RESEARCH ARTICLE

Theoretical Study of the Subsequent Decomposition Mechanisms of 1,1-Diamino-2,2-dinitroethene (FOX-7)

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ABSTRACT

This computational study focuses on the mechanism of the consecutive decomposition of FOX-7 and compares the results with recent experimental study [*J. Phys. Chem. A* **2023**, *127*, 7707] under 202 nm photolysis (592 kJ/mol). The mechanisms of forming these compounds, including cyanamide variants (HNCNH and NH₂CN), hydroxylamine (NH₂OH), nitrosamine (NH₂NO), diaminoacetylene (H₂NCCNH₂), cyanogen (NCCN), water (H₂O), ammonia (NH₃), urea ((NH₂)₂CO), hydroxyurea (NH₂C(O) NHOH), and formamide (NH₂CHO), have only been speculated on without any energetic information previously. This study employed an unsupervised potential energy profile search protocol and ab initio molecular dynamics (AIMD) simulations to identify reaction pathways leading to these compounds. The calculations reveal that although some products (e.g., HNCNH, NH₂CN, H₂NCCNH₂, and NCCN) can be formed via unimolecular decomposition, other products (e.g., NH₂OH, NH₂NO, H₂O, NH₃, (NH₂)₂CO, NH₂C(O)NHOH, and NH₂CHO) are energetically favored if they are formed via bimolecular recombination between unimolecular decomposition products or a product and a FOX-7 molecule.

1 | Introduction

1,1-Diamino-2,2-dinitroethene (FOX-7), first synthesized in 1998 [1], has emerged as a powerful energetic material due to its low sensitivity and high detonation capabilities [2–6]. Compared to widely utilized explosives like cyclo-1,3,5-trimethylene-2,4,6trinitramine (RDX), which is known for its high detonation capabilities and straightforward manufacturing processes [7, 8], FOX-7 offers reduced sensitivity to heat, impact, and friction [9], which mitigates several challenges associated with its storage, transport, and handling. As a result, FOX-7 has been considered a viable alternative to RDX [10–12] and a comprehensive understanding of the decomposition mechanism is crucial for harnessing its capabilities. Over the past decade, the decomposition of FOX-7 has been extensively studied both experimentally and computationally [13–21]. A series of gas-phase products, for example, nitrogen dioxide (NO₂) [13, 15, 17–27], amino radical (NH₂) [13, 14, 17, 19, 21, 22, 25], nitric oxide (NO) [14, 15, 17–21], nitrous acid (HONO) [14, 19–21], carbon monoxide (CO) [14, 18, 20], and hydrogen isocyanide (HNC) [14], have been reported. Different research groups employed various strategies to tackle this problem, and their results differed in detail, but the consensus is that the nitro-to-nitrite isomerization and the intermolecular hydrogen bonds directly correlate with the sensitivity (e.g., initial decomposition) of FOX-7. Recently, an experiment–computation combined study on the initial decomposition of photon-excited FOX-7 (with 532 and 355 nm photons) conducted by our groups

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UTATIONAL ISTRY also highlighted the role of conical intersections and nonadiabatic dynamics, with molecular oxygen detected as a primary product for the first time [28]. Interestingly, although gas-phase products NO and O_2 were detected in this study, the crystal structure changed negligibly before and after the radiation, indicating that an overwhelming majority of the molecules remained intact.

Compared to the mechanism of initial decomposition, the mechanism of subsequent decomposition is less clear from experiments. This is due to the energetic nature of these materials-if the excitation energy is above the threshold of the detonation, the decomposition reaction is vicious and fast (by the very definition of an energetic material), making it difficult to capture the intermediates. Computational studies are not limited by such issues. For example, following the initial decomposition study [17, 28], our group characterized the full subsequent unimolecular decomposition of FOX-7 on the singlet surface which includes 54 intermediates and 37 transition states. Twenty gas-phase products were reported in this study, which were later used to compare with the decomposition products observed at a higher level of excitation (202 nm or 592 kJ/mol) [29]. A good match was found in some of the products, including NO, NO2, CO, and carbon dioxide (CO_2) ; however, certain products observed in the experiment clearly indicate that they are unlikely to have been formed via unimolecular decompositions, for example, water (H₂O), ammonia (NH₃), cyanogen (NCCN), hydroxylamine (NH₂OH), and nitrosamine (NH₂NO), without a significant rearrangement of atoms or breaking the molecule into smaller fragments first.

The current research reveals the significant role of bimolecular recombination in the subsequent decomposition of FOX-7. There has been only one computational study [30] on the bimolecular reaction mechanism of FOX-7, where it collides with OH and NO₂ radicals. Four pathways were reported for OH + FOX-7 (H abstraction, forming H₂O; OH addition to either of the two carbon atoms; and OH addition to the nitrogen atom of the nitro groups), and two pathways were reported for NO₂ + FOX-7 (O abstraction, forming NO₂ radical; H abstraction, forming HNO₂). These bimolecular recombination reactions possess activation energies that are significantly lower than the decomposition of FOX-7. Although this pioneering research points to the importance of bimolecular recombination during the subsequent decomposition of FOX-7, the species that it employed (e.g., OH and NO₂ radical) are not among the products of initial decomposition. Further, there are disagreements between the reported products and the experiments. For example, NO₃ radical (formed in the O abstraction channel of $NO_2 + FOX-7$ reaction) has not yet been detected in any of the experiments [18, 20, 28, 29].

Our study focuses on the complex processes involved in the formation of various compounds (CO, CO₂, NH₃, H₂O, NH₂OH, NH₂CN, NH₂CHO, H₂N₂O, NCCN, (NH₂)₂CO, H₂NCCNH₂, and NH₂C(O)NHOH) detected in the experiment [29]. These compounds have been considered to be formed from subsequent decomposition, but many of their reaction pathways remain largely speculative [28, 29, 31]. Although the current study focuses on the reactions in the gas phase as a starting point of this complicated system, by no means it should be viewed as diminishing the importance of the encapsulated environment in the decomposition. As our previous research shows, the intermolecular hydrogen bonds stabilize the molecules and increase the activation energy of the decomposition in general [17]. It is also worth noting that as the decomposition progresses, particularly in the context of an explosive event, the system undergoes a significant transformation from a condensed (crystal) phase and releases gas-phase products, enabling bimolecular collisions between them with high excess energy. Accounting for this factor is critical, which greatly enhances the relevance of the calculations in the gas phase.

2 | Computational Methods

This study explores the single-molecule decomposition of FOX-7 and bimolecular reactions between an initial decomposition product and another FOX-7 molecule in a gaseous environment. All relevant stationary points (e.g., intermediates and transition states) were optimized using the dispersion-corrected density functional theory M06-2X-D3 [32]/def2-TZVPP [33] in NWChem (version 6.8.1) [34]. This level of theory has been selected based on its proven accuracy in a previous study on the same system [28]. The stationary points were validated with vibrational frequency analyses using the same level of theory by ensuring that intermediates possess 3N-6 positive vibrational frequencies and transition states possess 3N-7 positive vibrational frequencies plus one imaginary vibrational frequency, where N is the number of atoms in the molecule. The unscaled zero-point energy (ZPE) was computed based on harmonic vibrational frequencies. The connections between the transition states and intermediates were confirmed using intrinsic reaction coordinate (IRC) [35-37] calculations. If the IRC calculations failed, such as hitting a shoulder or a small barrier in potential energy along the reaction coordinate, geometry optimizations were performed at the failed configuration. Attempts were made to locate potential transition states for the association between two separate molecules. These molecules were initially separated by over 10Å while aligning them to mimic the target intermediate, and the system was allowed to relax along the energy gradient. If a consistent decrease in both distance and potential energy was observed until the system stabilized at the target intermediate configuration, a barrierless association was inferred. In cases where this was not observed, the presence of a transition state or a van der Waals complex may be indicated. To further investigate these scenarios, the nudged elastic band (NEB) [38] methodologies were applied. This method has been proven to be effective in identifying transition states and van der Waals complexes for reaction systems of similar complexity [39, 40]. To refine the energy calculations of all stationary points, CCSD(T)-F12A/ccpVTZ-F12 [41-44] was carried out with Molpro (version 2021.2) [45, 46]. The built-in acceleration features of Molpro, such as density fitting (DF) [47] and resolution of the identity (RI) approximations [48], render the computational cost of CCSD(T)-F12/ cc-pVTZ-F12 just slightly higher than CCSD(T)/cc-pVTZ, yet maintaining accuracy comparable to CCSD(T) with a complete basis set (CBS) limit [49, 50]. The choice of CCSD(T)-F12A over CCSD(T)-F12B is based on the former's suggested superior performance with triple-zeta basis sets [44].

