



Further Decomposition Pathways of Mixtures of the Nitramines HMX, RDX and CL20 with the Energetic Binder Glycidyl Azide Polymer (GAP) – A Computational Study II

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Abstract: The energetic plasticizer glycidyl azide polymer (GAP) is used for new types of rocket propellants which are formulated with the objective of achieving higher burning rates. While the homolytic fission of an N-NO₂ bond, which we discussed previously, is energetically favored as the initial decomposition step, experiments show that the decomposition of mixtures of the nitramines octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and hexanitrohexaazaisowurtzitane (CL20) with a monomer of GAP-diol is more complex. Therefore we investigated further possible decomposition pathways. Comparison of the calculated activation energies for the decomposition of the mixtures with those for the decomposition of the isolated nitramines shows that the presence of GAP-diol decreases the activation energies of certain decomposition steps by up to 20 kJ mol⁻¹. GAP-diol facilitates the decomposition of CL20 and RDX to a larger extent than the decomposition of HMX. However, the investigated decomposition pathways of GAP-diol were inhibited by the presence of the nitramines.

Keywords: calculation, decomposition, energetic binder, nitramine, solid rocket propellants

Introduction

A mixture of the nitramine CL20 (hexanitrohexaazaisowurtzitane) with the energetic binder GAP is being developed as a base for a new, faster burning rocket propellant [1, 2]. Experimental investigation has shown that the decomposition of mixtures of ϵ -CL20 and β -HMX with GAP proceeds in different ways. Mixtures of CL20 with GAP decompose more quickly and with an autocatalytic increase in rate, whereas the decomposition of mixtures of HMX with GAP shows a linear increase in reactivity [3].

We already discussed the N-NO₂ bond fission as a possible initial decomposition step for the decomposition of nitramine-GAP mixtures. In this report, further initial steps of the gas-phase decomposition of the nitramines HMX, RDX and CL20 with a monomer of GAP-diol are modeled computationally in order to gain a better understanding of the complex processes involved in the decomposition of these mixtures.

Results and Discussion

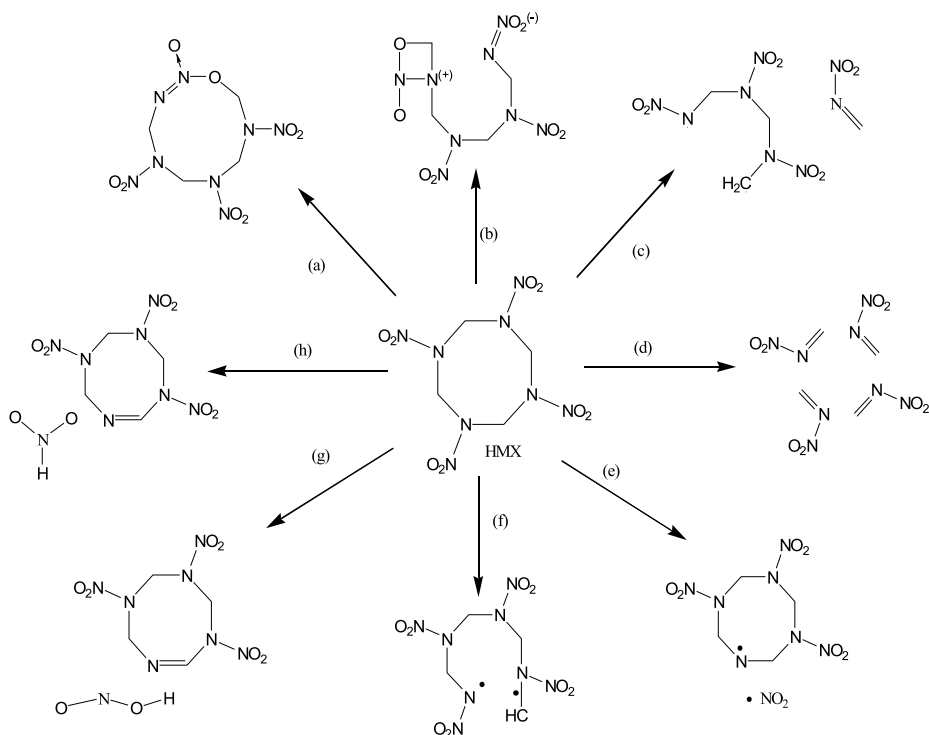
The decomposition of GAP-diol is discussed first in order to identify similarities and differences in the behavior of the mixtures of the nitramines with GAP-diol. The decomposition of the nitramines was already discussed in a previous report [4]. Scheme 1 illustrates the possible initial decomposition steps [11].

Decomposition of GAP

The decomposition of GAP is a complex process, but in contrast to the nitramines [4] the mechanism of the decomposition is only influenced slightly by pressure and heating rate [5-7]. Changes in these variables affect secondary reactions between the more reactive gaseous decomposition products [7].

