

Computational Studies of FOX-7, A New Insensitive Explosive

Helen Dorsett

**Weapons Systems Division
Aeronautical and Maritime Research Laboratory**

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ABSTRACT

First-principles quantum chemical calculations are used to predict the initial steps of decomposition in solid FOX-7 (1,1-diamino-2,2-dinitroethylene). Three possible reaction paths were studied: (1) intra- or inter-molecular hydrogen transfer; (2) nitro-nitrite rearrangement; and (3) scission of the C-nitro bond. These computational studies suggest that the preferred path for FOX-7 decomposition will depend upon the conditions which cause initiation. For example, under gentle heating (thermolysis), intermolecular hydrogen transfer is likely, resulting in the production of reactive radical intermediates and water. Conversely, scission of a C-nitro bond requires a large energy input to cause electronic (singlet-to-triplet) excitation of the molecule, suggesting that this reaction is more likely to occur under the high-pressure/high-temperature conditions typically generated by shock or impact.

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Executive Summary

In order to reduce the hazards to Defence personnel associated with the use, storage and transport of explosives, the Australian Defence Force established a policy (DI(G) LOG 07-10) to adopt insensitive munitions (IM) into its inventory "where it is sensible, practicable and cost-effective to do so." In 1998, the FOA Defence Research Establishment (Sweden) reported the successful synthesis of FOX-7 (1,1-diamino-2,2-dinitroethylene), an explosive which they claim exhibits both high performance and low sensitivity. Hence, FOX-7 shows promise as an RDX replacement in explosives ordnance designed to comply with IM standards.

Qualifying new explosives for military use is a lengthy, expensive and hazardous process, particularly for explosives displaying 'non-ideal' detonation behaviour. Repetitive testing of explosives performance and sensitivity can be augmented or even replaced by computer simulation, thereby reducing cost and risk to personnel. For instance, computational estimates of the performance of an explosive formulation can be obtained from chemical thermodynamics, using as input the measured heats of formation of the pure ingredients. However, it is more difficult to model the sensitivity of an explosive, which can depend upon several factors, perhaps the most important being the nature of the initial chemical decomposition reactions. Characterising these 'initiation reactions' is often beyond the scope of standard experimental techniques, or impossible to extract from practical sensitivity tests. Fortunately, some fundamental chemical properties of energetic materials can be determined non-empirically using 'first-principles' quantum mechanics.

Since FOX-7 is a relatively new energetic material, little is known about its physical and chemical properties. Therefore, first-principles quantum chemical calculations are used to predict the initial steps of decomposition in solid FOX-7. Since some chemical properties of FOX-7 are similar to those of another insensitive explosive, TATB (triaminotrinitrobenzene), three possible reaction paths were investigated based upon observed decomposition in solid TATB. The results of this study agree with, and expand upon, the results of previously reported calculations, and suggest that the decomposition of solid FOX-7 will depend upon the nature of initiation. For example, gentle heating (thermolysis) is likely to cause hydrogen transfer between molecules, producing highly reactive chemical species. Conversely, rupture of a C-nitro bond (resulting in the production of NO_2) requires a large amount of energy, suggesting that this reaction is more likely to occur when the explosive has been subjected to shock or impact.

Finally, it is worth noting that solid FOX-7, unlike many energetic materials, is relatively easy to model, since it is composed of small, symmetric molecules arranged in a simple crystal structure. FOX-7 is therefore a convenient vehicle for studies of initiation and growth of reaction to detonation. Extrapolation to other systems will ultimately contribute to the development of better explosive formulations for IM compliant ordnance in ADF applications.

Authors

Helen Dorsett

Weapons Systems Division

Helen Dorsett holds a BA in Physics from Rutgers University (USA), an MS in Chemical Physics and a PhD in Physical Chemistry from the University of Maryland (USA). She joined DSTO in 1998 after completing a collaborative post-doctoral project between the University of Melbourne (VIC) and Pacific Northwest National Laboratory (USA) to model solvation of salts in water. Her DSTO research includes computational studies of energetic molecules and small scale testing of underwater explosives.

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1. Introduction

In order to reduce the risk to Defence personnel and materiel associated with the hazards of using, storing and transporting explosives, the Australian Defence Organisation established a policy to adopt insensitive munitions (IM) into its inventory “where it is sensible, practicable and cost-effective to do so” [1]. However, for conventional explosive formulations, IM compliance often comes at the cost of reduced performance [2]. In 1998, the FOA Defence Research Establishment of Sweden reported the successful synthesis of FOX-7 (1,1-diamino-2,2-dinitroethylene) [3]. FOX-7 is expected to be a high-performance explosive, since it has the same elemental composition as RDX (cyclotrimethylenetrinitramine) as well as a relatively high crystal density. Indeed, the thermochemical code CHEETAH 1.4 predicts a FOX-7 velocity of detonation $V_{oD} = 8870$ m/s and a detonation pressure $P_{CJ} = 34.0$ GPa¹. The developers of FOX-7 also claim that it has a much lower sensitivity than RDX to friction, shock, and impact [5], and thus shows promise as a high-performance replacement for RDX in IM-compliant formulations.

Compared with typical C-H-N-O explosives, FOX-7 is a small and relatively symmetric energetic molecule (Figure 1a). The structure of solid FOX-7 is also simple, consisting of a small crystal unit cell containing four molecules. These characteristics make FOX-7 an attractive system for theoretical studies, particularly as a prototype for modelling the complex physics and chemistry associated with initiation and growth of reaction to detonation in solid energetic materials. Such studies can be used to identify and characterise phenomena that contribute to explosives sensitivity, thereby creating a theoretical means with which to screen energetic materials for IM applications. In this way, theoretical simulations serve to reduce the risk associated with time-consuming and repetitive testing of these hazardous materials.

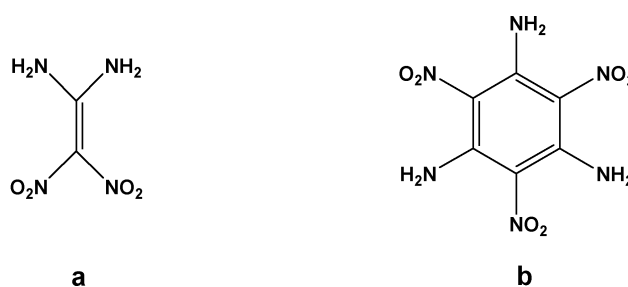


Figure 1. (a) FOX-7 (1,1-diamino-2,2-dinitroethylene); (b) TATB (triaminotrinitrobenzene).

