



Contemplation on the Protonation of TEX

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Abstract: The possibility of acid catalyzed decomposition of TEX, a well known explosive, is considered by investigating the stability of cations formed by protonation at different sites in the molecule. For this purpose, density functional theory has been employed at the B3LYP/6-31++G(d,p) and B3LYP/6-31G(d,p) levels. Various simple cations, as well as hydrogen-bridged cations of TEX and carbocations formed from protonated TEX, are considered which may undergo further acid catalyzed cleavage routes of the molecule.

Keywords: TEX, explosives, ethers, acetals, decomposition, DFT calculations

1 Introduction

4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (TEX) (see Figure 1) is one of the energetic materials which has attracted attention in recent years [1]. Boyer and coworkers were the first to manage the synthesis of TEX, starting with formamide and glyoxal in a two-step synthesis involving a piperazine derivative as an intermediate [2]. TEX is a nitramine and additionally contains two embedded five-membered cyclic di-etheric (also can be considered as acetals) structures resembling 1,3-dioxalane.

TEX is much less sensitive to impact and friction than the well known explosives RDX and HMX. In addition it has a high density (1.99 g/cm³), excellent thermal stability (m.p >240 °C) as well as a high detonation velocity (8665 m/s) and pressure (370 kbar) [1-7].

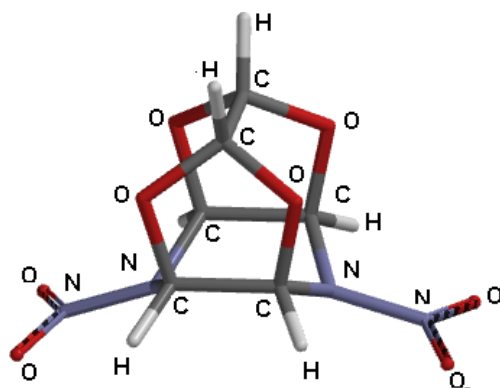


Figure 1. Structure of TEX.

The presence of two embedded 1,3-dioxalane units in TEX suggests some well known reactions of ethers and acetals (cyclic or acyclic). One of these is the acid catalyzed ring opening reaction of cyclic ethers [8-10]. Furthermore, the embedded 1,3-dioxalane unit(s) in TEX can be considered as a full acetal of glyoxal. It is known that acetal formation and destruction are acid catalyzed reactions [8-10]. In such reactions it is sometimes difficult to predict from which part of the ether (or acetal) unit an alcohol or an alkyl halide is derived. Obviously, quantum chemical calculations could help to find the answer without performing any chemical treatment. Computations based on density functional theory (DFT) have been widely employed on the TEX molecule in order to predict the crystal density [11], bond dissociation energies and impact sensitivity [12], detonation velocity [13], and sensitivity and performance relations [14]. The influence of RDX and HMX on the thermal stability of TEX has been investigated [15]. Türker used DFT calculations in modeling work which involved TEX and other explosives [16-18]. The heats of reaction of free dinitramidic acid ($\text{HN}(\text{NO}_2)_2$) with derivatives of 4,10-(R)-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane ($\text{R} = \text{H}, \text{F}, \text{CH}_3, \text{NO}_2$ (TEX)) were calculated using density functional theory at the B3LYP/6-31+G(d,p) level of theory [19]. The heat of formation (HOF) for a caged isowurtzitane analog, 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclododecane (TEX) was obtained by the density functional theory (B3LYP method with a 6-31+G(d,p) basis set) [20].

Since TEX is prepared in concentrated acid medium, it is worth studying the protonation of it, which might give some clues concerning the low yield of it which may be due to the decomposition of it rather than its low formation rate.

2 Methods of Calculation

Since all of the structures are closed shell systems (no radicals), all the theoretical methods were applied using the restricted level of theory [21]. The initial optimizations of the structures leading to energy minima were achieved by using the MM2 method followed by the semi-empirical PM3 self-consistent fields molecular orbital (SCF-MO) method [21, 22]. Subsequently, further structure optimizations were achieved using STO and RHF levels of theory (6-31G(d,p)), and then within the framework of Density Functional Theory (DFT, B3LYP) [22-24] at the level of 6-31G(d,p). All of the structures were treated in their singlet states (restricted type calculations have been done). The exchange term of B3LYP consists of hybrid Hartree-Fock and local spin density (LSD) exchange functions with Becke's gradient correlation to LSD exchange [25]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [26] and the Lee, Yang, Parr (LYP) correlation correction functional [27].