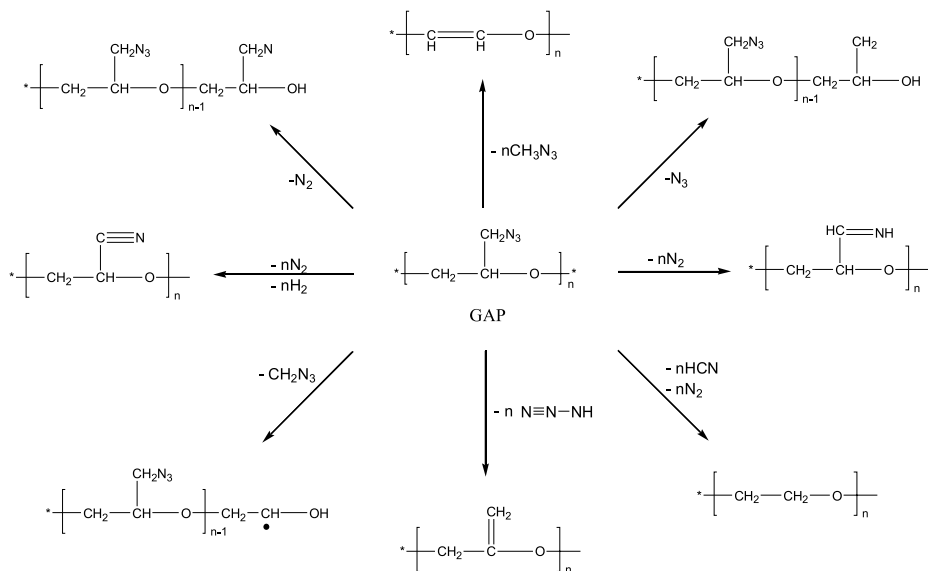
The thermal decomposition of azides is usually a first order reaction [8] which leads to a complex mixture of N₂, H₂, HN₃, NH₃, HCN, alkanes, alkenes and imine polymers. A singlet nitrene is believed to be the primary product, formed after initial N-N₂ bond fission, despite the fact that the triplet state is the ground state of most nitrenes. Promotion to the triplet state would require 590 kJ mol⁻¹. The elimination of N₂ can be coupled with or followed by a 1,2-hydrogen shift, giving a more stable imine product. Products observed during the decomposition of GAP include N₂, H₂, HCN, NH₃, CH₄, C₂H₄ and C₂H₂ as well as CO and CH₂O. This is in agreement with the products expected from the decomposition of an azide. Species with higher molecular masses have also been detected.

These include furane as well as the monomer, dimer and oligomers of GAP [7-10]. Mass spectrometric investigations showed that N_2 and CO together comprise 56% of the total product yield [10]. As expected, the decomposition of GAP is a first order reaction, [6, 8] but has also been proposed to consist of three phases, of which the second is believed to be autocatalytic [10].



Scheme 1. Proposed pathways for the first step in the decomposition of HMX.

(a) Transfer of an oxygen atom from an NO_2 group to an adjacent CH_2 group. (b) Heterolytic C-N bond fission. (c) Elimination of H_2CNNO_2 . (d) Concerted depolymerization to four molecules of H_2CNNO_2 . (e) Homolytic N- NO_2 bond fission. (f) Homolytic C-N bond fission. (g) Elimination of HONO (nitrous acid). (h) Elimination of HNO_2 (nitrous acid).



Scheme 2. Proposed pathways for the first step in the decomposition of GAP-diol.

As for all azides, fission of the weak N-N₂ bond is the most favorable initial step in the decomposition of GAP [6-11]. Other possible decomposition pathways are shown in Scheme 2 [9]. Several decomposition temperatures have been reported. While initial elimination of N₂ has been reported at temperatures as low as 120 °C, [11] other references observed decomposition at 215 °C, [8] 221 °C, [8] 260 °C [6] and 280 °C [9]. Experimentally determined activation energies for the decomposition have been reported between 135.7 kJ mol⁻¹ [6] and 176.6 kJ mol⁻¹ [11]. The azide groups decompose before the polymer backbone [6, 7]. At a temperature of 257 °C all azide groups of the polymer have decomposed, [7] but the rest of the polymer chain remains unchanged [7] and decomposes only at higher temperatures. The observed monomer and oligomers of GAP can be explained by depolymerization reactions, which lead primarily to the monomer and random chain scissions which yield the oligomers [9].

The nitrene formed during the decomposition of the azide side chains can rearrange during or after the decomposition *via* a 1,2-H shift to form a polyimine, [7, 9] which can undergo inter- or intramolecular cross-linking reactions. This explains the high percentage of products with a low molecular weight, as it is less likely for cross-linked polymers to undergo depolymerization [9]. The decomposition of the nitrene follows two pathways [8]. The most important of

these is C-N fission giving HCN; the other, C-N fission with a hydrogen shift, yields ammonia [11]. The polyimine can eliminate molecules such as H_2CNH or HCN to form other polymeric structures [9].

