Decomposition of 2,4,6-trinitrotoluene (TNT) and 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO) by Fe$_{13}$O$_{13}$ nanoparticle: density functional theory study

Leonid Gorb$^{1,2}$ · Mykola Ilchenko$^3$ · Jerzy Leszczynski$^1$

Received: 10 January 2022 / Accepted: 26 April 2022 / Published online: 11 May 2022
© The Author(s), under exclusive licence to Springer-Verlag GmbH Germany, part of Springer Nature 2022

Abstract

To obtain more insight into the mechanisms of the decomposition of energetic compounds, we performed a computational study of the interaction of Fe$_{13}$O$_{13}$ nanoparticles with two energetic molecules such as 2,4,6-trinitrotoluene (TNT) and 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO). The density functional theory using M06-2X, B3LYP, and BLYP density functionals was applied. We found that the reactivity of these molecules strongly depends on the place of adsorption (so-called top and bottom planes of Fe$_{13}$O$_{13}$). Namely, only the interaction with the bottom plane results in the thermodynamic characteristics of the decomposition that provide a medium reaction rate for the studied processes. Several pathways for such decomposition were found. One of them is the inter-complex oxygen transfer of nitro-group oxygen to Fe$_{13}$O$_{13}$. This pathway results in the formation of adsorbed nitroso compounds. The second pathway describes a more complex decomposition that includes the transfer of the nitro-group oxygen accompanied by the hydrogen transfer. In all cases, the interaction of energetic molecules with Fe$_{13}$O$_{13}$ nanoparticles takes place along with a barrier-less electron transfer from Fe$_{13}$O$_{13}$ to TNT or NTO species.

Keywords NTO · TNT · Decomposition · Nanoparticles · Nano-cluster · Iron oxide · Density functional theory

Introduction

The interest in the reactivity of nitro-compounds is caused by the wide involvement of such compounds in industrial activities. They are used as antioxidants, (de Resende et al. 2019; Alegria et al. 2018; Castonguay and Van Vunakis 1979; Díaz-Araya et al. 1998), dyes (Castonguay and Van Vunakis 1979), insecticides (Ooth et al. 1988; Becker et al. 2001; López et al. 2005; Ju and Parales 2010), and energetic compounds (Bretherick 1989; Li 2010; Salter-Blanc et al. 2015; Chang et al. 2020). Our interest in the properties of the compounds of this class has been mainly related to natural and designed ways of their utilization, i.e., decomposition and degradation. This is mainly because nitro-compounds are used as energetic materials. Let us give just one example. In 2010, more than 12 million pounds of energetic materials were released into waterways by the US Army’s Radford Ammunition Plant (Mahbub and Nesterenko 2016). Investigations of the decomposition products of toxic species (including nitro-compounds) require the application of reliable techniques. Therefore, in addition to different experimental methods, computational modeling has been applied to study the transformations of energetic materials.

The application of efficient computational methods allows the prediction of a wide spectrum of properties and processes, starting from calculations of environmentally important physicochemical characteristics of a
compound (Qasim et al. 2007), followed by an estimation of the rate of its decomposition (Sviatenko et al. 2014, 2015). Currently, the predictions of reactivity mainly cover the area of the gas phase and water solution reactions. Let us illustrate this statement by just two of the most striking examples. Computational modeling was able to predict an aqueous solubility of more than 2500 environmental pollutants (Kovdienko et al. 2010) and temperature dependence of the solubility for a few hundreds of them (Klimenko et al. 2016). Another example demonstrates the ability of computational methods to model the rate of the alkaline hydrolysis of such pollutants as TNT and HMX (one of the modern energetic materials) with an accuracy comparable with experimental data (Sviatenko et al. 2014, 2015).

Modeling the decay of any chemical species on the surface of minerals is usually a much more complicated task, compared to similar modeling in water solutions. Nevertheless, such processes are of environmental concern. Not surprisingly, the reactivity of Fe(II) containing minerals is one of the most complex topics among the research studies related to surface chemistry. This is due to the number of theoretical and computational problems associated with the open-shell electronic structure of these systems. To our knowledge, there was only one attempt to study the reactivity of nitro-compounds with Fe(II) species (Zilberberg et al. 2004). However, the models used in that study very crudely described the state of Fe(II) in the considered minerals. In addition, the situation was complicated by the lack of reliable experimental data on the structure of the active site(s) that can catalyze the decomposition of nitro-compounds on the surface of iron-containing minerals.

