

On the Possibility of Autoxidation of TEX – A DFT Study

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Abstract: TEX is an explosive with interesting isowurtzitane cage structure. It exhibits successful explosion performance and good sensitivity. Herein, the tendency of TEX to form hydroperoxide structure under storage conditions was examined by density functional treatment. Additionally the possible decomposition products of the hydroperoxides

were investigated. Moreover, the detonation performance values for TEX itself and two isomeric hydroperoxide derivatives were calculated. Detonation products and explosive power index values were investigated and the effect of O₂ molecule on sensitivity and detonation properties was studied.

Keywords: TEX · Autoxidation · Explosives · Detonations · Density functional calculations · Hydroperoxidation; Decomposition

1 Introduction

Recent researches on explosives concentrate on explosives with superior detonation characteristics having low sensitivity to exterior stimuli [1–4]. Strained cyclic caged nitramine explosives satisfy the demanded requirements. The strain energy associated with some cage structures also leads to an increase in the ΔH_f° , which in turn increases explosive performance [5].

The interesting cage structure, which can be synthesized quite easily, is based on the isowurtzitane structure (Figure 1). There are two molecules representing this group of energetic high density substances: 2,4,6,8,10,12-(hexanitro-hexaaza)-tetracyclododecane (HNIW, CL-20) [6,7] and 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclododecane (TEX) [8]. In the structure of TEX structure one can easily visualize two cyclic ether structures (1,3-dioxolane, each of which can be considered as cyclic acetal formed in between formaldehyde and ethylene glycol).

Some theoretical and experimental analysis of the production and application of TEX have already been done [9–13] but the interaction of TEX with O₂ molecule resulting in hydroperoxide formation has not been investigated.

Although slight thermal degradation takes place in non-oxidizing atmosphere, the presence of oxygen or active species such as hydroperoxides significantly speed up the oxidation of explosives [14].

The formation of hydroperoxide compounds in partial oxidations of hydrocarbons is a preliminary idea for the understanding of consequent cracking mechanisms in organic materials [15,16]. Ethers of almost any type that have been exposed to the atmosphere for certain period of time invariably form peroxides (autoxidation) [17–19]. Five-membered cyclic ether, tetrahydrofuran (THF) is to be mentioned in that sense [17,18]. Autoxidation occurs by a free radical mechanism. In the reaction, ether hydrogen atoms are replaced by a hydroperoxide moiety.

Although the reaction mechanistically is a multi-step process the overall reaction is shown in Figure 2. Such autoxidation reactions also occur with hydrocarbons, such as fuels [20]. It is thought that the C–H groups (linked to heteroatoms) of TEX molecule may serve as a potential moiety to be vulnerable to oxidation through hydroperoxide formation. This has prompted to investigate hydroperoxide formation of TEX theoretically. The biradical O₂ molecule may easily cause C–H groups to lose a hydrogen radical and adds itself to the carbon radical of the molecule. The

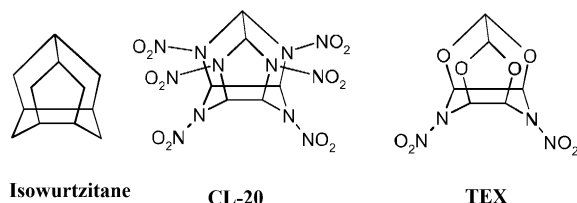


Figure 1. The structures of isowurtzitane, CL-20, and TEX.

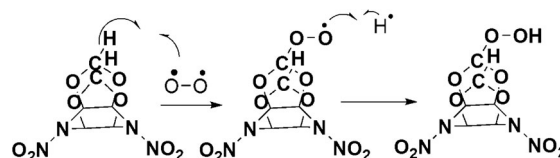


Figure 2. The formation of hydroperoxide by O₂ molecule.

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formed radical abstracts the hydrogen radical to form a hydroperoxide molecule as shown in Figure 2.

