**ORIGINAL RESEARCH**

# Density functional theory investigation on the degradation mechanisms of 3-nitro-1,2,4-triazol-5-one (NTO) in water

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**Abstract**

The degradation mechanisms of 3-nitro-1,2,4-triazol-5-one (NTO) in the bulk water were explored at the density functional theory (DFT) level using the M06-2X functional and the 6-311G(d,p) basis set; the effect of bulk water solution was considered using the conductor-like polarizable continuum model (CPCM) approach. The initial dissociation step of NTO may be triggered by UV light, radicals, and heat. Our computed results suggest that radical-induced reactions should be suitable for the initial degradation of NTO in water. The follow-up further degradation illustrated that the product fragments may include urazole, NO, $NO_2$, HONO, $CO_2$, di-imide, and $N_2$. It was revealed that hydroxide ions can accelerate the degradation of NTO in water.

**Keywords** NTO · Degradation mechanism · Urazole · CPCM · Urea

## Introduction

The 5-nitro-1,2-dihydro-1,2,4-triazol-3-one or 3-nitro-1,2,4-triazol-5-one (NTO) is an insensitive energetic material which was first reported in 1905 [1] and was first studied by Lee et al. [2] as an explosive. NTO is thermally stable as a pure ingredient and is a potential insensitive explosive ingredient in insensitive explosive formulations [3]. NTO can form amine and metal salts, which have potential to be used in propulsion systems as an energetic combustion catalyst and for primary and secondary explosives [3]. NTO can be reduced to their amine derivatives by microbial isolates [3–6]. It can be decomposed by X-ray, UV, laser, and photochemical irradiation [7, 8]. Oxley et al. [9] explored the thermal decomposition on NTO and NTO/TNT system. Thermal decomposition of NTO undergoes through C-N homolysis either by direct scission of $C-NO_2$ bond, especially at high temperature, or by initial transfer of hydrogen and subsequent $C-NO_2H$ cleavage. At low temperatures, the rate-determining step in NTO thermolysis is related to hydrogen transfer to the nitro group followed by subsequent loss of HONO. It has also been suggested that triazol (TO) is not an intermediate in the principal NTO decomposition pathway [9]. In the presence of iron/copper (Fe-Cu) bimetal particles, a nitro-to-amino pathway that may lead to partial mineralization of NTO is proposed and aminotriazolone was detected [10]. Heating the crystal of $[Pb(NTO)_2 \cdot (H_2O)]$, the ligand water is dissociated first and $NO_2$ group is favored to leave [11]. Three types of intramolecular proton migration and the direct scission of $C-NO_2$ were proposed to be the initial steps for the unimolecular decomposition of NTO, and radical induced $C-NO_2$ scission was considered to be the dominant path at higher temperatures [12]. Theoretical studies suggested several proposed initial decomposition mechanisms of NTO, and the $C-NO_2$ bond homolysis was proposed to be the most probable initial step for unimolecular decomposition of NTO [13].

Density functional theory with dispersion-correction (DFT-D) was applied to investigate the effects of vacancy and pressure on the structure and initial decomposition of crystalline 5-nitro-2,4-dihydro-3H-1,2,4-trazole-3-one (beta-NTO) [14]. Initial decomposition process of NTO dimer was found to have a potential energy barrier of 87.8 kcal/mol at B3LYP/6-31G(d,p) level to be decomposed to form $CO_2$. The reaction of NTO dimer formed nitroso-TO, $CO_2$, $N_2$, HONO, and HCN in that order, and $CO_2$ is produced through a cluster of NTO in the gas phase [15]. The ab initio molecular dynamics method was used to explore a priori elucidation of the mechanism in unimolecular decomposition of NTO. The

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results demonstrated that C-NO$_2$ homolysis is the dominant channel at high temperatures. At lower temperature, the dissociation channels initiated by hydrogen migrations would be activated first and followed by ring opening and HONO loss. The NTO ring could also be ruptured in the two C-N bonds connected to the carbonyl carbon [16].