Total electronic energy calculations of all of the structures considered have been performed at the B3LYP/6-31++G(d,p) (for the protonated cations) and B3LYP/6-31G(d,p) (for the other species considered) theoretical levels. The normal mode analysis for each structure yielded no imaginary frequencies, which indicates that each compound has at least a local minimum on the potential energy surface. The total electronic energies were corrected for zero point vibrational energies (ZPVE or ZPE). Aqueous energies were calculated by the computer program based on the Crammer-Truhlar SM54 solvation method for water [28-30]. All of these computations were performed by using the Spartan 06 package program at the standard conditions of 298.15 K and 1.00 atm [31].

3 Results and Discussion

The TEX molecule, which contains many heteroatoms, has several potential sites for protonation. In the present work only mono protonation cases at different sites have been considered. Since protonation leads to cation formation, a second protonation is generally less likely under ambient conditions.

Initially four different protonation sites were considered for mono protonation; etheric (or acetal) oxygen, amine nitrogen (protonation at the exo- and endo-positions) and oxygen in the nitro groups. All of these protonated structures are shown in Figures 2 and 3. Note that the proton in structure-1 occupies the outward position of the cage, whereas in structure-2 it is on the inward position.

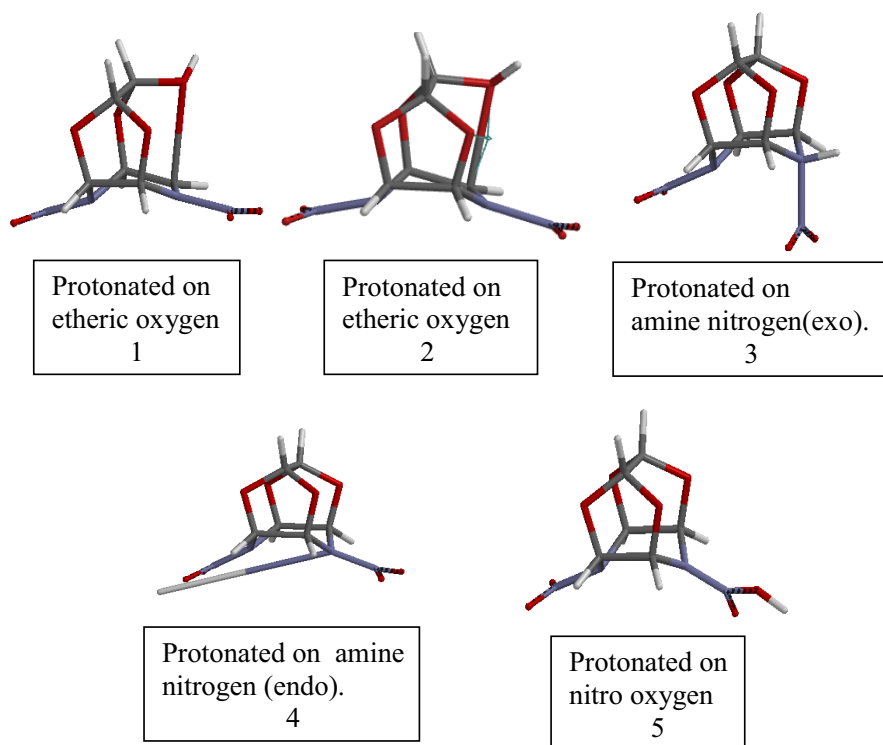


Figure 2. Structure-optimized appearance of TEX protonated at different sites (B3LYP/6-31++G(d,p)).

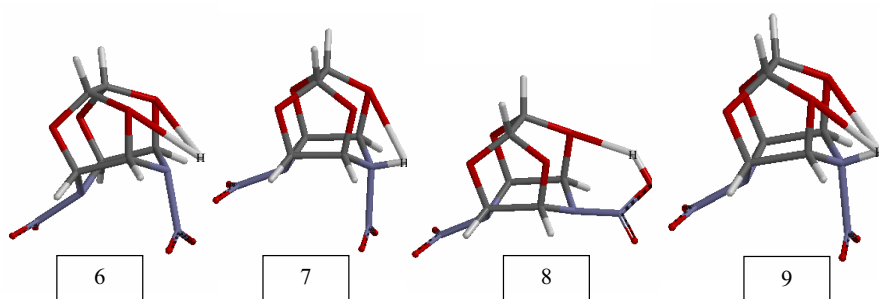


Figure 3. Structure-optimized hydrogen-bridged structures of TEX protonated at different sites (B3LYP/6-31++G(d,p)).