Calculations

As in our previous study, diaxial RDX, β -HMX and ϵ -CL20, which are the most stable solid-state polymorphs were used [4]. We used GAP-diol as we could not include more monomer units due to calculational cost and we wanted to stay close to the commercial product, which has hydroxide groups at the end of the polymer. In order to evaluate the effect of different alignments of GAP-diol on the activation energies, two different alignments were used. Alignment I is the minimum energy arrangement of the respective nitramines with GAP-diol, and alignment II was specifically chosen for the interaction of the azide groups with a nitramine group.

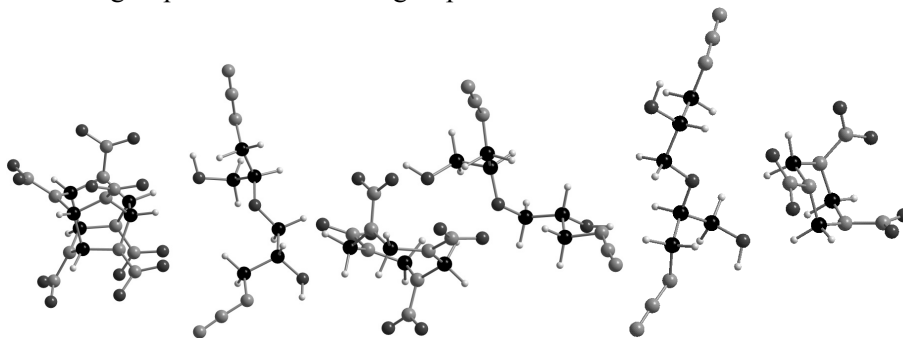


Figure 1. Alignment I of the mixtures of the nitramines HMX, RDX and CL20 with GAP.

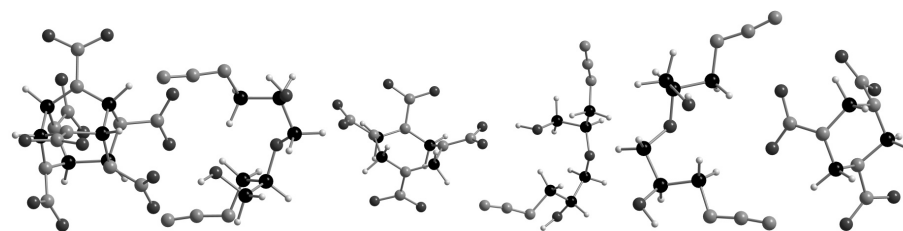


Figure 2. Alignment II of the mixtures of the nitramines HMX, RDX and CL20 with GAP.

We then determined the transition states for the decomposition pathways given in Scheme 1 at the B3LYP/6-31G(d) level of theory, which has been applied in previous studies [12, 13]. As discussed before [4], the decomposition pathways given in Scheme 1 for HMX also apply, with some deviations, for RDX and CL20.

We did not find transition states for any of the nitramines for decomposition pathway (c) in Scheme 1. This suggests that this decomposition pathway does not play a role in the decomposition of the nitramines. The formation of the HNO₂ tautomer of nitrous acid was not observed; all calculations resulted in the elimination of the HONO tautomer. For decomposition pathways (b) and (f), we did not find transition states for all of the nitramines.

Our results in Table 1 are in very good agreement with the reported values for the decomposition of the respective nitramines.

Table 1. Calculated activation energies for the decomposition pathways given in Scheme 1

Ea/kJ mol ⁻¹	Ref.	(a)	(b)	(d)	(e)4	(f)	(g)	(h)
HMX	B3LYP/6-31G(d) (β -HMX) [12]		231.4		166.5		186.6	
	B3LYP/cc-pVDZ (α -HMX) [23]				166.2		177.5	
	determined by comparison of bond breaking energies [24]				193.3	251.0	159.0	159.0
	BLYP/6-311G(d,p) (HMX) [16]		172.4	201.3	174.9		179.5	
	B3LYP/6-311G(d,p) (HMX) [16]		234.3	300.4	169.5			
	B3LYP/6-31G(d)	192.5	229.0	-	178.5	292.8	182.0	-
	B3LYP/3-21G	182.5	-	-	162.8	299.0	149.6	-
HMX + GAP	B3LYP/3-21G / I	215.6	-	-	161.2	-	173.4	
	B3LYP/3-21G / II	-	-	-	169.3	-	166.4	
RDX	B3LYP/6-31G(d) [12]	220.5						
	BPW91/cc-pVDZ [25]			228.9	143.5			
	B3LYP/6-31G(d) [13]			248.5	163.2		164.0	
	B3LYP/6-31G(d)	219.9	262.4	248.6	173.2	-	164.1	-
	B3LYP/3-21G	213.8	-	244.7	152.1	-	133.6	-
RDX + GAP	B3LYP/3-21G / I	209.6	261.9	-	174.0	-	152.7	-
	B3LYP/3-21G / II	-	-	-	154.7	-	115.7	-
CL20	solution of CL20 in acetone [26]				177			
	B3LYP/6-31G(d) [18 ¹]	269.2			157.4			
	B3LYP/6-31G(d)	267.9	-	-	-	-	246.7	-
	B3LYP/3-21G	244.4	-	-	153.1	-	222.1	-
CL20 + GAP	B3LYP/3-21G / I	241.7	-	-	151.7	-	-	-
	B3LYP/3-21G / II	225.3	-	-	145.4	-	224.4	-