2 Methods of Calculation

The initial geometry optimizations of TEX, TEX hydroperoxides, TEX radicals (note that open shell structures are in doublet state), and other structures were achieved by following the order as done in the previous study [20]: MM2 method, PM3 method, STO and HF 6-31G(d,p) and DFT-B3LYP/6-31G(d,p) were applied. The normal mode analysis for each compound yielded no imaginary frequencies. The total electronic energies were corrected for zero point vibrational energies (ZPE). Gas phase heats of formation of the molecules were calculated by a semi-empirical approach (PM3) over DFT optimized geometries. These computations were performed by using the Spartan 06 program package at standard conditions of 298.15 K and 1.013×10^5 Pa [21]. The geometry optimizations and the single point calculations of all the structures were performed at UB3LYP/6-31G(d,p) theoretical level for bond dissociation energy (BDE) calculations. In BDE calculations, the basis set superposition error (BSSE) analysis was done with the counterpoise method, presented by Boys and Bernardi [22]. BSSE analyses and molecular volume calculation were performed at the same theoretical levels by the Gaussian 03 software package [23].

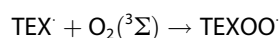
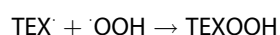
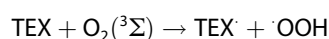
3 Results and Discussion

Hydrogen abstraction from TEX molecule produces TEX radicals indicated by a_1 and b_1 . The former one is the radical occupying the bridgehead position (C–C bridge between the 1,3-dioxalane moieties) of TEX, whereas the later one (b_1) is on the carbon next to the nitramine group. Table 1 includes the corrected total energies of these radicals. The UB3LYP/6-31G(d,p) level of calculations indicate that a_1 is more stable than b_1 (6.68 kJ mol^{-1}). Note that a_1 radical could be stabilized mesomerically by two oxygen atoms of the dioxalane moiety, whereas only one oxygen atom is available for the b_1 radical. In addition to that, it is somewhat destabilized by the nitramine group.

Table 1. The total electronic energy values of the radicals and hydroperoxides originated from TEX.

Atoms involved	Label	Energy [kJ mol^{-1}]
$\text{C}_1\text{--H}_1$	a_1	–2761883.96
$\text{C}_3\text{--H}_1$	b_1	–2761877.29
$\text{C}_1\text{--OO}_{10}$	a_2	–2959474.98
$\text{C}_3\text{--OO}_{10}$	b_2	–2959351.19
$\text{C}_1\text{--OOH}_1$	A	–3158349.70
$\text{C}_3\text{--OOH}_1$	B	–3158312.46

The reactions of TEX with oxygen can be outlined as:



Note that $^3\Sigma$ state of oxygen is its ground state having two parallel-spin unpaired electrons. Under photochemical conditions, $^1\Delta$ and $^1\Sigma$ states of oxygen exist [24], but the less likely photochemical insertion of O_2 molecule to TEX is not considered presently.

3.1 Geometries

The geometry optimizations of the structures shown in Figure 3 have been done at the (DFT) B3LYP/6-31G(d,p) level. The bond length data for the geometry optimized structure of TEX is consistent with the literature data in Ref. [25]. The similarity of the literature and the calculated bond length values for TEX increases the reliability of the selected method employed in the present study.

TEX was found to be a polar explosive. The value of dipole moment orienting from the middle of $\text{C}_1\text{--C}_2$ bond to area between C_3 , C_4 , C_5 , and C_6 (see Figure 4 for the labeling) was calculated as 1.73 Debye. TEX-hydroperoxide-A is less polar (1.47 Debye) than TEX, whereas TEX-hydroperoxide-B is more polar (2.44 Debye) than TEX.

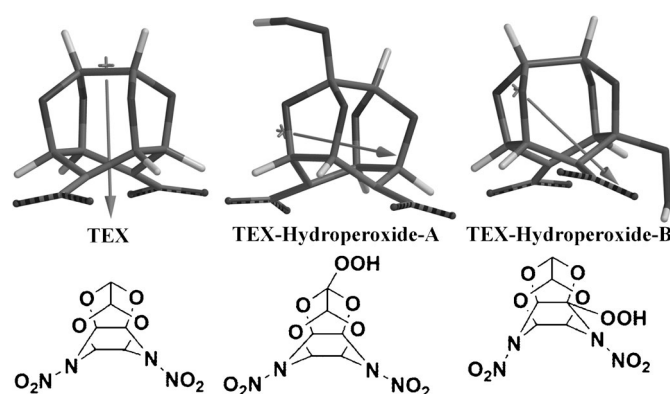


Figure 3. The structures of TEX and its hydroperoxides.