¹ CHEETAH 2.0 [4] estimates for RDX performance are $V_{oD} = 8930$ m/s and $P_{CJ} = 35.6$ GPa.

A natural starting point for theoretical studies of FOX-7 initiation is to investigate chemical decomposition at the molecular scale. For this purpose, *ab initio* ('first-principles') quantum chemical calculations provide the most accurate and detailed description of the reaction chemistry in the absence of empirical data. However, this accuracy comes at relatively high computational expense, so efficient use of quantum chemical calculations requires intuitive postulates of possible reaction paths. Generally, these premises can be made from experimental measurements, however, little chemical data is currently available for FOX-7. Nevertheless, some chemical properties of FOX-7 are similar to TATB (triaminotrinitrobenzene), another insensitive explosive which has undergone extensive experimental characterisation [6]. Based upon the observed decomposition of TATB and similar nitroanilines subjected to thermal or mechanical insult, three possible initiation mechanisms for FOX-7 were investigated, namely: (1) unimolecular or intermolecular hydrogen transfer; (2) nitro-nitrite isomerisation and (3) scission of a C-NO₂ bond. These studies show that, like TATB, the type of chemical decomposition likely to occur in FOX-7 will depend upon the external conditions that cause initiation.

2. Method

For a description of the mathematical basis of *ab initio* quantum chemical calculations, the reader is referred to a DSTO general document [7] discussing molecular modelling techniques suitable for use with energetic materials.

All calculations were performed using the *Gaussian98* [8] suite of programs. Generally, sophisticated 'multi-configuration' Hartree-Fock methods are recommended for modelling the close-lying electronic states within nitro groups [9]. However, the computational expense of these techniques currently renders them untenable for calculations on large energetic molecules. From their studies of nitromethane, Manaa and Fried [10] demonstrated that computationally inexpensive methods based upon density functional theory (DFT) qualitatively reproduce features of open-shell systems. Furthermore, they claim that calculations using the B3LYP functional² are accurate to within 5 kcal/mol for treatments of bond cleavage in energetic materials similar to nitromethane. Therefore, the B3LYP functional was used in conjunction with Dunning's correlation-consistent basis sets cc-pVDZ and aug-cc-pVDZ³ for these calculations.

² B3LYP' is a combination of Becke's three parameter exchange functional [11] with the Lee-Yang-Parr correlation functional [12].

³ The acronym 'cc-pVDZ' stands for 'correlation-consistent polarised double-zeta (split valence)' basis sets which were developed with consideration of electron correlation effects (electron-electron interactions) in atoms [13]. The prefix 'aug' indicates the basis has been expanded with diffuse functions to better describe delocalised electrons. Unless otherwise specified, the larger basis set, aug-cc-pVDZ, was used for calculations.

For calculations of reaction enthalpies, all initial- and final-state chemical species were allowed to relax to a minimum-energy structure, from which vibrational properties were calculated. All heats of reaction are based upon room-temperature enthalpies, which include the zero point energy and the enthalpy change as temperature increases from 0 K to 298 K.

3. Results and Discussion

3.1 Ground-state properties of FOX-7

3.1.1 General comments on structure vs. sensitivity

As shown in Figure 1, the FOX-7 molecule consists of nitro (-NO₂) and amino (-NH₂) functional groups attached to a carbon (C-C) 'backbone.' The close proximity of amino hydrogens to nitro oxygens has prompted speculation that the stability of FOX-7 is due to hydrogen bonding within the molecule [3,14]. However, part of the increased stability can be attributed to other electronic effects. It is well known that the presence of amino groups tends to desensitise nitroaromatic molecules to shock or impact initiation. For example, TATB is much more stable than trinitrobenzene, which contains no amine groups. This increase in stability is attributed to 'push-pull' electron delocalisation which allows partial charge transfer between 'electron-withdrawing' nitro groups and 'resonance donating' amine groups. The nearly planar configuration of FOX-7 indicates that it has an electronic structure with delocalised electrons, as with TATB. A theoretical study by Politzer *et al.* [15] confirmed the presence of 'push-pull' electron delocalisation in FOX-7. By comparing various amino/nitro derivatives of ethylene, Politzer *et al.* conclude that the stability FOX-7 is due to more to resonance effects than to hydrogen bonding.

3.1.2 B3LYP/aug-cc-pVDZ predictions

The minimum energy B3LYP/aug-cc-pVDZ configuration obtained by an unconstrained optimisation of an isolated FOX-7 molecule is shown in Figure 1. The calculations predict a nearly planar molecule with a slight (11°) twist of the C=C axis coupled with some rotation of the amine and nitro groups. Calculated bond lengths and bond angles are listed in Table 1 along with corresponding experimental values for solid FOX-7 [14]. Aside from the N-H bond lengths⁴ the calculated gas-phase is quite similar to the experimental structure. However, the isolated molecule has C2

⁴ Hydrogen atoms are difficult to measure accurately with x-ray diffraction, and their positions are generally estimated using a "riding" model. Hence, values for hydrogen bond lengths are best measured by neutron diffraction, which can detect hydrogen, or estimated by *ab initio* calculations. For calculations involving the x-ray structure of FOX-7, optimised N-H bond lengths were obtained by fixing all the heavy atoms in the x-ray structure and allowing all the hydrogen atoms to relax to a minimum-energy configuration. N-H bond lengths obtained this way range from 1.009 to 1.01Å.

symmetry, whereas interactions between neighbouring molecules in solid FOX-7 causes an accentuated twist of one nitro group. Accounting for differences in N-H bond lengths⁴, the energy required to distort FOX-7 from the gas-phase configuration to the x-ray configuration is relatively small, approximately 2 kcal/mol⁵. B3LYP/aug-cc-pVDZ predictions of the structures and energies of FOX-7 and its isomers (*see* Table 3) are nearly identical to those obtained by Politzer *et al.* using B3P86/6-31+G** [15].