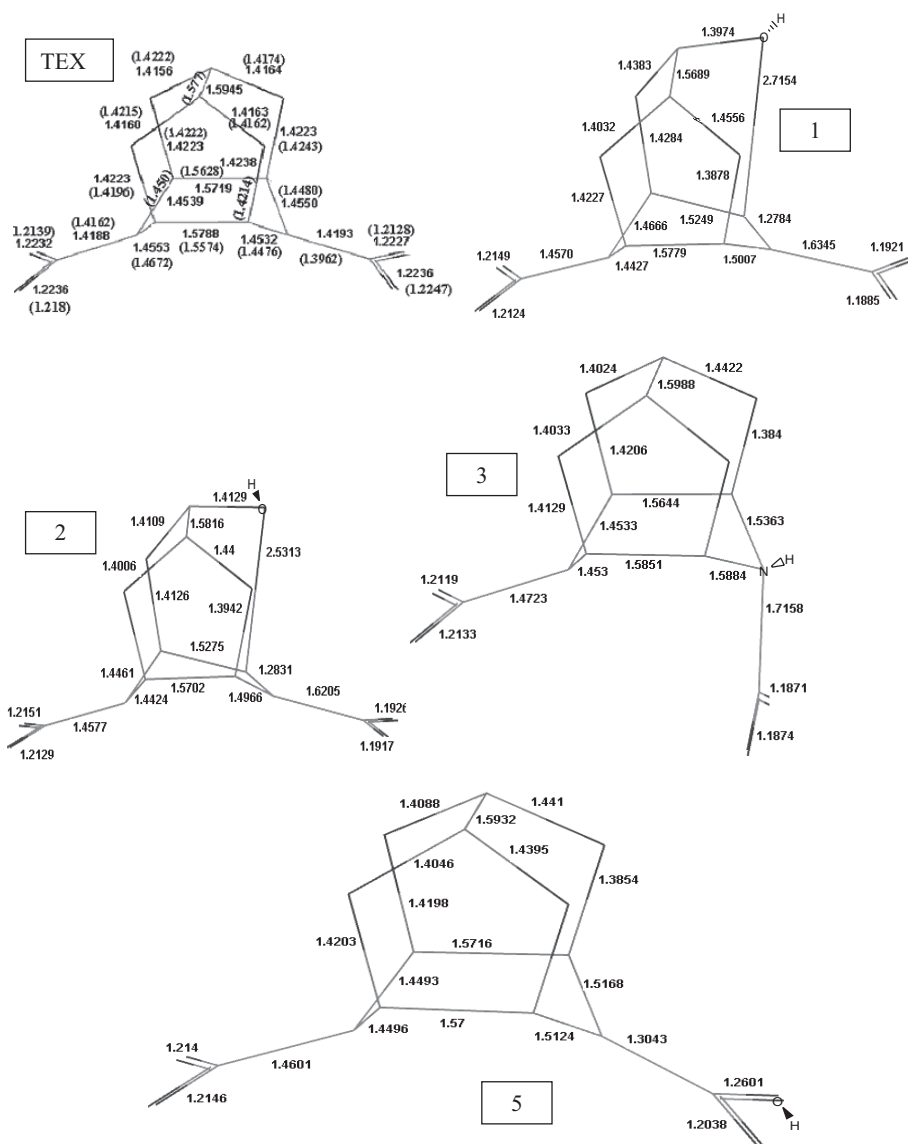


Figure 4. Some bond lengths (Å) in some of the protonated structures considered. (B3LYP/6-31++G(d,p), hydrogens omitted except proton, experimental values are in parenthesis [7]).

Protonation of TEX at different sites was investigated at the level of B3LYP/6-31++G(d,p), whereas the carbocations were studied at the B3LYP/6-31G(d,p) level of the theory.

Protonation on the etheric oxygen leads to an oxonium ion (1) which has an elongated C-O bond (2.71 Å; normally the C-O bond length is *ca.* 1.42 Å [32], 1.42 in TEX) suggesting etheric cleavage (see Figures 2 and 4). In oxonium ion-2 (conformer of 1), the elongated C-O bond is 2.53 Å. Note that in structure-2, the proton faces the other dioxalane ring (inward). Figure 4 shows some selected bond lengths in the case of protonation at the etheric oxygen and the amine nitrogen. Note that in each of these protonated cases, one of the N-N bonds (nitramine) is noticeably longer (the right N-N bond of the structures in Figure 4) than the other nitramine bond (1.634 , 1.457 in structure-1, 1.620, 1.457 in structure-2 and 1.715, 1.472 Å in structure-3. For comparison the N-N bond lengths in N,N-dimethylnitramine and TEX are 1.382 Å [32] and 1.41 Å, respectively).