As discussed previously [4], the calculations of the transition states were repeated at the B3LYP/3-21 G level of theory due to the high computational cost. Whilst the decomposition energies for pathways (a), (d), (e) and (f) are only slightly lower than the energies at the 6-31G(d) level, the results for the elimination of HONO from HMX are 30 kJ mol⁻¹ lower than the 6-31G(d) results. Therefore, the decomposition energies obtained for the decomposition of the mixtures at this level of theory should be lower than the actual energies of decomposition.

We used the same alignments of GAP-diol with the nitramines for the calculation of the activation energies as in our previous study [4]. Alignment I is the minimum energy arrangement of the respective nitramines with GAP-diol, and alignment II was specifically chosen for the interaction of the azide groups with a nitramine group.

Elimination of nitrous acid

The elimination of HONO or HNO₂, the tautomers of nitrous acid, is an important decomposition pathway for the cyclic nitramines. The breaking of a C-H bond is the rate determining step in the first step of the decomposition [14, 15]. It has been suggested that the intramolecular C-H bond fission is accompanied by the breaking of an N-NO₂ bond [16, 17].

Despite the fact that N-NO₂ homolysis is the lowest energy initial step of the decomposition, theoretical investigations have shown that overall, the consecutive elimination of three or four molecules of HONO is a more favorable process [12, 13].

The transition states for the axial and equatorial elimination of HONO from HMX and RDX have been calculated at the B3LYP/6-31G(d) level of theory and are given in Table 2.

Table 2. Axial and equatorial elimination of HONO from HMX and RDX at the B3LYP/6-31G(d) level of theory (with *zpe*)

	Axial elimination	Equatorial elimination
HMX	204.42 (182.95)	203.64 (182.95)
RDX	184.84 (164.12)	194.56 (173.40)

Our calculations showed that the bond dissociation energy of the equatorial N-NO₂ group is about 10 kJ mol⁻¹ lower than the bond dissociation energy of the axial bond [4]. This was not observed in the activation energies for the elimination of HONO, which have the same value in both cases. The non-bonded O...H distance from the equatorial group is shorter than the O...H distance from the

axial group, which favors proton elimination in the equatorial case [12]. For RDX axial elimination of HONO is favored by 9.72 kJ mol^{-1} over equatorial elimination. This difference is larger than that of 2 kJ mol^{-1} which was observed for the elimination of NO_2 , in which the shorter $\text{O}\cdots\text{H}$ distances from the axial groups also play a part.

For CL20 we calculated the elimination of HONO from a non-planar nitro group attached to a five membered ring, which was found to be favored by 37.7 kJ mol^{-1} over the elimination from a six membered ring [18]. The activation energy is $266.0 \text{ kJ mol}^{-1}$ ($246.74 \text{ kJ mol}^{-1}$ with *zpe*) and is in agreement with the literature [18]. This reaction pathway is less favorable for CL20 than for the cyclic nitramines due to the formation of a bridgehead double bond.