Table 1. Selected geometric parameters for FOX-7 (Å, degrees).

parameter	Expt. [14]	Calc.	parameter	Expt. [14]	Calc.
C=C	1.456	1.430	N-H(t)	0.88, 0.87	1.008
C-NH ₂	1.319, 1.325	1.344	N-H(s)	0.84	1.018
C-NO ₂	1.399, 1.426	1.433	N-O(t)	1.252, 1.242	1.255
O(s)-H(s)	1.97, 2.03	1.790	N-O(s)	1.249, 1.242	1.222
∠ H ₂ N-C-NH ₂	118.4	117.7	∠ O-N-O	120.9, 121.0	122.4
∠ O ₂ N-C-NO ₂	116.3	116.9	∠ H(t)-N-C	121.0, 121.1	120.3
∠ H ₂ N-C=C	120.7, 120.8	121.1	∠ H(s)-N-C	119.8, 121.9	117.0
∠ O ₂ N-C=C	119.8, 123.9	121.6	∠ O(s)-N-C	118.6, 118.9	117.9
∠ H-N-H	118.3, 118.1	122.2	∠ O(t)-N-C	120.1, 120.4	119.7
∠ H ₂ N-C=C-NO ₂	172.9, 177.8	169.2	∠ O(t)-N-C-C	171.0, 143.6	156.0
∠ H(t)-N-C-C	-179.6, -178.3	-170.4	∠ O(s)-N-C-C	-5.8, -34.3	-21.7
∠ H(s)-N-C-C	0.5, 10.1	2.1			

(t) - terminal bond (bond nearly parallel to C=C axis) (s) - side bond

Table 2. Vibrational normal modes of FOX-7. Frequencies are in wavenumbers (cm⁻¹).

freq	type	freq	type
61	C=C stretch + NO ₂ scissor	806	NO ₂ -C-NO ₂ scissor + N-O stretch
88	NH ₂ -C-NH ₂ rock + N-H(t) stretch	870	N-O(s) stretch + N-O(t) oop rock
114	NH ₂ -C-NH ₂ rock + N-H(t) stretch	1068	C-NH ₂ torsion + N-H(s) stretch
212	C=C stretch + N-H(t) stretch	1083	C-NH ₂ torsion + N-H(s) stretch
266	N-H(t) stretch	1149	NH ₂ -C-NH ₂ bend
296	C-N stretch + N-H(t) stretch	1214	C-NH ₂ torsion + C-NO ₂ stretch
335	C-N stretch	1272	C-NO ₂ bend
376	N-H(t) stretch	1341	C-NO ₂ bend + N-H(t) oop rock
387	N-H(t) stretch	1481	N-H(s) stretch + NH ₂ -C-NH ₂ bend
442	NH ₂ torsion + N-H stretch	1519	C-NH ₂ stretch + N-H oop rock
465	C=C stretch + NO ₂ -C-NO ₂ scissor	1565	N-H(s) stretch + C-NH ₂ bend
471	C=C torsion	1602	C-N stretch + NO ₂ stretch
610	C-NH ₂ torsion + C-N stretch	1624	NH ₂ -C-NH ₂ bend + C-NH ₂ bend
643	N-H(s) stretch + NH(s) rock	1632	C-NH ₂ bend
690	C=C stretch + NH ₂ -C-NH ₂ scissor	3446	C-NH ₂ bend + C-NH ₂ rock
751	NO ₂ -C-NO ₂ rock + N-O stretch	3460	C-NH ₂ bend + C-NH ₂ rock
751	N-H(s) stretch + NH(s) rock	3681	N-H(t) rock
771	C=C stretch + NO ₂ -C-NO ₂ scissor	3683	N-H(t) rock

(t) - terminal bond; (s) - side bond; oop - out of plane

⁵ In SI units, 1 kcal/mol = 4.184 kJ/mol = 6.95 × 10⁻²¹ J.

Calculated vibrational frequencies (unscaled) for FOX-7 in the gas phase are listed in Table 2.⁶ Since the normal modes tend to be a combination of several types of bond motion (*e.g.*, 'stretching' or 'bending'), identification of mode type is limited to a description of the most significant displacements. Of particular interest are the stretching modes of terminal N-H bonds. The frequencies of these vibrations are several hundred wavenumbers below those expected for amine groups. As will be discussed in Section 3.3, the low frequencies of these modes indicate that they will be activated at low temperatures, and may play a role in FOX-7 thermal decomposition.

Table 3. Configuration energies and enthalpies of possible reaction species. Values are in atomic units (1 au = 4.3597 × 10⁻¹⁸ J).

Chemical formula	Mass		E	H (T=298K)
(H ₂ N) ₂ C=C(NO ₂) ₂	148	singlet neutral	-598.427356	-598.325528
"	"	cation	-598.093807	-597.992254
"	"	anion	-598.471705	-598.373691
"	"	triplet neutral	-598.342738	-598.244256
"	"	x-ray	-598.306302	--
"	"	relaxed H-bonds	-598.421341	--
(H ₂ N)(O ₂ N)C=C(NO ₂)(H ₂ N)		<i>cis</i> isomer	-598.401490	-598.299490
		<i>trans</i> isomer	-598.420218	-598.320104
(H ₂ N)(H ₂ ON)C=C(NO ₂) ₂	164		-673.600674	-673.493737
•(H ₂ N) ₂ C=C(NO ₂)(ONOH)	149		-599.018113	-598.905803
(H ₂ N) ₂ C=C(NO ₂)(ONO)	148	nitrite isomer	-598.431014	-598.330776
•(H ₂ N)(HN)C=C(NO ₂) ₂	147	end deprotonation	-597.750901	-597.663956
"	"	side deprotonation	-597.751534	-597.663562
(H ₂ N)(ON)C=C(NO)(NO ₂)	146	furoxan derivative	-597.157186	-597.079491
•(H ₂ N) ₂ C=C(NO ₂)	102		-393.208040	-393.123943
•(H ₂ N)C=C(NO ₂) ₂	132		-542.360098	-542.289787
(H ₂ N) ₂ C=C(NO ₂)(NO)	132		-523.217935	-523.122288
•(H ₂ N)(HN)C=C(NO ₂)(NO)	131		-522.574147	-522.491694
(H ₂ N)(N)C=C(NO)(NO ₂)	130	furazan derivative	-521.982617	-521.909682
•(H ₂ N) ₂ C=CO(NO ₂)	118		-468.517425	-468.469437
•(H ₂ N)(HN)C=C(NO ₂)	101		-392.556021	-392.485309
HONO	47		-205.743025	-205.718668
•NO ₂	46		-205.112659	-205.100000
"	"	anion	-205.196358	-205.184661
•NO	30		-129.913296	-129.905494
OH ₂	18		-76.444642	-76.419636
•OH	17		-75.749004	-75.737037
•NH ₂	16		-55.891079	-55.868425
"	"	anion	-55.918054	-55.895804
NH	15		-55.152140	-55.141365
H ₂	2		-1.174025	-1.160796
•H	1		-0.501657	--

⁶ There is currently no experimental spectra available for FOX-7, however, it is expected that measured vibrational frequencies will be red-shifted with respect to the predictions due to significant hydrogen bonding within the solid.

