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# Thermal decomposition pathways for 1,1-diamino-2,2-dinitroethene (FOX-7)

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In this study, we computationally investigate the initial and subsequent steps in the chemical mechanism for the gas-phase thermal decomposition of 1,1-diamino-2,2-dinitroethene (FOX-7). We determine the key exothermic step in the gas-phase thermal decomposition of FOX-7 and explore the similarities and differences between FOX-7 and other geminal dinitro energetic materials. The calculations reveal a mechanism for NO loss involving a 3-member cyclic intermediate, rather than a nitro-nitrite isomerization, that occurs in the radical intermediates formed throughout the decomposition mechanism. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4896165]

## INTRODUCTION

Over the last few decades there have been numerous experimental and theoretical studies detailing the structure and decomposition pathways of energetic materials. Despite the large body of work on this subject, the initial decomposition steps in energetic materials are still debated and the decomposition steps responsible for the large exothermicity are often unresolved.[1–9] For energetic materials containing nitro groups, the three most likely initial steps are: HONO elimination, $NO_2$ loss, and NO loss via a nitro-nitrite isomerization.[1] For example, gas-phase[1] studies of the thermal decomposition of dimethylnitramine (DMNA) and 1,3,3-trinitroazetidine (TNAZ) conclude that C-$NO_2$ fission is the first step in the thermal decomposition mechanism, in agreement with prior infrared multiphoton dissociation experiments in molecular beams. Interestingly, the first step in the decomposition of many energetic materials changes based on the type of excitation. For example, there have been several studies from Bernstein and co-workers[2–5] investigating the mechanistic differences between thermal and photo-initiated decomposition of several energetic materials (RDX, PETN, HMX, and CL-20). Specifically, while the lowest calculated barrier in the thermal decomposition of PETN is C-$NO_2$ bond fission, upon gas-phase UV photodissociation the dominant first step is NO loss via a nitro-nitrite isomerization. Similarly, a study by Garland and Nelson[6] concluded that the initial step in the UV photodecomposition of solid samples of TNAZ was also NO loss. In our computational study presented herein, we seek to determine the initial and subsequent decomposition steps in the unimolecular thermal decomposition of a relatively new material, 1,1-diamino-2,2-dintiroethene (FOX-7).

FOX-7 is an insensitive energetic material making it a promising and potentially useful replacement for other energetic materials currently in use. FOX-7 is a relatively small molecule composed of an ethene moiety separating two amino groups and two nitro groups. While there have been numerous experimental and theoretical studies on the explosive and crystalline properties of FOX-7,[10–21] there have been only a few quantum mechanical studies on the unimolecular decomposition mechanism.[22,23] In 1998, Östmark *et al.*[10] experimentally determined the thermal activation energy for solid FOX-7 as 58 kcal/mol. Later, in 2005, Burnham *et al.*[11,12] used FTIR to analyze the final products of the thermal decomposition of solid FOX-7 and determined the activation energy to be 56.9 kcal/mol. Zheng *et al.*[21] used molecular dynamics simulations to model the thermal decomposition of crystalline FOX-7 at high temperatures and concluded that the main products were $N_2$ and $H_2O$. Dorsett[22] investigated nitro-nitrite isomerization and intermolecular hydrogen transfer as possible initial steps in the unimolecular thermal decomposition of FOX-7 using the B3LYP functional. Her calculations demonstrated that direct C-$NO_2$ bond fission has a significantly higher barrier than either of these steps and is unlikely to compete in gas phase thermal decomposition. Gindulyte *et al.*[23] also used density functional theory to investigate unimolecular FOX-7 decomposition; they concluded that the initial step is a nitro-nitrite isomerization due to the low calculated barrier energy of 59.1 kcal/mol. Following this isomerization, their calculations showed that the end products are NO, HONO, CO, $NH_2$, and HNC. Interestingly, recent calculations by Kiselev and Gritsan[24] done at the CCSD(T) level[24] postulate that an intramolecular hydrogen shift between the amine and the carbon adjacent to the nitro groups has a lower barrier than the nitro-nitrite isomerization and would likely dominate in gas-phase thermal decomposition. However, this new barrier is significantly lower than the experimentally determined activation energy for crystalline FOX-7.

The study presented herein computationally investigates all possible thermally-initiated decomposition pathways available for gas-phase FOX-7 as well as the subsequent dissociation channels. These calculations, performed at the G4//B3LYP/6-311++g(3*df*,2*p*) level, detail a complete picture of the unimolecular dissociation pathways available to FOX-7 following thermal excitation. The main decomposition pathways in this system begin with four possible initial steps: direct $NO_2$ loss, nitro-nitrite isomerization to yield NO, a hydrogen transfer to the nitro-carbon, and a cyclization reaction to form an oxazete-N-oxide moiety. Due to the unsaturated hydrocarbon backbone of FOX-7, initial C-$NO_2$ bond fission

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has the highest calculated barrier of all four initial steps and is not expected to compete thermally in the gas phase.

In addition to studying decomposition mechanisms in energetic materials, FOX-7 also serves as an ideal system for studying the specific mechanism for NO loss in nitroalkyl radicals. Despite its relatively small size compared to other energetic materials, FOX-7 has a complex decomposition mechanism that passes through several different nitroalkyl radical intermediates. While the nitro-nitrite isomerization mechanism has been heavily studied among closed-shell nitroalkanes[25–31] and remains largely unchanged across different nitroalkanes, NO loss in nitroalkyl radicals occurs through an entirely different process. Recently, we published calculations[32] detailing the NO-loss mechanism in the 2-nitro-2-propyl radical at the G4//B3LYP/6-311++g(3*df*,2*p*) level and confirmed the mechanism experimentally. We found that the radical does not go through a nitrite intermediate but rather undergoes isomerization through a tight three-member ring formed between the C, N, and O atoms. This cyclic intermediate is defined as "tight" since the calculated bond distances between each of the atoms is approximately equivalent to a covalent bond. This ring intermediate is not a stable minimum but rather loses NO in a concerted process. In addition, the barrier to this tight cyclic isomerization is 27 kcal/mol lower than a "traditional" nitro-nitrite isomerization. Since FOX-7 has five different species (four radicals) in the initial and subsequent decomposition steps that can lose NO, it serves as an ideal system to study this mechanism and provide further evidence for the relevance of this low barrier pathway in the decomposition of nitroalkyl radical species. Furthermore, calculations on FOX-7 reveal that the most exoergic decomposition pathway passes through one of these tight cyclic NO-loss transition states.