Even in the gas phase, finding an exhaustive list containing all the unimolecular decomposition and bimolecular recombination pathways for a molecule like FOX-7 represents a tremendous challenge as the enormous number of possible ways of breaking apart the molecule into fragments, each of which could potentially have constitutional and conformational isomers [40]. Ab initio molecular dynamics (AIMD) simulation has been proven to be an effective way of exploring the potential energy surface that is most relevant to chemical reactions. In AIMD, molecules are excited in a controlled manner (e.g., collision energies or temperatures) to start with and the subsequent trajectories are sorted through to find distinct isomers. To assist in finding new bimolecular recombination pathways, a series of small molecules observed from the early stages of FOX-7 decomposition (NO, NO₂, OH, CO, CO_2 , NH₂, and triplet atomic O) were set to collide with one FOX-7 molecule. The rotations and vibrations of FOX-7 and the small molecules were set to the ground state. The collision energies were set to equal to the maximum accessible energy as a result of the unimolecular decomposition of FOX-7 under 202nm photolysis (592kJ/mol). For example, the heat of reaction for forming (H₂N)₂CC(O)NO₂ (I4) and NO via the FOX-7 \rightarrow I4 + NO pathway is -15 kJ/mol [28]; thus, the maximal translational energy of NO was set to 607 kJ/mol (592+15kJ/mol). In addition, the relative orientation between FOX-7 and the small molecule was randomly sampled and as they were separated by 12 Å. The positions and momenta of the atoms were propagated by VENUS [51, 52] using the velocity Verlet algorithm with a timestep of 0.1 fs, with the energy gradients calculated in NWChem [34]. We could not afford AIMD simulations with M06-2X-D3/def2-TZVPP; thus, B3LYP/6-31G* [53, 54] was used, which has good efficiency and reasonable accuracy for reactions of similar sizes [17, 55, 56]. Hundred trajectories were sampled for each pair of reactants, and the trajectories were halted once the products were formed, or when they returned to the reactants. The reactive trajectories were visualized in VMD [57] and examined for the reaction mechanisms. The distinct geometries found in the trajectories were used as an initial guess to find the new stationary points of the potential energy profile.

3 | Results and Discussion

It is important to note that almost all the intermediates reported in the figures in this section have multiple reaction pathways. The focus, however, is not to present a comprehensive reaction map of all these pathways but, instead, to show the reaction pathways of the lowest energy barrier that lead to the products identified in the experiment.

3.1 | The Formation of Cyanamide (HNCNH, 114 and NH, CN, 119)

Both **I14** and **I19** could be formed via unimolecular decomposition. Krisyuk and Sypko propose that **I14** and **I19** are both formed from FOX-7 via a two-step process: Hydrogens are first transferred from amine group(s) to nitro group(s), which is followed by a C–C bond cleavage [58]. For **I14**, one hydrogen from each of the two amine groups migrates to the nitro groups, while for **I19**, both hydrogens are eliminated from the same amine group. The highest barriers of both pathways are associated with the step of the C-C bond cleavage (322 and 309 kJ/mol for I14 and I19, respectively). Our previous study suggests that the formation of I14 could be a sequential decomposition product of I4, which is the initial decomposition product of FOX-7 via a nitroto-nitrite isomerization (forming NO as the gas-phase product, Figure 1) [31]. Another nitro-to-nitrite isomerization takes place in I4, which is then followed by the C-C bond cleavage to form methanediamine (C(NH₂)₂, I13) and CO₂. I13 could undergo different H₂ loss reactions to form either HNCNH (I14, the hydrogen atoms are from two different NH₂ groups) or NH₂CN (I19, the hydrogen atoms are from the same NH_2 group). The energy barriers for these H₂ loss reactions are 136 and 204kJ/ mol, respectively, both of which are lower than that of the initial nitro-to-nitrite isomerization of 273 kJ/mol [31]. Therefore, the overall barriers for the pathways leading to I14 and I19 are determined by the highest energy barrier in the pathway, which is the initial isomerization step of 273 kJ/mol. This value is lower than the 322 and 309kJ/mol barriers proposed by Krisyuk and Sypko [58], where they are formed directly from FOX-7. We note that I14 and I19 are interconvertible through a high hydrogen transfer barrier.

3.2 | The Formation of Hydroxylamine (NH₂OH) and Nitrosamine (NH₂NO)

Intuitively, NH₂OH and NH₂NO are not likely to be primarily produced via unimolecular dissociations of FOX-7 as the amine group would have to migrate to react with the nitro groups, which reside at the opposing ends of FOX-7. However, as Figure 1 shows, radicals such as NH2 (formed with I58), OH (formed with I34, a sequential dissociation product of I4), and NO (formed with I4) can be readily formed via unimolecular decomposition of FOX-7. Thus, NH₂OH and NH₂NO could potentially be formed via bimolecular recombination $(NH_2 + OH \rightarrow NH_2OH)$ and $NH_2 + NO \rightarrow NH_2NO$). These mechanisms were proposed by the experimental study [29] without providing the energetics. Both recombination reactions forming NH2OH and NH2NO are exothermic and releasing 256 and 189 kJ/mol, respectively. These energies are in good agreement with the experimental heat of formation data at 0K (259 and 195 kJ/mol, respectively) [59]. NEB calculations were performed to prove that both recombination reaction pathways occur without a transition state.

3.3 | The Formation of Diaminoacetylene (H₂NCCNH₂, I126)

The recent experimental study proposed that diaminoacetylene (H_2NCCNH_2 , **I126**) was formed via the bimolecular collision of two CNH_2 fragments, which were sequential decomposition products of $H_2NCC(NO_2)_2$ (**I7**), the initial decomposition product of FOX-7 after NH_2 cleavage [29]. A potential issue with this mechanism is the high energy barrier—the formation of **I7** is endothermic by 461 kJ/mol [28], and the following C–C bond cleavage takes another 513 kJ/mol, a total of 974 kJ/mol. Our calculations partially agree with the proposed products' recombination pathway, except that the CNH_2 fragments should be generated from the C– NH_2 bond cleavage in $C(NH_2)_2$ (**I13**, see its genesis in Figure 1). The energy



FIGURE 1 | The potential energy profile (in kJ/mol) of the decomposition pathways of FOX-7 calculated at the CCSD(T)-F12/VTZ-F12A//M06-2X-D3/Def2-TZVPP + ZPE(M06-2X-D3/Def2-TZVPP) level of theory. Intermediates and products are labeled as "I" in black, and the transition states are labeled as "TS" in red.

required for this pathway (311 kJ/mol with respect to FOX-7, see Figure 1) is much lower than the previously proposed C—C bond cleavage of $H_2NCC(NO_2)_2$ (**17**). The potential energy and NEB calculations show that two CNH_2 fragments can recombine to form H_2NCCNH_2 (**1126**) without a transition state, releasing 448 kJ/mol of energy.