Briefly and simplistically, the initial step of the decomposition (reduction) of nitro-compounds is considered a donation of two electrons from Fe(II)-containing species to the nitro-group of a nitro-compound with further formation of the nitroso-group. The simplest scheme, which is most appropriate for Fe(II)-containing water solutions or for Fe(II) ions adsorbed on the surface of different minerals, can be described as follows:

\[
\text{R-NO}_2 + 2\text{H}^+ + 2\text{e} \rightarrow \text{R-NO} + \text{H}_2\text{O} \quad (1)
\]

It is important to highlight that the two protons in this equation come from the water solution. However, as follows from the results presented in Zilberberg et al.’s study (2004), there is a pathway of the nitro-group reduction, which at least at the initial step does not need the participation of protons. Such a mechanism includes an intra-complex transfer of one of the oxygen atoms of the nitro-group to Fe(II) containing species. The study (Zilberberg et al. 2004) considered the following reaction:

\[
\text{R-NO}_2 + \text{FeO} \rightarrow \text{FeO}_2 + \text{R-NO} \quad (2)
\]

The successful thermodynamic execution of the chemical reaction (2) requires the ability of a mineral surface to compensate for the value of energy necessary for the breaking of the N–O bond by the formation of an o xo ferrous iron bond. As follows from the data presented in Zilberberg et al.’s 2004 study, the elucidation of this issue at the computational level is not certain. Namely, calculations using pure DFT functionals such as BLYP and BPW91 reveal the thermochemical data quite close to the exothermic effect of this reaction. In contrast, calculations that use such a hybrid functional as B3LYP, which has been found quite successful in the studies of numerous physicochemical properties of Fe$_x$O$_y$ systems [9], result in quite significant endothermicitry of the reaction (2).

Two more important findings are described in the literature. First, a study using B3LYP functional predicts the highest value of activation energy for the considered process to be 29.7 kcal/mol. Such a value corresponds to a rather slow chemical reaction rate. In contrast, calculations applying such a pure DFT functional as BLYP predict just 12.0 kcal/mol of activation energy for the same process. This classifies the reaction (2) as proceeding at a medium rate. Second, the initial stage of the interaction of nitrobenzene and FeO results in a non-barrier one-electron transfer from the d-shell of iron into the antibonding LUMO localized mostly on the nitro group of nitrobenzene. This transfer results in the formation of the open-shell electronic configuration of the NB-FeO intermediate with a pair of α and β electrons occupying the $d_\alpha$(Fe) and $\pi^*$(–NO2) orbitals, in addition to the unpaired four α electrons on the $d(\text{Fe})$ orbitals. Interestingly, the transferred electron is an addition to the remaining unpaired four α electrons on the $d(\text{Fe})$ orbitals. In other words, the adsorption of the nitro-compounds on ferrous iron could be accompanied by a non-barrier one-electron reduction of nitro-compounds. Similar to the topics explored in Zilberberg et al.’s 2004 study, here we investigate the initial steps of the reduction of energetic materials. For this purpose, we have designed nanoparticles possessing the composition of Fe$_{13}$O$_{13}$ as presented in Fig. 1.

Such Fe$_{13}$O$_{13}$ species could be considered an approximate but certainly more complex and realistic model of Fe(II)-containing minerals, compared to the one considered by Zilberberg et al. (2004). The current study will provide new data on the interaction between nitro-compounds and Fe(II)-containing species in the gas phase.

To study the nitro-to-nitroso conversion on the Fe$_{13}$O$_{13}$ surface, we have chosen genuine energetic molecules belonging to two different classes of energetic materials. NTO (5-nitro-2,4-dihydro-1,2,4-triazol-3-one) belongs to a relatively new class called insensitive munition, and TNT (2,4,6-trinitrotoluene) represents a traditional energetic
material, which is the standard component for most military loads. Both compounds have been shown to be resistant to degradation under environmentally relevant conditions and are therefore recognized as persistent contaminants. Two-dimensional structural formulas of TNT and NTO are presented in Scheme 1.

**Scheme 1** Structural formulas of TNT and NTO

![Structural formulas of TNT and NTO](image)

**Computational details**

The structure of Fe$_{13}$O$_{13}$ drawn in Fig. 1 was chosen to mimic a cubic closed packed array since most Fe(II)-containing minerals crystallize in such a manner (Zhang 1999). The nanoparticle shown in Fig. 1 has specific features—its top and bottom planes are not equivalent. The top plane (TP) has 4 iron and 9 oxygen atoms, and the bottom plane (BP) has an inverted structure—9 iron and 4 oxygen atoms (see Fig. 1). In addition, since all iron and oxygen atoms of Fe$_{13}$O$_{13}$ lay on the surface, they downgraded the coordination numbers (lower than six, which is the coordination number of each bulk ion of a face-centered cubic arrangement). This is one of the reasons for elevated reactivity that we expected for the considered nanoparticle.