## COMPUTATIONAL METHODS

All calculations were performed at the G4//B3LYP/6-311++g(3*df*,2*p*) level of theory using the GAUSSIAN 09 software package.[33] Intrinsic reaction coordinate (IRC) calculations were performed on most transition states unless the transition state was relatively simple, (e.g., hydrogen transfer). Natural Bond Order (NBO) analysis was performed on certain structures in order to characterize the bonding between atoms. Atomic spin density was determined at the B3LYP/6-311++g(3*df*,2*p*) level for all open-shell species. The carbon atoms are designated as in the IUPAC nomenclature, that is, C1 is bonded to the amino groups and C2 is bonded to the nitro groups. Each minimum geometry is designated as an intermediate structure and identified with an I (i.e., I2). If the species is a transition state (TS) then the label TS will be added to its respective number (i.e., TS2).

## RESULTS

### Initial thermal decomposition steps

Figure 1 shows our calculated results for three possible initial steps for the gas-phase thermal decomposition of FOX-7: loss of $NO_2$ to form intermediate 4 (I4) + $NO_2$, with a barrier equal to the endoergicity of 69.3 kcal/mol (Eq. (1)); a nitro-nitrite isomerization (TS5) with a barrier of 58.4 kcal/mol producing I6 (Eq. (2); and a hydrogen shift from an amine to C2 (TS2) at 47.9 kcal/mol producing I3 (Eq. (3)). The structures of each local minimum and transition state species, with labeled bond lengths and angles, are given in Fig. 2.

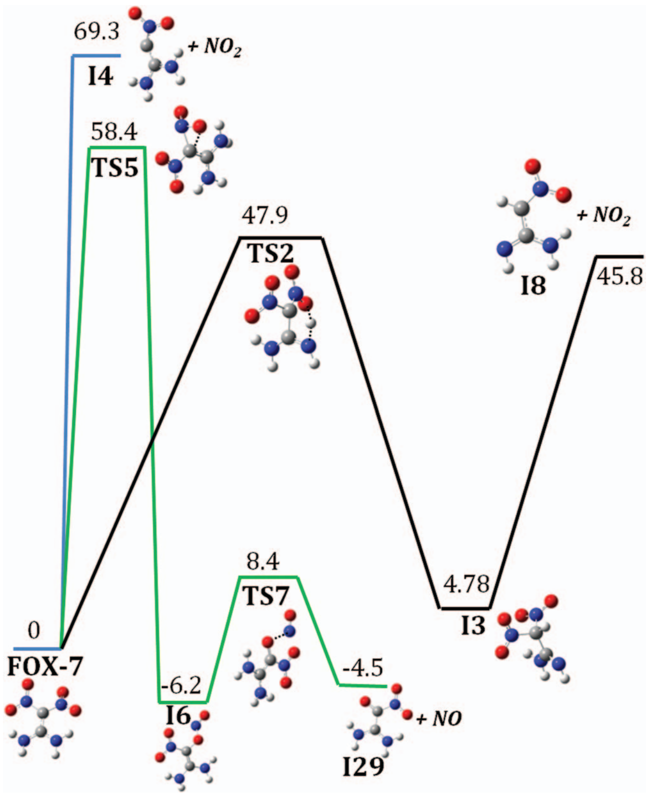

FIG. 1. Calculated minima and transition states for the possible initial dissociation channels of 1,1-diamino-2,2-dinitroethene (FOX-7) on the ground state potential energy surface. All values are expressed in units of kcal/mol relative to FOX-7 (structure I1) and were calculated at the G4//B3LYP/6-311++g(3*df*,2*p*) level. The geometries for each stationary point are shown in Fig. 2 with the numbering system unchanged.

Cleavage of the C-N bond yields $NO_2$ and a nitroalkene radical (I4) where the lone electron is only slightly delocalized across the remaining $NO_2$ group. This is demonstrated by the fact that there is only minimal change in the length of each of the remaining bonds (max of ~3% or ~0.05 Å). This is partly what results in the high barrier to $NO_2$ loss. Thus, we do not expect direct C-$NO_2$ bond fission to be the dominant initial step in the gas-phase thermal decomposition of FOX-7:

$$(NH_2)_2C=C(NO_2)_2 \rightarrow (NH_2)_2C=C(NO_2) + NO_2, \tag{1}$$

$$\begin{aligned}(NH_2)_2C &= C(NO_2)_2\\ &\rightarrow (NH_2)_2C=C(NO_2)(ONO)\\ &\rightarrow (NH_2)_2C=C(NO_2)(O) + NO,\end{aligned} \tag{2}$$

$$\begin{aligned}(NH_2)_2C &= C(NO_2)_2\\ &\rightarrow (NH_2)(NH)C-C(H)(NO_2)_2\\ &\rightarrow (NH_2)(NH)C-C(H)(NO_2) + NO_2.\end{aligned} \tag{3}$$

The second of the possible initial steps in FOX-7 decomposition is nitro-nitrite isomerization via a barrier of

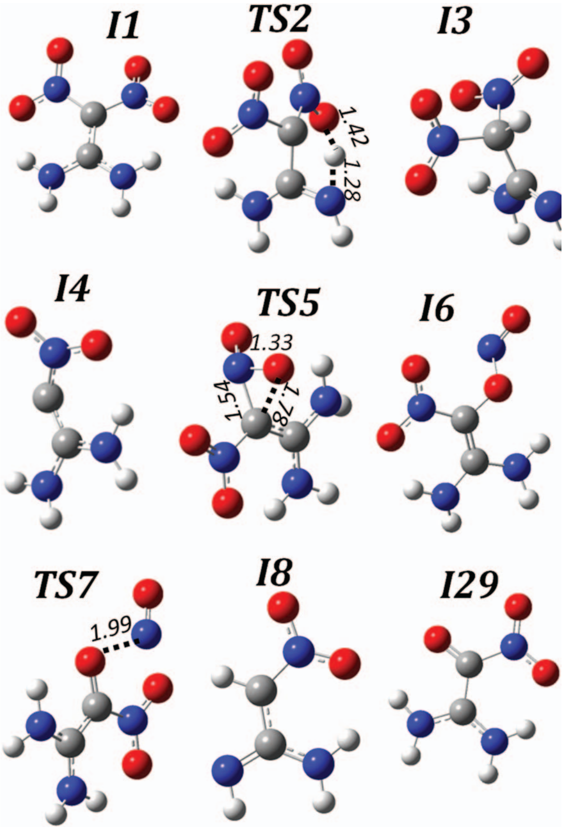

FIG. 2. Calculated geometries for each stationary point shown in the PES in Fig. 1. All of the geometries were calculated at the B3LYP/6-311++g(3*df*,2*p*) level. The designation of the geometries is identical to their respective energetic shown in Fig. 1. Important geometric parameters are shown for each transition state geometry and are reported in units of Å.