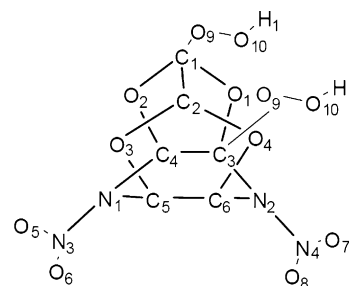


Figure 4. The numbering pattern of the presented structures.

3.2 The Formation Tendencies of TEX Radicals and Hydroperoxides

The route in this study is as follows: the O_2 molecule, which is a biradical simply causes C–H group of TEX to lose a hydrogen radical forming a TEX radical and then adds itself to the TEX radical. The formed hydroperoxy radical abstracts the hydrogen radical to form the hydroperoxide molecule (see Figure 2).

Numberings of the carbon, nitrogen, and oxygen atoms of TEX and its derivatives are shown in Figure 4. Numberings of the radicals and hydroperoxides have been done in the same manner. Table 1 shows the labeling of both the radicals and hydroperoxides originated from the corresponding atoms and their corrected total electronic energies (UB3LYP/6-31G(d,p) for open shell systems).

TEX is a quite symmetrical molecule. Therefore, in the presented study two central carbon atoms (C_1 and C_3) were investigated. The radical formed by the dissociation of the C_1 – H_1 bond was named as “ a_1 ” and the one formed by the dissociation of the C_3 – H_1 bond was named as “ b_1 ” radical. The total electronic energy values presented in Table 1 reveal that radical “ a_1 ” is more stable (with lower energy) than radical “ b_1 ”. They are both carbon radicals and “ a_1 ” is flanked by two oxygen atoms, whereas “ b_1 ” is flanked by a nitramine nitrogen. The lower stability of the radical “ b_1 ” compared to a_1 can be associated with different stabilizing effects of the etheric (acetal) oxygen atoms and nitramine nitrogen.

The O_2 molecule easily adds itself to either a_1 or b_1 radical to produce the radicals a_2 and b_2 . Table 1 shows that radical “ a_2 ” is more stable (with lower energy) than radical “ b_2 ”. These radicals may immediately react with hydrogen radicals (or abstract hydrogen) to form TEX hydroperoxides “A” and “B”. TEX hydroperoxide-A is more stable than hydroperoxide-B.

Another supporting calculation for the hydroperoxidation of TEX molecule is $\Delta G_{\text{rxn}}^\circ$ values. $\Delta G_{\text{rxn}}^\circ$ was calculated as the difference between the G° values of the products and the reactants at B3LYP/6-31G(d,p) level of theory. The G° values of TEX, O_2 molecule, and both hydroperoxides were calculated (Table 2). $\Delta G_{\text{rxn}}^\circ$ for the formation of TEX-hydroperoxide-A is $-203.45 \text{ kJ mol}^{-1}$ and $\Delta G_{\text{rxn}}^\circ$ for the formation of TEX-hydroperoxide-B is $-164.99 \text{ kJ mol}^{-1}$. The both hydroperoxide formations seem to be spontaneous as a result of the negative $\Delta G_{\text{rxn}}^\circ$. The formation of TEX-hydroperoxide-B is more reluctant due to less negative $\Delta G_{\text{rxn}}^\circ$. By comparing the total electronic energies of the hydroperoxide molecules, “the most vulnerable central carbon” was selected. This is the central carbon atom, which is able to be oxidized through hydroperoxidation. Carbon C_1 (which leads to more stable radical, “ a_1 ” compared to radical “ b_1 ”) was found to be quite susceptible to oxidation through hydroperoxidation since the corresponding radicals a_1 , a_2 , and hydroperoxide-A are lower in total electronic energy (more stable) than their counterparts b_1 , b_2 , and hydroperoxide-B.