In this study, the possibility of forming H₂NCCNH₂ (**I126**) via unimolecular decomposition mechanisms was also explored. As shown in Figure 2, starting from the initial decomposition product $NO_2 + (NH_2)_2CCNO_2$ (I6, 300 kJ/mol) reported in Turner et al. [28], the NH₂ group that is further away from the remaining NO₂ group can migrate from one carbon atom to another via a C-C-N three-membered ring transition state TS6 (544 kJ/ mol) to form a more stable intermediate H₂NCC(NH₂)NO₂ (I166, 284 kJ/mol). Similarly, the NH₂ group closer to the NO₂ group can form I166 following a similar procedure (e.g., crossing a C-C-N three-membered ring transition state TS165, 506 kJ/mol), where a very shallow intermediate I165 (468 kJ/ mol) is involved. It should be noted that the potential energy of TS166 is higher than that of I165 by 0.5kJ/mol without ZPE. I166 will further undergo C-NO₂ bond cleavage to form H₂NCCNH₂ (I126) and NO₂ via an exit barrier TS167 (356 kJ/ mol). The major barriers associated with these unimolecular decomposition pathways are the C-C-N three-membered ring transition states (TS165 and TS6), which are feasible in the ultraviolet photolysis experiment using 202nm photons (592kJ/ mol). However, the overall barriers involved in the unimolecular decompositions are much higher than the bimolecular reaction route discussed in the previous paragraph.

3.4 | The Formation of Cyanogen (NCCN, I128)

Turner et al. also proposed the formation of cyanogen (NCCN, **I128**) via two CN fragments recombination [29]. The source of CN was hypothesized to be from the hydrogen loss of hydrogen isocyanide (CNH, **I18**). **I18** is produced from the unimolecular decomposition of $(NH_2)_2CCO_2$ (**I11**, see its genesis from FOX-7 in Figure 1). A hydrogen atom first migrates from the $-NH_2$ group to the oxygen atom, which is followed by the C–C bond cleavage, making HNCNH₂ (**I17**) and HCO₂ (243 kJ/mol, Figure S1). **I17** can further dissociate into CNH (**I18**) and NH₂ [29, 31]. However, the calculations show that the hydrogen loss step of CNH (**I18**) to form CN requires an additional 463 kJ/mol of energy, resulting in a total of 807 kJ/mol above FOX-7 (Figure S1).

In this study, a new reaction pathway of forming cyanogen (NCCN, **I128**) with significantly lower barrier is proposed. This pathway starts from diaminoacetylene (H_2NCCNH_2 , **I126**), the product reported in the previous section. As Figure 3 shows, each of the $-NH_2$ groups in H_2NCCNH_2 (**I126**) undergoes a molecular hydrogen loss reaction and eventually forms cyanogen



FIGURE 2 | The potential energy profile (in kJ/mol) of the decomposition pathways of FOX-7 calculated at the CCSD(T)-F12/VTZ-F12A//M06-2X-D3/Def2-TZVPP + ZPE(M06-2X-D3/Def2-TZVPP) level of theory. Intermediates and products are labeled as "I" in black, and the transition states are labeled as "TS" in red.



FIGURE 3 | The potential energy profile (in kJ/mol) of the H_2 decomposition pathways of I126 calculated at the CCSD(T)-F12/VTZ-F12A//M06-2X-D3/Def2-TZVPP + ZPE(M06-2X-D3/Def2-TZVPP) level of theory. Intermediates and products are labeled as "I" in black, and the transition states are labeled as "TS" in red.

(NCCN, **I128**). The barrier of the dissociation of the first and second H₂ is 349 and 319 kJ/mol, respectively. It is important to note that if H₂NCCNH₂ (**I126**) is formed by the recombination of CNH₂ (**I58**), as the previous section shows, it would be highly vibrationally excited as the recombination releases 448 kJ/mol of (electronic) potential energy. Therefore, it is reasonable to expect that the barriers involved in the **I126** \rightarrow **TS126** \rightarrow **I127** \rightarrow **TS127** \rightarrow **I128** pathway are feasible and the overall barrier of forming cyanogen (NCCN, **I128**) is actually the same as the one reported in the previous section (forming CNH₂, 311 kJ/mol with respect to FOX-7). Comparing the potential energy profiles of the two reaction pathways (CN recombination vs. **I126** \rightarrow **I128** via H₂ loss), the latter is much more energetically favored.

3.5 | The Formation of H₂O and NH₃

The experimental study proposed that the H_2O and NH_3 can be formed via atomic hydrogen in addition to OH and NH_2 radicals, respectively [29]. According to Figure 1, the energies required for the fragments of these reactions, H, OH, and NH_2 , are 219, 181, and 311 kJ/mol (Table 1), respectively, accessible under the experimental conditions using 202 nm photons (592 kJ/mol) [31]. As a result, after irradiation, H, OH, and NH_2 fragments generated in the system could form H_2O and NH_3 via barrierless and exothermic $H + OH \rightarrow H_2O$ (-491 kJ/ mol in this work; -492 kJ/mol according to experiments [59]) and $H + NH_2 \rightarrow NH_3$ (-442 kJ/mol in this work; -444 kJ/mol according to experiments [59]) recombination reactions, respectively. The overall barriers and heats of reaction for forming H_2O and NH_3 are summarized in Table 2.

Additionally, bimolecular collision pathways for forming H₂O and NH₂ are characterized in this study. Considering the decomposition products such as OH and NH₂ from FOX-7, they could collide with other FOX-7 molecules. Similar radical elimination mechanisms have been previously investigated by Lyu et al., where they explored the potential energy profile and reactive MD simulations leading to the formation of H_2O and NH_3 [21]. Compared to Lyu et al., the heats of reaction for the two reaction pathways (forming H₂O and NH₃) are similar, but the energy barrier of the transition state calculated in our study at the CCSD(T)-F12A level is higher. In our study, the potential energy profile of OH+FOX-7 (Figure 4) shows that they can directly associate with each other and form two distinct van der Waals complexes depending on the approaching angle. The OH fetches the hydrogen atom in the -NH₂ group of FOX-7 via transition states TS113 and TS114 to form H₂O with HNC(NH₂)C(NO₂)₂ (I111/I112). I111 and I112 can isomerize to each other via transition state TS110. In AIMD simulations, both bimolecular reaction pathways are observed, and the animations can be found in Movie S1 (forming I111+H₂O) and Movie S2 (forming $I112 + H_2O$) in Supporting Information. The lowest barrier of FOX-7 + OH \rightarrow HNC(NH₂)C(NO₂)₂ + H₂O is as low as 28 kJ/ mol (TS114) and the reaction releases 61 kJ/mol potential energy

TABLE 1 | The summary of the reaction fragments and their corresponding minimum energy pathways and barriers in kJ/mol. The highest barrier is with respect to FOX-7.