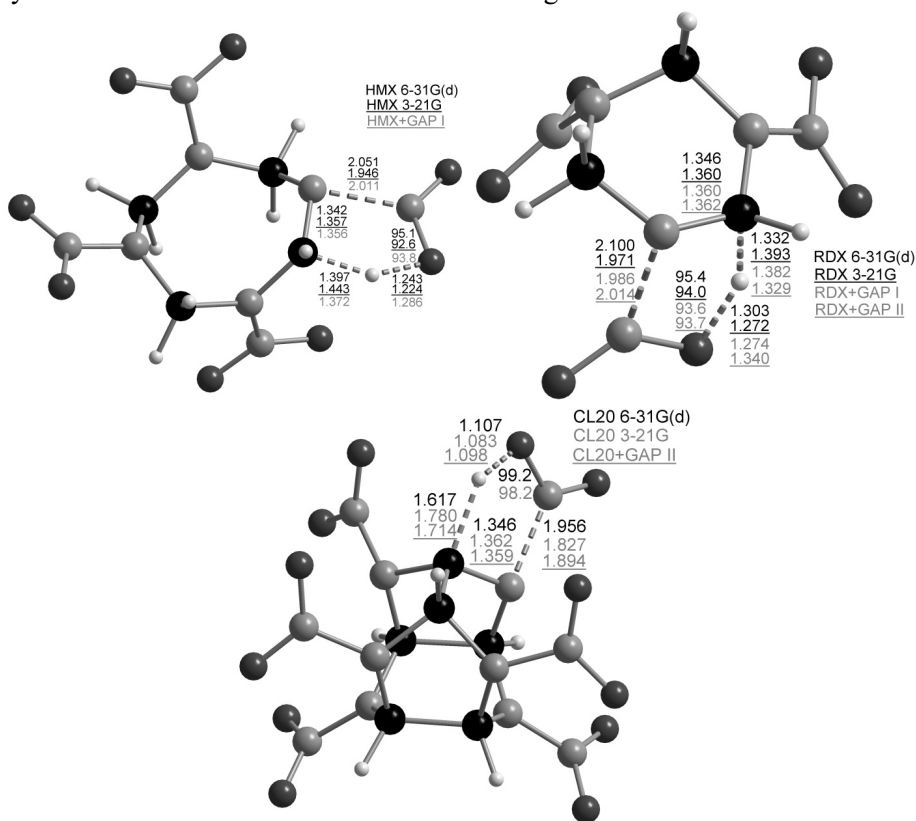


Figure 3. Transition states for the elimination of HONO from HMX, RDX and CL20 and mixtures of these nitramines with GAP-diol. The bond distances in the transition states are given in Å.

The transition states for the HONO elimination from mixtures of GAP-diol with the respective nitramines at the B3LYP/3-21G level of theory with different alignments are given in Figure 3, and the values of the activation energies in Table 1.

In general, the presence of GAP-diol inhibits the elimination of HONO from the nitramines. Only for alignment II of RDX with GAP-diol was the activation energy lowered, by about $18.80 \text{ kJ mol}^{-1}$ ($17.90 \text{ kJ mol}^{-1}$ with *zpe*). The differences in the activation energy between the pure nitramines and the mixtures are fairly large for HMX and RDX, whereas the activation energy for the elimination of HONO from CL20, which is already fairly high, is only increased by 3.92 kJ mol^{-1} (2.21 kJ mol^{-1} with *zpe*).

We did not find a transition state for the elimination of HNO_2 , the second tautomer of nitrous acid. All attempts led to the same transition states as found for the elimination of HONO.

Oxygen Transfer

The transfer of an oxygen atom from an NO_2 group to an adjacent CH_2 group has only previously been calculated for RDX [12]. For HMX an acyclic transition state has been found, which is similar to a transition state found for the homolytic cleavage of a C-N bond [5].

Calculations at the B3LYP/6-31G(d) level of theory gave transition states for all three nitramines, for which the geometries are given in Figure 4.

The activation energy for HMX is $203.53 \text{ kJ mol}^{-1}$ ($192.54 \text{ kJ mol}^{-1}$ with *zpe*), for CL20 $276.63 \text{ kJ mol}^{-1}$ ($267.91 \text{ kJ mol}^{-1}$ with *zpe*) and for RDX $230.57 \text{ kJ mol}^{-1}$ ($219.90 \text{ kJ mol}^{-1}$ with *zpe*), which compares well with the literature value for RDX [5]. For HMX, the activation energy for the oxygen transfer reaction is in the same range as the elimination of HONO. The transition states of the mixtures of the nitramines with GAP-diol were calculated at the B3LYP/3-21G level. The geometries are given in Figure 4. Here, the interaction with GAP-diol has different outcomes on the decomposition of the different nitramines. An increase of $23.15 \text{ kJ mol}^{-1}$ ($22.89 \text{ kJ mol}^{-1}$ with *zpe*) in the activation energy was found for HMX, but the activation energy was lowered by almost the same amount for RDX ($12.86 \text{ kJ mol}^{-1}$, $17.50 \text{ kJ mol}^{-1}$ with *zpe*). The addition of GAP-diol to CL20 leads to only a small decrease of 4.55 kJ mol^{-1} (2.68 kJ mol^{-1} with *zpe*) in the activation energy. As there was a large distance between the oxygen transfer site and GAP-diol we repeated the calculation of the oxygen transfer reaction with a second alignment of the mixture, where GAP-diol and the oxygen transfer site were closer together. Here the activation energy was lowered by $19.32 \text{ kJ mol}^{-1}$ ($19.10 \text{ kJ mol}^{-1}$ with *zpe*), highlighting the influence of the alignment of the molecules on the activation energy.