Three density functional theory functionals in conjunctions with 6-311++G(d,p) basis set: M06-2X, BLYP, and B3LYP were used in this work. The B3LYP and BLYP functionals were also modified by a D3 version of Grimme’s dispersion with Becke–Johnson damping (D3BJ) (Grimme et al. 2011). Fe$_{13}$O$_{13}$ nanoparticle is constructed as an associate of 13 (FeO) molecules. According to the experimental and theoretical data (Bretherick 1989; Allen et al. 1996; Gutsev et al. 2000; Rollason and Plane 2000), each FeO molecule has a $^5\Delta$ ground state ($S_z = 2$). Therefore, the initial electronic and spin states of a Fe$_{13}$O$_{13}$ were assigned as having a spin equal to 26. In other words, the initial electronic state of Fe$_{13}$O$_{13}$ was treated as a quintet of unpaired d-electrons located on each iron atom. Optimized geometry for such a system was obtained at the M06-2X level, keeping the molecular symmetry as C$_{4v}$. The equilibrium interatomic distance of Fe-O was found equal to 2.02 Å. Since it is not obvious that the final spin state for Fe$_{13}$O$_{13}$ is just a simple sum of the spin states of FeO components, the

![Geometrical structure of Fe$_{13}$O$_{13}$ nanoparticle. Fe: light blue, O: red](image)

![Relative energy, kcal/mol](image)

**Fig. 1** Geometrical structure of Fe$_{13}$O$_{13}$ nanoparticle. Fe: light blue, O: red

**Fig. 2** The dependence of the total energy of Fe$_{13}$O$_{13}$ on its spin state

---

@ Springer
dependence of the total energy value in the vicinity of the state characterized by \( S = 26 \) was studied for a fixed \( \text{Fe}_{13}\text{O}_{13} \) C\(_{4V}\)-geometry, using BLYP, M06-2X, and B3LYP levels of theory (the addition of a dispersion correction is not necessary in such cases). Results presented in Fig. 2 illustrate the tendency that was established early (Zilberberg et al. 2004). Namely, the spin states that are higher than 26 are favored in the case of application of the hybrid type for functionals like B3LYP and M06-2X (the minimum was found in the area corresponding to \( S_z = 28 \) or 29 (see Fig. 2). However, slightly lower spin states are favored in the case when BLYP functional was used. Still, as follows from the shape of the curves presented in Fig. 2, the situation is less clear in the case of BLYP.

Therefore, in this work, we decided to study the decomposition of NTO and TNT only in the case of high-spin states of \( \text{Fe}_{13}\text{O}_{13} \). Namely, we investigated the decay of NTO and TNT adsorbed by nanoparticle \( \text{Fe}_{13}\text{O}_{13} \) characterized by spin 29. Some of those adsorbed complexes were also checked for SCF instability (Seeger and Pople 1976; Bauernschmitt and Ahlrichs 1996) to ensure that all obtained solutions are stable.

Considering that the top and bottom planes of the \( \text{Fe}_{13}\text{O}_{13} \) (see Fig. 1) are not equivalent, the interaction of both NTO and TNT with \( \text{Fe}_{13}\text{O}_{13} \) was probed for both planes.

The limited geometry optimization performed in this work for the interacting species included a fully relaxed geometry of NTO and TNT (\( C_1 \) symmetry was assumed) and a frozen geometry of \( \text{Fe}_{13}\text{O}_{13} \). We perfectly understand that our choice of the optimal spin state for the \( \text{Fe}_{13}\text{O}_{13} \) moiety would be more convincing in the case of a full optimization of nitro-compound—\( \text{Fe}_{13}\text{O}_{13} \) complexes. However, all our attempts to include the geometry of \( \text{Fe}_{13}\text{O}_{13} \) into the optimization during the adsorption process were unsuccessful due to numerous SCF non-convergences. The local minima and transition states were verified by harmonic vibrational frequencies analysis. All calculations were carried out within the Gaussian-09 and 16 packages (Frisch 2009; Frisch et al., 2016).

To make the analysis of the obtained data more informative, the spin difference density was obtained for the complex formed between TNT and \( \text{Fe}_{13}\text{O}_{13} \). The spin difference density \( \Delta \rho(r) \) is defined as:

\[
\Delta \rho(r) = \rho(r) - \rho_{\text{TNT}}(r) - \rho_{\text{Fe}_{13}\text{O}_{13}}(r)
\]

where \( \rho(r) \) is the density for the complex; \( \rho_{\text{TNT}}(r) \) is the density of TNT calculated for the geometry of the TNT moiety of the complex, using the “complete” basis set, i.e., including functions for the \( \text{Fe}_{13}\text{O}_{13} \) moiety of the complex. The \( \rho_{\text{Fe}_{13}\text{O}_{13}}(r) \) density of \( \text{Fe}_{13}\text{O}_{13} \) is calculated similarly to that of TNT.

To predict the ability of TNT and NTO to be reduced during the considered process, the value Gibbs free energy calculated as \( \Delta H - T\Delta S \) at 293.15 K was used.