		Minimal		
		excess		
	Minimum energy	energy		
Fragment	pathways	required		
Н	$\mathrm{FOX}\text{-}7 \mathop{\rightarrow} I4 \mathop{\rightarrow} TS11 \mathop{\rightarrow} I11 \mathop{\rightarrow} TS12 \mathop{\rightarrow}$	219		
	$I12 \mathop{\rightarrow} I13 \mathop{\rightarrow} I16 \mathop{+} \mathrm{H}$			
OH	$\mathrm{FOX}\text{-}7 \rightarrow I4 \rightarrow TS31 \rightarrow I31 \rightarrow I34 + \mathrm{OH}$	181		
NH ₂	$\mathrm{FOX}\text{-}7 \mathop{\rightarrow} \mathbf{I4} \mathop{\rightarrow} \mathbf{TS11} \mathop{\rightarrow} \mathbf{I11} \mathop{\rightarrow} \mathbf{TS12} \mathop{\rightarrow}$	311		
$I12 \rightarrow I13 \rightarrow I58 + NH_2$				

Note: Intermediates and transition states are marked in bold.

(**I112**). This makes the minimal excess energy required for the FOX-7 + OH reaction to be 209 kJ/mol with OH formation (with $(NH_2)_2CC(NO_2)$, **I34**) being the rate-limiting step. Therefore, FOX-7 + OH recombination pathway should be favored over the H + OH pathways reported by the experiment [29], because (1) forming H requires more excess energy in the system (219 kJ/mol, Tables 1 and 2) more importantly, for the initial phase of the decomposition, the abundance of FOX-7 should be much greater than that of H.

Similarly, as shown in Figure 5, the NH₂ radicals can also abstract a hydrogen atom from the -NH₂ groups of FOX-7. The minimum energy path of these hydrogen abstraction pathways is the colinear abstraction (TS112, 40 kJ/mol), leading to the formation of hydrogen loss products HNC(NH₂)C(NO₂)₂ (I112) and NH₃. As shown in Movies S3 and S4, NH₂ could also approach perpendicularly to FOX-7 and abstract a hydrogen atom via higher transition states TS111a (60kJ/mol) and TS111b (66 kJ/mol), forming hydrogen loss products I111 (an isomer of I112) and NH₃. Both hydrogen abstraction reactions are slightly exothermic (-12 and -15kJ/mol), with low reaction barriers as low as 40 kJ/mol. Similar to the case of FOX-7+OH recombination, the preparation of NH₂ (endothermic by 311 kJ/mol) is the rate-limiting step of FOX-7+NH₂ recombination, which requires a minimal excess energy of 351 kJ/mol. Although this value is higher than what is required for the $H + NH_2 \rightarrow NH_3$ reaction (Table 2), colliding with another FOX-7 molecule is much more likely for NH₂ during the initial phase of the decomposition. As the decomposition progresses, the abundance of free H fragments is expected to increase, making the $H + NH_2 \rightarrow NH_3$ reaction more predominant.

3.6 | The Formation of Urea $((NH_2)_2CO, I29)$

The experimental study proposed that the singlet **I29** is a recombination reaction product of diaminocarbene (**I13**, $C(NH_2)_2$) and atomic oxygen [29]. Previous experiment and computation have revealed that (triplet) atomic oxygen is one of the two gas-phase products (the other is NO) of the initial decomposition. In this study, a recombination pathway between (triplet) atomic oxygen and FOX-7 is characterized. As shown in Figure 6, triplet atomic oxygen is able to bond to the carbon atom connecting to $-NO_2$ groups of FOX-7 via a small entrance reaction barrier **TS135a**

TABLE 2 Th	e summary of the recombination	reactions and their corresponding	total reactions, barriers,	, and total heat of reaction in kJ/mol
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Recombination reactions	Total reactions	Minimal excess energy required	Heats of reaction
$H + OH \rightarrow H_2O$	(2)FOX-7 \rightarrow I16 + I34 +CO ₂ +(3) NO+H ₂ O	219	-91
$\rm FOX-7+OH \rightarrow I111+H_2O$	$(2) \text{FOX-7} \rightarrow \textbf{I34} + \textbf{I111} + \text{NO} + \text{H}_2\text{O}$	213	117
$\rm FOX-7+OH \rightarrow I112+H_2O$	$(2) \text{FOX-7} \rightarrow \textbf{I34} + \textbf{I112} + \text{NO} + \text{H}_2\text{O}$	209	119
$H + NH_2 \rightarrow NH_3$	(2)FOX-7 \rightarrow I16 + I58 + (2) CO ₂ + (4)NO + NH ₃	311	88
$\rm FOX-7 + \rm NH_2 \rightarrow I111 + \rm NH_3$	(2)FOX-7 \rightarrow I58 + I111 + CO ₂ + (2) NO + NH ₃	371	296
$\rm FOX-7 + \rm NH_2 \rightarrow \rm I112 + \rm NH_3$	(2)FOX-7 \rightarrow I58 + I112 + CO ₂ + (2) NO + NH ₃	351	298

Note: Intermediates and transition states are marked in bold.



FIGURE 4 | The potential energy profile (in kJ/mol) of the bimolecular collision pathways of FOX-7 and OH calculated at the CCSD(T)-F12/VTZ-F12A//M06-2X-D3/Def2-TZVPP+ZPE(M06-2X-D3/Def2-TZVPP) level of theory. Intermediates and products are labeled as "I" in black, the Van der Waals prereaction complexes are labeled as "Pre," and the transition states are labeled as "TS" in red.



FIGURE 5 | The potential energy profile (in kJ/mol) of the bimolecular collision pathways of FOX-7 and NH_2 calculated at the CCSD(T)-F12/VTZ-F12A//M06-2X-D3/Def2-TZVPP + ZPE(M06-2X-D3/Def2-TZVPP) level of theory. Intermediates and products are labeled as "I" in black, and the transition states are labeled as "TS" in red.

(29 kJ/mol) and form triplet intermediate **I135a** (-25 kJ/mol). The carbon–carbon bond is weakened, as it only takes 41 kJ/mol to dissociate (via **TS135b**), yielding the targeted product singlet **I29** and triplet $C(NO_2)_2$ (**I115**). The energy required for the formation of **I29** is 373 kJ/mol, which is primarily due to the formation

of atomic oxygen (with $(H_2N)_2CC(NO)NO_2$, **19**, 344 kJ/mol) [28]. Through **TS115** (40 kJ/mol), **I115** can further decompose into NO₂ and the unstable intermediate OCNO (doublet, **I116**), which can eventually decompose into a CO and a NO molecule. The energy required for this reaction pathway is 384 kJ/mol, but the



FIGURE 6 | The potential energy profile (in kJ/mol) of the bimolecular collision pathways of FOX-7 and triplet ground state atomic O calculated at the CCSD(T)-F12/VTZ-F12A//M06-2X-D3/Def2-TZVPP + ZPE(M06-2X-D3/Def2-TZVPP) level of theory. Intermediates and products are labeled as "I" in black, and the transition states are labeled as "TS" in red.

overall heat of reaction from FOX-7+triplet oxygen to the five decomposition products (**I9**, **I29**, NO₂, CO, and NO) is -139 kJ/mol. The full animation (Movie S5) of this pathway is reported in Supporting Information. Between the two recombination hypotheses (**I13**, C(NH₂)₂+atomic oxygen vs. FOX-7+triplet oxygen), the latter is favored during the early stages of the decomposition due to the abundance of FOX-7 molecules.