In the case of amine protonation (aminium ion formation), elongation of the N-N bond (1.716 Å) can be readily justified because two positively charged centers (protonated nitrogen and nitrogen of the nitro group) are adjacent. By contrast, the explanation of the elongation of the N-N bond when the etheric oxygen is protonated needs some contemplation (see section 3.2 below). Figure 4 also shows the crystallographic data of the bond lengths (in parenthesis). The experimental and the presently calculated bond lengths are in accord with each other. In most of the cases the absolute magnitudes of the deviations are less than 1%.

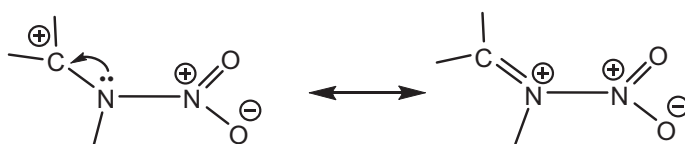
3.1 Hydrogen bridged cations

To get more insight into the protonation of TEX, hydrogen-bridged cations have also been considered. Hydrogen-bridged structures have been proposed, especially for boron hydrides [33, 34]. Although, in the case of simple hydrogen bonding, the hydrogen donor and acceptor molecules/sites (both intermolecular and intramolecular hydrogen bonding are intended) are well defined, in some intricate cases even the interaction of the hydrogen-bond acceptor with the cation (protonated heteroatoms acting as the hydrogen donor) are to be considered [35]. In the present case, four hydrogen-bridged cations of TEX are considered (see Figure 3). Structure-9 is the extreme one, where the proton is interacting with three heteroatoms (bifurcated H-bond, chelated H-bond [35-38]). All of the structures presented in Figure 3 have hydrogen bridges between two or three heteroatoms. In these structures, one of the hydrogen-heteroatom linkages is longer than the other(s), which suggests

a preferential tendency of the proton to attach itself to one site when a choice of more than one site of exists.

3.2 Carbocations

Actually, such an elongated etheric linkage in 1 (2.71 Å and 2.63 Å at B3LYP/6-31++G(d,p) and B3LYP/6-31G(d,p) levels, respectively, normally it is *ca.* 1.42 Å [32]) means only carbocation formation, and is labeled as cation-12 (see Figures 2 and 4). In this cation, the lone-pair on the amino nitrogen shifts towards the carbocation and becomes positively charged itself.



As seen in the above resonance structures, the situation of two positively charged nitrogen atoms which are adjacent causes the elongation of the N-N bond due to the repulsion of the two positive charges. Note that the present C-N bond, adjacent to the carbocation, is only 1.27 Å, whereas in N,N-dimethylnitramine it is about 1.46 Å [32]. The alternative cleavage leading to cation-13 (carbocation) is obtained by cleavage of the other etheric oxygen-carbon bond at the protonation site of the molecule. The resultant carbocation is not planar, contrary to the general geometrical features of carbocations, hence it should be more energetic. Also, the resultant structure has a highly elongated O-H bond (1.90 Å) inclined towards the NO₂ group (see Figure 5). As for its stabilization, only the inductive effect of the methine carbon of the other 1,3-dioxalane ring system and the mesomeric effect of the etheric oxygen of the broken ring are considered. However, such a mesomeric effect, if it could happen would result in the formation of a planar carbocation. The results indicate that structurally it is the most energetic structure of all (see the section 3.3). On the other hand, if the C-N bond in the protonated nitramine is broken, then cation-14 is formed. This can be stabilized by the mesomeric effect of the etheric oxygen. Indeed, the bond length of the C-O adjacent to the carbocation center is 1.378 Å, whereas the other C-O bond at the symmetrical position in the same 1,3-dioxalane ring is 1.415 Å, indicating some double bond character. Thus a shift of some electron density from the oxygen to the carbocation center should have occurred.