The lase-induced decomposition of a solid sample of NTO shows that the early unimolecular reactions include loss of NO$_2$ and nitro-nitrite rearrangement followed by loss of NO [17]. To determine the early stages of thermal decomposition of NTO under rapid heating conditions, thin films of NTO were treated by a pulsed infrared laser. The first observed product of the decomposition is CO$_2$ and no proof was found for formation of NO$_2$ or HONO. It shows that the CO$_2$ reaction product is formed by bimolecular oxygenation of the carbonyl group by the nitro group of an adjacent NTO molecule, which is contrasted with proposed mechanisms based upon slow heating experiments [18]. The mineralization of $^{14}$C-labelled NTO was monitored by the remediation method based upon photochemical decomposition and Fenton oxidation of NTO. No significant photo-degradation of NTO was detected in the absence of the catalyst [19]. Laser ionization mass spectrometry was used to detect the degradation fragments of NTO. It is proposed that the degradation is dominated by nitro-nitrite rearrangement and NO loss as the shear-induced decomposition [20]. Electron paramagnetic resonance spectroscopy (EPR) and high-performance liquid chromatography (HPLC) were used to detect the decomposition of neat NTO and mixed systems containing NTO in acetone and NTO in TNT through thermochemical and photochemical conditions. Neat thermochemical decomposition of NTO involves a solid-phase global auto-catalytic reaction scheme, which both initiation and propagation reactions contribute to the overall loss of the starting material of NTO. Both room-temperature photochemical decomposition of NTO and higher temperature (370 K) thermochemical decompositions show the NTO nitro group/hydrogen abstraction reactions and the nitrogen-hydrogen bond cleavage plays an important role in the loss of NTO [21].

There are different pathways proposed for the mechanisms of the initial degradation steps of NTO. Photolysis, radicals, or thermo-chemical processes may decompose NTO. To further understand the initial steps and the follow-up pathways for NTO degradation in water at room temperature, theoretical calculations at the M06-2X/6-311G(d,p) level with CPCM model were performed to illustrate the detailed mechanisms of the NTO degradation in the present work. Computed results show that the degradation fragments of NTO may include urazole, NO, NO$_2$, HONO, CO$_2$, di-imide, and N$_2$.

## Computational methods

Minnesota density functional M06-2X [22] was applied in exploring the pathways for the NTO decomposition with the standard 6-311G(d,p) basis set [23, 24]. The force constants were determined analytically in the analysis of harmonic vibrational frequencies for all of the complexes. An intrinsic reaction coordinate (IRC) analysis was carried out to ensure that each transition state links to the corresponding reactants and products (both as local minima on the potential energy surface). Thus, the mechanisms of the thermal chemical processes of the decomposition of the corresponding compounds are detailed to every elementary reaction steps. The conductor-like polarizable continuum model (CPCM) [25, 26] was employed to simulate the entire reactions in water solvent (with a dielectric constant of 78.4). The Gaussian-09 package of programs [27] was used for all computations.

## Results and discussions

NTO is a weak acid with pKa 3.76 [28]. Hence, NTO can exist as a neutral or anionic form depending upon the pH of the solution. Several isomers of neutral and anionic forms of NTO were optimized at M06-2X/6-311G(d,p) level in the bulk water using the CPCM approach. The most stable forms of neutral and anionic form of NTO are shown in Fig. 1 and have been used for further investigation.

### Initial degradation step of NTO

In the environment, several aspects such as solar radiation, heat, or reactive species in water may affect stability of NTO. While NTO can be degraded through X-ray, UV, laser, and photochemical irradiation [4, 7, 8], no significant photo-degradation of NTO was detected in the absence of the catalyst [19]. Hence, we will focus on the NTO degradations caused by the factors of hydroxide ion, hydroxyl radical, and heat in the present study.

### NTO degradation initiated by hydroxyl radical

Le Campion et al. [18] studied the photocatalytic degradation of NTO in aqueous suspension of TiO$_2$ and proposed a degradation mechanism of NTO by hydroxyl radicals. When hydroxyl radical attacks the carbon C5 of the

