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Computational Chemistry Investigation

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Preface

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Catalytic role of solvated electron in the spontaneous degradation of insensitive munition compounds: Computational chemistry investigation

Abstract

The DNAN (2,4-dinitroanisole), NTO (3-nitro-1,2,4-triazol-5-one), and NQ (nitroguanidine) are important insensitive energetic materials used in military applications. They may find their way to the environment during manufacturing, transportation, storage, training, and disposal. A detailed investigation of possible mechanisms for self-degradation of radical anions formed by addition of solvated electron to DNAN, NTO, and NQ species was performed by computational study using the PCM(Pauling)/M06-2X/6-311++G(d,p) approach. Obtained results suggest that only NQ radical anion is able for self-degradation by elimination of nitrite anion. Formation of urea radical on the earlier stage of the NQ radical anion degradation was also predicted.

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Introduction

Manufacturing, transportation, and storage of traditional munition compounds are challenging due to their sensitivity towards external stimuli such as temperature, pressure, and shock, which can result in an unplanned detonation. To avoid unintentional detonations, a new class of munition compounds known as insensitive munitions (IMs) are currently being developed. Examples of some of the IM compounds are 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO), and nitroguanidine (NQ) [1]. Production, storage, transportation, and application of IMs may lead to their way in the environment. For example, use of IMs in Army training ranges can find their way in the soils and water bodies. Therefore, it is not surprising that detailed environmental fate, transport, and effects of these molecules are continued to be under investigation [2]. Moreover, due to high solubility of NQ (5000 mg/L) [3] and NTO (16,642 mg/L) [4] compared to DNAN (276 mg/L)[5] in water, it is expected that NQ and NTO would be more prevalent in water bodies than on the soil surface.

In the environment, residues of munitions undergo biotic or abiotic degradation caused by soil microorganisms and plants or hydrolysis and photolysis [6–8]. Some studies have suggested the photosensitive nature of these compounds when left exposed to solar or simulated solar radiation [9]. The degradation rate constants of DNAN, NQ, and NTO during photolysis have been reported to be 0.262, 1.181, and 0.349 d⁻¹, respectively [6]. Photo-oxidation has been found to be the dominant mechanism for DNAN photo-transformation [7, 8]. The major reaction intermediates and products identified during

both sunlight and UV photolysis of DNAN in different environments were nitrite (NO_2^-), nitrate (NO_3^-), and minor amounts of deprotonated 2,4-dinitrophenol [7], 2-methoxy-5-nitroaniline, and 4-methoxy-3-nitrophenol [8]. The photolysis of DNAN is expected to take place in photo-excited triplet state that undergoes photo-substitution ($\text{S}_{\text{N}}2\text{Ar}^*$ type) by OH^- to form phenolic products [9]. DNAN, NQ, and NTO, irradiated with 350-nm UV light, demonstrated some photo-degradation products such as dinitrophenol (from DNAN), guanidine (from NQ), and 1,2,4-triazol-3,5-dione (from NTO) [6]. NTO transforms to 1,2,4-triazol-5-one and urazole under X-ray radiation [10]. NTO photo-transformation was enhanced in acidic and basic solutions [2]. It has also been shown that under acidic conditions, NTO and DNAN degrade in the presence of iron/copper bimetal particles [11]. Urea was identified as a degradation product of NTO, and para- and ortho-aminonitroanisole as products for DNAN degradation [11]. The loss of nitroguanidine in the aqueous environment is dominated by photolysis, with half-lives ranging from 1.6 days in the summer to 3.9 days in the winter [12]. The nitroguanidine is initially photolyzed to nitrite and hydroxyguanidine; nitrite is photochemically converted to nitrate [13]. Laboratory studies of the UV photolysis of nitroguanidine showed the products to be primarily guanidine, urea, and nitrite, with lesser quantities of cyanoguanidine, ammonia, and nitrate [14, 15].