### Results and discussion

#### Electronic structure of TNT and NTO-adsorbed complexes

To understand the reactivity of TNT and NTO during the initial steps of reduction, it is appropriate to start with analyzing some electronic and geometrical parameters of adsorbed complexes. First, we would like to analyze the data related to the interaction of both TNT and NTO compounds with the \( \text{Fe}_{13}\text{O}_{13} \). The interactions of the title compounds with \( \text{Fe}_{13}\text{O}_{13} \) are characterized by the formation of several adsorbed complexes that differ in the orientation of adsorbed molecules regarding the TP and BP planes of the nanoparticle. The molecular structures of those complexes are presented in ESI (see Fig. 1S and 1S and Table 1S). The complexes that are the most stable according to relative
values of Gibbs free energy are presented in Fig. 3. Table 1 collects the most important parameters of charge distribution, spin state, and geometry, which are necessary for future discussion.

As follows from the data presented in Table 1, both TNT and NTO compounds are predicted to be chemosorbed on the surface of Fe$_{13}$O$_{13}$, since the intermolecular NO…Fe (R4 and R5) distances are virtually the same (sometimes even shorter) as the Fe-O distances in the isolated nanoparticle (2.02 Å). Therefore, the case of a very strong interaction between the nanoparticle and adsorption moieties is revealed.

There are at least two reasons for such strong adsorption. First, all atoms of Fe$_{13}$O$_{13}$ are characterized by downgraded coordination numbers. Second, as follows from the data presented in Table 1, adsorption of both considered species is accompanied by a barrier-less electron transfer from Fe$_{13}$O$_{13}$ to TNT and NTO (actually, this is a typical case of chemical reduction). A similar effect was observed in our early study (Zilberberg et al. 2004) devoted to the interaction of nitrobenzene and FeO. However, there are also some specifics due to the different nature of the two adsorbed species. Namely, since the electron affinity of TNT is much stronger than that of nitrobenzene (−2.2 eV and −1.04 eV, respectively, at the M06-2X level of the theory), the former molecule can accept up to two electrons from Fe$_{13}$O$_{13}$. The indication of this ability is the values of electron charge transfer to TNT, which approaches −2 a.u. depending on the type of DFT approximation and values of spin density (which in the case of BLYP and B3LYP functionals even exceeds 2 a.u.). We would also like to mention that most of this spin-density is located on the nitrogen and oxygen atoms of the nitro-groups of TNT (see Figs. 3S and 4S, where the shape of TNT LUMO, LUMO+1, and LUMO+2 orbitals, along with spin difference density, is presented). Additional evidence of the nature of redistribution of electron density after adsorption of TNT on Fe$_{13}$O$_{13}$ is provided by a mean value of $<S^2>$ operator. The data presented in Table 1 suggest that all three considered DFT approximations predict it as 870 a.u. This corresponds exactly to an eigenvalue of S(S + 1), S = 29 and means that more than six of the d-electrons located on each Fe atom are unpaired. During the adsorption of TNT, up to two unpaired electrons are transferred to the TNT molecule. This is in full correspondence with our recently published results (Zilberberg et al. 2004) where we also established that more than six unpaired electrons per Fe atom participate in the electron transfer to a molecule of nitrobenzene. Adsorbed NTO demonstrates behavior similar to that of TNT. However, since it has an electron affinity lower than TNT (1.84 eV, M06-2X), only up to one electron is transferred from Fe$_{13}$O$_{13}$. There is one more important conclusion. In the case of the nitrobenzene-FeO interaction, we stated that pure and hybrid functionals behave differently. Namely, a pure functional (BLYP) does not reveal a profound effect regarding electron transfer, but it demonstrates quite good correspondence with the experiment related to the thermodynamics of the reaction: nitrobenzene + FeO. The calculations carried out using hybrid functional B3LYP demonstrated the opposite trends that disagree with an experiment that approaches −2 a.u. depending on the type of DFT approximation and values of spin density (which in the case of BLYP and B3LYP functionals even exceeds 2 a.u.). Additional evidence of the nature of redistribution of electron density after adsorption of TNT on Fe$_{13}$O$_{13}$ is provided by the mean value of $<S^2>$ operator. Analyzing the data collected in Table 1, one can conclude that all three functionals qualitatively describe similar trends in the electronic structure of TNT and NTO complexes adsorbed by Fe$_{13}$O$_{13}$. Namely, both molecules interact tightly with the surface of Fe$_{13}$O$_{13}$. The adsorption initiates a transfer