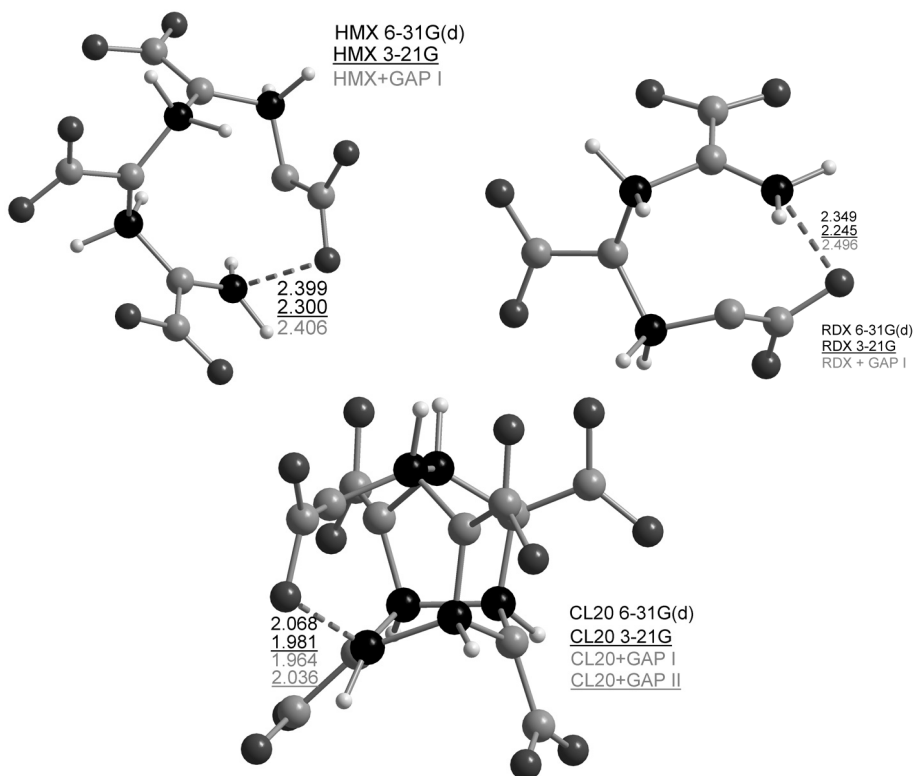


Figure 4. Transition states for the transfer of an oxygen atom from the NO₂ group of HMX, RDX and CL20 to an adjacent CH₂ group. The bond distances of the transition states of the nitramines at the B3LYP/3-21G and B3LYP/6-31G(d) level of theory and the bond distances of the transition states of the mixtures of the nitramines with GAP-diol at the B3LYP/3-21G level of theory are given in Å.

Other Transition States

All other transition states given in Scheme 1 require higher activation energies, which makes them more unlikely candidates for the initial step in the decomposition of the nitramines or their mixtures with GAP. Some transition states for the decomposition pathways given in Scheme 1 could not be located for all nitramines.

The transition states for the heterolytic fission of a C-N bond were found for HMX and RDX at the B3LYP/6-31G(d) level of theory and are shown in Figure 5. The activation energies are, at 236.54 kJ mol⁻¹ (229.04 kJ mol⁻¹ with

zpe) for HMX and $272.13 \text{ kJ mol}^{-1}$ ($262.40 \text{ kJ mol}^{-1}$ with *zpe*) for RDX, in agreement with previously calculated values [5, 16]. The activation energies for this decomposition pathway are about 30 kJ mol^{-1} higher than the activation energies for the elimination of HONO or the oxygen transfer reaction.

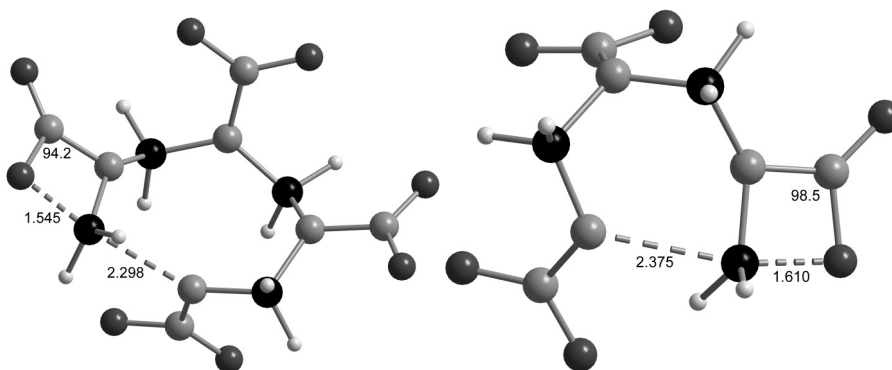


Figure 5. Transition states for the heterolytic fission of a C-N bond of HMX and RDX. The bond distances of the transition states of the nitramines at the B3LYP/6-31G(d) level of theory are given in Å.

A concerted depolymerization reaction to methylene nitramine molecules has only been detected experimentally for RDX [19]. Theoretical investigation of the concerted depolymerization of HMX reported a very high activation energy [16]. We only found a transition state for the concerted depolymerization of RDX at the B3LYP/6-31G(d) level of theory with an activation energy of $270.53 \text{ kJ mol}^{-1}$ ($248.55 \text{ kJ mol}^{-1}$ with *zpe*) which agrees with previous results [13].