There are other reactive species such as solvated electron, which can also cause degradation of IM compounds in the aqueous environment and needs to be investigated. Under environmentally relevant conditions, the reductive transformation of nitrocompounds may take place due to presence of different species that can easily give an electron forming radical anionic species of munition compounds and that may lead to their spontaneous degradation. The reduction of nitrogroup of aromatic compounds in acidic solution can give nitroso-, hydroxylamino-, and amino-compounds [16]. The same result is observed in case of reduction by nitroreductase [17]. Earlier, some of us studied mechanism of reduction of some nitrocompounds to nitrosocompounds by *flavin mononucleotide* (FMN) [18]. Calculations showed that reduction of nitro group to nitroso group in 2,4-dinitroanisole (DNAN), 2,4-dinitrotoluene (DNT), trinitrotoluene (TNT), 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO), and 5-amino-3-nitro-1H-1,2,4-triazole (ANTA) is thermodynamically feasible with 56–59 kcal/mol Gibbs free energy release [18]. The activation barrier for these reactions is 3.63–14.79 kcal/mol. Calculated thermodynamics of the reduction of nitro group to nitroso group suggests consecutive four-step process (electron–proton–electron–proton transfer) where the first proton comes from solution, while the second one from FMN.

In the present work, we have investigated the catalytic role of solvated electron in the spontaneous degradation of IM compounds using density functional theory (DFT) level

approach. It was predicted that DNAN and NTO radical anion are stable for self-degradation and specific conditions like acidic or alkaline medium, high temperature, UV/vis irradiation, and other reactive species would be necessary to facilitate degradation of these compounds' radical anion in the water solution. On the other hand, NQ radical anion is susceptible to self-degradation through the elimination of nitrite anion and formation of urea radical.

Computational methods

All calculations were performed using the Gaussian 09 suite of programs [19]. The M06-2X functional of the DFT was chosen for the study because it was recommended for applications involving thermochemistry, kinetics, and noncovalent interactions on the basis of assessment of its performance over broad amounts of data [20]. Its estimated mean unsigned error, which includes the averages of the absolute deviations of calculated values from database reference values, is about 1.3 kcal/mol.

The influence of bulk water has been simulated within PCM approach [21]. Our earlier study of different solvation models for the alkaline hydrolysis of nitroaromatic compounds and comparison of obtained results with experimental data suggests selecting PCM model in a combination with Pauling radii as a reliable approach for the present study [22]. The relevant stationary points (intermediates, transition states, and products) in aqueous solution were fully optimized at the PCM(Pauling)/M06-2X/6-311++G(d,p) level [20, 21, 23]. Since our computational analysis is based on the values of Gibbs free energy, stationary points were further characterized by calculation of the analytic harmonic vibrational frequencies at the same theory level as geometry optimization.