**Fig. 1** Structure of NTO molecule and NTO anion with the labels used in the discussion



NTO neutral molecule          NTO anion
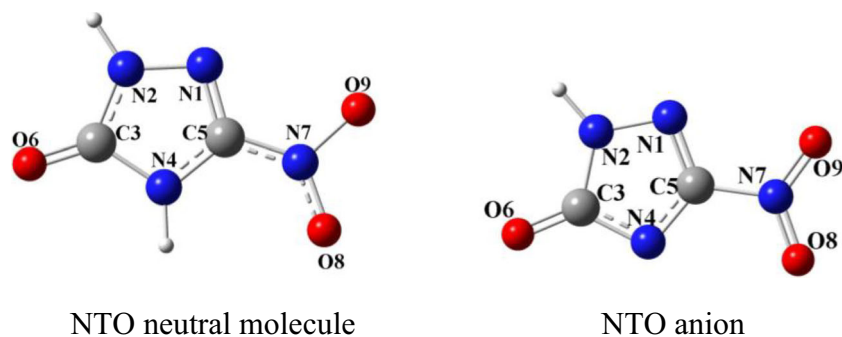
five member ring of neutral NTO, the near attacking (NA) complex (R1_A in Route R1, Fig. 2) was formed with the atomic distance of O-C5 as 2.579 Å and the bond length of C5-N7 is measured as 1.449 Å. The transition state (R1_TS) of the step revealed that the C5-N7 bond was slightly stretched to 1.459 Å while the hydroxyl radical moved closer to C5 (2.087 Å). The energy barrier was estimated to be 3.6 kcal/mol which implies a fast reaction step. The yielded product (R1_B) is the complex of the hydroxyurazole and the leaving nitro group whose nitrogen is about 1.62 Å away from the C5, and it is about 39 kcal/mol lower in energy than that of the reactant.

For the NTO anion, the reaction pathway (Route R2, Fig. 2) is similar to that of NTO neutral molecule in route R1. Hydroxyl radical attached to C5 of NTO while the nitro group was ruptured from the five-member ring simultaneously. The energy barriers for Route R2 were calculated to be 3.9 kcal/mol. Given the low energy barriers for both the neutral and anionic NTO, hydroxyl radical makes the dissociation of NTO a viable process.

## NTO degradation initiated by water and hydroxide ion

We also investigated the catalytic role of water and hydroxide ion on the degradation of NTO in the water solution. With the help of one water molecule, it is predicted that 45.8 kcal/mol and 45.2 kcal/mol of energy barriers need to be overcome to form nitrous acid (HONO) and hydroxyurazole from the decomposition of the neutral (Route T1, Fig. 3) and anionic NTO molecules (Route T2, Fig. 3), respectively. This illustrates that the water hydrolysis of NTO is difficult to occur due to the high energy barrier.

However, the energy barrier is predicted to be significantly reduced to 5.7 kcal/mol when the reaction was assisted by hydroxide ion to form the $NO_2^-$ and hydroxyurazole anion (Route T3, Fig. 3). This reveals that the NTO anion may be decomposed in the alkaline solutions. Thus, based upon data shown in Figs. 2 and 3, it is evident that at room temperature, the hydroxyl radical will play dominant role in the degradation of NTO in the water solution.
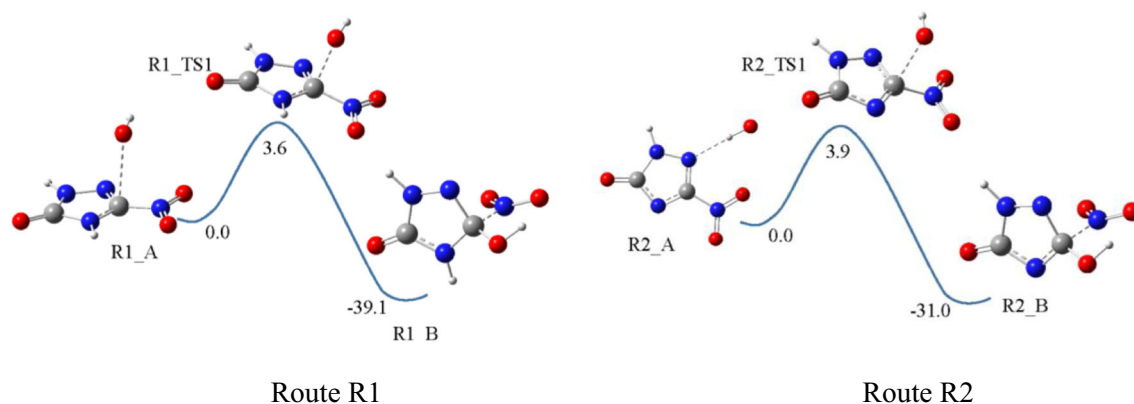


Route R1          Route R2

**Fig. 2** Reaction coordinates of NTO degradation with hydroxyl radical. Route R1 is for NTO neutral molecule and Route R2 is for NTO anion molecule. (M06-2X/6-311G(d,p) level with CPCM; energy differences in kcal/mol with zero-point energy correction)