3.7 | The Formation of Hydroxyurea (NH₂C(O)NHOH, 1177)

Upon the formation of $(NH_2)_2CO$ (**129**), the experimental study proposed that a singlet atomic oxygen could be inserted into one of the four nitrogen–hydrogen bonds of **129** [29]. However, we are not able to locate any transition state of the insertion pathway connecting **129** + singlet oxygen and **1177**. The NEB calculation also rejects the barrierless insertion mechanism. Instead, it confirmed a barrierless addition pathway, which shows that the potential energy of the system monotonically decreases as the singlet atomic oxygen approaches perpendicularly to one of the nitrogen atoms of **129**. As shown in Figure 7, the forming intermediate $NH_2C(O)N(O)H_2$ (**1176**) of this barrierless addition pathway is highly exothermic. A hydrogen migration via transition state **TS176** (107 kJ/mol above **1176**) results in a more stable complex $NH_2C(O)NHOH$ (**1177a**), which can also isomerize to **I177b** via transition state **TS177**. Both **I177a** and **I177b** are the reported product $NH_2C(O)NHOH$ from experimental study [29]. Here, we acknowledge that the association between $(NH_2)_2CO$ (**I29**) and $O(^1D)$ reaction has multireference character; thus, the entrance channel (i.e., forming **I176**) in Figure 7 could be inaccurate. The most trustworthy number of the association should be computed from multireference method but is beyond the scope of this manuscript. Considering that **I29** can only be formed after several decomposition steps starting from FOX-7, at which point, the access energy in the system is hypothesized to allow the association to take place. The consecutive isomerization of **I176** (Figure 7), nonetheless, should still be valid.

3.8 | The Formation of Formamide (NH₂CHO, 1171)

I171 was detected in the experimental study [29] and was proposed to be formed via radical—radical recombination: $HCO + NH_2 \rightarrow NH_2CHO$ (-407kJ/mol). The genesis of NH_2 in the system has been discussed earlier (Figure 1 and Table 1, 311kJ/mol). As Figure 8 shows, HCO is produced by the C–C bond cleavage of $NH_2C(NH)CHO$ (**I41**) and **I41** (and NO) is the product of a nitro-to-nitrite isomerization of **I5**, another initial decomposition product of FOX-7. The energy required to break the C–C bond in **I41** is 373 kJ/mol, making the total energy of



FIGURE 7 | The potential energy profile (in kJ/mol) of the bimolecular collision pathways of **I29** and singlet first excited state atomic O calculated at the CCSD(T)-F12/VTZ-F12A//M06-2X-D3/Def2-TZVPP + ZPE(M06-2X-D3/Def2-TZVPP) level of theory. Intermediates and products are labeled as "I" in black, and the transition states are labeled as "TS" in red.



FIGURE 8 | The potential energy profile (in kJ/mol) of the decomposition pathways of FOX-7 calculated at the CCSD(T)-F12/VTZ-F12A//M06-2X-D3/Def2-TZVPP + ZPE(M06-2X-D3/Def2-TZVPP) level of theory. Intermediates and products are labeled as "I" in black, and the transition states are labeled as "TS" in red.

HCO + HNCNH₂(**I17**) 414 kJ/mol with respect to FOX-7. Overall, the reaction pathway FOX-7 → **I18** + NO₂ + NO + NH₂CHO is endothermic (108 kJ/mol). The highest barrier involved in this process is **TS17**, 538 kJ/mol with respect to FOX-7, which is accessible under the experimental excitation of 592 kJ/mol. However, the previous theoretical study [31] found that the C–C bond is weakened after the hydrogen is transferred from the carbon back to the –NH group (**TS42**). As shown in Figure 8, **TS42** is only 227 kJ/mol above **I41**, in comparison with the 372 kJ/ mol C–C dissociation energy [31], and leads to the formation of CO and C(NH₂)₂ (**I13**). CO can react with H to form HCO $(H+CO \rightarrow HCO, -60 \text{ kJ/mol})$, which then reacts with NO₂ to form NH₂CHO as discussed at the beginning of the paragraph. The minimal excess energy required for this pathway is the preparation of NH₂ (Table 1, 311 kJ/mol).

3.9 | Reactive Trajectories Observed in AIMD Simulations

To elucidate potential bimolecular reaction pathways, AIMD simulations were conducted on FOX-7 colliding with a suite of seven small molecules. Among these, NO_2 , CO, and CO_2 exhibited no reactivity, while NO, OH, NH_2 , and atomic triplet O reacted with FOX-7. Table 3 shows the energetics of the observed reactions. The AIMD simulation of FOX-7 with the NO radical (Movie S6)

TABLE 3 \mid The summary of the reaction pathways observed in the AIMD simulations and their heat of reaction in kJ/mol.

	Heat of	Animation
Reactive trajectories	reaction	in SI
$FOX-7 + NO \rightarrow I10 + NO_2$	23	Movie <mark>S6</mark>
$\rm FOX-7+OH \rightarrow I111+H_2O$	-64	Movie <mark>S1</mark>
$FOX-7 + OH \rightarrow I112 + H_2O$	-61	Movie <mark>S2</mark>
$FOX-7 + OH \rightarrow I119 + NO_2 + NO$	-204	Movie <mark>S7</mark>
$FOX-7 + OH \rightarrow (2) I33 + I17 + CO$	-51	Movie <mark>S8</mark>
$FOX-7 + OH \rightarrow I195 + I33 + NO_2 + NH_3$	62	Movie <mark>S9</mark>
$FOX-7 + OH \rightarrow I9 + O_2H$	74	Movie S10
$FOX-7 + NH_2 \rightarrow I111 + NH_3$	-15	Movie S3
$FOX-7 + NH_2 \rightarrow I112 + NH_3$	-12	Movie <mark>S4</mark>
$FOX-7 + NH_2 \rightarrow I121 + NO_2$	-157	Movie <mark>S11</mark>
$FOX-7+O \rightarrow I29 + NO_2 + NO + CO$	-483	Movie <mark>S5</mark>
$FOX-7 + O \rightarrow NO + OH + I144$	-199	Movie S12
$FOX-7+O \rightarrow NO_2 + I33 + I16 + CO$	-177	Movie S13
$FOX-7+O \rightarrow I9+O_2$	-149	Movie S14
$FOX-7+O \rightarrow I10+O_2$	-169	Movie S15
$FOX-7 + O \rightarrow (2) NO_2 + I13 + CO$	-155	Movie <mark>S16</mark>
$FOX-7 + O \rightarrow I137 + NH_2$	-77	Movie S17
$FOX-7+O \rightarrow I112+OH$	4	Movie S18

Note: Intermediates and transition states are marked in bold.

reveals a direct oxygen abstraction pathway, slightly endothermic at 23 kJ/mol, forming $(H_2N)_2CC(NO)NO_2$ (**110**) + NO₂.

The FOX-7 + OH bimolecular collision results in a series of reactive trajectories. Section 3.5 introduces two pathways leading to H_2O formation (I111+ H_2O and I112+ H_2O) through direct hydrogen abstraction, as depicted in Movies S1 and S2. Moreover, an $S_N 2$ reaction is observed (Movie S7) wherein the OH radical attacks the carbon atom on the nitro side of FOX-7, promptly repelling one nitro group $(-NO_2)$. The trajectory continues as the remaining nitro group seizes a hydrogen atom from an amine group $(-NH_2)$, followed by NO radical loss. Subsequently, a hydrogen atom from one of the hydroxyl groups transfers back to the --NH group, forming (H2N)2CC(O)OH (I119). The reaction FOX-7 + OH \rightarrow I119 + NO₂ + NO is highly exothermic (-204 kJ/mol). In a similar S_N2 reaction (Movie S8), the departing $-NO_2$ captures a hydrogen atom from an $-NH_2$ group, resulting in the formation of HONO (I33). Subsequently, the remaining -NO₂ also captures a hydrogen atom from another -NH₂ group, making an additional I33. This process leaves behind H₂N(NH)CCO (I32), which further dissociates into I17 and CO, marking the reaction FOX-7 + OH \rightarrow (2) I33 + I17 + CO with the heat of reaction of 51 kJ/mol. Additionally, Movie S9 showcases the C-OH bond formation (OH radical with FOX-7), facilitating a hydrogen transfer from -OH to -NH₂ and leading to NH₃ production. The final products of this reaction are HNCCO (I195) + I33 + NO_2 + NH_3 with a heat of reaction of 62 kJ/mol. The last reactive trajectory



Unimolecular Decomposition

FOX-7 and Radical Recombination

Radical and Radical Recombination

FIGURE 9 | The left panel shows the unimolecular decomposition pathways (solid black arrow), the middle panel shows the pathways of bimolecular recombination involving a FOX-7 molecule and a radical observed from the unimolecular decomposition (hollow black arrow), and the right panel shows the pathways of bimolecular recombination products involving two radicals observed from the unimolecular decomposition (solid yellow arrow). Products in green dashed boxes were identified in the ultraviolet photolysis experiment [29].