3.2 Reaction products and energies

As mentioned in the introduction, possible mechanisms for initiation of reaction in solid FOX-7 include (1) intra- or intermolecular hydrogen transfer; (2) nitro-nitrite isomerisation and (3) C-nitro bond cleavage. To determine the energy cost of these reactions, and consequently how likely they are to occur, the energies and enthalpies of reactants and products were calculated, and the results listed in Table 3.

3.3 Hydrogen transfer

The crystal structure of FOX-7 consists of molecules aligned end-to-end in infinite two-dimensional wave-shaped layers [14]. This type of packing structure (Figure 2) maximises hydrogen bonding between the amine groups of one molecule and the nitro groups on its nearest neighbour, and also increases the probability of hydrogen transfer between the two molecules.

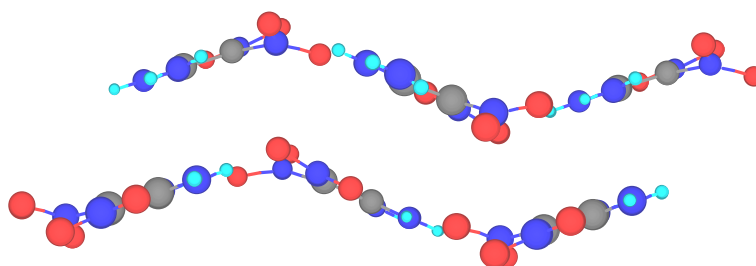


Figure 2. 'Ball-and-stick' representation of molecular packing in crystalline FOX-7.

There is evidence to suggest that intermolecular hydrogen transfer occurs via vibration-assisted bond cleavage during thermolysis of FOX-7. The reported temperature of ignition for FOX-7 is 215 °C, while differential scanning calorimetry (DSC) shows initiation of reaction at 238 °C [3]. In isolated FOX-7, several vibrational modes associated with the motion of terminal hydrogens are activated at temperatures between 110 °C to 270 °C. These terminal hydrogens lie closest to neighbouring molecules in the solid, and participate in hydrogen bonding, which further weakens the N-H bond. It is therefore likely that heating FOX-7 excites vibrations of terminal hydrogens to the point of N-H bond cleavage, thereby liberating the hydrogen for further reactions with neighbouring molecules.

3.3.1 HONO formation

Intramolecular hydrogen transfer resulting in HONO formation (Figure 3) has been proposed as the initial step for decomposition of 2-nitroaniline [6]. *Ab initio* calculations suggest that the analogous unimolecular reaction for FOX-7 is unlikely to occur as a

result of thermolysis, since the product is unstable and relaxes back to the original FOX-7 configuration.⁷

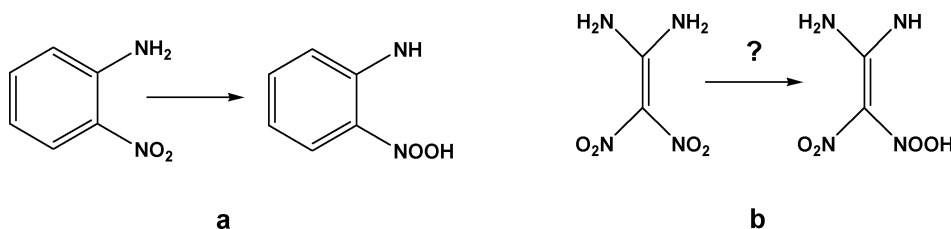


Figure 3. (a) Hydrogen transfer in 2-nitroaniline. (b) Analogous reaction in FOX-7.

However, hydrogen transfer between molecules in solid FOX-7 is possible. Irradiation of solid TATB with UV light leads to formation of long-lived radicals consistent with the structure shown in Figure 4a [6]. Calculations predict that the analogous structure for FOX-7 is stable and can be produced by an endothermic process of intermolecular hydrogen transfer.

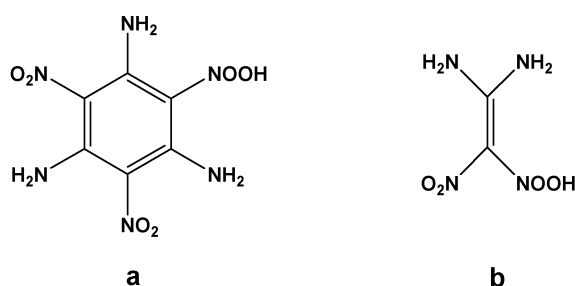
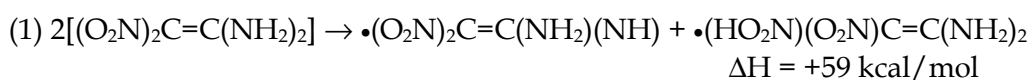


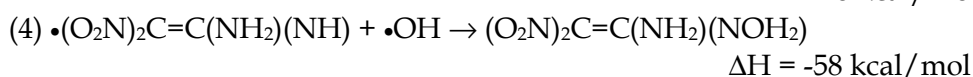
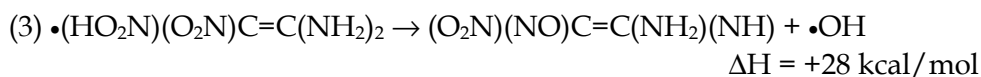
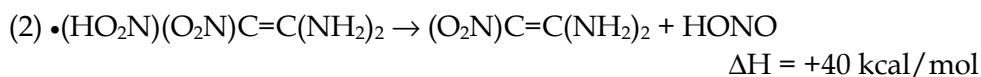
Figure 4. (a) HONO derivative of TATB. (b) Analogous product for FOX-7.

Deprotonation of FOX-7 is energetically costly, requiring an input of 100 kcal/mol; however, hydrogenation of FOX-7 to form the structure in Figure 4b releases 59 kcal/mol of energy. This calculated heat of reaction is quite close to activation barrier of +58 kcal/mol determined from analysis of the DSC isotherms of FOX-7 [3]. The reaction for intermolecular hydrogen transfer and its associated enthalpy (including intermolecular hydrogen bonding and distortion effects) is



⁷ More specifically, the 'singlet' product is unstable. A recent *ab initio* study by C.J. Wu and L.E. Fried [16] suggest that intramolecular hydrogen transfer in TATB results in formation of 'biradical' products (i.e., the product contains two unpaired electrons, and therefore has a triplet ground state). Subsequent calculations of the analogous 'biradical' product for FOX-7 is also stable. However, formation of a triplet product from ground-state (singlet) FOX-7 is 'spin-forbidden.' Therefore, H-transfer is unlikely to occur under relatively gentle heating.