**Fig. 3** Reaction coordinates of NTO degradation with water (Route T1 and T2) and hydroxide ion (Route 3). Route T1 is for NTO neutral molecule and Route T2 and T3 are for anionic NTO molecule. (M06-2X/6-311G(d,p) level with CPCM; energy differences in kcal/mol with zero-point energy correction)



Route T1



Route T2



Route T3
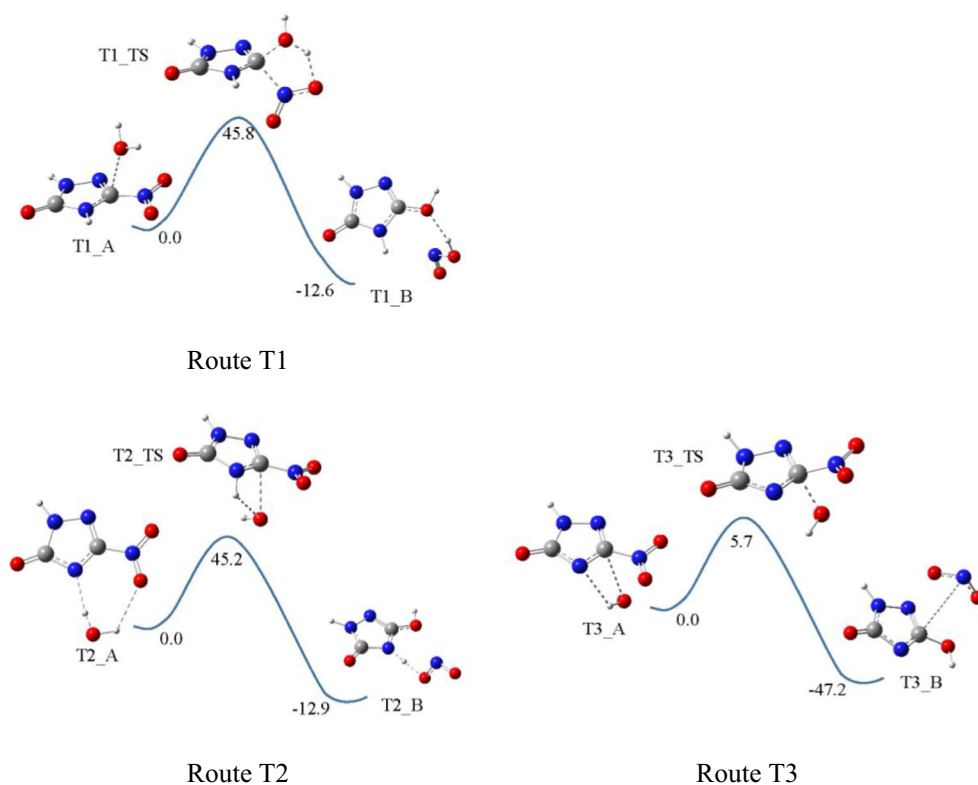
## Further degradation of urazole

The dione tautomeric form is the most stable among all tautomers of urazole, and this form can be easily formed from hydroxylurazole discussed in Figs. 2 and 3 through intramolecular proton transfer as studied by Erdogan and Ism [29]. The dione tautomeric form will be only discussed for the further discussion of urazole. Urazole does not absorb UV/Vis light reaching on the earth surface. Therefore, it is expected that further degradation would be motivated by either the thermal or chemical processes. Water can react with urazole to break the five-membered ring. As shown in Route TU1 (Fig. 4), the energy barriers are around 52 kcal/mol for the reactions between water and urazole. This illustrated that the energy barriers are too high for the degradation to proceed at room temperature. Hence, without any additional assistance (such as heat, pressure, etc.), this pathway will not be favored for the urazole decomposition.

Similar to the NTO degradation, hydroxyl radicals are also possible to take part in the urazole degradation. It was observed that there are three steps for the hydroxyl radicals to break the urazole. The hydroxyl radical will first attack the carbon of the triazol ring and rupture the ring to form intermediate RU1_B (Route RU1 in Fig. 4).