| Table 1 | The details of geometrical (Å) and electronic structures (a.u.) of TNT and NTO adsorbed on Fe$_{13}$O$_{13}$ |
|---------|----------------------------------------------------------------------------------------------------------------------------------|
|         | Charge transfer | Spin density | $<S^2>$ | R1   | R2   | R3   | R4   | R5   |
| TNT isolated | M06-2X | 0 | 0 | 0.0 | 1.21 | 1.21 | 1.22 | |
|           | BLYP-D3BJ | 0 | 0 | 0.0 | 1.24 | 1.24 | 1.27 | |
|           | B3LYP-D3BJ | 0 | 0 | 0.0 | 1.22 | 1.22 | 1.28 | |
| TNT adsorbed | M06-2X | −1.53 | 1.84 | 870.33 | 1.29 | 1.31 | 1.31 | 2.03 | 2.01 |
|           | BLYP-GD3BJ | −1.76 | 2.39 | 870.26 | 1.30 | 1.36 | 1.38 | 2.04 | 1.96 |
|           | B3LYP-D3BJ | −1.87 | 2.32 | 870.29 | 1.45 | 1.37 | 1.29 | 2.04 | 2.03 |
| NTO isolated | M06-2X | 0 | 0 | 0.0 | 1.20 | 1.21 | 1.20 | |
|           | BLYP-GD3BJ | 0 | 0 | 0.0 | 1.23 | 1.25 | 1.22 | |
|           | B3LYP-D3BJ | 0 | 0 | 0.0 | 1.21 | 1.23 | 1.20 | |
| NTO adsorbed | M06-2X | −0.88 | 0.16 | 870.31 | 1.34 | 1.37 | 1.25 | 2.09 | 2.20 |
|           | BLYP-GD3BJ | −1.01 | 0.60 | 870.20 | 1.38 | 1.40 | 1.25 | 2.00 | 2.42 |
|           | B3LYP-D3BJ | −1.13 | 0.35 | 870.23 | 1.35 | 1.40 | 1.25 | 2.03 | 2.27 |
of up to two electrons to the antibonding LUMOs of TNT and up to one electron to the antibonding LUMO of NTO.

Pathways of TNT decomposition

More complex and representative structures of both iron-containing moiety and species adsorbed on its surface, as considered in the current work, could generate pathways that could be different than the ones found for oversimplified models (Zilberberg et al. 2004). The thermodynamical parameters related to the computationally generated pathway computed in this study are collected in Tables 2, 3, and 4.

Let us start from the analysis of pathways similar to those found in the earlier study (Zilberberg et al. 2004). As we already mentioned in the Introduction, such a model describes an intra-complex transfer of one of the oxygen ... of the nitro-group to Fe(II)-containing species. We found that TNT adsorbed on both considered planes of Fe$_{13}$O$_{13}$ is able to participate in such a type of decomposition. The corresponding thermodynamical parameters are collected in Table 2. However, the thermodynamical parameters that characterize the course of this reaction on the top plane could be considered ineffective from the practical point of view (high activation barrier and endergonicity). For the corresponding energetic profile, see ESI Fig. 5s.

Much more interesting for the analysis are the results presented in Fig. 4. Namely, the BLYP-D3BJ and M06-2X level calculations predict low enough values of activation barriers to consider that the transfer of oxygen to the Fe$_{13}$O$_{13}$ could be carried out with an observable chemical rate. Also, according to the B3LYP-D3BJ and BLYP-D3BJ level data, the breaking of one of the nitrogen-oxygen bonds of the nitro-group is quite satisfactorily compensated by the formation of two additional oxo ferrous iron bonds in Fe$_{13}$O$_{13}$. This results in significant exergonicity of this reaction. However, the M06-2X level calculations predict this reaction to be just slightly endothermic. To explain this difference, we assumed that in the case of B3LYP-D3BJ and BLYP-D3BJ the oxygen atom transfer includes a more significant transfer of charge and electron density than in the case of M06-2X. However, we did not find a convincing explanation since both electronic characteristics are virtually the same at the B3LYP-D3BJ, BLYP-D3BJ, and M06-2X levels of theory.

As we already mentioned, a more complex structure of Fe$_{13}$O$_{13}$ considered in this study could, in principle, generate the pathways that are different from a simple oxygen transfer from the nitro-group to a Fe(II)-containing mineral or species. An example of such a pathway is presented in Fig. 5. The main feature of this pathway is the participation of the hydrogen atom of the CH$_3$-group in the decay of the ortho-nitro-group of TNT. The structures of located transition state and product are presented in Fig. 5. Intuitively, one expects the appearance of an intermediate on the path from the transition state to the product. However, we did not locate such a structure at any of the DFT approximations considered here. We would also like to highlight that the predicted decay of the ortho-nitro-group is kinetically less effective than a simple oxygen transfer that characterizes the decay of the para-nitro-group of TNT. However, it is characterized by an even more pronounced exothermic effect that is predicted in the case of the ortho-nitro-group.