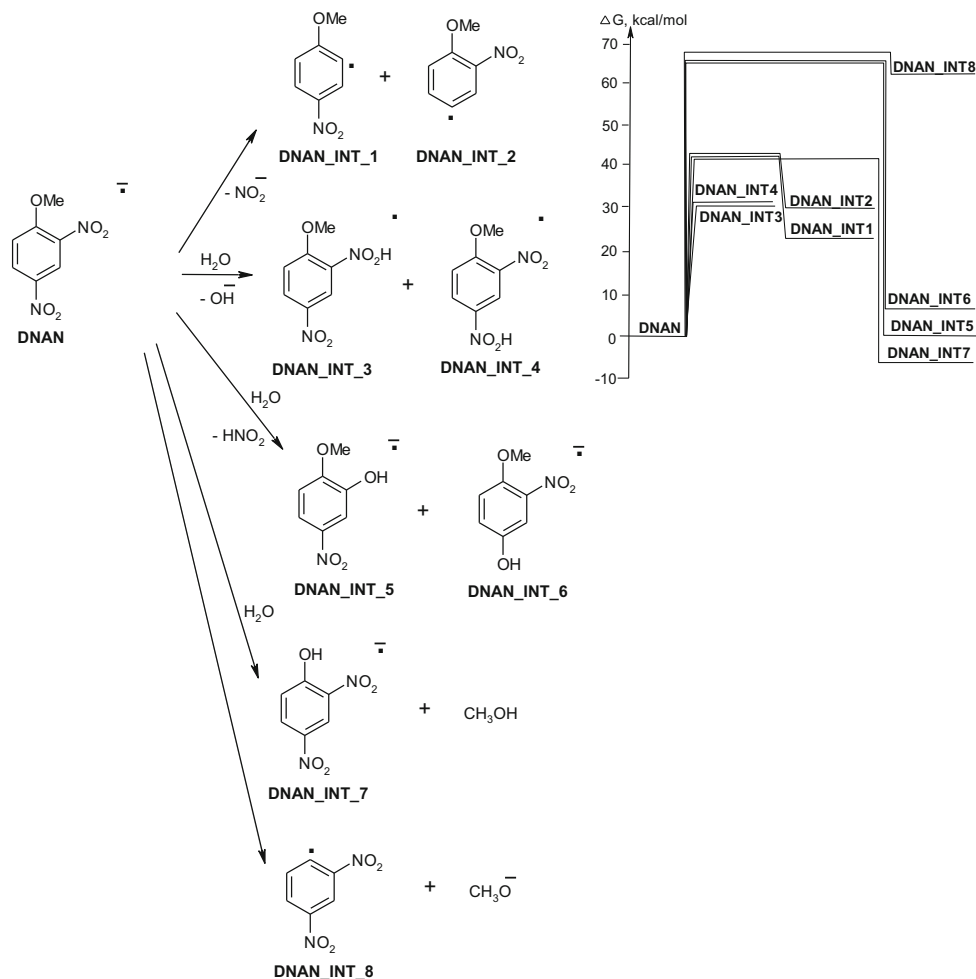
Results and discussion

Reduction of 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO), and nitroguanidine (NQ) leads to formation of radical anions of these nitrocompounds. Different pathways for further decomposition of radical anions were examined to evaluate the possibility of their self-degradation in aqueous solution.

DNAN

Detailed scheme following various paths of radical anion transformation is provided in Fig. 1 along with Gibbs free energy diagrams. Values for activation Gibbs free energy and Gibbs free energy of reaction are listed in Table 1. Elimination of nitrite, attaching of proton from water molecule, and substitution of nitrogroup by hydroxyl were

Fig. 1 Computationally predicted pathways of DNAN radical anion self-degradation in aqueous solution along with the corresponding Gibbs free energy diagrams



examined. Obtained result show that radical anion of DNAN cannot be easily degraded in an aqueous solution. Nitrite anion elimination requires more than 40 kcal/mol of activation energy, and leads to unstable radicals DNAN_INT_1 and DNAN_INT_2 which are 22 and 28 kcal/mol, respectively, less stable than the initial DNAN radical anion.

Attaching proton from water molecules occurs without energy barrier; however, this leads to the formation of

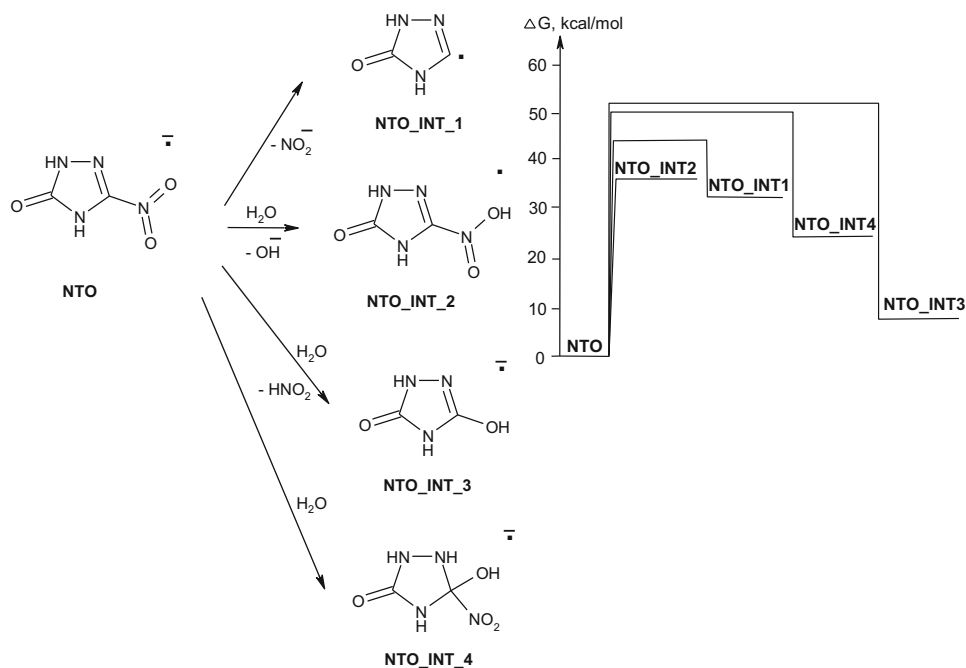
DNAN_INT_3 and DNAN_INT_4 radicals which are 28 and 30 kcal/mol less stable than the initial DNAN radical anion. Substitution of nitro group by hydroxyl group from water molecule requires more than 60 kcal/mol activation energy.