58.4 kcal/mol (TS5). The nitrite isomer (see I6 in Fig. 2) is slightly more stable than FOX-7 and the isomerization is exothermic by 6.2 kcal/mol. The nitrite species then undergoes O-NO bond fission with a barrier of 13.3 kcal/mol (TS7) yielding I29 + NO. Although the barrier to this pathway is lower than that for direct C-$NO_2$ bond fission, it is still slightly higher than the third possible initial step discussed in the next paragraph. Nevertheless, as discussed throughout the paper, it is this NO loss that leads to radical intermediates that undergo net exothermic product channels in gas-phase FOX-7. Thus, NO loss Eq. (2) is probably the most important of the three possible initial steps in FOX-7 decomposition.

The third possible initial step is a H-shift pathway with a barrier of 47.9 kcal/mol (TS2) and a total endoergicity of 4.8 kcal/mol. The H-shifted isomer (I3) can then undergo $NO_2$ loss with a barrier of 41.0 kcal/mol (relative to I3). Alternatively, this isomer can also undergo a nitro-nitrite isomerization with a barrier of 57.9 kcal/mol, but that barrier is so much higher than that to direct C-$NO_2$ bond fission that it is not expected to be competitive. See Figure S1 in the supplementary material for further details of this isomerization pathway.[34] The fourth possible initial step is a cyclization pathway yielding a strained four-member ring with a C-C-N-O framework. This pathway is detailed in Figure S1 in the supplementary material.[34]

Due to the ethene sub-structure in FOX-7, the nitro-nitrite isomerization TS is significantly different than that observed for alkanes and merits further investigation. The nitro-nitrite isomerization TS in FOX-7 (TS5) has a fairly short C-N bond at 1.54 Å and a longer C-O bond of 1.78 Å. These bonds are significantly shorter than is observed in $sp^3$ carbons where both bonds range from 1.9 Å to 2.2 Å; an example of these longer bonds is observed in the nitro-nitrite isomerization from H-shifted FOX-7 (I3). The presence of the double bond allows the carbon and nitrogen to remain bonded throughout most of the isomerization and this in turn lowers the barrier height to such an extent that it is competitive with C-$NO_2$ fission. NBO analysis confirms that the C-N bond remains a two-electron bond at the TS while the C-O bond only involves one electron. The TS geometry is slightly different than the calculated geometry for the nitro-nitrite isomerization TS in the analogous 2-nitropropene[32] where both the bonds were longer (C-N = 1.7 Å, C-O = 1.8 Å). These differences are most likely due to the electron withdrawing effects of the second $NO_2$ group in FOX-7; this allows stronger bonds between C2 and the isomerizing $NO_2$ group. After isomerization the nitrite species has an elongated O-N bond (1.7 Å) that is extremely weak and undergoes bond fission with a barrier (TS7) of only 13.3 kcal/mol. NBO calculations show that despite the long bond length, the O-NO bond involves two electrons. The nitrite isomer of FOX-7 has two conformers: *cis* and *trans* (I6) relative to the carbon attached to the nitrite group. The *cis* conformer is lower in energy by 1.3 kcal/mol, perhaps due to weak $\pi$-$\pi$ interactions between the $NO_2$ group and the C=C bond. The transition state for NO loss appears to only exist for the *trans* conformer and as such only the *trans* conformer is shown in Figs. 1 and 2.

### Decomposition pathways after H-shift and subsequent $NO_2$ loss

We suggest in Sec. "Initial thermal decomposition steps" that an intramolecular hydrogen transfer followed by $NO_2$ loss would be the dominant initial step in isolated FOX-7 molecules due to the low barrier. Note, however, that the low barrier is only likely to exist for isolated FOX-7 molecules since the amino hydrogens would be involved in extensive hydrogen bonding in the condensed and solid phases; this would likely raise the barrier to the H-shift pathway significantly.

Figure 3 details all of the subsequent pathways for FOX-7 following a H-shift and subsequent $NO_2$ loss. The resulting radical (I8) can undergo two subsequent steps: a hydrogen transfer back to the amino group with a barrier of 50.7 kcal/mol (TS22) or a 3-center transition state (TS9) involving a tight cyclic intermediate, followed by NO fission. This NO-loss TS, with a barrier of 40.0 kcal/mol, circumvents traditional nitro-nitrite isomerization. In Fig. 3, this pathway is designated as I8 → I10. Due to the low barrier, the tight cyclic NO loss TS (TS9) is expected to dominate during thermal decomposition. The energies of the stationary points for all subsequent dissociation events are shown in Fig. 3 and the geometries for each point are shown in Fig. 4 with the relevant geometric parameters labeled. The energies reported in Fig. 3 are relative to structure I8.

The lowest pathway after the initial H-shift and $NO_2$ loss is via a 3-center TS (TS9) that passes through a cyclic