(Movie **S10**) of FOX-7 + OH involves a direct oxygen abstraction forming $(H_2N)_2CC(NO)NO_2$ (**I9**) and hydroperoxyl radical (O₂H), with a heat of reaction of 74 kJ/mol.

In addition to the NH₃ formation pathways (Movies S3 and S4, hydrogen abstraction) outlined in Section 3.5, an S_N2 reaction (Movie S11) is observed in the AIMD simulation of FOX-7+NH₂. This reaction features the NH₂ radical substituting an $-NO_2$ group on FOX-7, resulting in the formation of $(H_2N)_2CC(NH_2)NO_2$ (I121). The reaction, FOX-7+NH₂ \rightarrow I121+NO₂, is highly exothermic, with a reaction heat of -157 kJ/mol.

The bimolecular collisions between FOX-7 and triplet atomic oxygen result in a diverse set of products. In addition to the highly exothermic reaction described in Section 3.6 (Movie S5), seven other reactions were discovered. The first reaction is $FOX-7 + O \rightarrow NO + OH + H_2N(NH)CC(O)NO_2$ (I144), where the triplet atomic oxygen attacks the carbon in the C-NO₂ group on FOX-7, triggering a nitro-to-nitrite transition and releasing a NO molecule. Subsequently, the oxygen atom abstracts a hydrogen atom from an adjacent -- NH₂, leading to the formation of OH (Movie S12), with a heat of reaction of -199 kJ/mol. The second reaction (Movie S13) involves oxygen replacing a -NO₂ group on FOX-7 to form I31, which then dissociates into I32+I33, with I32 eventually breaking down into $HNCNH_2$ (I16) and CO. The overall reaction, $FOX-7 + O \rightarrow NO_2 + I33 + I16 + CO$, has a heat of reaction of -177 kJ/mol. There are also two direct O abstraction reactions (Movies S14 and S15), where oxygen abstracts an oxygen atom from $-NO_2$ of FOX-7, respectively, producing **I9** + O_2 (colinear colliding) and $I10 + O_2$ (perpendicular colliding) with heats of reaction of -149 and -169kJ/mol, respectively. The fifth reaction (Movie S16) sees oxygen bound to a carbon atom on the nitro side of FOX-7, leading to the rapid breaking of bonds between carbon and two -NO2 groups, followed by the cleavage of the C–C bond to produce I13 + CO. The total reaction, FOX-7 + O \rightarrow (2) NO₂ + **I13** + CO, has a reaction heat of -155 kJ/ mol. The sixth reaction (Movie S17) involves oxygen substituting an $-NH_2$ group on FOX-7, forming $H_2N(O)CC(NO_2)$ (I137) with a reaction heat of -77 kJ/mol (FOX-7 + O \rightarrow **I137** + NH₂). The final reaction (Movie S18) features oxygen abstracting an end hydrogen atom on FOX-7, producing I112 and OH, with the reaction being slightly endothermic at 4kJ/mol $(FOX-7+O \rightarrow I112+OH).$

4 | Conclusions

This study has elucidated several unimolecular decomposition and bimolecular recombination key pathways involved in the subsequent decomposition of FOX-7. Figure 9 illustrates the various experimentally identified decomposition products characterized in this study. The left, middle, and right panels show unimolecular decomposition pathways, bimolecular recombination pathways involving a FOX-7 molecule and a radical, and bimolecular recombination pathways involving two radicals from the unimolecular decomposition, respectively. The formation of cyanamide variants (HNCNH, **I14** and NH₂CN, **I19**) through unimolecular decomposition and hydrogen transfer, as well as their interconversion, highlights the complexity of the decomposition process. Notably, the barriers reported for these reactions are substantially lower than previously reported [58]. The calculations confirm the exothermic and barrierless pathways for the formation of NH₂OH and NH₂NO through bimolecular recombination of decomposition products (NH₂, OH, and NO). Our study also sheds light on the formation of diaminoacetylene (H2NCCNH2, I126), cyanogen (NCCN, I128), and formamide (H₂NC(O)H, **I171**), revealing alternative pathways with lower energy barriers compared to those previously proposed. Our study reports novel bimolecular collision pathways, where OH and NH₂ radicals abstract hydrogen from FOX-7 molecules, leading to the formation of H₂O and NH₃. These pathways should be more favored at the initial stages of the decomposition due to the abundance of FOX-7 compared to free-roaming hydrogen atoms. The recombination reaction involving triplet atomic oxvgen and FOX-7 plays an important role in the formation of urea (H₂NC(O)NH₂, **I29**) and hydroxyurea (H₂NC(O)N(H)OH, **I177**). These reactions are highly exothermic with low barriers, thus are hypothesized to promote efficient chain reactions and substantial energy release.

In conclusion, this study offers a more comprehensive understanding of the subsequent decomposition pathways of FOX-7, revealing the complexity and diversity of reactions that occur. These findings not only enhance our understanding of FOX-7's behavior but also contribute to the broader knowledge of energetic material decomposition, with potential implications for their synthesis, stability, and safety.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

1. N. V. Latypov, J. Bergman, A. Langlet, U. Wellmar, and U. Bemm, "Synthesis and Reactions of 1,1-Diamino-2,2-dinitroethylene," *Tetrahedron* 54, no. 38 (1998): 11525–11536, https://doi.org/10.1016/S0040-4020(98)00673-5.

2. H. H. Krause, *New Energetic Materials* (Weinheim, Germany: Wiley Online Books, 2004).

3. G. D. Kozak, "Factors Augmenting the Detonability of Energetic Materials," *Propellants, Explosives, Pyrotechnics* 30, no. 4 (2005): 291–297, https://doi.org/10.1002/prep.200500014.

4. R. P. Singh, R. D. Verma, D. T. Meshri, and J. M. Shreeve, "Energetic Nitrogen-Rich Salts and Ionic Liquids," *Angewandte Chemie International Edition* 45, no. 22 (2006): 3584–3601, https://doi.org/10.1002/anie.200504236.

5. A. J. Bellamy, "FOX-7 (1,1-Diamino-2,2-dinitroethene)," in *Structure and Bonding*, vol. 125, ed. T. M. Klapötke (Berlin, Heidelberg: Springer Berlin Heidelberg, 2007), 1–33.

6. T. M. Klapötke, *Chemistry of High-Energy Materials*, ed. D. Gruyter (Berlin, Germany: Walter de Gruyter, 2019).

7. S. N. Bulusu, ed., *Chemistry and Physics of Energetic Materials* (Dordrecht: Springer Netherlands, 1990).

8. P. F. Pagoria, "Synthesis of Pure RDX," 1994 10162021, p UCRL-ID-117229, https://doi.org/10.2172/10162021.

9. H. Östmark, H. Bergman, K. Ekvall, and A. Langlet, "A Study of the Sensitivity and Decomposition of 1,3,5-Trinitro-2-oxo-1,3,5-triazacyclo -hexane," *Thermochimica Acta* 260 (1995): 201–216, https://doi.org/10. 1016/0040-6031(95)90496-4.