Decomposition of DNAN radical anion through the elimination of methoxy anion will also not proceed due to the presence of high activation energy of 67.02 kcal/mol. However,

Table 1 Activation Gibbs free energy and Gibbs free energy of reaction for self-degradation of DNAN anion radical in aqueous solution

Reaction	Activation Gibbs free energy, kcal/mol	Gibbs free energy of reaction, kcal/mol
DNAN → DNAN_INT_1 + NO ₂ ⁻	42.19	21.88
DNAN → DNAN_INT_2 + NO ₂ ⁻	43.12	28.07
DNAN + H ₂ O → DNAN_INT_3 + OH ⁻	–	27.85
DNAN + H ₂ O → DNAN_INT_4 + OH ⁻	–	29.68
DNAN + H ₂ O → DNAN_INT_5 + HNO ₂	62.15	-2.77
DNAN + H ₂ O → DNAN_INT_6 + HNO ₂	69.27	4.61
DNAN + H ₂ O → DNAN_INT_7 + CH ₃ OH	41.53	-7.84
DNAN → DNAN_INT_8 + CH ₃ O ⁻	67.02	60.78

Fig. 2 Computationally predicted pathways of NTO radical anion self-degradation in aqueous solution along with the corresponding Gibbs free energy diagrams



substitution of methoxy group by hydroxyl has smaller energy barrier (41.53 kcal/mol) and leads to more stable 2,4-dinitrophenole radical anion DNAN_INT_7.

Based on the obtained results, one may predict that none of these pathways for DNAN radical anion degradation is energetically favorable. The smallest energy barrier is predicted for formation of 2,4-dinitrophenole radical anion; however, it is still high (41.53 kcal/mol). Thus, transformation of DNAN radical anion in aqueous solution requires specific conditions. Those may include photo-irradiation and presence of strong reductants or oxidants.

NTO

Scheme for different pathways of radical anion transformation of NTO is provided in Fig. 2 along with Gibbs free energy diagrams. Values for activation Gibbs free energy and Gibbs free energy of reaction are listed in Table 2. Behavior of NTO radical anion is similar to DNAN radical anion. Nitrite anion elimination requires more than 41 kcal/mol activation energy and leads to unstable radical NTO_INT_1. This radical is

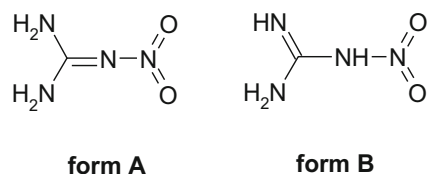
32 kcal/mol less stable than the initial NTO radical anion. Barrierless attachment of proton from water molecule to nitrogroup of NTO radical anion leads to radical NTO_INT_2 which is 34 kcal/mol less stable than the NTO radical anion. More than 50 kcal/mol are required for substitution of nitro group by hydroxyl group from water molecule or for addition of water molecule to C=N double bond of NTO radical anion. Similar to above conclusions regarding degradation of DNAN radical anion, we predict that the considered degradation pathways would not materialized due to high activation energies and formation of very unstable products.

NQ

Nitroguanidine is a nitroimino compound that exists in two tautomeric forms A and B in aqueous solutions (Scheme 1). Form A predominates in acidic, neutral, or slightly basic media. According to our calculation, form A is 18.44 kcal/mol more stable than form B in aqueous solution. Therefore, form A was selected for further investigation.

Table 2 Activation Gibbs free energy and Gibbs free energy of reaction for self-degradation of NTO anion radical in aqueous solution

Reaction	Activation Gibbs free energy, kcal/mol	Gibbs free energy of reaction, kcal/mol
$\text{NTO} \rightarrow \text{NTO_INT_1} + \text{NO}_2^-$	40.77	32.03
$\text{NTO} + \text{H}_2\text{O} \rightarrow \text{NTO_INT_2} + \text{OH}^-$	–	34.08
$\text{NTO} + \text{H}_2\text{O} \rightarrow \text{NTO_INT_3} + \text{HNO}_2$	52.39	6.05
$\text{NTO} + \text{H}_2\text{O} \rightarrow \text{NTO_INT_4}$	50.86	22.98