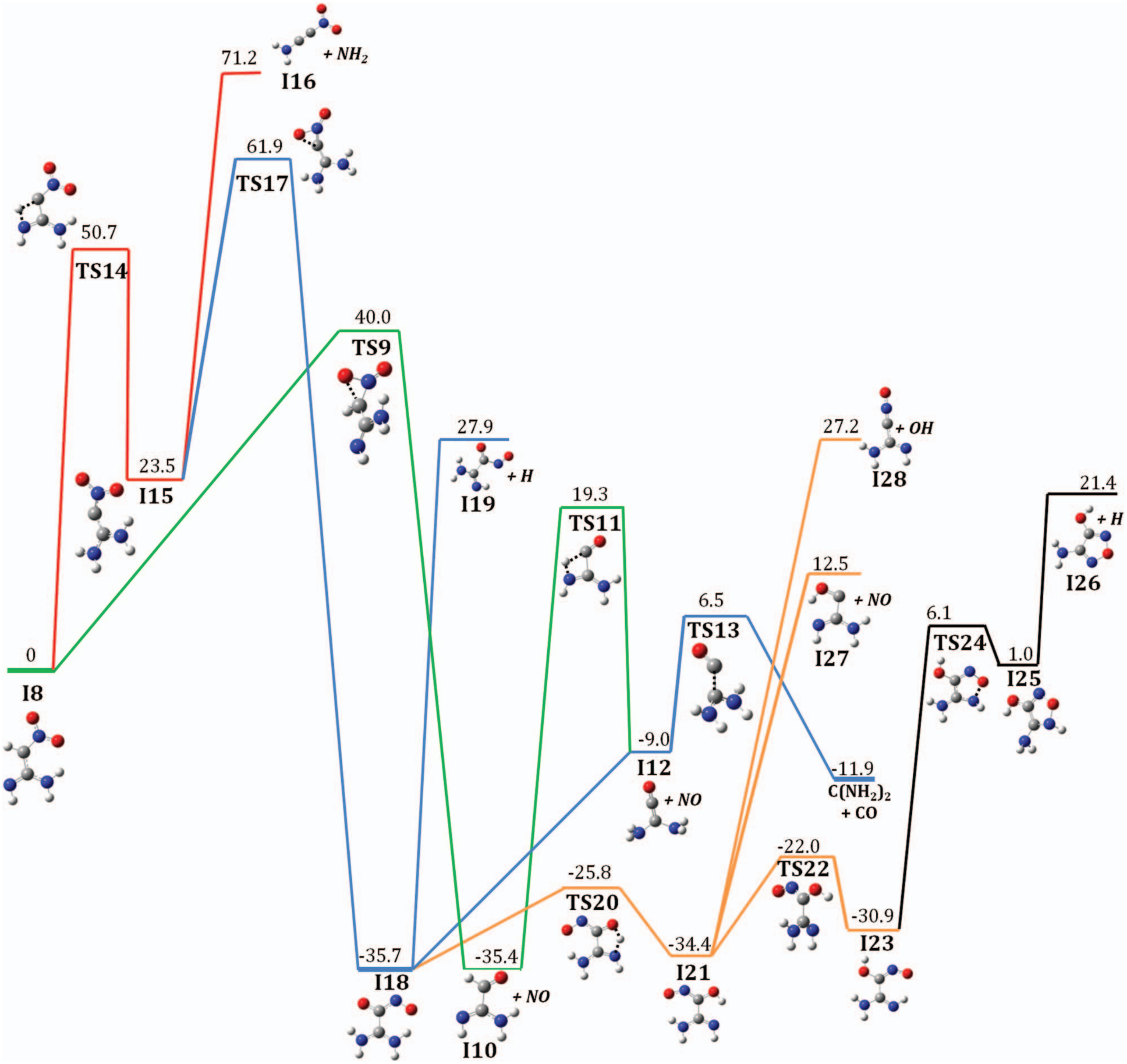

FIG. 3. Calculated minima and transition states for the possible dissociation channels of the radical formed from a H-shift and subsequent $NO_2$ loss in FOX-7 (1-amino-1-imino-2-nitro-2-ethyl radical) on the ground state potential energy surface. All values are expressed in units of kcal/mol relative to structure I8 and were calculated at the G4//B3LYP/6-311++g(3*df*,2*p*) level. The geometries for each stationary point are shown in Fig. 4 with the numbering system unchanged.

structure on the reaction coordinate of the TS en route to NO loss (I8 → TS9 → I10 + NO). The TS for this isomerization does not resemble traditional nitro-nitrite isomerization geometry but rather has a short C-N bond of only 1.40 Å and a long C-O bond length of 1.82 Å. Furthermore, this isomerization does not yield a stable isomer but proceeds through a shoulder (not a local minimum) along the reaction coordinate; this shoulder is a heterocyclic three-member ring involving the C-N-O atoms formed en route to fission of the C-N and O-N bonds yielding NO + $H_2NC(NH)CHO$ (I10) in a concerted process. This shoulder along the I8 → I10 + NO reaction coordinate in Fig. 3 is shown in detail in Fig. 5. The intermediate cyclic structure (not a stable minimum) is confirmed by the use of an IRC calculation that clearly shows both ring formation and subsequent bond fission occurring along the downhill slope of the reaction coordinate path (Fig. 5); this channel is exoergic by 35.4 kcal/mol from I8. However, since the first step in this pathway (FOX-7 → I8, see Fig. 1) is endoergic by 45.8 kcal/mol, this NO loss pathway is net endoergic.

The resulting conjugated species (I10) then undergoes a H-shift from the carbon to the amino group yielding $(NH_2)_2CCO$ (I12) with a barrier of 54.7 kcal/mol via TS11. In this reaction, the molecule retains its C=O group and gains a double bond between the two carbon atoms. Despite the apparent double bond between the carbons the transition state (TS13) to break the C=C bond and form CO and $C(NH_2)_2$ is only 15.5 kcal/mol. TS13 has a long C-C bond (1.74 Å) and a C=O bond length of 1.16 Å. Interestingly, NBO calculations on this species (TS13) show that there is a lone pair on C2, creating a negative formal charge on C2 and a positive formal charge on C1; this situation leads to efficient cleavage