Further decomposition of 'hydrogenated' FOX-7 may involve endothermic production of a hydroxyl radical, which can then bond exothermically to neighbouring unreacted or deprotonated FOX-7 molecules. Proposed reaction sequences are listed below with calculated reaction enthalpies.



Validation of this sequence as a possible route for FOX-7 decomposition requires detection of HONO (produced in reaction 3) or derivatives of FOX-7 containing HONO or NO groups.

3.3.2 Formation of furazan and furoxan derivatives

Intermolecular hydrogen transfer may also result in cyclisation reactions to form furazan and furoxan derivatives. Such reactions were observed in TATB crystals subjected to shock or impact [17], and the resulting furoxan products were found to be much more sensitive than the unreacted TATB. The reaction to form furazan and furoxan products is illustrated for 2-nitroaniline in Figure 5.

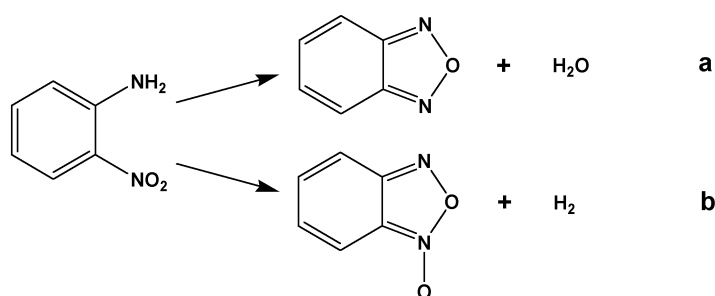
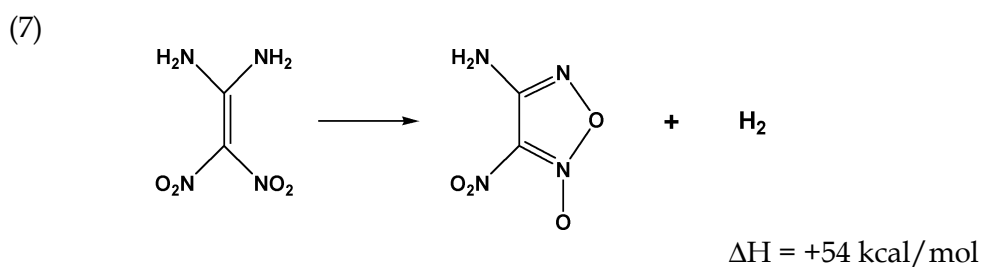
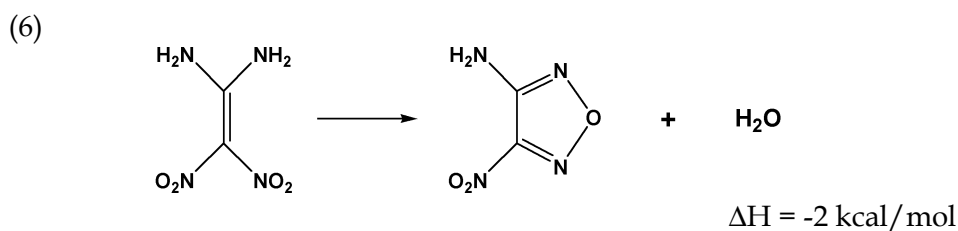


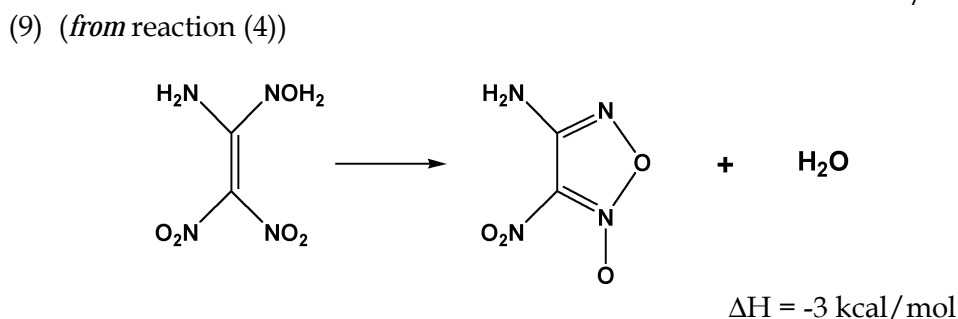
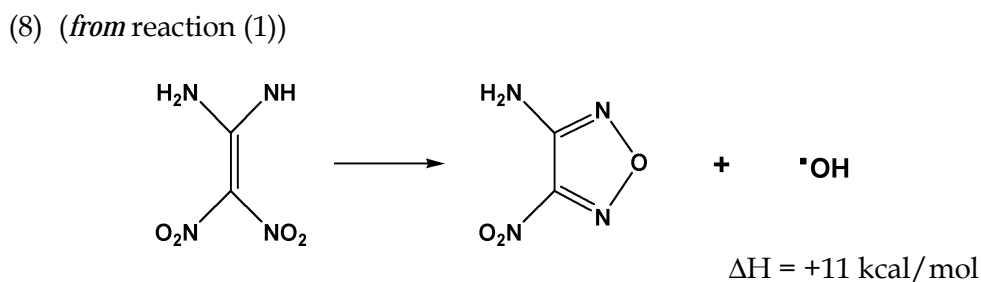
Figure 5. Decomposition of 2-nitroaniline into (a) furazan and (b) furoxan derivatives.

The analogous reactions in FOX-7 and their associated enthalpies are:



The calculated heats of reaction suggest that furazan formation, a slightly exothermic process, is more likely than production of the furoxan derivative, which requires a large input of energy. However, the actual mechanism of unimolecular hydrogen transfer is unclear in this case, since both reactions require transfer of *two* hydrogens.

For the solid state, furazan and furoxan derivatives of FOX-7 can be formed from products of previous intermolecular hydrogen transfer (reactions (1) and (4) above), in reactions that are nearly energetically neutral:



The low predicted enthalpies suggest that these reactions are likely to occur at 'hot spot' decomposition centres in solid FOX-7. If FOX-7 thermolysis leads to formation of

the furazan product, then the simultaneous production of the highly reactive hydroxyl radical indicates that reaction (8) could contribute to growth of reaction to detonation.