Scheme 1 Nitroguanidine in two tautomeric forms A and B in aqueous solutions

Scheme for different mechanistic pathways of NQ radical anion transformation is provided in Fig. 3 along with Gibbs free energy diagrams. Values for activation Gibbs free energy and Gibbs free energy of reaction are listed in Table 3. One can see that elimination of nitrite anion from NQ radical anion is energetically favorable process with Gibbs free energy barrier of 16.67 kcal/mol that leads to the formation of radical NQ_INT_1. This radical is 6.90 kcal/mol more stable than the initial NQ radical anion, while barrierless proton attachment

leads to radicals NQ_INT_2 and NQ_INT_3, which are more than 24 kcal/mol less stable than NQ radical anion. Addition of water molecule to C=N double bond of NQ radical anion requires 37.19 kcal/mol activation energy and leads to unstable NQ_INT_4 radical anion. Thus, according to our calculation, degradation of NQ radical anion in aqueous solution may occur by elimination of nitrite anion and formation of guanidine radical NQ_INT_1.

Further transformation of NQ_INT_1 may occur by addition of water molecule to C=N double bond with the formation of unstable radical NQ_INT_5, which readily decomposes through elimination of ammonia and formation of stable urea radical NQ_INT_6. However, addition of water molecule to NQ_INT_1 requires high activation energy of 34.80 kcal/mol; therefore, it is not likely to take place. Another pathway for NQ_INT_1 decomposition is elimination of ammonia. This process has smaller activation energy of 31.87 kcal/

Fig. 3 Computationally predicted pathways of NQ radical anion self-degradation in aqueous solution along with the corresponding Gibbs free energy diagrams