10. H. Dorsett and Defence Science and Technology Organisation (Australia), Aeronautical and Maritime Research Laboratory (Australia), Weapons Systems Division, *Computational Studies of FOX-7, a New Insensitive Explosive* (Salisbury, South Australia: DSTO Aeronautical and Maritime Research Laboratory, 2000).

11. W. Trzciński and A. Belaada, "1,1-Diamino-2,2-dinitroethene (DADNE, FOX-7)—Properties and Formulations (A Review)," *Central European Journal of Energetic Materials* 13, no. 2 (2016): 527–544, https://doi.org/10.22211/cejem/65000.

12. T. L. Jensen, E. Unneberg, and T. E. Kristensen, "Smokeless GAP-RDX Composite Rocket Propellants Containing Diaminodinitroethylene (FOX-7)," *Propellants, Explosives, Pyrotechnics* 42, no. 4 (2017): 381–385, https://doi.org/10.1002/prep.201600278.

13. P. Politzer, M. C. Concha, M. E. Grice, J. S. Murray, P. Lane, and D. Habibollazadeh, "Computational Investigation of the Structures and Relative Stabilities of Amino/Nitro Derivatives of Ethylene," *Journal of Molecular Structure: THEOCHEM* 452, no. 1–3 (1998): 75–83, https://doi.org/10.1016/S0166-1280(98)00136-5.

14. A.Gindulytè, "Proposed Mechanism of 1,1-Diamino-dinitroethylene Decomposition: A Density Functional Theory Study," *Journal of Physical Chemistry A* 103, no. 50 (1999): 11026–11033.

15. R. S. Booth and L. J. Butler, "Thermal Decomposition Pathways for 1,1-Diamino-2,2-dinitroethene (FOX-7)," *Journal of Chemical Physics* 141, no. 13 (2014): 134315, https://doi.org/10.1063/1.4896165.

16. V. G. Kiselev and N. P. Gritsan, "Unexpected Primary Reactions for Thermolysis of 1,1-Diamino-2,2-dinitroethylene (FOX-7) Revealed by *Ab Initio* Calculations," *Journal of Physical Chemistry A* 118, no. 36 (2014): 8002–8008, https://doi.org/10.1021/jp507102x.

17. K. Yadav, Y. Luo, R. I. Kaiser, and R. Sun, "Initial Decomposition Pathways of 1,1-Diamino-2,2-dinitroethylene (α -FOX-7) in the Condensed Phase," *Physical Chemistry Chemical Physics* 26, no. 15 (2024): 11395–11405, https://doi.org/10.1039/D4CP00001C.

18. A. M. Turner, J. H. Marks, Y. Luo, et al., "Electron-Induced Decomposition of Solid 1,1-Diamino-2,2-dinitroethylene (FOX-7) at Cryogenic Temperatures," *Journal of Physical Chemistry*. A 127, no. 15 (2023): 3390–3401, https://doi.org/10.1021/acs.jpca.3c01035.

19. B. Yuan, Z. Yu, and E. R. Bernstein, "Initial Decomposition Mechanism for the Energy Release From Electronically Excited Energetic Materials: FOX-7," *Journal of Chemical Physics* 2014, no. 140 (2014): 074708, https://doi.org/10.1063/1.4865266.

20. M. Civiš, S. Civiš, K. Sovová, K. Dryahina, P. Španěl, and M. Kyncl, "Laser Ablation of FOX-7: Proposed Mechanism of Decomposition," *Analytical Chemistry* 83 (2011): 1069–1077.

21. J.-Y. Lyu, Q. Zhu, X. Bai, et al., "A Detailed Chemical Kinetic Mechanism of 1,1-Diamino-2,2-dinitroethylene (FOX-7) Initial Decomposition in the Gas Phase," *Combustion and Flame* 255 (2023): 112877, https://doi.org/10.1016/j.combustflame.2023.112877.

22. A. V. Kimmel, P. V. Sushko, A. L. Shluger, and M. M. Kuklja, "Effect of Charged and Excited States on the Decomposition of 1,1-Diamino-2,2-dinitroethylene Molecules," *Journal of Chemical Physics* 126, no. 23 (2007): 234711, https://doi.org/10.1063/1.2741530. 23. I. Borges, "Electronic and Ionization Spectra of 1,1-Diamino-2,2-d initroethylene, FOX-7," *Journal of Molecular Modeling* 20, no. 3 (2014): 2095, https://doi.org/10.1007/s00894-014-2095-x.

24. L. Türker and S. Vari, "Effects of Epoxidation and Nitration on Ballistic Properties of FOX-7—A DFT Study," *Zeitschrift fur Anorganische und Allgemeine Chemie* 639, no. 6 (2013): 982–987, https://doi.org/10. 1002/zaac.201300086.

25. S. N. Rashkeev, M. M. Kuklja, and F. J. Zerilli, "Electronic Excitations and Decomposition of 1,1-Diamino-2,2-dinitroethylene," *Applied Physics Letters* 82, no. 9 (2003): 1371–1373, https://doi.org/10. 1063/1.1557768.

26. Z. Zheng, J. Xu, and J. Zhao, "First-Principles Studies on the Thermal Decomposition Behavior of FOX-7," *High Pressure Research* 30, no. 2 (2010): 301–309, https://doi.org/10.1080/08957959.2010.485390.

27. Q. Wu, W. Zhu, and H. Xiao, "DFT Study on Crystalline 1,1-Diamino-2,2-dintroethylene Under High Pressures," *Journal of Molecular Modeling* 19, no. 9 (2013): 4039–4047, https://doi.org/10.1007/s00894-013-1931-8.

28. A. M. Turner, Y. Luo, J. H. Marks, et al., "Exploring the Photochemistry of Solid 1,1-Diamino-2,2-dinitroethylene (FOX-7) Spanning Simple Bond Ruptures, Nitro-to-Nitrite Isomerization, and Nonadiabatic Dynamics," *Journal of Physical Chemistry A* 126, no. 29 (2022): 4747– 4761, https://doi.org/10.1021/acs.jpca.2c02696.

29. A. M. Turner, J. H. Marks, J. T. Lechner, T. M. Klapötke, R. Sun, and R. I. Kaiser, "Ultraviolet-Initiated Decomposition of Solid 1,1-Diamino-2,2-dinitroethylene (FOX-7)," *Journal of Physical Chemistry*. *A* 127, no. 37 (2023): 7707–7717, https://doi.org/10.1021/acs.jpca.3c03215.

30. J.-D. Zhang and L.-L. Zhang, "Theoretical Study on the Mechanism of the Reaction of FOX-7 With OH and NO₂ Radicals: Bimolecular Reactions With Low Barrier During the Decomposition of FOX-7," *Molecular Physics* 115, no. 23 (2017): 2951–2960, https://doi.org/10.1080/00268976. 2017.1339917.

31. Y. Luo, C. Kang, R. Kaiser, and R. Sun, "The Potential Energy Profile of the Decomposition of 1,1-Diamino-2,2-Dinitroethylene (FOX-7) in the Gas Phase," *Physical Chemistry Chemical Physics* 24, no. 43 (2022): 26836–26847, https://doi.org/10.1039/D2CP03719J.