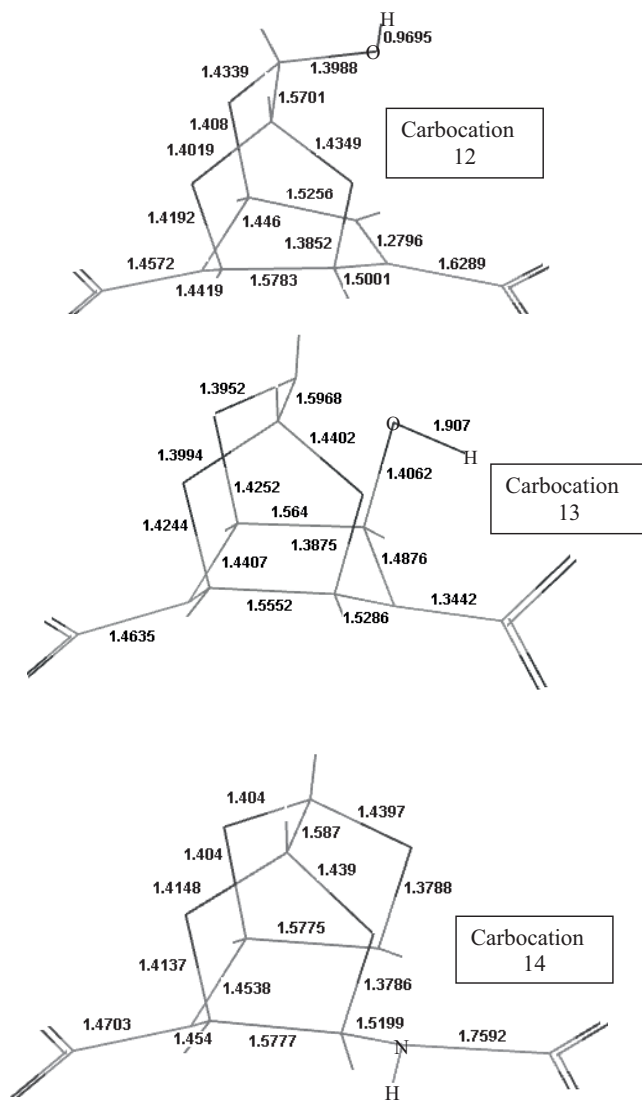


Figure 5. Some bond lengths of the carbocation structures considered. (B3LYP/6-31G(d,p), hydrogens omitted except original proton).

3.3 Energies

Table 1 shows the zero point energies (ZPE), the corrected total energies of all of these isomeric structures (1-9, $C_6H_7N_4O_8$), and the relative energies, as well as the dipole moments. Analysis of the energetics and the dipole moments shows

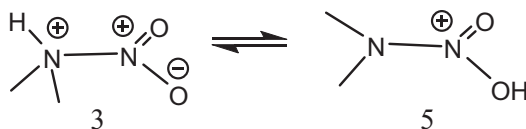
that structure-1 and structure-12 are in reality similar species. The relative energies indicate that the stability order is $8 > 5 > 1 > 9 > 6 > 3 > 7 > 2$ in vacuum and $5 > 2 > 1 > 9 > 6 > 3 > 7 > 8$ in water.

Table 1. Various properties of the protonated cations considered (B3LYP/6-31++G(d,p))

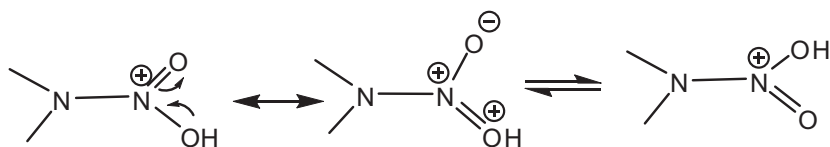
Compd. No.	Cation type	ZPE	E_{corr}	Relative energy in vacuum	$E(\text{aq})_{\text{corr}}$	Relative energy in water	Dipole moment
1	Oxonium	451.029821	-2764476.091	187.638	-2764683.290	31.58	4.840395
2	Oxonium	449.529683	-2764461.741	201.988	-2764686.040	28.83	4.970087
3	Aminium (exo)	458.465381	-2764465.735	197.994	-2764679.895	34.975	6.275386
5	N-hydroxy-N-oxoaminium derivative	458.730199	-2764480.300	183.429	-2764714.870	0.0	8.716505
6	H-bridged	458.474548	-2764465.855	197.874	-2764680.095	34.775	7.041872
7	H-bridged	458.596705	-2764465.443	198.286	-2764679.833	35.037	7.058799
8	H-bridged	458.190681	-2764663.729	0.0	-2764663.729	51.141	5.972981
9	H-bridged	458.445755	-2764465.954	197.775	-2764680.294	34.576	6.293666

All possess C1 symmetry. Energies in kJ/mol. Dipole moments in Debye.

