TS1 [36] and (7) TS2 that hydrogen atom plays an important role in the transition state of tautomerism transformation of nitromethane to *aci*-nitromethane. Thus, a better processing of this system necessitates the application of polarization functions and diffuse functions for the hydrogen atom considered. The 6-311++G (d,p) basis set was used in calculations of the transition state.

It was estimated that the activation barrier for this tautomerism in the presence of water is $151.46 \text{ kJ mol}^{-1}$; on the other hand, the calculated activation energy in the presence of methylamine was $104.60 \text{ kJ mol}^{-1}$. These values are valid for the temperature of 0 K and are corrected for the zero-point energy. The corresponding energy values are presented in Table 1. These calculation results indicate that the conversion of nitromethane to *aci*-nitromethane is feasible in the presence of this admixtures and the effect of methylamine is higher than that of water (the relative energy difference between the two transition states is $46.86 \text{ kJ mol}^{-1}$). The B3LYP/6-311++G (d,p) geometries of proposed TS1 and TS2 transition states are given in Figure 1.

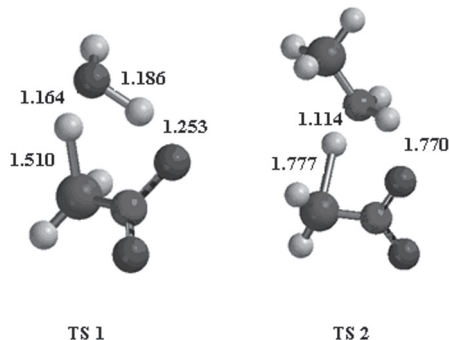


Figure 1. Bond lengths and distances in B3LYP/6-311++G (d,p) optimized structures of TS1 and TS2 transition states (in Å).

Discussion

The homolytic fragmentations or reactions of the C–NO₂, N–NO₂, N–NO, and O–NO₂ groupings, or other bearers of explosibility (i.e. explosophores), are common primary fission processes of energetic materials under thermal, impact, shock and electric spark stimuli [34]. Therefore, it is natural that relationships

exist between characteristics of non-autocatalyzed low-temperature thermal decomposition and impact or electric spark sensitivities and also detonation characteristics of polynitro compounds [34, 35]. The last fact means that the primary fragmentation of polynitro compounds in their detonation transformation should proceed under milder conditions than those present at the front of detonation wave or in its reaction zone [34, 35]. It was already mentioned that two chemical mechanisms of the NM detonation should correspond to the two found mechanisms of its low-temperature thermolysis (see [30, 32]). Primary fission of one of them should proceed in the sense of Scheme (5) (i.e. for neat NM). The second kind of the mechanism is related to Scheme (3) with subsequent fission in the sense of Scheme (6). From the calculated *BDE* energies is obvious that homolytic fission of N–OH bond in nitromethane *aci*-form is more favorable than the fission of C–NO₂. The significant difference of *BDE* energies (56 kJ mol⁻¹) indicates that the reaction rate in the reaction zone of the detonation wave of *aci*-NM detonation will be higher in comparison to detonation of neat NM. This statement corresponds to reality – an increase in detonation parameters [1] and/or decrease in failure diameter [5, 7, 8, 14] of NM owing to a little addition of amines to its charge confirm this fact. A relatively higher (percentage) content of water in NM should have a similar effect [8]. Our analysis also shows that processes in the sense of Schemes (1) and (2) are thermodynamically unfavourable, which means that alkyl ammonium cation formation in the sense of Scheme (2) should not be probable either; hence we should speak about a complex of NM or its *aci*-form with amine (similar to that considered in the case of water [36]).

On the basis of quantum molecular-dynamics simulation of a shocked NM near detonation conditions the formation of *aci*-NM by 1,3-intramolecular hydrogen shift is considered by Reed et al. [45]. They discovered that the wide-bandgap insulator nitromethane undergoes chemical decomposition and a transformation into a semimetallic state for a limited distance behind the detonation front. According to Rice et al. [46] the metallization of explosive due to compression cannot be dismissed as the initiating step in the sequence of reactions leading to detonation. However, physicists of explosion do not take account of metallization [13, 14, 46] because generation of this state during detonation of the conventional explosives is not possible. It is convenient to introduce here that Dremine compares this initiation with initiation of photochemical reaction [13].

Scrutinizing the facts given above the following pathways of the *aci*-NM formation might come into the account during the initiation of NM: either 1,3-intramolecular hydrogen shift or catalytic influence of water and/or amine. Figure 2 presents a mutual comparison of the corresponding reaction coordinates with relevant energies of transition states.