The energy barrier is estimated to be 17.6 kcal/mol. Secondly, the intermediate RU1_B can further produce a carbon dioxide $CO_2$ and lead to intermediate RU2_B ($NH_2CON_2H_2$) with assistance of one water molecule with energy barriers of 15.3 kcal/mol (Route RU2 in Fig. 4). Further degradation reaction of intermediate RU2_B was followed through reaction with hydroxyl radical (Route RU3 in Fig. 4). The hydroxyl radical attacks the carbon of RU2_B and forms intermediate RU3_B through transition state RU3_TS1 with energy barrier of 33.7 kcal/mol. The C-N bond in RU3_B undergoes dissociation through an energy barrier of 6.3 kcal/mol and leads to the formation of intermediates of carbamic acid $NH_2COOH$ and di-imide NHNH. Di-imide is not very stable and can easily lead to formation of $N_2$ and hydrazine $NH_2NH_2$ through the thermal process with energy barrier of only 3 kcal/mol as shown in Route T4 in Fig. 4.

## Further degradation of nitrous acid HONO

In the presence of high temperature, NTO may be dissociated to produce intermediate nitrous acid HONO (Route T1, Fig. 3), which can be further degraded. The decomposition reaction takes place between two HONO molecules by elimination

**Fig. 4** Reaction coordinates for urazole degradation. Route TU1 is for the thermal degradation with water. Routes RU1, RU2, and RU3 are for radical induced degradations. Route T4 is for thermal degradation of di-imide. (M06-2X/6-311G(d,p) level with CPCM; energy differences in kcal/mol with zero-point energy correction)
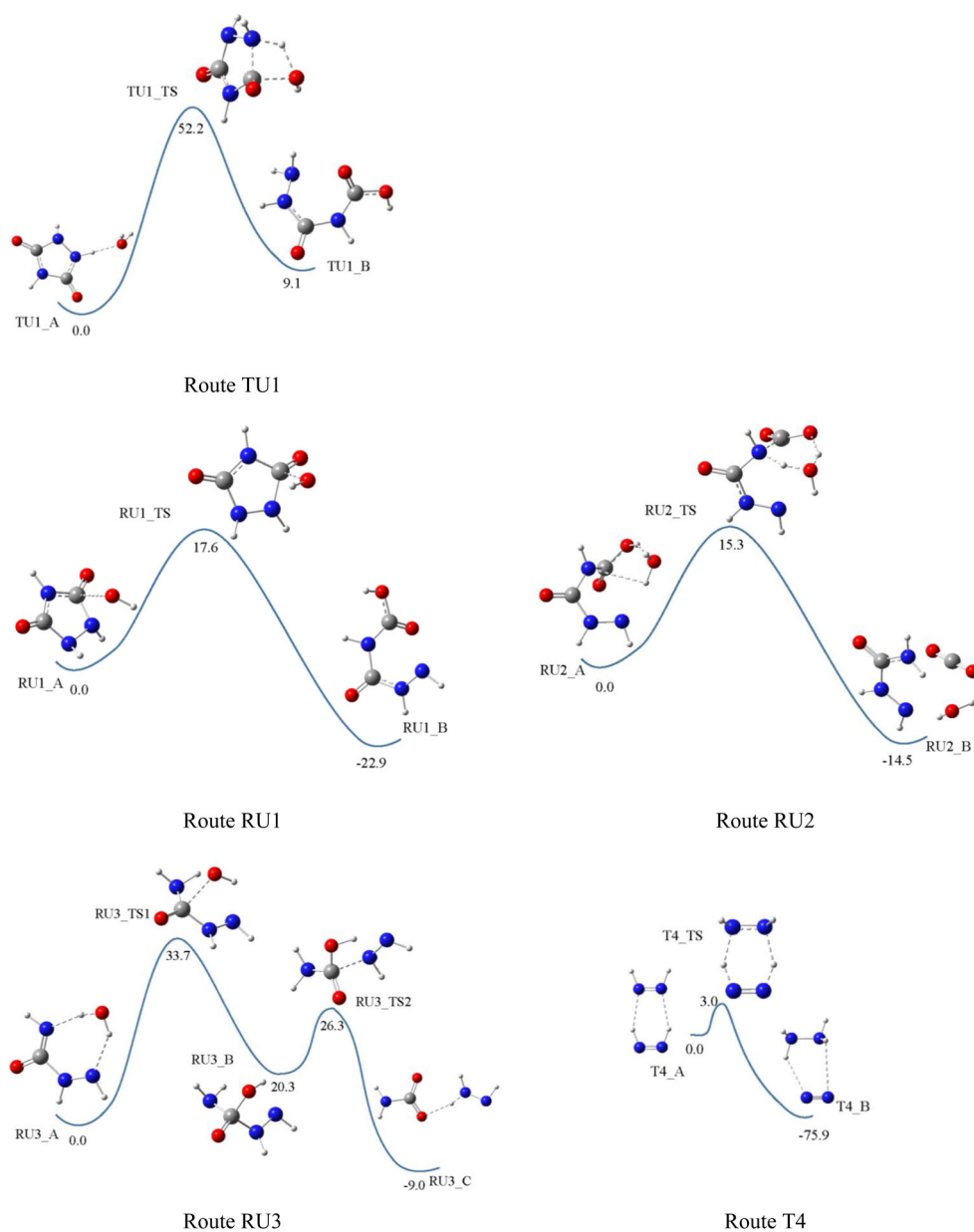
of a water. As shown in Route T5 (Fig. 5), with the assistance of one water molecule, the two HONO were bonded by three hydrogen bonds with atomic distances from 1.588 Å to 2.253 Å as the near attacking compound T5_A. The hydrogen H1 of the second HONO attacked the oxygen O2 of the hydroxide group from the first HONO to form the transition state structure T5_TS. The bond length of N11-O11 was stretched from 1.183 Å in T5_A to 1.235 Å in T5_TS while the bond length of N11-O22 was shortened from 1.337 Å in T5_A to 1.261 Å in T5_TS. The OH (O2H site) from the first HONO and H1 from the second HONO formed a water molecule and yielded

