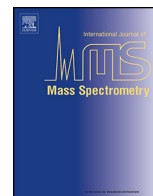




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Exploration of decomposition pathways of 2,4,6-trinitrotoluene (TNT) radical ions by means of density functional theory

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ABSTRACT

Methods of mass spectrometry are widely used for effective detection and identification of explosives and high density energy materials. During last decade mass spectrum of most popular explosives such as PETN, HMX, RDX and TNT have been obtained and carefully inspected. Nevertheless, the reactivity of ionized nitro compounds and the mechanisms of their fragmentation are still to be understood. Inspired by the work of Sulzer et al. [23] on fragmentation of TNT under dissociative electron attachment, we carried out theoretical exploration of unimolecular decomposition of TNT radical ions. It was found that elimination of hydroxyl is the predominant fragmentation channel for both positively and negatively ionized TNT molecules, whereas in general decomposition of TNT radical ions involves complex stepwise processes.

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1. Introduction

Increased threats of terrorist attacks arouse public interest in the fast real-time detection and the development of highly sensitive detection techniques. Careful inspection of the literature points toward two main methods, which can be employed for effective detection and identification of explosives. The first method is based on variation in luminescence or fluorescence of the sensing media [1–11], whereas the second involves wide variety of the methods of mass spectrometry [12–15]. The ability of nitro containing molecules easily trap extra electron and form negatively charged ions is taken into consideration in corona discharge [16], glow discharge [17,18] electrospray ionization [19], and electron attachment [20–25] techniques. Results of recent experimental study [26] clearly demonstrates ability of electron attachment to effectively trace and distinguish different isomeric forms of nitrotoluene. Moreover, low-energy electrons have the ability to selectively break specific bonds in complex molecules [27–30]. Nevertheless, despite numerous experimental studies, our knowledge on mechanisms and kinetics of fragmentation of ionized nitro compounds is still scarce and only reaction energies of simple reaction steps are usually reported (see for example Refs. [20–22,31]). It is not surprising, especially taking into consideration complexity

of fragmentation mechanisms of the charged molecules compared to their neutral ground state counterparts [32].

We carried out the present theoretical study with the purpose of studying the mechanism of fragmentation pathways of the radical ions of TNT. TNT is well-known explosive material and is often used in military and industrial applications owing to its relatively low sensitivity and attractive thermal stability. Wide range of application of TNT as explosive together with its toxicity emerges concerns covering environmental and security issues and, hence, reliable detection techniques able to trace negligible amount of this hazardous material are of great demand.

Results of desorption electrospray ionization [13] and electron attachment [21,24] studies point toward two main fragmentation pathways of TNT radical anion which involve formation of ions m/z 210 and m/z 197 and proceed via elimination of OH and NO radicals, respectively. On the other hand SPI TOF-MS (Single Photon Laser Ionization Time-of-Flight Mass Spectrometry) spectrum of TNT consists of the parent peak at m/z 227 and the $(M-OH)^+$ product ion at m/z 210 [14] which demonstrates that loss of hydroxyl radical will be predominant decomposition channel also for TNT radical cation.

From our point of view, results of present work will be undoubtedly useful for interpretation of mass spectrum and also for understanding reactivity of ionized nitro compounds. Moreover, decomposition behavior of charged nitro molecules is of great interest in the light of recent papers which discuss effect of polar surfaces on stability of molecular materials [33,34] and laser

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induced decomposition of explosive on inorganic–organic interfaces [35].

2. Theory/calculation

Fragmentation pathways of TNT radical ions were studied within density functional theory (DFT) [36,37] with M06 [38] functional as implemented in the Gaussian 09 package [39]. All calculations were performed by using valence split double-zeta 6-31+G(2df,p) basis set. According to results of previous theoretical studies, DFT levels of theory can be successfully used for exploration of isomerization and fragmentation channels of ionized organic molecules [40–44]. Furthermore, DFT calculations do not usually suffer from consequences of spin contamination [45–48] which is very often the case for ab initio post-HF methods (see, for example [49] and references therein). Nevertheless, we checked the $\langle S^2 \rangle$ values not to exceed ideal $S(S+1)$ counterpart by more than 10%.

Transition states structures for reactions with well-defined saddle points were localized using Berny algorithm and were positively identified with one imaginary frequency. IRC analysis was carried for each transition state to make sure that the transition state connects desired reactants and products. All IRC calculations were performed using the Hessian-based predictor–corrector integrator algorithm [50,51].

3. Results and discussion

The content of the manuscript is arranged in the following manner. Geometry and electronic structures of neutral ground state and ionized TNT molecules are discussed in Section 3.1. Discussion of decomposition pathways of negatively and positively ionized TNT molecules are performed in Sections 3.2 and 3.3, respectively. Since fragmentation of TNT radical ions is complex multi-stage process, we decided to include in the text of present manuscript only geometry structures of initial reagents and only those intermediates, which are of the most interest. In addition we compiled Cartesian coordinates of all structures involved in fragmentation of TNT radical ions including structures of transition states in [Supplementary Information](#).