Similarly, structures-4 and -5 are almost the same. The proton is close to the NO_2 group in 4 which, by a symmetry operation, almost becomes 5 (the N-H bond is so elongated in 4 that the proton is close to the oxygen atom of the other nitramine NO_2 moiety, tending to form structure-5). The total energies follow the stability order of $8 > 5 > 1 > 9 > 6 > 3 > 7 > 2$ in vacuum. Structure-8 is the most stable due to the larger ring for the H-bridge. Structure-5 (protonation on nitro-oxygen) is the next most stable because that site is sterically less hindered. Structures-7 and -9 contain 4-membered rings. Ring strain seems to be more pronounced in 7. The stability of 9 over 7 can be attributed to the fact that in 9 the proton is bridged to three centers, thus the charge is better distributed. Structures-3 and -5 should be interrelated through 1,3-proton tautomerism, which is briefly and partially shown below.



Structure-5 should be more favorable than structure-3 due to the lack of repulsive interactions between the nitrogen atoms. However, the hydrogen atom of structure-5 should be rather mobile because of the following mesomeric form, which may be prone to the tautomeric equilibrium shown.



The hydrogen atom might preferably migrate to the other oxygen atom (negatively charged) or to the other nitrogen atom of the nitramine bond.

Table 1 also shows the energies of the species in aqueous medium. In general these species are more stable in water. The stability order in aqueous medium is $5 > 2 > 1 > 9 > 6 > 3 > 7 > 8$. The carbocations considered possess the same stability order ($14 > 12 > 13$) in both vacuum and aqueous conditions.

Table 2. Various properties of the carbocations considered (B3LYP/6-31G(d,p))

Compd. No.	ZPE	E_{corr}	Relative corrected energy in vacuum	$E(\text{aq})_{\text{corr}}$	Relative corrected energy in water	Dipole moment
12	452.342857	-2764386.347	2.618	-2764608.417	13.558	4.83981
13	459.391361	-2764360.779	28.186	-2764593.059	28.916	5.72209
14	459.174947	-2764388.965	0.0	-2764621.975	0.0	5.65612

All possess C1 symmetry. Energies in kJ/mol. Dipole moments in Debye.

When compared with the corresponding order in vacuum conditions, structure-9 in aqueous medium is slightly more stable than 6 and structures-8 and -2 exhibit a dramatic change in terms of the stability. These changes can be attributed to effects arising from the special geometry of the structures in which any stabilizing effects occurring in the vacuum conditions might have been reduced or removed in aqueous media by the orientation of water molecules around the above mentioned cations.

Carbocation-13 is the least stable (most energetic) of the carbocations. It is not a planar structure and it is known that whenever the hybridization of a carbocation is not sp^2 (trigonal) it has a higher energy [39]. Structure-14 (carbocation) is more stable than 12 (carbocation) because in 14 the oxygen atom mesomerically stabilizes the carbocation whereas in 12, a similar role has to be performed by the nitramine amino nitrogen, but its lone pair electrons are already engaged by the nitro group. Consequently it cannot stabilize the carbocation center in 12 as effectively as the oxygen atom in 14.

Carbocations easily undergo various reaction [40, 41]. Although, bridged structures-6 and -9 have a high tendency to form structure-3 (see Figures 2

and 4), they are more stable than 3 because the proton is linked to more than one center in 6 and 9, thus decreasing the effective charge. Compared to the case of 3, structure-7 is quite energetic, most probably because of the presence of a 4-membered ring.

In the structure of TEX, there are four oxygen atoms (NO₂), two amino nitrogens (in the piperazine unit) and four etheric (acetal) oxygen atoms capable of being protonated. This statistical situation might influence the likelihood of protonation tendencies. The present calculations indicate that protonation of TEX under aqueous conditions occurs preferentially on the nitro oxygen atoms (leading to structure-5), if only thermal factors are considered, but under vacuum conditions structure-8 is favored. On the other hand, carbocations 14 or 12 may form under either vacuum or aqueous conditions, wherever the initial attack of the proton occurs. As soon as a carbocation forms, it is susceptible to attack by various nucleophiles present in the medium, as well as to elimination and ring opening reactions [40, 41].

4 Conclusion

By using the DFT approach, the protonation of TEX has been intensively researched, considering various alternatives. The results reveal that H-bridged structures play some role in vacuum but are less effective in water. The resultant cations in each case are more stable in aqueous conditions compared to the vacuum. Anion formation initiates decomposition of TEX.

5 References

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