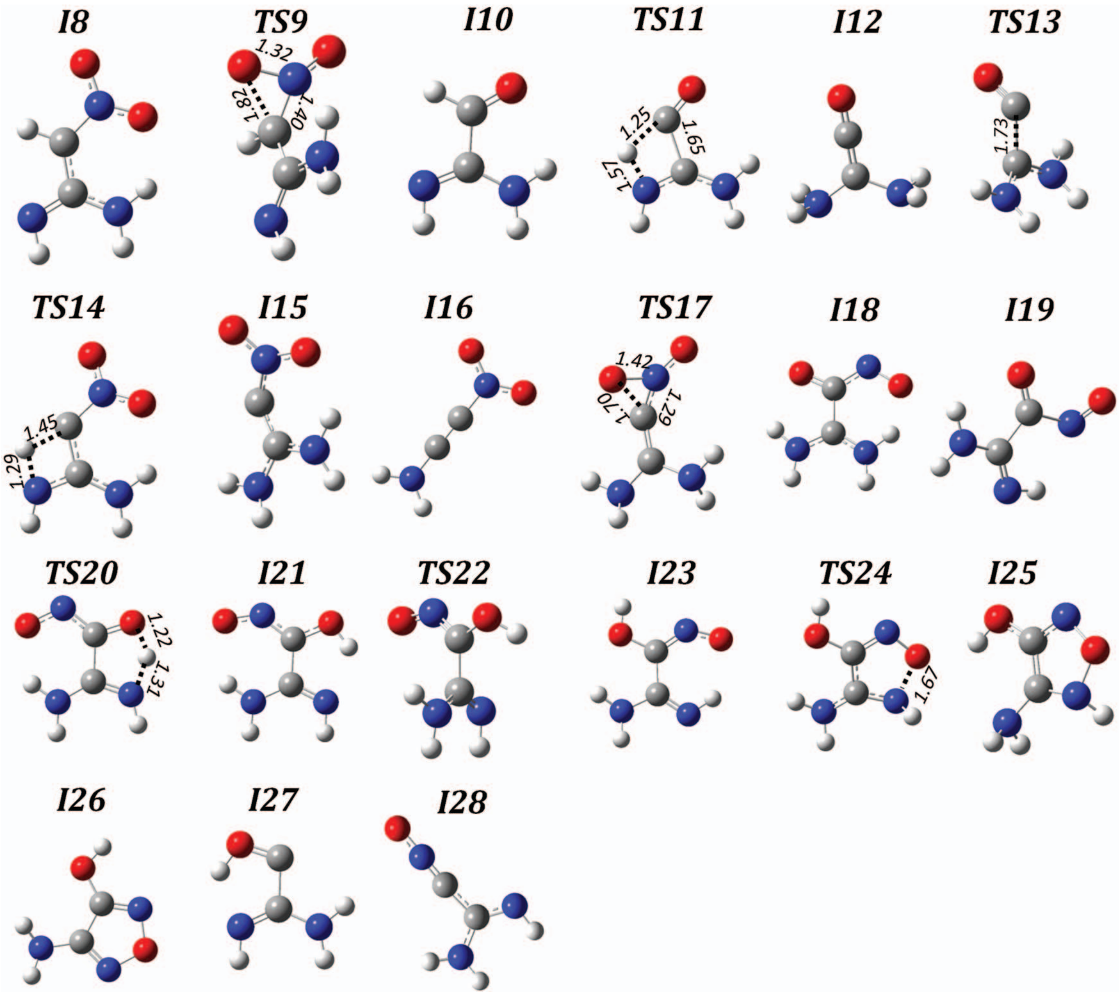

FIG. 4. Calculated geometries for each stationary point shown in Fig. 3. All of the geometries were calculated at the B3LYP/6-311++g(3*df*,2*p*) level. The designation of the geometries is identical to their respective energetic shown in Fig. 3. Important geometric parameters are shown for each transition state geometry and are reported in units of Å.

of the C-C bond yielding CO and singlet diaminomethylene; this reaction is exothermic by 3 kcal/mol relative to I12. The exothermicity of this dissociation is likely due to the stability of the resulting diaminocarbene species; this is one of the few classes of persistent carbenes.

The pathway with the highest barrier is I8 → I15 (shown as red in Fig. 3). This path consists of a H-shift from C2 to the imine group creating a vinyl radical geminal to a nitro group. Note that this structure (I15) is the same structure that results from direct C-$NO_2$ fission in FOX-7 Eq. (1); however, the much lower barrier to the H-shift channel Eq. (3) ensures that the C-$NO_2$ fission pathway in Eq. (1) does not occur in isolated FOX-7 and that species I15 is formed almost exclusively via TS14 (Fig. 3). This isomer (I15) is slightly less stable and is endoergic by 23.5 kcal/mol; this is most likely due to the localization of the radical on the alkene carbon. This isomer (I15) has two possible decomposition pathways: loss of $NH_2$ with a bond dissociation energy of 47.7 kcal/mol (I16) and a tight cyclic NO-loss TS (TS17) with a barrier energy of 38.4 kcal/mol (both of these endoergicities are relative to I15). The tight TS to NO loss (TS17) has an extremely short C-N bond of 1.29 Å, a C-O bond length of 1.70 Å, and a relatively long N-O bond of 1.42 Å. Due to the ethenyl-like radical center,

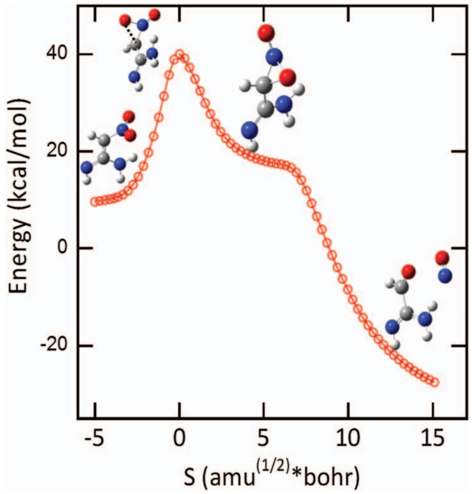

FIG. 5. Intrinsic reaction coordinate (IRC) calculations performed at the B3LYP/6-311++g(3*df*,2*p*) level. The IRC follows the NO-loss pathway from 1-amino-1-imino-2-nitro-2-ethyl radical (I8 → TS9 → I10). Energy is reported relative to the energy of structure 16 (Fig. 3) calculated at the B3LYP/6-311++g(3*df*,2*p*) level and is not corrected for zero-point energy. Geometries of the transition state and intermediate are shown on the IRC plot. All geometry optimizations were performed at the B3LYP/6-311++g(3*df*,2*p*) level.

this pathway does not form a nitrite functionality but rather an isomer with geminal nitroso and carbonyl groups (I18). This NO-loss pathway is exothermic by 59.2 kcal/mol relative to I15. NBO analysis of the $(H_2N)_2CC(O)(NO)$ isomer (I18) shows that the radical is heavily delocalized through both the NO group and the lone oxygen. This delocalization creates a slight positive charge on C1 that is stabilized via electron donation from the neighboring amino group(s). This electronic configuration creates intense electron withdrawing from the $C(NH_2)_2$ group which effectively removes electron density from the C-N and C-O bonds. While this withdrawing effect does not appear to affect the C-O bond to a large degree, the C-NO bond is significantly weakened. Consequently, the C-NO bond is moderately weak, and breaks (I18 → I12, see Fig. 3) with an endoergicity of only 26.7 kcal/mol. This C-NO bond fission yields species I12 whose dissociation events were described in the previous paragraph.

The $(H_2N)_2CC(O)(NO)$ species (I18) is not likely to undergo the bond fission event (I18 → I12) described above, however, because it can undergo a keto-enol tautomerization (I18 → I21) with a much lower barrier (TS20) of 9.9 kcal/mol. The resulting enol tautomer (I21) can then undergo two bond fission events: loss of NO or OH with endoergicities of 46.9 and 60.6 kcal/mol, respectively, relative to I21. The lowest barrier, however, is a conformational isomerization where one half of the molecule undergoes a 180 rotation via TS22. This conformer can then form a radical heterocyclic ring after a bonding event between the nitroso and the imine group with a barrier of 37 kcal/mol (TS24). This cyclic species (I25) can efficiently lose a hydrogen atom with a bond dissociation energy of 20.4 kcal/mol yielding 3-amino-4-hydroxylfurazan, an aromatic heterocyclic ring (I26).