32. Y. Zhao and D. G. Truhlar, "The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Function," *Theoretical Chemistry Accounts* 120, no. 1–3 (2008): 215–241, https://doi.org/10.1007/s00214-007-0310-x.

33. F. Weigend and R. Ahlrichs, "Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy," *Physical Chemistry Chemical Physics* 7, no. 18 (2005): 3297–3305, https://doi.org/10.1039/ b508541a.

34. M. Valiev, E. J. Bylaska, N. Govind, et al., "NWChem: A Comprehensive and Scalable Open-Source Solution for Large Scale Molecular Simulations," *Computer Physics Communications* 181, no. 9 (2010): 1477–1489, https://doi.org/10.1016/j.cpc.2010.04.018.

35. K. Fukui, "Formulation of the Reaction Coordinate," *Journal of Physical Chemistry* 74, no. 23 (1970): 4161–4163, https://doi.org/10.1021/j100717a029.

36. J. Ischtwan and M. A. Collins, "Determination of the Intrinsic Reaction Coordinate: Comparison of Gradient and Local Quadratic Approximation Methods," *Journal of Chemical Physics* 89, no. 5 (1988): 2881–2885, https://doi.org/10.1063/1.454992.

37. S. Maeda, Y. Harabuchi, Y. Ono, T. Taketsugu, and K. Morokuma, "Intrinsic Reaction Coordinate: Calculation, Bifurcation, and Automated Search," *International Journal of Quantum Chemistry* 115, no. 5 (2015): 258–269, https://doi.org/10.1002/qua.24757. 38. D. Sheppard and G. Henkelman, "Paths to Which the Nudged Elastic Band Converges," *Journal of Computational Chemistry* 32, no. 8 (2011): 1769–1771, https://doi.org/10.1002/jcc.21748.

39. K. Fujioka, K.-M. Weitzel, and R. Sun, "The Potential Energy Profile of the HBr⁺ + HCl Bimolecular Collision," *Journal of Physical Chemistry A* 126, no. 9 (2022): 1465–1474, https://doi.org/10.1021/acs.jpca. 1c08300.

40. K. Fujioka, R. I. Kaiser, and R. Sun, "Unsupervised Reaction Pathways Search for the Oxidation of Hypergolic Ionic Liquids: 1-Ethyl-3-methylimidazolium Cyanoborohydride (EMIM⁺/CBH⁻) as a Case Study," *Journal of Physical Chemistry A* 127, no. 4 (2023): 913–923, https://doi.org/10.1021/acs.jpca.2c07624.

41. T. B. Adler, G. Knizia, and H.-J. Werner, "A Simple and Efficient CCSD(T)-F12 Approximation," *Journal of Chemical Physics* 127, no. 22 (2007): 221106, https://doi.org/10.1063/1.2817618.

42. K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, "A Fifth-Order Perturbation Comparison of Electron Correlation Theories," *Chemical Physics Letters* 157, no. 6 (1989): 479–483, https://doi. org/10.1016/S0009-2614(89)87395-6.

43. K. A. Peterson, T. B. Adler, and H.-J. Werner, "Systematically Convergent Basis Sets for Explicitly Correlated Wavefunctions: The Atoms H, He, B–Ne, and Al–Ar," *Journal of Chemical Physics* 128, no. 8 (2008): 084102, https://doi.org/10.1063/1.2831537.

44. G. Knizia, T. B. Adler, and H.-J. Werner, "Simplified CCSD(T)-F12 Methods: Theory and Benchmarks," *Journal of Chemical Physics* 130, no. 5 (2009): 054104, https://doi.org/10.1063/1.3054300.

45. H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schütz, "Molpro: A General-Purpose Quantum Chemistry Program Package," *Wiley Interdisciplinary Reviews: Computational Molecular Science* 2, no. 2 (2012): 242–253, https://doi.org/10.1002/wcms.82.

46. H.-J. Werner, P. J. Knowles, F. R. Manby, et al., "The Molpro Quantum Chemistry Package," *Journal of Chemical Physics* 152, no. 14 (2020): 144107, https://doi.org/10.1063/5.0005081.

47. T. B. Adler and H.-J. Werner, "An Explicitly Correlated Local Coupled Cluster Method for Calculations of Large Molecules Close to the Basis Set Limit," *Journal of Chemical Physics* 135, no. 14 (2011): 144117, https://doi.org/10.1063/1.3647565.

48. K. E. Yousaf and K. A. Peterson, "Optimized Auxiliary Basis Sets for Explicitly Correlated Methods," *Journal of Chemical Physics* 129, no. 18 (2008): 184108, https://doi.org/10.1063/1.3009271.

49. T. H. Dunning, "Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron Through Neon and Hydrogen," *Journal of Chemical Physics* 90, no. 2 (1989): 1007–1023, https://doi.org/10.1063/1.456153.

50. A. J. C. Varandas, "Basis-Set Extrapolation of the Correlation Energy," *Journal of Chemical Physics* 113, no. 20 (2000): 8880–8887, https://doi.org/10.1063/1.1319644.

51. X. Hu, W. L. Hase, and T. Pirraglia, "Vectorization of the General Monte Carlo Classical Trajectory Program VENUS," *Journal of Computational Chemistry* 12, no. 8 (1991): 1014–1024, https://doi.org/10.1002/jcc.540120814.

52. U. Lourderaj, R. Sun, S. C. Kohale, et al., "The VENUS/NWChem Software Package. Tight Coupling Between Chemical Dynamics Simulations and Electronic Structure Theory," *Computer Physics Communications* 185, no. 3 (2014): 1074–1080, https://doi.org/10.1016/j.cpc.2013. 11.011.

53. A. D. Becke, "Density-Functional Exchange-Energy Approximation With Correct Asymptotic Behavior," *Physical Review A* 38, no. 6 (1988): 3098–3100, https://doi.org/10.1103/PhysRevA.38.3098.

54. R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, "Self-consistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wave

Functions," Journal of Chemical Physics 72, no. 1 (1980): 650–654, https://doi.org/10.1063/1.438955.

55. C. He, G. R. Galimova, Y. Luo, et al., "A Chemical Dynamics Study on the Gas-Phase Formation of Triplet and Singlet C 5 H 2 Carbenes," *Proceedings of the National Academy of Sciences* 117, no. 48 (2020): 30142–30150, https://doi.org/10.1073/pnas.2019257117.

56. S. Doddipatla, C. He, R. I. Kaiser, et al., "A Chemical Dynamics Study on the Gas Phase Formation of Thioformaldehyde (H_2CS) and Its Thiohydroxycarbene Isomer (HCSH)," *Proceedings of the National Academy of Sciences of the United States of America* 117, no. 37 (2020): 22712–22719, https://doi.org/10.1073/pnas.2004881117.

57. W. Humphrey, A. Dalke, and K. Schulten, "VMD: Visual Molecular Dynamics," *Journal of Molecular Graphics* 14, no. 1 (1996): 33–38, https://doi.org/10.1016/0263-7855(96)00018-5.

58. B. E. Krisyuk and T. M. Sypko, "New Thermolysis Routes of Diaminodinitroethylene (DADNE)," *Propellants, Explosives, Pyrotechnics* 46, no. 7 (2021): 1079–1096, https://doi.org/10.1002/prep.202000324.

59. B. Ruscic, R. E. Pinzon, M. L. Morton, et al., "Introduction to Active Thermochemical Tables: Several "Key" Enthalpies of Formation Revisited," *Journal of Physical Chemistry A* 108, no. 45 (2004): 9979–9997, https://doi.org/10.1021/jp047912y.

Supporting Information

Additional supporting information can be found online in the Supporting Information section.