3.1. Geometry and electronic structures of TNT radical ions

TNT belongs to the wide class of nitroaromatics. Equilibrium geometry structure of neutral ground state TNT molecule is depicted in [Fig. 1a](#). Highest occupied molecular orbital (HOMO) is predominantly formed from $2p_z$ atomic functions of aromatic ring carbon and oxygen atoms ([Fig. 2a](#)). Lowest unoccupied molecular orbital (LUMO) lies 5.53 eV above HOMO and mainly formed from $2p_z$ atomic functions of nitrogen and oxygen atoms of nitro groups and carbon atoms of aromatic ring ([Fig. 2b](#)).

Attachment of extra electron causes negligible changes of molecular geometry. Equilibrium structure of TNT radical anion ([Fig. 1b](#)) has slightly shortened C–N and elongated N–O and C4–C7 bond distances compared to neutral molecule ([Fig. 1a](#)). Calculated electron affinity of TNT is 2.31 eV ([Table 1](#)), which means that trapping of electron by molecule is energetically favorable process. It should be noted that TNT has significantly higher electron affinity among other well-known nitro molecules such as FOX-7 (0.76 eV) [52], RDX (0.9 eV) [53], HMX (1.4 eV) [53], PETN (1.7 eV) [53], and TATB (1.3 eV) [53] and close to electron affinity of novel high density energy material, BNFF, (2.3 eV) [53]. Inspection of the coefficients of the highest singly occupied α -spin molecular orbital, corresponding to electron component of TNT anion radical, indicates large contribution of $2p_z$ atomic functions from nitrogen and oxygen

Table 1
Calculated electron affinities (EA) and ionization potentials (IP).

Compound	EA (eV)	IP (eV)
C ₇ H ₅ N ₃ O ₆ (TNT)	2.31	10.43 (10.59) ^c
C ₇ H ₅ N ₂ O ₄ [*]	2.52	9.08
NO ₂ [*]	2.26 (2.27) ^{a,b}	9.50 (9.60) ^d

^a Experimental values are shown in parentheses.

^b Experimental was taken from [55,56].

^c Experimental value taken from [54].

^d Experimental value was taken from [57,58].

atoms of nitro groups and carbon atoms of aromatic ring ([Fig. 2c](#)) similar to LUMO of neutral molecule.

Ionization of the molecule is usually energetically highly unfavorable process. Calculated adiabatic ionization potential (IP) of TNT is 10.43 eV ([Table 1](#)), which is in good agreement with experimental estimation of 10.59 eV [54]. Removing of electron from TNT molecule does not have any noticeable effect on molecular structure as one can see from [Fig. 1a](#) and [c](#).

3.2. Fragmentation of TNT radical anion

3.2.1. Cleavage of C–NO₂ bond

We began our theoretical study with modeling of homolytic (**A1–A2**, [Scheme 1](#)) and heterolytic (**A1–A3**, [Scheme 1](#)) cleavage of C–N bond ([Scheme 1](#)) in TNT radical anion. Our calculations showed that former channel requires by ~6 kcal/mol lower energy than the latter process. Advantage of homolytic bond cleavage over heterolytic can be explained through inspection of the calculated electron affinities of NO₂^{*} and C₇H₅N₂O₄^{*} radical moieties ([Table 1](#)). As one can see from [Table 1](#), NO₂ has slightly lower electron affinity than C₇H₅N₂O₄^{*}. Therefore, we are in right to assume that extra electron of TNT radical anion will remain with higher probability on the C₇H₅N₂O₄ moiety during C–N bond cleavage rather than on NO₂ group.

3.2.2. Formation of anion *m/z* 210 via hydroxyl loss

Formation of ion *m/z* 210 via hydroxyl loss happened to be complex multi-step reaction ([Scheme 2](#)). The first step (**A1–A4**, [Scheme 2](#)) involves formation of aci-isomer of TNT radical anion and requires 26.5 kcal/mol. Aci-isomer **A4** lies 17.8 kcal/mol above **A1**, and undergoes series of subsequent conformational transitions **A4–A5** and **A5–A6** with activation barriers as low as 3 and 5 kcal/mol, respectively. Elimination of OH radical from aci-isomer **A6** (**A6–A7**, [Scheme 2](#)) requires 21.5 kcal/mol. Alternative pathway of OH loss (**A5–A8**, [Scheme 2](#)) is more demanding process and requires 31.1 kcal/mol.

We additionally studied fragmentation pathway of TNT radical anion proceeding via elimination of hydroxyl radical from *para*-aci-form **A10** ([Scheme 3](#)). According to our calculations, this reaction demands significantly higher energy (72.4 kcal/mol) than OH elimination from *ortho*-aci-isomers **A6** (37.2 kcal/mol, [Scheme 3](#)) and **A5** (49.2 kcal/mol, [Scheme 3](#)).

3.2.3. Formation of anion *m/z* 197 via loss of nitric oxide

Elimination of nitric oxide (NO) from neutral ground state [59–61] and optically excited [62,63] nitro compounds is a step-wise process which usually involves two main steps: (1) formation of nitrite isomer via pseudo rotation of nitro group (nitro-nitrite isomerization) and (2) subsequent NO elimination. The primary step is usually considered as the rate limiting step, whereas NO loss demands always significantly lower energy [64,65]. According to theoretical investigations [66,67] elimination of NO radical from molecular ions of 1-nitropropane and nitromethane does not require nitro-nitrite rearrangement on the first step and proceeds via completely different mechanisms.

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