## Decomposition pathways post NO loss

After FOX-7 loses NO (FOX-7 → I29 + NO, see Fig. 1) via the isomerization reaction detailed in Eq. (2), the resulting radical species (I29) has several subsequent decomposition pathways available. The energetics of these various pathways are detailed in Fig. 6 and the optimized geometries are shown in Fig. 7 (note that all energies in Fig. 6 are relative to I29). This radical species (I29) possesses a carbonyl-like group on the C2 with a C=O bond length of 1.22 Å adjacent to the remaining $NO_2$ group with the radical delocalized onto C1 and the carbonyl oxygen. NBO analysis shows that there are three-electron bonds between each of the four heavy atoms ($O$-$C$-$C$-$NH_2$) and confirms the delocalization of the radical. The backbone of this intermediate is planar, allowing for hydrogen bonding between the $O$-$NH_2$ and the $NO_2$-$NH_2$ groups. There are three possible dissociation pathways for this radical: the pathway with the highest barrier is loss of NO via a tight cyclic TS with a barrier of 35.1 kcal/mol (TS38), and the two lowest are H-shifts between an amino group and either the O or $NO_2$ (on C2) groups with barriers of 15.2 kcal/mol (TS34) and 12.7 kcal/mol (TS30), respectively. The H shift to the O group is endoergic by 12.7 kcal/mol forming species I35 and to the $NO_2$ is 3.7 kcal/mol forming species I31. Calculations show that almost the entirety of the radical spin density is delocalized throughout the HONO moiety in I31 with a very small amount present on either carbon. In contrast, the enol species (I35) has half of the total unpaired spin density on C2 with the rest spread between the three oxygen atoms. An increased radical density on the carbon is likely the reason for the higher endoergicity. Both of these H-shifted species remain flat demonstrating significant hydrogen bonding.

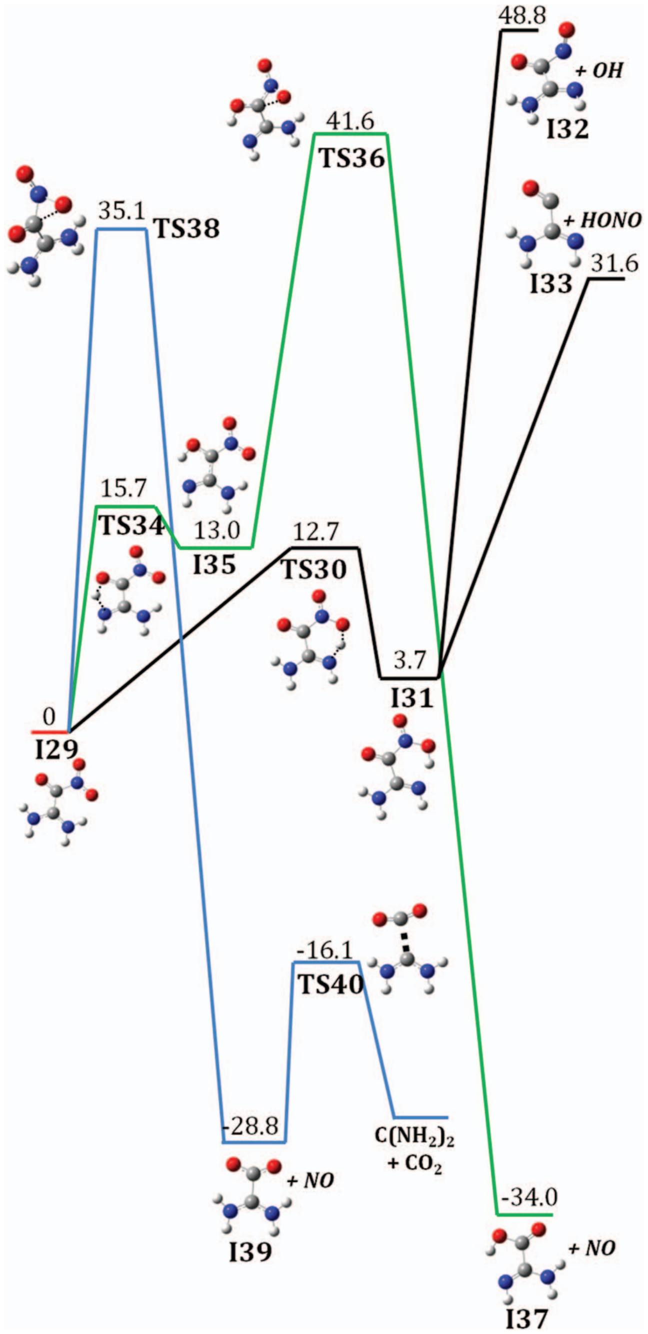

FIG. 6. Calculated minima and transition states for the possible dissociation channels of the radical formed from a NO loss in FOX-7 (1,1-diamino-2-nitroethen-2-al radical) on the ground state potential energy surface. All values are expressed in units of kcal/mol relative to structure I29 and were calculated at the G4//B3LYP/6-311++g(3*df*,2*p*) level. The geometries for each stationary point are shown in Fig. 7 with the numbering system unchanged.

The higher energy dissociation event for I29 is loss of a second NO fragment in the mildly exothermic pathway shown as the blue line in Fig. 6. In this pathway, I29 loses NO after passing through a tight three-member ring intermediate that

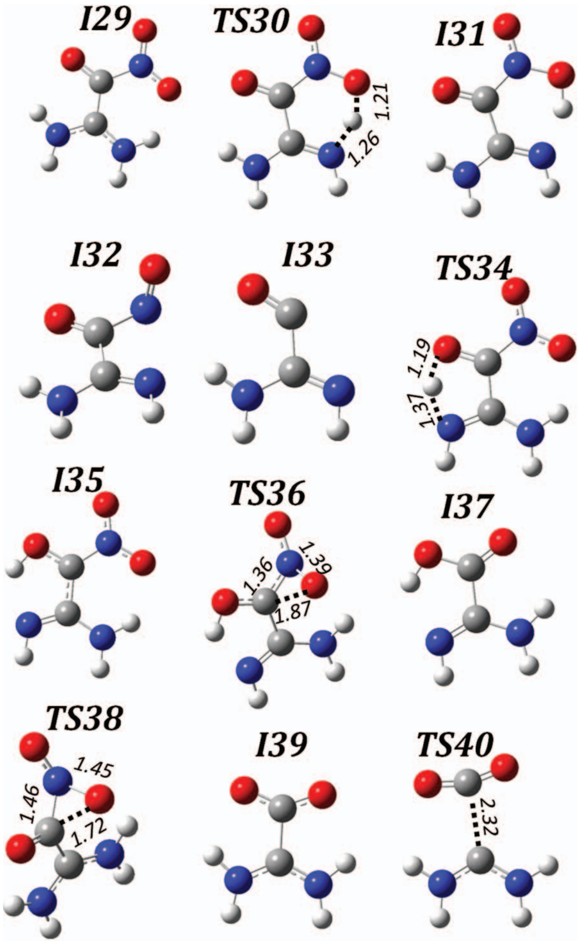

FIG. 7. Calculated geometries for each stationary point shown in the PES in Fig. 6. All of the geometries were calculated at the B3LYP/6-311++g(3*df*,2*p*) level. The designation of the geometries is identical to their respective energetic shown in Fig. 6. Important geometric parameters are shown for each transition state geometry and are reported in units of Å.