### Table 2
Calculated thermodynamical parameters of nitro-group decomposition derived at the M06-2X level of the DFT theory (kcal/mol)

| Reaction                                           | $\Delta H_{298}$ | $\Delta G_{298}$ | $\Delta H^\ddagger$ | $\Delta G^\ddagger$ |
|----------------------------------------------------|-----------------|-----------------|---------------------|---------------------|
| TNT intra-complex oxygen transfer (TP)             | 57.0            | 55.9            | 58.8                | 59.4                |
| TNT intra-complex oxygen transfer (BP)            | -4.8            | -4.8            | 33.6                | 31.8                |
| Decay of TNT ortho-nitro-group (BP)               | -55.7           | -57.7           | 19.0                | 19.7                |
| Decay of NTO nitro-group (BP)                     | -40.5           | -44.1           | 9.4                 | 9.2                 |

| Reaction                                           | $\Delta H_{298}$ | $\Delta G_{298}$ | $\Delta H^\ddagger$ | $\Delta G^\ddagger$ |
|----------------------------------------------------|-----------------|-----------------|---------------------|---------------------|
| TNT intra-complex oxygen transfer (TP)             | 27.7            | 27.8            | 26.9                | 28.9                |
| TNT intra-complex oxygen transfer (BP)            | -31.5           | -32.0           | 9.2                 | 9.2                 |
| Decay of TNT ortho-nitro-group (BP)               | -51.2           | -51.6           | 23.7                | 24.9                |
| Decay of NTO nitro-group (BP)                     | -45.3           | -44.1           | 12.9                | 13.0                |

### Table 3
Calculated thermodynamical parameters of nitro-group decomposition derived at the BLYP-GD3BJ level of the DFT theory (kcal/mol)

| Reaction                                           | $\Delta H_{298}$ | $\Delta G_{298}$ | $\Delta H^\ddagger$ | $\Delta G^\ddagger$ |
|----------------------------------------------------|-----------------|-----------------|---------------------|---------------------|
| TNT intra-complex oxygen transfer (TP)             | n/f*            | n/f*            | n/f*                | n/f*                |
| TNT intra-complex oxygen transfer (BP)            | -15.8           | -15.8           | 25.6                | 24.0                |
| Decay of TNT ortho-nitro-group (BP)               | -53.2           | -54.3           | 19.5                | 20.8                |
| Decay of NTO nitro-group (BP)                     | -37.3           | -40.8           | 12.6                | 12.8                |

| Reaction                                           | $\Delta H_{298}$ | $\Delta G_{298}$ | $\Delta H^\ddagger$ | $\Delta G^\ddagger$ |
|----------------------------------------------------|-----------------|-----------------|---------------------|---------------------|
| TNT intra-complex oxygen transfer (TP)             | n/f*            | n/f*            | n/f*                | n/f*                |
| TNT intra-complex oxygen transfer (BP)            | -15.8           | -15.8           | 25.6                | 24.0                |
| Decay of TNT ortho-nitro-group (BP)               | -53.2           | -54.3           | 19.5                | 20.8                |
| Decay of NTO nitro-group (BP)                     | -37.3           | -40.8           | 12.6                | 12.8                |
Fig. 4  Gibbs free energy profiles (kcal/mol) for TNT oxygen transfer (adsorption by bottom plane). Fe: light blue, O: red, N: blue, C: grey, H: light gray

Fig. 5  Gibbs free energy profile (kcal/mol) for the decay of TNT meta-nitro-group (adsorption by bottom plane). Fe: light blue, O: red, N: blue, C: grey, H: light gray
Pathways of NTO decomposition

In the case of NTO, only the pathway that is very similar to the one characterizing the decay of the ortho-nitro-group of TNT was predicted. As follows from the Gibbs energy profile presented in Fig. 6, the first step, in this case, is a transfer of the closest NH proton in the direction of the nitro-group oxygen. Since the mobility of this hydrogen is greater than in the case of the mobility of the hydrogen from the CH₃-group (it is more acidic (Golius et al. 2015), the observable reaction barriers are smaller than the ones that relate to TNT transformation. Similar to TNT, the reaction is characterized by high exothermic effects.

Finally, we would like to convey two details of the computational challenges of this project.

First, during the performed calculations, for several initial geometries, we faced multiple cases of SCF non-convergences. Due to such failures of calculation procedures, we cannot assure that there are no additional minima corresponding to reactive intermediates in addition to the structures presented in the profiles in Figs. 4, 5, and 6. This relates especially to the cases of the decay of the ortho-nitro-group of TNT and to the decay of NTO. For example, we found an intermediate that corresponds to an intramolecular proton transfer in NTO (see Fig. 6s of ESI). This pathway starts from another adsorption state, which is less effective than the one presented in Fig. 6. However, it has approximately the same values of Gibbs free energy barriers as the profile presented in Fig. 6.

Second, one may argue that the relaxation of the Fe₁₃O₁₃ nanoparticle could quantitatively change the results described above. We tried to perform full optimization of the Fe₁₃O₁₃ nanoparticle with and without the adsorbed NTO molecule. However, we met even more problems than already described. Therefore, we present here just two trustworthy results.