a NO and a $NO_2$ simultaneously. The energy barriers were calculated to be 14.7 kcal/mol, which suggests that HONO is not stable in water and can be easily decomposed at the room temperature.

## Conclusions

In the present study, the degradation pathways of unimolecule 3-nitro-1,2,4-triazol-5-one (NTO) in water solution were explored at the DFT level. Our results suggest that the initial

**Fig. 5** Reaction coordinates for HONO thermal degradation in the presence of one water molecule. (M06-2X/6-311G(d,p) level with CPCM; energy differences in kcal/mol with zero-point energy correction; bond length in Å)



Route T5
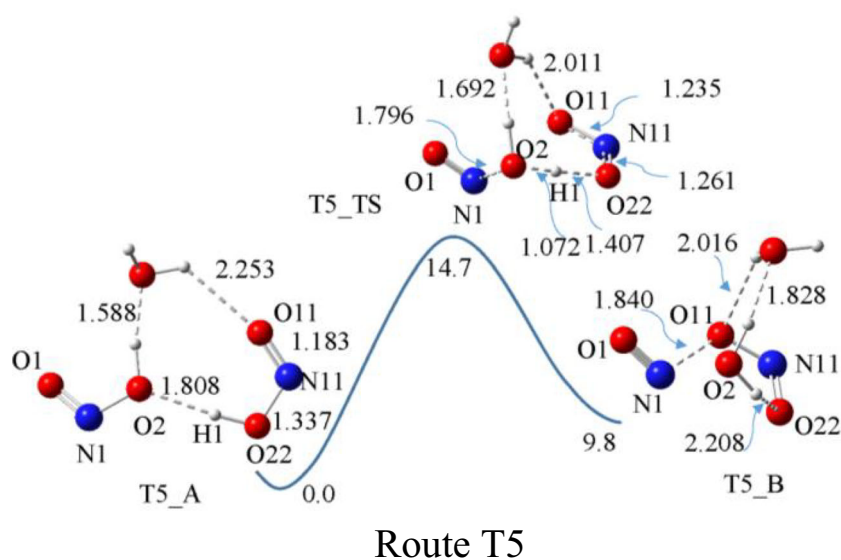
degradation step of NTO is more likely to go through the hydroxyl radical reaction pathway. Further dissociation of the intermediates of the initial degradation appears to favor the thermal and radical reaction pathways; the presence of hydroxide ions is expected to speed up the degradation process. The investigated pathways suggested that the fragments of the NTO degradation may contain urazole, NO, $NO_2$, HONO, $CO_2$, di-imide, and $N_2$.

**Data availability** Data can be obtained from the corresponding authors through email.

## Declarations

**Ethical approval** Not applicable

**Consent to participate** Not applicable

**Consent to publish** Yes

**Competing interests** The authors declare no competing interests.

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