Table 2. The $\Delta G_{\text{rxn}}^\circ$ values of the reactions in Figure 5.

Reaction	$\Delta G_{\text{rxn}}^\circ [\text{kJ mol}^{-1}]$
TEX \rightarrow A	–203.45
A \rightarrow 1	–340.05
1 \rightarrow 2	28.36
A \rightarrow 3	–283.21
3 \rightarrow 4	100.67
4 \rightarrow 5	–161.53
TEX \rightarrow B	–164.99
B \rightarrow 6	–234.61
6 \rightarrow 7	–116.59
6 \rightarrow 8	–30.17
B \rightarrow 9	–256.41
9 \rightarrow 10	30.20
10 \rightarrow 11	–169.55

3.3 Decomposition of TEX Hydroperoxides

The hydroperoxide molecules may decompose to a variety of molecules with less total electronic energies. The decomposition mechanisms for hydroperoxides in the literature [15,16,20,26] have been considered in this work; namely the carboxylic acid (ester)-alkane, alcohol-aldehyde and alcohol-ketone mechanisms. The selection of these mechanisms is based on analytic information along with the distribution of products formed from the oxidative cracking of hydroperoxides [27].

Currently, the decompositions of the TEX-hydroperoxides, labeled as “A” and “B”, were considered in view of the proposed mechanisms stated. As can be seen from Figure 5, thermodynamic energy calculations on these fifteen different products were made over DFT optimized structures (using B3LYP method and 6-31G(d,p) basis set). The $\Delta G_{\text{rxn}}^\circ$ values for the conversion of hydroperoxide “A” to the products are shown in Table 2. $\Delta G_{\text{rxn}}^\circ$ values were calculated as the difference between the G° values of the products and the reactants.

As expressed in the previous sections and according to Table 2, the hydroperoxidation of TEX molecule is a spontaneous process in the presence of O_2 molecule under the storage conditions. The suggested decomposition reactions are shown in Figure 5. Hydroperoxide-A molecule may decompose in two ways; it may either prefer to form product-1 having a ketone and an alcohol group or product-3 having a diol structure. Since the $\Delta G_{\text{rxn}}^\circ$ for the conversion of A to product-1 is more negative than that of A to product-3, it prefers to yield product-1 rather than product-3. Further conversion of product-1 to product-2 seems to be a non-spontaneous reaction due to the positive $\Delta G_{\text{rxn}}^\circ$. In the same way, rearrangement of product-3 to –4 is a non-spontaneous reaction under normal conditions. Therefore, product-1, 6-hydroxy-4,8-dinitrohexahydrobis[1,3]dioxolo-[4,5-b:4',5'-e]pyrazin-2-one, was assigned to be the most feasible decomposition product of hydroperoxide-A in terms of the thermodynamic considerations.