3.4 Nitro-nitrite rearrangement

Thermal decomposition of solid nitroaromatic compounds below 500 °C produces a large amount of NO gas, whereas NO₂, when it is observed, is present only in small quantities. One explanation for this observation is an initiation step involving nitro-nitrite rearrangement, which then leads to formation of NO and acyl radicals. Recently, Brill and James used mass spectroscopy to demonstrate nitro-nitrite isomerisation in nitroaromatics [18].

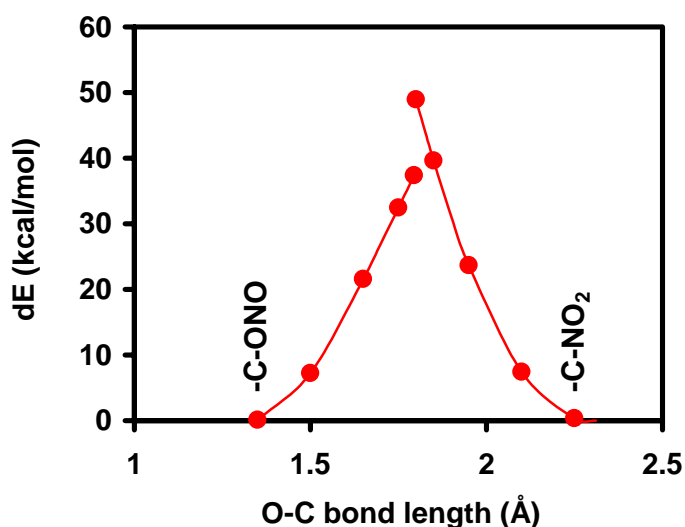
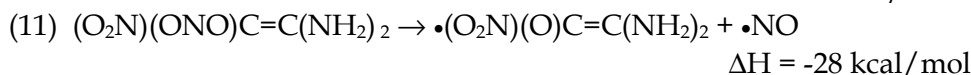


Figure 6. B3LYP/cc-pVDZ reaction path for nitro-nitrite rearrangement in FOX-7. All energies are given with respect to the minimum energy ground state structure.

For FOX-7, nitro-nitrite isomerisation and the production of NO and acyl radicals can be written:



Since nitro-nitrate isomerisation in FOX-7 leads to exothermic production of radicals, a cursory attempt was made to determine the activation energy required to initiate the reaction. To do this, configurational energies were calculated as the distance between a carbon and oxygen atom is incrementally reduced. To speed calculation, only the

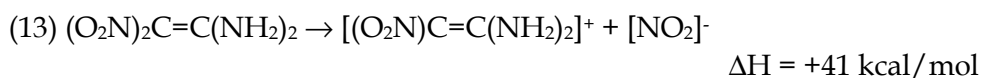
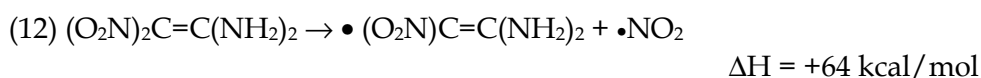
positions of the nitrogen and the second oxygen in the nitro group were optimised; all other atoms were fixed. Results are plotted in Figure 6.

The most prominent feature of Figure 6 is the cusp in energy at $R_{O-C} = 1.80\text{\AA}$. As the C-O distance decreases from 1.800\AA to 1.795\AA , the C-N distance increases from 1.35\AA to 2.58\AA , and the total energy drops by 12 kcal/mol. This non-physical result can be explained by examination of the final state structure at $R_{O-C} = 1.35\text{\AA}$. In this configuration, the N-O distance within the 'nitrite' group is 1.61\AA which, given the limits of this calculation, probably indicates a broken bond⁸. Hence, the calculated energy profile effectively describes two reactions, the first being scission of the C-nitro bond ($2.31\text{\AA} > R_{O-C} \geq 1.80\text{\AA}$), and the second being simultaneous formation of NO and the carbonyl moiety ($1.80\text{\AA} > R_{O-C} \geq 1.35\text{\AA}$). This calculation is not accurate enough to determine whether nitro-nitrite rearrangement proceeds in the two steps described above, or combines reactions (10) and (11) in a single concerted step. However, it does indicate that an accurate model of the reaction must include a description of radical formation, which is beyond the scope of spin-restricted singlet calculations.

3.5 C-nitro bond scission

In nitroaliphatics, nitramines and nitrate esters, the attachment of nitro groups is relatively weak, and therefore scission of the X-NO₂ bond is an important step in decomposition of these energetic materials. In nitroaromatics, the C-NO₂ bond is comparatively strong. For instance, the absence of detectable NO₂ in the decomposition products of solid bulk substituted nitrobenzenes indicates that other decomposition reactions exist with lower activation energies than that required for C-NO₂ homolysis [6]. Nevertheless, C-NO₂ bond scission occurs under high temperature decomposition, and appears to be the predominant reaction path under shock or impact conditions.

For FOX-7, C-nitro bond homolysis would lead to formation of either radical or charged species:



The calculated reaction enthalpies indicate that for gaseous FOX-7, radical formation requires an energy input of more than 20 kcal/mol over formation of charged products, suggesting that ion formation is more likely to occur.

⁸ In general, density functional methods cannot accurately model bond scission since they describe only a single electron configuration.

To better determine the outcome of C-nitro bond scission, a detailed reaction profile was calculated as a function of C-NO₂ bond length in FOX-7. For each fixed C-NO₂ distance, the system was allowed to relax to a minimum-energy configuration. The results are shown in Figure 7. Calculations were performed for both singlet and triplet electronic configurations for FOX-7, with the assumption that a singlet calculation will favour formation of charged products (*i.e.*, two products in singlet ground states), and triplet calculations will better describe the unpaired electrons of radical products.

From Figure 7, it is clear that singlet DFT calculations are not adequate for predicting ion formation via C-NO₂ scission in FOX-7. As the bond is stretched, the predicted energy increases until it exceeds the heat of reaction for ion formation by more than 50 kcal/mol. In the calculation, spin contamination is evident beyond $R_{\text{C-NO}_2} = 4.2 \text{ \AA}$, and worsens to the point that the spin-unrestricted calculation fails at $R_{\text{C-NO}_2} = 4.5 \text{ \AA}$. Also, Mulliken population analysis of the two singlet 'products' predicts a *decrease* in excess charge with increasing separation, contrary to expected behaviour for ion formation. Hence, if ion formation is a possible consequence of C-NO₂ bond scission in FOX-7, *ab initio* studies of this process will likely require more sophisticated multiconfigurational treatments.