is extremely similar to the one described in Sec. "Decomposition pathways after H-shift and subsequent $NO_2$ loss". This intermediate is not a stable minimum and consequently undergoes concerted O-N and C-N bond fission to yield species I39 (Fig. 6); this pathway is exothermic by 28.8 kcal/mol. The structure of the resulting singlet ($(NH_2)_2CCO_2$) (I39) is particularly interesting because its lowest energy configuration resembles an ethane substructure with a carboxalate group on C2 and a positive charge delocalized across C1 and its two amino groups. This species has an extremely weak C-C bond demonstrated by low energy bond fission TS (TS40) of only 12.7 kcal/mol.

The second lowest barrier for the decomposition of I29 (the radical resulting from FOX-7 losing NO shown in Eq. (2)) is a H-shift from the amine to the lone oxygen atom forming species I35 (and a hydroxyl group). This molecule (I35) has two high-energy dissociation channels: OH loss and $NO_2$ loss, neither of which is energetically accessible, and a lower pathway shown in green in Fig. 6 (I35 → TS36 → I37). This low energy path passes through a tight TS and a cyclic intermediate en route to NO loss and has a transition state energy of 28.6 kcal/mol relative to I35. As described in previous paragraphs, this NO-loss pathway proceeds through a tight three-member ring intermediate and not a traditional nitrite species. After NO loss, the resulting structure contains a carboxylic acid moiety on C2. This species can then undergo either C-C bond fission or a H-shift from the O atom to the imine group. The lowest barrier from I29 is a hydrogen shift to the $NO_2$ group, forming a HONO moiety adjacent to the carbonyl-like group (I31); this species can subsequently lose either HONO or OH. The total endoergicity to undergo N-OH bond fission ($I31 \rightarrow I32 + OH$) is 45.1 kcal/mol relative to species I31. The pathway to C-$NO_2$H bond fission ($I31 \rightarrow I33 + HONO$) has a much lower total endoergicity of 27.9 kcal/mol and is expected to dominate over the OH loss pathway during gas-phase thermal decomposition.

Interestingly, the only net exothermic unimolecular decomposition pathways for FOX-7 occur from the I29 radical species formed when FOX-7 loses a NO group. These pathways are shown in blue and in green in Fig. 6; the lower barrier blue pathway occurs from I29 to I39 with a barrier of 35.1 kcal/mol. The only pathway expected to compete with this exothermic dissociation is HONO loss from species I31 with an endoergicity of 31.6 kcal/mol.

## DISCUSSION

In organic energetic materials with saturated hydrocarbon backbones or strained rings and C-$NO_2$ and N-$NO_2$ groups, $NO_2$ loss tends to dominate over NO production in gas-phase thermal decomposition.[1] This is due to the high barrier of the nitro-nitrite isomerization. However, the addition of an unsaturated moiety adjacent to a nitro group (as demonstrated in FOX-7) creates new decomposition pathways usually thermally inaccessible in other energetic materials. For example, the nitro-nitrite isomerization barrier in isolated FOX-7 is actually lower in energy than the barrier to C-$NO_2$ bond fission. This is due to the alkene group allowing the C-N bond to retain a small amount of bonding throughout the isomerization (this is opposed to nitroalkanes where the C-N bond is stretched almost to the breaking point). In addition, direct C-N fission creates a radical geminal to an alkene, which is significantly more unstable than in the analogous alkane. Thus, in gas-phase FOX-7, the NO-loss pathway is expected to dominate over the direct C-$NO_2$ bond fission in thermal decomposition.

In addition, the double bond allows for efficient hydrogen transfer from the amino group to the nitro-carbon with a barrier of only 47.8 kcal/mol. This H-shifted species subsequently loses $NO_2$, which resembles the likely first thermal decomposition step in energetic materials with saturated hydrocarbon backbones. While the hydrogen transfer is the lowest calculated barrier by ~10 kcal/mol, it is also ~10 kcal/mol lower than the experimentally determined activation energy for thermal decomposition of solid FOX-7 (~58 kcal/mol). In fact, the experimental activation energy matches almost perfectly with the calculated TS energy for the initial nitro-nitrite isomerization but this NO-loss channel is not expected to compete with the lower energy H-shift pathway in gas-phase FOX-7. While the H-shift pathway is significantly lower than the NO-loss pathway in isolated FOX-7, the condensed and crystalline phases of FOX-7 are expected to have significant hydrogen bonding of the amino hydrogens to the nitro groups. This hydrogen bonding would be expected to increase the barrier to an H-shift reaction significantly because of the increased energetic cost of breaking the intermolecular hydrogen bonds. Therefore, we postulate that the NO-loss pathway may be the lowest barrier available in the thermal decomposition of condensed and crystalline phase FOX-7. This conclusion is supported by the experimentally determined activation energy of ∼58 kcal/mol.[10] Although the direct C-$NO_2$ bond fission (FOX-7 → I4 + $NO_2$) pathway cannot compete thermally in the gas phase, the radical intermediate formed in the reaction (I4) could still be important in the decomposition of FOX-7. Since this intermediate can be formed through a lower energy pathway (following a H-shift and subsequent $NO_2$ loss Eq. (3) via the I8 → I15 pathway) it is possible that this alkene radical intermediate may be present in relatively small amounts throughout the thermal decomposition of FOX-7.

The majority of the calculated dissociation channels for FOX-7 are standard bond fission reactions and not particularly notable. The NO production channels, however, are interesting in that many of them differ from the "traditional" nitro-nitrite isomerization transition states seen in nitroalkanes. Furthermore, while the nitro-nitrite isomerization has been extremely well studied in closed-shell nitroalkanes and nitroalkenes, it has not been well studied in open-shelled systems. We recently published calculations[32] on the NO production in the 2-nitro-2-propyl radical and found that rather than passing through a nitrite intermediate it formed a three-member ring between the C, N, and O atoms with a transition state energy of only 35.7 kcal/mol. While the lower energy of the calculated transition state (designated as TS-$\alpha$ in the FOX-7 study) in our prior work[32] was confirmed by experimental results, this type of NO-loss pathway has not been calculated for any "real-world" energetic materials until now. Several of the NO-loss channels available to radical intermediates occurring throughout the gas-phase decomposition of FOX-7 resemble this "novel" nitro-nitrite transition state and pass through a similar cyclic structure. The five NO-loss transition states in the FOX-7 decomposition mechanism calculated herein are shown in Fig. 8 along with the TS for 2-nitro-2-propyl radical (TS-$\alpha$).[32] Most importantly, both NO loss via TS9 (from a radical intermediate) and via TS5 (from the singlet FOX-7) have lower barriers than expected for NO loss via a traditional nitro-nitrite isomerization because they pass through one of these tight three-member ring NO-loss pathways.