1. The geometry of the optimized cluster did relax significantly compared to ... considered in this work (compare the structures presented in Fig. 1 and Fig. 7s). The structure with the lowest energy corresponds to the spin equal to 26 compared to the structure having S = 29 and studied in this work.

2. During the optimization, we were not able to locate a transition state of NTO decomposition. However, we found that the product (see Fig. 8s) of such decomposition is similar to the one presented in Fig. 5. We concluded that most probably the relaxed structure has a similar electron donor ability to transfer barrierless electron(s) to the adsorbed species.
Therefore, we believe that the electron-donor properties of the relaxed structure of Fe$_{13}$O$_{13}$ and its decomposition ability are similar to the one considered in this work.

**Conclusion**

We performed a computational analysis of the spin states of Fe$_{13}$O$_{13}$ nanoparticles in a wide range of spin states. We found that in the case of B3LYP and M06-2X DFT functionals, the state with the lowest total energy corresponds to $S_z = 29$. The computational analysis of the decomposition pathways of TNT and NTO adsorbed by Fe$_{13}$O$_{13}$ nanoparticle that has the abovementioned $S_z$ suggests that both molecules will undergo a chemical reduction under investigated conditions. In the case of TNT, we found two possible routes for that decomposition: an intra-complex transfer of one of the para-nitro-group oxygen atoms and a synchronous movement of one of the CH$_3$-group hydrogen and nitro-group oxygen. In the case of NTO, the predicted pathway included a synchronous movement of the NH hydrogen and nitro-group oxygen. Generally, the values of activation Gibbs free energy indicated a medium reaction rate for the considered decomposition of TNT and NTO. It is important to highlight that all considered DFT approximations predicted that the interaction between TNT and NTO was accompanied by a barrierless electron transfer from the Fe$_{13}$O$_{13}$ nanoparticle to the energetic material molecule.

**Supplementary Information** The online version contains supplementary material available at https://doi.org/10.1007/s11356-022-20547-w.

**Acknowledgements** The computation time was provided by the Extreme Science and Engineering Discovery Environment (XSEDE) by the National Science Foundation Grant Number OCI-1053575 and XSEDE award allocation Number DMR110088 and by the Mississippi Center for Supercomputer Research.

**Author contribution** M. I. performed the calculations and contributed to the writing of the manuscript. L. G. contributed to the writing of the manuscript and the formulation of the idea of the research. J. L. contributed to the conceptualization of the research.

**Funding** This study was supported by the ARO grant award number W911NF-20-1-0116.

**Data availability** Not applicable.

**Declarations**

**Ethics approval and consent to participate** Not applicable.

**Consent for publication** Not applicable.

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

**References**

Alegria E, Ribeiro A, Mendes M et al (2018) Effect of phenolic compounds on the synthesis of gold nanoparticles and its catalytic activity in the reduction of nitro compounds. Nanomaterials 8:320–338. https://doi.org/10.3390/nano8050320

Allen MD, Ziurys LM, Brown JM (1996) The millimeter-wave spectrum of FeO in its X5Δ state ($v = 0$): a study of all five spin components. Chem Phys Lett 257:130–136. https://doi.org/10.1016/0009-2614(96)00521-0

Bauernschmitt R, Ahlrichs R (1996) Stability analysis for solutions of FeO in its X5Δ state (v = 0): a study of all five spin components. Chem Phys Lett 257:130–136. https://doi.org/10.1016/0009-2614(96)00521-0

Bauerlami R, Ahlrichs R (1996) Stability analysis for solutions of FeO in its X5Δ state (v = 0): a study of all five spin components. Chem Phys Lett 257:130–136. https://doi.org/10.1016/0009-2614(96)00521-0

Bretherick L (1989) Safety in the chemical laboratory Y. J Chem Educ 66:A220–A224

Castonguay A, Van Unakis H (1979) Nitrosation and transnitrosation of nornicotine: inhibitory effect of some antioxidants. Toxicol Lett 4:475–480. https://doi.org/10.1016/0378-4247(79)90114-0

Chang SJ, Bai HL, de Ren F, et al (2020) Theoretical prediction of the impact sensitivities of energetic C-nitro compounds. J Mol Model 26:219. https://doi.org/10.1007/s00894-020-04481-7

de Resende MF, Lino CI, de Souza-Fagundes EM et al (2019) Assessment of anti-diabetic activity of a novel hydrazine-thiazole derivative: in vitro and in vivo method. Brazilian J Pharm Sci 55:1–14. https://doi.org/10.1590/s2175-979020190001182

Díaz-Araya G, Godoy L, Naranjo L et al (1998) Antioxidant effects of 1,4-dihydropyridine and niitroso aryl derivatives on the Fe+3/ascorbate-stimulated lipid peroxidation in rat brain slices. Gen Pharmacol 31:385–391. https://doi.org/10.1016/S0306-3623(98)00034-2