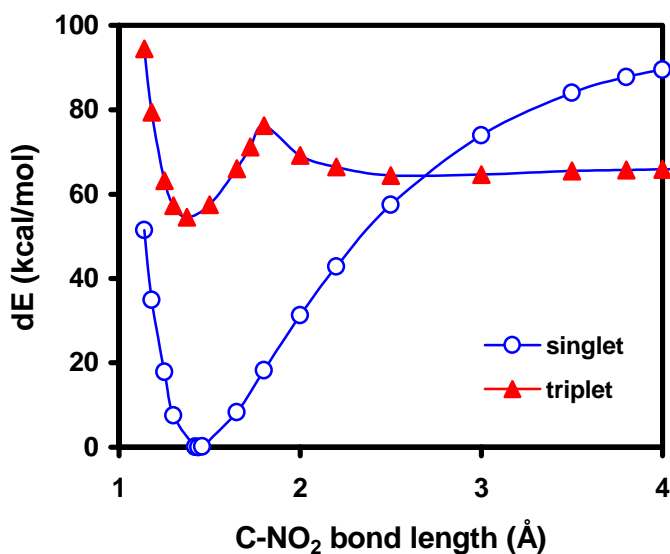
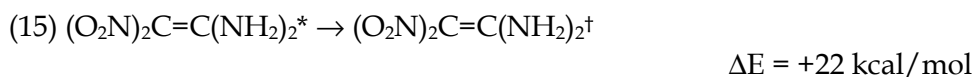
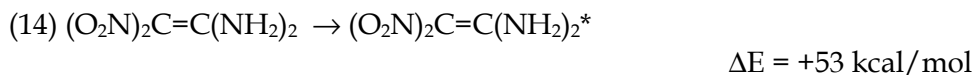


Figure 7. B3LYP/cc-pVDZ reaction path for C-NO₂ bond scission in FOX-7. All energies are given with respect to the minimum energy of the singlet ground state.

Triplet B3LYP/cc-pVDZ calculations appear to be more successful at modelling radical formation via rupture of the C-NO₂ bond. From an optimum configuration of $R_{\text{C-NO}_2} = 1.37 \text{ \AA}$, the triplet energy increases by nearly 22 kcal/mol, to a maximum at $R_{\text{C-NO}_2} = 1.80 \text{ \AA}$. Beyond $R_{\text{C-NO}_2} = 2.50 \text{ \AA}$, the triplet energy settles to a value of +64 kcal/mol relative to the singlet minimum, a value identical to the calculated heat of reaction for radical formation. These calculations indicate that radical formation via

C-nitro scission in FOX-7 requires excitation to the triplet electronic state. Modelling the reaction as a two-step process,



where (14) represents singlet-triplet excitation and (15) represents further excitation to a transition state between reactants and products. These results are similar to the DFT calculations of Manaa and Fried for nitromethane, nitramine and nitric acid [10]. Extrapolating from their comparisons to multiconfiguration calculations, it is likely that the actual activation barrier of reaction (15) reaches a maximum value at $R_{\text{C-NO}_2} \sim 2.0 \text{ \AA}$, and is at least 10 kcal/mol greater than the B3LYP predictions. The estimated total activation energy is then approximately 70 kcal/mol – a value only slightly greater than thermal energy contributions to the total energy (from Table 3, $\Delta E = +62$ to $+64$ kcal/mol), suggesting that scission of the C-NO₂ bond would proceed once FOX-7 is excited to the triplet state.

3.6 Fragmentation via mass spectroscopy

Electron impact mass spectroscopy (EI-MS) is a standard method for determining the nature and purity of chemical samples. EI-MS involves ionising molecules in a sample by electron impact, and then measuring the mass/charge (m/e) ratio of the resulting fragments. Although the primary use of EI-MS is sample analysis, there is some evidence to suggest that the EI-MS fragmentation pattern of some energetic materials is similar to their thermal fragmentation [19].

EI-MS of FOX-7 has been performed at FOA using 20eV and 70eV electron impact energies [20] and at DSTO using 20eV electron impact [4]. Table 4 lists the major m/e peaks observed in 70eV FOA spectra and the 20eV DSTO spectra.

The presence of $m/e = 148$ indicates that FOX-7 is very stable compared to conventional high explosives like RDX. What is rather surprising is the comparative lack of NO₂ ($m/e = 46$) and NO ($m/e = 30$) among the fragmentation products, particularly at 20eV impact energies. The FOA claim that the presence of $m/e = 130$ and 18 in their 20eV and 70eV EI-MS spectra indicates production of water due to furazan formation. However, these products were not observed in DSTO EI-MS results taken after standard instrument decontamination procedures.

Table 4. *EI-MS spectra for FOX-7 subjected to 20 eV (DSTO results) and 70 eV (FOA results) electron impact energies.*

M/z	20 eV peak int (%)	70eV peak int (%)	possible species
18	n/a	20.0	H ₂ O
27	n/a	4.9	HCN
28	n/a	33.2	CO, N ₂
29	n/a	6.0	
30	n/a	32.5	NO
41	--	4.9	
42	3.5	16.2	
43	13.3	100.0	C(NH)(NH ₂), CNO
44	100.0	80.0	C(NH ₂) ₂ , CO ₂
45	37.2	1.9	
46	0.7	7.9	NO ₂
53	--	12.8	
54	0.6	3.4	
55	--	9.1	
60	24.1	< 0.5	
69	--	33.2	
70	--	6.4	
72	--	9.1	
86	--	21.9	
88	25.2	< 0.5	C(NO)(NO ₂)
89	1.0	< 0.5	
130	--	< 0.2	
148	21.2	69.4	FOX-7
149	1.5	12.5	FOX-7 + H