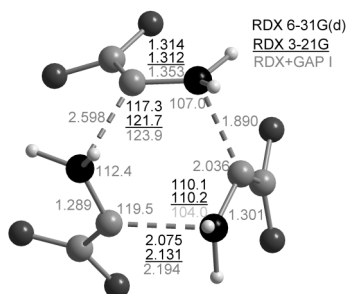


Figure 6. Transition state for concerted depolymerization of RDX. The bond distances of the transition states of RDX are given in Å.

The calculation of the transition state for the concerted depolymerization of RDX and its mixture with GAP-diol was repeated at the B3LYP/3-21G level of theory (Figure 6). The activation energy of the RDX / GAP-diol mixture is $19.60 \text{ kJ mol}^{-1}$ ($17.17 \text{ kJ mol}^{-1}$ with *zpe*) higher than for isolated RDX.

For a homolytic C-N bond fission reaction we only found a transition state for the decomposition of HMX (Figure 7) at the B3LYP/6-31G(d) level of theory. The activation energy is, at $317.69 \text{ kJ mol}^{-1}$ ($292.80 \text{ kJ mol}^{-1}$ with *zpe*), higher than all other calculated decomposition pathways. Thus we refrained from carrying out further calculations on the nitramine / GAP-diol mixtures.

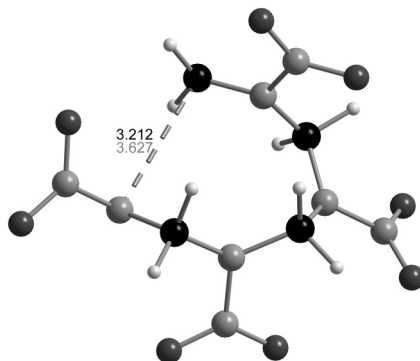


Figure 7. Transition state for the homolytic C-N bond fission of HMX. The bond distances at the B3LYP/6-31G(d) (upper value) and B3LYP/3-21G level of theory (lower value) are given in Å.

A transition state leading to the elimination of methylene nitramine was not found for any of the nitramines which were investigated.

Decomposition of GAP-diol

The elimination of N_2 through fission of the weak N-N₂ bond is the most favorable initial step in the decomposition of GAP [6-11], as for all azides [20]. After the elimination of N_2 a nitrene intermediate is formed either in the singlet or triplet state. The transition states for the decomposition of GAP-diol leading to singlet and triplet nitrenes were calculated at the B3LYP/6-31G(d) level of theory. The optimization of the geometry of the singlet nitrene always gave an imine product following a 1,2-hydrogen shift. The activation energies were calculated to be $204.82 \text{ kJ mol}^{-1}$ ($190.72 \text{ kJ mol}^{-1}$ with *zpe*) for the singlet nitrene and $188.66 \text{ kJ mol}^{-1}$ ($173.88 \text{ kJ mol}^{-1}$ with *zpe*) for the triplet nitrene. The transition states are shown in Figure 8.

The thermolysis of azides should give singlet nitrenes due to spin conservation; the excitation of a singlet nitrene to a triplet nitrene would require 590 kJ mol^{-1} [21]. Therefore further calculations were performed using only the singlet nitrene. The transition states for GAP-diol and mixtures of GAP-diol with RDX and HMX are given in Figure 8. We could not find a transition state for the mixture of CL20 with GAP-diol. The activation energy for the elimination of N_2 from isolated GAP-diol is $204.82 \text{ kJ mol}^{-1}$ ($190.72 \text{ kJ mol}^{-1}$ with *zpe*). In the presence of the nitramines the activation energy for the elimination of N_2 increases by $38.28 \text{ kJ mol}^{-1}$ ($41.16 \text{ kJ mol}^{-1}$ with *zpe*) for the second alignment of the HMX / GAP-diol mixture and by $17.69 \text{ kJ mol}^{-1}$ ($16.09 \text{ kJ mol}^{-1}$ with *zpe*) for a RDX / GAP-diol mixture.

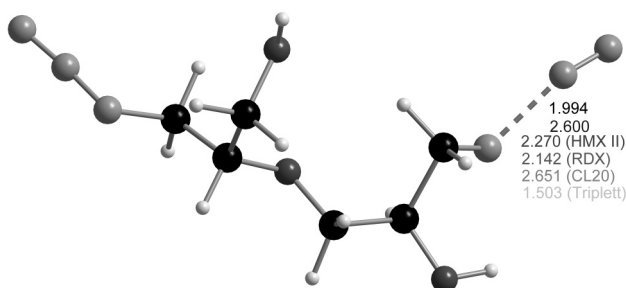


Figure 8. Transition states for the elimination of N_2 from GAP-diol and mixtures of GAP-diol with HMX, RDX and CL20. The N- N_2 bond distances are given in Å, the first value representing isolated GAP-diol at the 6-31G(d) level of theory, the second at the 3-21G level of theory.