Díaz-Araya G, Godoy L, Naranjo L et al (1998) Antioxidant effects of 1,4-dihydropyridine and niitroso aryl derivatives on the Fe+3/ascorbate-stimulated lipid peroxidation in rat brain slices. Gen Pharmacol 31:385–391. https://doi.org/10.1016/S0306-3623(98)00034-2

Frisch GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenb DJMJT (2009) Gaussian 09, Revision C.01

Golius A, Gorb L, Michalkova Scott A et al (2015) Computational study of NTO (5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one) tautomeric properties in aqueous solution. Struct Chem 26:1281–1286. https://doi.org/10.1007/s11224-014-0526-z

Grimme S, Ehrlich S, Goerigk L (2011) Effect of the damping function in dispersion corrected density functional theory. J Comp Chem 32:1456–1465

Gutsev GL, Khanna SN, Rao BK, et al (2000) Electronic structure and properties of FeO n and FeO n - clusters. 5812–5822

Ju K-S, Parales RE (2010) Nitroaromatic compounds, from synthesis to biodegradation. Microbiol Mol Biol Rev 74:250–272. https://doi.org/10.1128/MMBR.00006-10

Klimenko K, Kuz’min V, Ognichenko L et al (2016) Novel enhanced energetic N-nitrocompounds based on bond dissociation energy. Nanomaterials 6:3623(98)

Kovalenko NA, Polishchuk PG, Muratov EN et al (2010) Application of random forest and multiple linear regression techniques to QSRR prediction of an aqueous solubility for military compounds. Mol Inform 29:394–406. https://doi.org/10.1002/minf.201000001

Li J (2010) A multivariate relationship for the impact sensitivities of energetic N-nitrocompounds based on bond dissociation energy. J Hazard Mater 174:728–733. https://doi.org/10.1016/j.jhazmat.2009.09.111

López Ö, Fernández-Bolaños JG, Gil MV (2005) New trends in pest control: the search for greener insecticides. Green Chem 7:431–442. https://doi.org/10.1039/b50733j

Frisch MG, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Petersson GA, Nakatsuji H, Li
X. Caricato M, Marenich AV, Bloino J, Janesko BG, Gomperts R, Mennucci B, Hratchian HP, JV and DJF Gaussian 16, Revision C.01 (2016)

Mahbub P, Nesterenko PN (2016) Application of photo degradation for remediation of cyclic nitramine and nitroaromatic explosives. RSC Adv 6:77603–77621. https://doi.org/10.1039/c6ra12565d

Ooth GEB, Services BC, House T (1988) Ullmann’s Encyclopedia of Industrial Chemistry. Nitro Compounds, Aromatic. Wiley-VCH Verlag GmbH & Co. KGaA

Becker OM, MacKerell AD, Jr, Benoît Roux MW (ed) (2001) Computational Biochemistry and Biophysics. Marcel Dekker, Inc., New York

Qasim M, Kholod Y, Gorb L et al (2007) Application of quantum-chemical approximations to environmental problems: prediction of physical and chemical properties of TNT and related species. Chemosphere 69. https://doi.org/10.1016/j.chemosphere.2007.03.067

Rollason RJ, Plane JMC (2000) The reactions of FeO with O3, H2, H2O, O2 and CO2. Phys Chem Chem Phys 2:2335–2343. https://doi.org/10.1039/b000877j

Salter-Blanc AJ, Bylaska EJ, Johnston HJ, Tratnyek PG (2015) Predicting reduction rates of energetic nitroaromatic compounds using calculated one-electron reduction potentials. Environ Sci Technol 49:3778–3786. https://doi.org/10.1021/es505092s

Seeger R, Pople JA (1976) Self-consistent molecular orbital methods. XVIII. Constraints and stability in Hartree-Fock theory. J Chem Phys 66:3045–3050. https://doi.org/10.1063/1.434318

Sviatenko L, Kinney C, Gorb L et al (2014) Comprehensive investigations of kinetics of alkaline hydrolysis of TNT (2,4,6-trinitrotoluene), DNT (2,4-dinitrotoluene), and DNAN (2,4-dinitroanisole). Environ Sci Technol 48:10465–10474. https://doi.org/10.1021/es5026678

Sviatenko LK, Gorb L, Hill FC et al (2015) Alkaline hydrolysis of hexahydro-1,3,5-trinitro-1,3,5-triazine: M06-2X investigation. Chemosphere 134:31–38. https://doi.org/10.1016/j.chemosphere.2015.03.064

Zhang J (1999) Room-temperature compressibilities of MnO and CdO: further examination of the role of cation type in bulk modulus systematics. Phys Chem Miner 26:644–648. https://doi.org/10.1007/s002690050229

Zilberberg I, Ilchenko M, Isayev O et al (2004) Modeling the gas-phase reduction of nitrobenzene to nitrosobenzene by iron monoxide: a density functional theory study. J Phys Chem A 108:4878–4886. https://doi.org/10.1021/jp037351v

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.