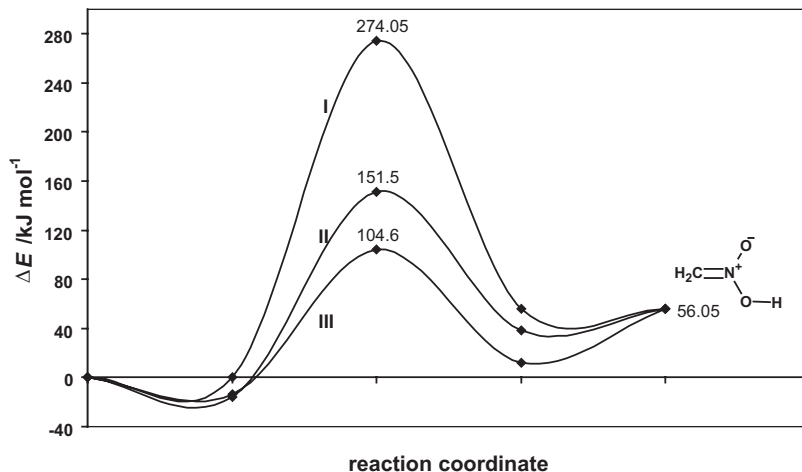


Figure 2. Equilibrium between neat nitromethane and its *aci*-form – a comparison of reaction coordinates for 1,3-intramolecular hydrogen shift (I), water-catalyzed (II) and methylamine-catalyzed (III) tautomerization.

On the basis of NMR spectroscopy it was found [44] that the amount of *aci*-nitro alkane is less than 1% for the neat NM. This amount has no influence on its velocity of detonation. However, increasing of this amount by addition of amine (or water) should lead to increased production of OH radicals during NM initiation. It was already mentioned the amount of this additive has its optimum (ca. 0.05% by wt.) [1]; a higher amount leads to decreasing the velocity of detonation – according to Walker’s results [1] NM with addition of about 0.8% by wt. of DETA detonates with the same velocity as neat NM, which means that the concentration of *aci*-NM does not need to be overly large for a significant increase in reaction rate in the reaction zone of detonation wave; the amount of the *aci*-form in the original NM should be secured by a detonation pressure of about 20 GPa (see data in the Walker’s paper [1]). Also secondary production of the *aci*-NM by increased shock influence in this case cannot be excluded.

Conclusions

It is well known that addition of amines [1, 2, 5, 7, 8, 14] or also of water [8] to nitromethane leads to change of its initiation reactivity. The most

widespread interpretation of this effect (namely failure diameter reduction) on the basis of *aci*-anion $[\text{CH}_2\text{NO}_2]^-$ formation [25] shows to be thermodynamically disadvantageous. Also the 1,3-intramolecular hydrogen shift is a higher barrier process [22, 23]. The acid dissociation of NM is highly endothermic and little dissociation occurs at equilibrium [23]. Similarly, intermolecular hydrogen atom transfer [16, 17-19] by effect of shock on nitromethane should be disadvantageous too, including *aci*-anion formation [27]. It must be repeated here that evidence for an increase in concentration of the anion in neat nitromethane under shock conditions (dynamic high pressure) has been found lacking [28]. With regard to the way of interaction of amines with nitromethane it would be better to speak about a complex of its *aci*-form with this additive (similar to that considered in the case of water [36]). As a result of the performed transition state calculations, admixtures of water or methylamine have important effect on the conversion of nitromethane to *aci*-form; the effect of methylamine is evidently more pronounced. Combination of these findings about transition states with calculated homolytic bond dissociation energies can explain why these admixtures (water and methylamine) change the performance values of nitromethane.

The bimolecular and higher interactions during the initiation of nitromethane (also containing amines) seem to be impossible (the intermolecular interaction in its liquid state are weaker [41, 42]). Experiments with initiation of NM detonation [5, 11, 25] were conducted under conditions in which the secondary termination reactions should be detected (i.e. under conditions of extinguishing detonation) which led to this concept of higher molecularity [35].

On the basis of knowledge about initiation reactivities of energetic materials [34, 35] it can be stated that the existence of two ways of the low-temperature thermal decomposition of nitromethane signalizes a possibility of existence of also two different fission pathways of its molecule during its detonation (i.e. it should have two detonation velocities). Walker's findings [1] confirm it; his results indicate that the primary fragments entering the reaction zone of detonation wave in the case of neat nitromethane are different from those in the case of nitromethane sensitized by addition of amines [35]. Two favorable primary mechanisms of fission in the nitromethane initiation and development of its detonation should be taken into account: homolysis of C–NO₂ bond in the neat compound and homolysis of N–OH bond in its *aci*-form. The second mentioned pathway is thermodynamically preferable and consequently the detonation wave in NM with admixture of amine and/or water substantially reduces the reaction zone length in comparison with the neat NM detonation.

Acknowledgements

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