While there are five NO-loss pathways calculated in this study, only one has a stable nitrite isomer (structure I6, see Fig. 1). While this molecule does isomerize to a nitrite species, the TS (TS5) is still markedly different than the one observed for saturated nitroalkanes. The C-N bond remains relatively strong in TS5 (1.54 Å) and while not as short as the C-N bond seen in nitroalkyl radical species, it is significantly shorter than in 2-nitropropane (2.2 Å);[32] the C-O bond is 1.78 Å. This shorter C-N bond lowers the nitro-nitrite isomerization barrier a small amount from the traditional nitro-nitrite isomerization seen in nitroalkanes (∼58 vs. ∼65 kcal/mol). Furthermore, the double bond in FOX-7 raises the barrier to direct C-$NO_2$ bond fission significantly due to the resulting unpaired electron density on the alkene. This increases the C-$NO_2$ bond fission barrier to 69.3 kcal/mol from the usual ∼60 kcal/mol barrier observed in most nitroalkanes. The lowering and raising, respectively, of these barriers demonstrates that NO loss will likely dominate relative to direct C-$NO_2$ fission in the gas-phase decomposition of FOX-7.

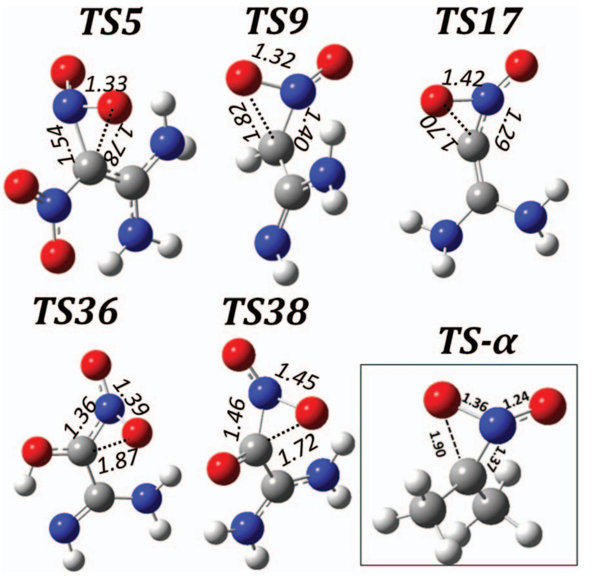

FIG. 8. Calculated geometries of the transition states leading to NO loss for the five pathways evident in FOX-7 decomposition. The numbered designation of each TS is identical to the label in Figs. 1, 3, and 6. TS-$\alpha$ is taken from Ref. 32 (it was denoted TS2 in Ref. 32) and is the NO-loss TS calculated for the 2-nitro-2-propyl radical. All geometries were calculated at the B3LYP/6-311++g(3*df*,2*p*) level. Important geometric parameters are labeled and reported in units of Å.

The other pathways to NO loss in FOX-7 (TSs 9, 17, 36, 38) occur in radical species and pass through a three-member ring intermediate, losing NO by cleaving a C-NO bond rather than the O-NO bond. Only one of these four channels has a stable isomer (I18) and this species consists of a carbonyl and a nitroso group rather than a nitrite functionality. The reason why this is the only stable isomer of the four is because the initial C2 in structure I15 has only two effective bonds (one to the $NO_2$ group and one to C1), and as such is able to form a carbonyl-like bond to the oxygen while still maintaining an un-ruptured single bond with the nitrogen atom. The other three transition states (TSs 9, 36, 38) do not have stable intermediates and lose NO in a concerted fashion during the isomerization. This is most likely due to the exothermicity of forming a double bond between the carbon and oxygen atoms, which in turn lowers the barrier en route to C-NO bond fission.

In summary, FOX-7 has four NO-loss pathways that proceed through a tight 3-centered cyclic transition state rather than a traditional nitro-nitrite isomerization (TSs 9, 17, 36, 38), three of which have the same effective geometry (TSs 9, 36, 38) and one that is significantly different (TS17). TS17 has an extremely short C-N bond length of 1.29 Å (equivalent to an imine) and a C-O bond of 1.7 Å. These bonds are significantly shorter than those in the 2-nitro-2-propyl radical, but the energy of the transition state (TS17) is only ∼3 kcal/mol higher than the barrier to NO loss in 2-nitro-2-propyl radical. The other three NO-loss pathways (TSs 9, 36, and 38) are much similar to the 2-nitro-2-propyl radical TS and have C-N bond lengths of 1.36-1.46 Å and C-O bond lengths of 1.72-1.82 Å. The C-N bonds are all longer in these three transition states for FOX-7 than in TS-$\alpha$ (from 2-nitro-2-propyl radical) and the C-O bonds shorter. This is likely due to delocalization of the radical away from C2 in FOX-7, yielding a slightly weaker C-N bond but allowing the C-O bond to be slightly stronger. In TS-$\alpha$, the radical is only slightly delocalized into the $NO_2$ group, where in TSs 9, 36, and 38 the radical can be delocalized among multiple atoms (including the two amino groups). Despite these differences, the similar geometries of TSs 9, 36, and 38 to TS-$\alpha$ from 2-nitro-2-propyl radical suggest that the unpaired electron still spends the majority of its time on C2 during these NO loss pathways.

The calculations presented in this study detail the various ground state dissociation pathways for isolated FOX-7 molecules. The calculations reveal that the initial NO-loss pathway (via a nitro-nitrite isomerization) is ∼11 kcal/mol lower than the barrier to C-$NO_2$ bond fission. Additionally, the lowest calculated barrier is shown to be intramolecular hydrogen transfer from the amino group to C2, demonstrating that this pathway would likely dominate in isolated FOX-7 molecules. In the condensed phase, however, this pathway would likely be significantly higher due to the presence of intermolecular hydrogen bonds. The subsequent dissociation steps have been shown to proceed through different nitroalkyl radical species many of which produce NO through a low energy pathway involving a tight cyclic three-member intermediate.

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