We also calculated the elimination of N_3 from GAP-diol at the B3LYP/6-31G(d) level of theory. The transition state is shown in Figure 9. The activation energy for this decomposition is $351.16 \text{ kJ mol}^{-1}$ ($329.79 \text{ kJ mol}^{-1}$ with *zpe*), which is much higher than the activation energy for the elimination of N_2 . Hence, we did not perform calculations for the GAP-diol / nitramine mixtures for this decomposition step. We did not find minima for the other decomposition pathways mentioned in Scheme 2.

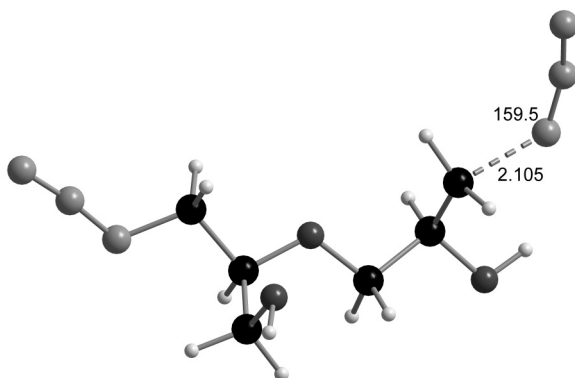


Figure 9. Transition state for the elimination of N_3 from GAP-diol. The C- N_3 bond distance at the 6-31G(d) level of theory is given in Å and the CNN bonding angle in $^\circ$.

Conclusions

Several reaction profiles of the decomposition of mixtures of the nitramines HMX, RDX and CL20 with the energetic binder GAP(glycidyl azide polymer)-diol, were investigated at the B3LYP/3-21G(d) level of theory and compared with the reaction profiles of the decomposition of the isolated nitramines and GAP-diol, which were calculated at the B3LYP level with 6-31G(d) and 3-21G basis sets. While homolytic N- NO_2 bond fission is energetically the most favored initial decomposition path, the energetics of the following reactions might still favor another initial decomposition path. Here, the elimination of nitrous acid, HONO, is more favorable for the cyclic nitramines as a bridgehead double bond would be formed during the elimination of HONO from CL20. The activation energies for the transfer of an oxygen atom of an NO_2 group to an adjacent CH_2 group are in the same range as the activation energies for the elimination of HONO. The transition states for the decomposition pathways initiated by a homolytic or a heterolytic C-N bond fission and the concerted depolymerization of the nitramines were not found for all nitramines. The concerted depolymerization is only viable for RDX.

The decomposition pathway with the lowest activation energy for GAP-diol is the elimination of N_2 . Due to spin conservation the resulting nitrene must be a singlet nitrene, as is found for the thermal decomposition of all azides, although a triplet nitrene has a lower energy.

For all mixtures we used two different conformations, the minimum energy conformation and a conformation that was believed to be particularly favorable for the decomposition of the nitramines. We found the activation energies for the two conformations to be quite different and either conformation can favor or disfavor a particular decomposition pathway. Due to the great conformational flexibility of the system, the values given for the increases or decreases in energy over the isolated compounds for a given reaction pathway are only estimates for the upper limit of the activation energy. Energy differences of up to 25 kJ mol^{-1} were found between different alignments of the same nitramine / GAP-diol mixtures. The actual activation energies might be lower for an alignment of the nitramines with GAP-diol that was not investigated here.

The addition of GAP to HMX did not favor any of the discussed decomposition pathways. For a RDX / GAP-diol mixture the elimination of HONO is favored by $18.80 \text{ kJ mol}^{-1}$ ($17.90 \text{ kJ mol}^{-1}$ with *zpe*) and the $\text{NO}_2\text{-CH}_2$ oxygen transfer is favored by $12.86 \text{ kJ mol}^{-1}$ ($17.50 \text{ kJ mol}^{-1}$ with *zpe*). For a CL20/GAP-diol mixture the N- NO_2 bond fission is favored by 8.01 kJ mol^{-1} (7.67 kJ mol^{-1} with *zpe*) and the $\text{NO}_2\text{-CH}_2$ oxygen transfer is favored by $19.32 \text{ kJ mol}^{-1}$ ($19.10 \text{ kJ mol}^{-1}$ with *zpe*). The decomposition of GAP-diol is inhibited by the addition of the nitramines.

In summary we conclude that the addition of GAP-diol to the nitramines HMX, RDX and CL20 alters the weight of the possible decomposition pathways by facilitating some pathways and impeding others. This agrees with the experimental observation of lower decomposition temperatures and different decomposition products found for the mixtures of the nitramines with GAP and suggests that the differences observed for the decomposition of the mixtures are due to an easier decomposition of the nitramines and a inhibited decomposition of GAP.

Computational Methods

All calculations were performed with the Gaussian 03 program at the B3LYP level using a 6-31G(d) and 3-21G basis sets [22]. The structures were minimized within the symmetry constraints stated above. All minima were confirmed by frequency analyses. The located transition states are of first order with Cartesian displacement coordinates of the imaginary frequency mode corresponding to a reaction of the starting materials to give the products.

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