1 eV = 1.602 x 10⁻¹⁹ J = 23.06 kcal/mol; n/a: out of range

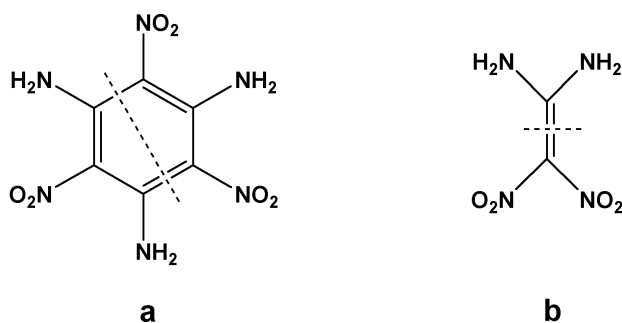


Figure 8. (a) *Ring scission in TATB; (b) analogous reaction in FOX-7.*

EI-MS may also cleave the C=C bond in FOX-7. In EI-MS studies of the thermal decomposition of TATB, Farber and Srivastava postulate that C=C homolysis occurs in the form of ring scission [21]. In this experiment, EI-MS spectra were taken of TATB sublimed from the solid by heating in an effusion cell to 200-300° C. Peaks observed at $m/e = 114$ and 144 are consistent with ring fission as shown in Figure 8a. The analogous reaction in FOX-7 – scission of the C=C bond – would result in fragments which, if singly ionised, have $m/e = 44$ and 104. Large peaks in both the 20eV and 70eV

EI-MS spectra of FOX-7 occur around $m/e = 44$.⁹ If C=C scission occurs, the absence of the complimentary peak at $m/e = 104$ indicates the $C(NO_2)_2$ cation product is extremely unstable, if it is produced at all.

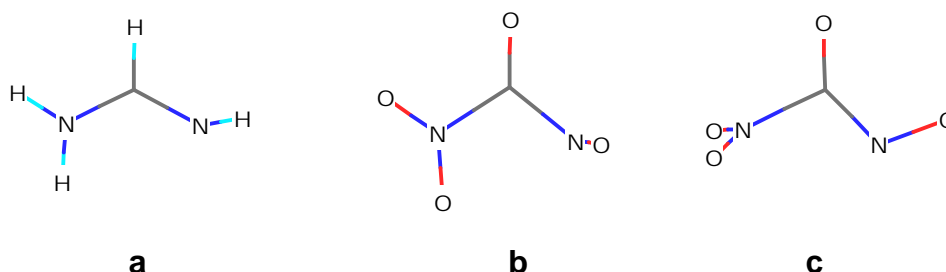
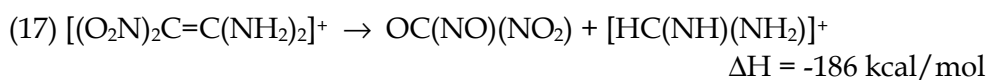
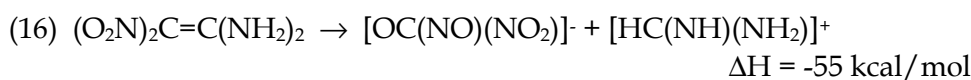


Figure 9. Optimised structures of FOX-7 EI-MS fragments: (a) mass 44 cation; (b) mass 104 neutral; (c) mass 104 anion. Shortened bonds indicate projection out of the x - y plane.

Ab initio calculations of C=C bond scission in FOX-7 agree with EI-MS results. The proposed mass 44 fragment and its cation is predicted to be stable, although the optimum structure involves transfer of one hydrogen from an amine group to the carbon atom (Figure 9). The proposed mass 104 fragment involves a similar transfer of an oxygen to the carbon atom, however only the neutral and anionic species is stable and therefore undetectable by EI-MS. Interestingly, C-C bond scission to produce the $HC(NH)(NH_2)$ cation is exothermic for reactions involving either the FOX-7 neutral molecule or cation, suggesting this reaction is likely to occur:



It is important to note that there are strong caveats for interpreting EI-MS results. As shown in Table 5, a particular peak could apply to any or all of several chemical species, and the number of possible species increases with m/e . Peaks at $m/e = 86$ and 88 strongly suggest the existence of simultaneous reactions leading to production of other species such as, for instance, $(O_2N)C=C(NH_2)$ and $(O_2N)HC=CH(NH_2)$. The FOA is currently running isotopic studies to precisely determine what species are produced in these EI-MS measurements [22].

⁹CO₂, a common contaminant in high-vacuum environments, also has $m/e = 44$. However, the spread around $m/e = 44$ in the 20eV spectra and $m/e = 43$ in the 70 eV spectra is not characteristic of isotopic abundances.

4. Conclusions

Ab initio quantum chemical calculations using density functional theory have been used to study three possible decomposition mechanisms in FOX-7: (1) hydrogen transfer, (2) nitro-nitrite rearrangement and (3) C-NO₂ homolysis. Calculations support intermolecular hydrogen transfer as a possible step for initiation of FOX-7 decomposition under thermolysis, which leads to formation of water and reactive intermediates like hydroxyl radicals and furoxan derivatives. If nitro-nitrite rearrangement occurs in FOX-7, preliminary calculations indicate the nitrite configuration is unstable, and decomposes exothermically to form NO and the associated radical fragment, thus suggesting the reaction would occur in a single concerted step. Detailed analysis of C-NO₂ bond scission support formation of radicals rather than ions, with strong contributions from the triplet excited state. This would suggest that C-NO₂ homolysis is more likely to occur under highly non-adiabatic conditions including those produced by shock or impact. A conservative analysis of reaction energetics indicates that facile generation of radical products can occur once FOX-7 is excited into the triplet state.

Although it has been proposed that decomposition via electron impact mass spectroscopy is similar to that initiated by thermolysis, EI-MS spectra obtained by both FOA and DSTO show a notable absence of proposed reaction products. *Ab initio* investigations support the existence of another path for FOX-7 decomposition, C=C bond scission, which has also been observed in EI-MS measurements of TATB.

Future research plans include a more sophisticated multiconfigurational treatment of the transition states of nitro-nitrite rearrangement and C-NO₂ bond scission, and detailed investigation of interactions between FOX-7 molecules. These studies will support the development of models for initiation and growth of reaction to detonation in solid FOX-7.

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19. ABSTRACT First-principles quantum chemical calculations are used to predict the initial steps of decomposition in solid FOX-7 (1,1-diamino-2,2-dinitroethylene). Three possible reaction paths were studied: (1) intra- or inter-molecular hydrogen transfer; (2) nitro-nitrite rearrangement; and (3) scission of the C-nitro bond. These computational studies suggest that the preferred path for FOX-7 decomposition will depend upon the conditions which cause initiation. For example, under gentle heating (thermolysis), intermolecular hydrogen transfer is likely, resulting in the production of reactive radical intermediates and water. Conversely, scission of a C-nitro bond requires a large energy input to cause electronic (singlet-to-triplet) excitation of the molecule, suggesting that this reaction is more likely to occur under the high-pressure/high-temperature conditions typically generated by shock or impact.					