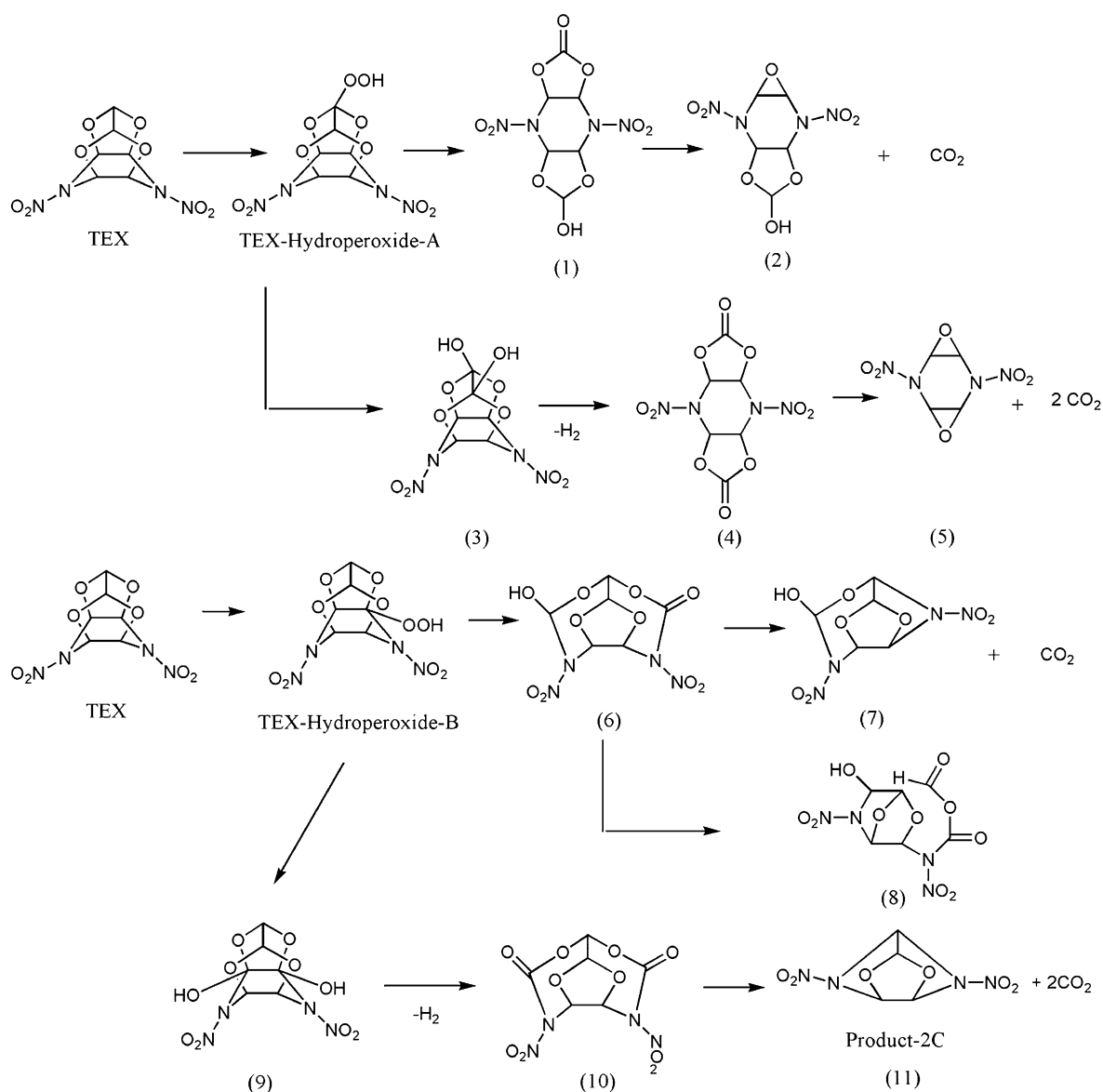


Figure 5. Decomposition of TEX hydroperoxides "A" and "B".

Hydroperoxide-B molecule may also decompose in two ways as in the case of hydroperoxide-A; it may either favor product-6 having a ketone and an alcohol group or may choose to form product-9, which contains a diol group (see Figure 5). Considering $\Delta G_{\text{rxn}}^\circ$ values, conversion of B to product-9 is more favored over product-6. Product-6 may spontaneously convert itself to product-7 liberating one mol of CO_2 molecule. It may also less favorably rearrange to product-8. Further decomposition of product-9 (Figure 5) is not a realistic reaction as a result of the positive $\Delta G_{\text{rxn}}^\circ$. Consequently, product-7 and product-9 have been taught to be the most achievable decomposition products of hydroperoxide-B regarding the thermodynamic calculations.