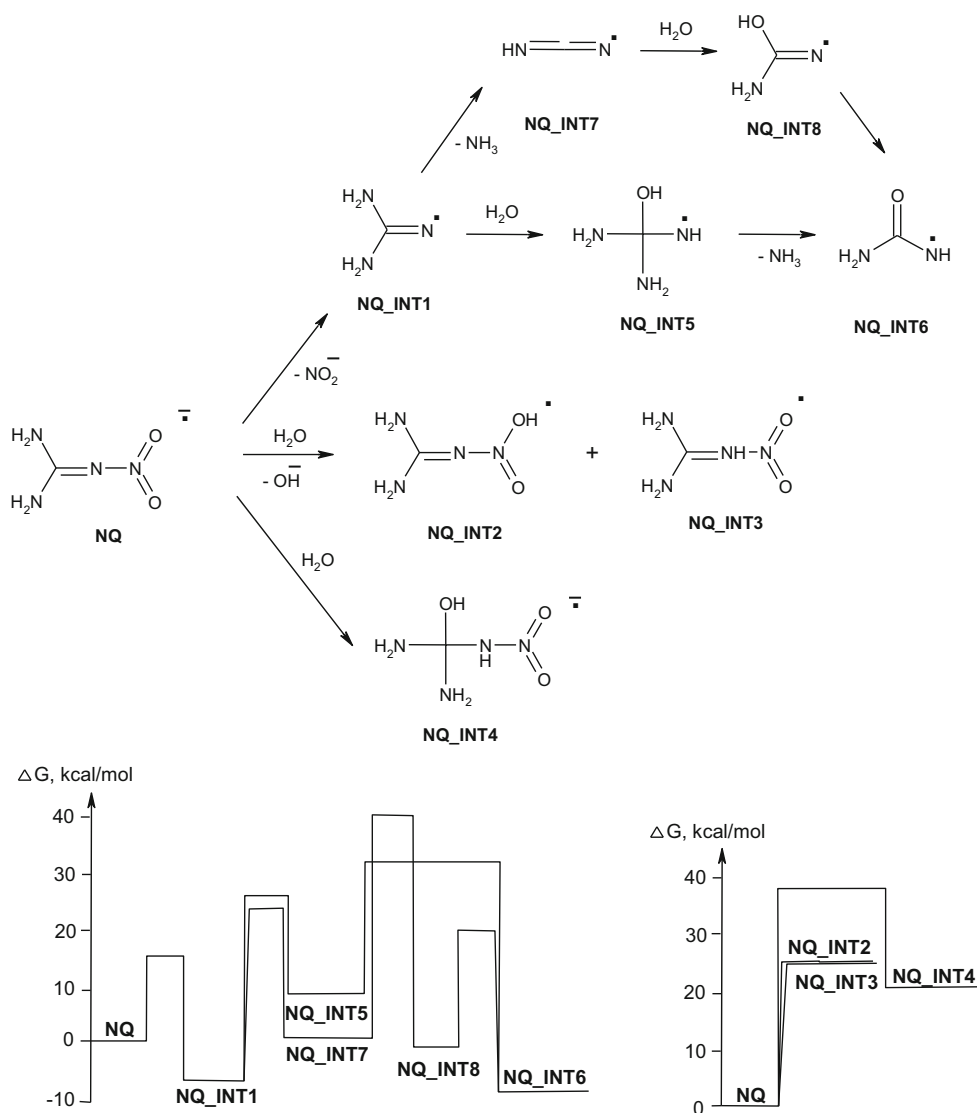


Table 3 Activation Gibbs free energy and Gibbs free energy of reaction for self-degradation of NQ anion radical in aqueous solution

Reaction	Activation Gibbs free energy, kcal/mol	Gibbs free energy of reaction, kcal/mol
$\text{NQ} \rightarrow \text{NQ_INT_1} + \text{NO}_2^-$	16.67	-6.90
$\text{NQ} + \text{H}_2\text{O} \rightarrow \text{NQ_INT_2} + \text{OH}^-$	-	24.75
$\text{NQ} + \text{H}_2\text{O} \rightarrow \text{NQ_INT_3} + \text{OH}^-$	-	24.17
$\text{NQ} + \text{H}_2\text{O} \rightarrow \text{NQ_INT_4}$	37.19	20.60
$\text{NQ_INT_1} + \text{H}_2\text{O} \rightarrow \text{NQ_INT_5}$	34.80	19.90
$\text{NQ_INT_5} \rightarrow \text{NQ_INT_6} + \text{NH}_3$	18.17	-23.58
$\text{NQ_INT_1} \rightarrow \text{NQ_INT_7} + \text{NH}_3$	31.87	4.97
$\text{NQ_INT_7} + \text{H}_2\text{O} \rightarrow \text{NQ_INT_8}$	42.83	-4.00
$\text{NQ_INT_8} \rightarrow \text{NQ_INT_6}$	21.14	-9.21

mol, but leads to unstable radical NQ_INT_7, whose further hydrolysis requires 42.83 kcal/mol activation energy. Based on obtained data, it is expected that degradation of guanidine radical NQ_INT_1 is unlikely without the presence of other reactive species and therefore it would represent very slow process. Possible pathways to increase rate for this process are variations of pH and temperature, irradiation, and presence of strong oxidants or reductants.

Conclusions

Different possible mechanistic pathways were investigated for self-degradation of radical anions formed by addition of solvated electron to DNAN, NTO, and NQ species. These pathways represent elimination of nitrite anion, attachment of proton from water molecule, substitution of nitrogroup by hydroxyl, and addition of water molecule to C=N double bond. Activation energies for such reactions were determined to shed light on possibility of such degradation. This investigation was limited to the initial steps. We predict that only NQ radical anion would enable degradation through elimination of nitrite anion. Formation of urea radical on the earlier stage of the NQ radical anion degradation was also predicted. Our calculation suggests that specific conditions such as change in pH, high temperature, UV/vis irradiation, and other reactive species would be necessary to facilitate degradation of DNAN and NTO radical anions in aqueous solution.

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Authors' contribution All authors (Liudmyla K. Sviatenko, Leonid Gorb, Danuta Leszczynska, Sergiy I. Okovytyy, Manoj K. Shukla, and Jerzy Leszczynski) made substantial contribution.

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Compliance with ethical standards

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14. ABSTRACT The DNAN (2,4-dinitroanisole), NTO (3-nitro-1,2,4-triazol-5-one), and NQ (nitroguanidine) are important insensitive energetic materials used in military applications. They may find their way to the environment during manufacturing, transportation, storage, training, and disposal. A detailed investigation of possible mechanisms for self-degradation of radical-anions formed by addition of solvated electron to DNAN, NTO, and NQ species was performed by computational study using the PCM(Pauling)/M06-2X/6-311++G(d,p) approach. Obtained results suggest that only NQ radical-anion is able for self-degradation by elimination of nitrite anion. Formation of urea radical on the earlier stage of the NQ radical-anion degradation was also predicted.					
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