3.4 Explosive Performance of TEX and the Hydroperoxides

Explosive performance of energetic materials depends on two key parameters: the detonation velocity (D) and detonation pressure (P). The empirical Kamlet-Jacobs [28–32] equations are used for the calculations of these properties as follows:

$$D = 1.01 (N M_{\text{ave}}^{1/2} Q^{1/2})^{1/2} (1 + 1.30\rho)$$

$$P = 1.558 \rho^2 N M_{\text{ave}}^{1/2} Q^{1/2}$$

where D is the detonation velocity (km s^{-1}), P is the detonation pressure (GPa), ρ is the density of a compound (g cm^{-3}), N is the moles of gaseous detonation products

Table 3. Predicted densities and detonation properties of TEX, hydroperoxides A and B, TNT, RDX, and HMX at B3LYP/6-31G(d,p) level.^{a)}

Compound	Ω [%]	ΔH_f° [kJ mol ⁻¹]	ρ [g cm ⁻³]	D [km s ⁻¹]	P [GPa]
TEX	-42.73	-397.82	1.95 (1.99)	8.33 (8.66)	32.25
A	-27.20	-496.90	1.97	8.71	35.48
B	-27.20	-476.90	2.02	8.89	37.52
TNT	-73.98	52.47	1.64	7.11 (6.95)	19.00
RDX	-21.61	168.9	1.78 (1.81)	8.88 (8.75)	34.75 (34.70)
HMX	-21.61	270.41	1.88 (1.90)	9.28 (9.10)	39.21 (39.30)

a) Data in parentheses are the literature values [35,36].

per gram of explosive, M_{aver} is the average molecular weight of gaseous products, and Q is the chemical energy of detonation (kcal g⁻¹). The parameters N , M_{aver} and Q are calculated according to the chemical composition of each explosive as revealed in Ref. [33]. For a $C_aH_bO_cN_d$ type explosive, if $2a + b/2 > c \geq b/2$ relation is satisfied, N is calculated using $(b + 2c + 2d)/4$, M_{ave} is calculated as $(56d + 88c - 8b)/(b + 2c + 2d)$, and Q is calculated as $[28.9b + 94.05(c/2 - b/4) + 0.239\Delta H_f^\circ]/M$. " M " is the molecular weight of the compound (in g mol⁻¹); ΔH_f° is the gas phase standard heat of formation of the compound (in kJ mol⁻¹). The gas phase standard heat of formation (ΔH_f°) is calculated at the PM3 level over DFT(B3LYP/6-31G(d,p)) optimized structure. The density of each compound was predicted from the molecular volume divided by molecular weight, while the molecular volume of each molecule was obtained from the statistical average of 100 single-point molar volume calculations for each optimized structure. The molar volume was evaluated using a Monte Carlo integration implemented in the Gaussian 03 software package [23].

TEX itself and its potential oxidation products (A and B) under storage conditions were examined to comprehend the effect of O₂ molecule on the explosive performance of TEX. The calculated density and detonation properties of TEX and hydroperoxide derivatives are listed in Table 3. It also includes experimental (in parenthesis) and theoretical performance values of TNT, RDX, and HMX [33,34] excerpted from the literature.

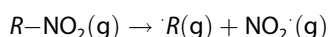
When oxygen balance (Ω %) values in Table 3 are considered, it is obvious that TEX and hydroperoxides are under-oxidized like TNT, RDX, and HMX. Since hydroperoxidation increases the number of oxygen atoms, oxygen balance values of both TEX hydroperoxides are greater than that of TEX. The density of TEX was calculated as 1.95 g cm⁻³ by Monte-Carlo integration technique. The literature value is 1.99 g cm⁻³. This value is not an experimental result, it has been determined from single crystal X-ray diffraction [25]. The calculated density data is quite close to the experimental results for TNT, RDX, and HMX. Hence, our calculated result may be employed in calculations, where experimen-

tal density data is required. It is clear from the Table that hydroperoxidation causes an increase in the density of TEX. Hydroperoxide "B" is denser than "A". This is the effect of hydroperoxide group on different central carbon atoms.

When detonation velocity and pressure values are considered, our calculated data for TEX (8.33 km s⁻¹) is relatively close to the experimental data (8.66 km s⁻¹). The hydroperoxide formation (the presence of extra oxygen) increases detonation performance of TEX. Both TEX and its hydroperoxide derivatives are better in performance when compared to TNT. The performance of TEX and its hydroperoxides lie between RDX and HMX.

3.5 The Bond Dissociation Energy (BDE) versus Sensitivity

In nitroaliphatics, nitramines, and nitrate esters, the connection of nitro groups is quite weak, and consequently scission of that bond is an essential step in decomposition of these energetic materials. The homolytic bond dissociation energy (BDE) calculations for the removal of nitrogen dioxide moiety from the main structures were done at UB3LYP/6-31G(d,p) level of theory for the determination of C–NO₂ and N–NO₂ bond strengths of the compounds. The expressions for the homolysis of $R\text{--NO}_2$ bond and for computing its homolytic BDE are shown as follows:



$$\text{BDE}(R\text{--NO}_2) = [E(\cdot R) + E(\text{NO}_2\cdot)] - E(R\text{--NO}_2)$$

where $R\text{--NO}_2$ indicates the neutral molecule and $\cdot R$ and $\text{NO}_2\cdot$ indicate the corresponding product radicals after the bond dissociation [35–37].

In the presented study, the "sensitivity" term describes the "impact sensitivity" of the energetic material. There are theoretical techniques for the computational determination of impact sensitivity. There are various appreciated studies in the literature [37–39] on the homolytic BDE of the nitro compounds, which have revealed that there is a parallel correlation between the BDE for the weakest $R\text{--NO}_2$ bond

Table 4. The homolytic bond dissociation energies (BDE) of TEX and derivatives calculated at (DFT) UB3LYP/6-31G(d,p) theoretical level.

	Bond	BDE [kJ mol ⁻¹]
TEX	N ₁ –N ₃	173.90
	N ₂ –N ₄	173.89
A	C ₁ –O ₉	310.09
	O ₉ –O ₁₀	71.54
	N ₁ –N ₃	173.28
	N ₂ –N ₄	173.85
B	C ₃ –O ₉	279.53
	O ₉ –O ₁₀	158.09
	N ₁ –N ₃	171.02
	N ₂ –N ₄	147.83
RDX	Nitro bond	175.26
HMX	Nitro bond	180.02

in the molecule and its sensitivity. The ordinary trend is that the greater the homolytic BDE value for scission of R–NO₂ or C–NO₂ bonds are, the lower the sensitivity is.

The nitro bond dissociation for TEX was calculated as 174 kJ mol⁻¹ (Table 4). TEX is as insensitive as RDX and HMX. The hydroperoxidation of TEX through C₁ carbon (hydroperoxide-A) has no significant effect on sensitivity if the nitramine bonds are considered. However, decomposition begins with the cleavage of O₉–O₁₀ bond. Since the nitramine BDEs in hydroperoxide-B are lower than the respective bonds of A, then B is expected to be more sensitive than A. Besides, the decomposition does not start with the cleavage of O₉–O₁₀ bond but the nitramine bond. The nitramine bond breakage is the initial step in the decomposition of TEX hydroperoxide-B. It can also be considered a more sensitive explosive than both RDX and HMX.

4 Conclusions

Herein, the tendency of TEX molecule to form hydroperoxide structure under storage conditions was examined. The $\Delta G_{\text{rxn}}^{\circ}$ values showed that hydroperoxide formation is a spontaneous process. TEX is able to produce two different hydroperoxide structures. The most susceptible “central carbon” to oxidation through hydroperoxidation formation was found to be C₁ since the corresponding radicals and the hydroperoxide is lower in total electronic energy and $\Delta G_{\text{rxn}}^{\circ}$ values. The thermodynamic calculations showed that these hydroperoxide structures may rearrange themselves or release small molecules to minimize their energy, forming different molecules. These molecules were identified using mechanisms suggested in the literature. The effect of the O₂ molecule on the detonation performance and sensitivity of TEX were examined. The results showed that hydroperoxide formation increases the detonation performance values and causes a slight increase in the sensitivity of TEX. As a whole, oxidation of TEX through hydroper-

oxidation under storage conditions does not create an adversity on the explosive performance.

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