Novel 1,3-Dipolar Cycloadditions of Dinitraminic Acid: Implications for the Chemical Stability of Ammonium Dinitramide

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Density functional theory at the B3LYP/6-31+G(d,p) level and ab initio calculations at the CBS-QB3 level have been used to analyze 1,3 dipolar cycloaddition reactions of dinitraminic acid (HDN) and its proton transfer isomer ($HO(O)NNNO_2$). It is shown that the nitro group of HDN and the −N−N=O functionality of the isomer react readily with carbon−carbon double bonds. Cycloadditions of HDN are compared with the corresponding reactions with azides and nitrile oxides as 1,3 dipoles. It is shown that the reactivities of HDN and its proton transfer isomer decrease with increasing electron withdrawing power of the substituents adjacent to the carbon−carbon double bond. In contrast, for azides and nitrile oxides, the highest reactivity is obtained with dipolarophiles with strongly electron withdrawing substituents. The observed reactivity trends allow for the design of unsaturated compounds that are highly reactive toward azides and chemically inert toward dinitramides. This may be of relevance for the development of binder materials for ammonium dinitramide based propellants.

1. Introduction

Ammonium dinitramide (ADN) $[NH_4N(NO_2)_2]$,[1−4] is considered to be a promising candidate as a new oxidizer in future solid rocket propellants. Today's dominant oxidizer ammonium perchlorate (AP) $[NH_4ClO_4]$, has one important downside. It is unfriendly to the environment. Tremendous amounts of chlorinated side products are produced during combustion.

In one of the earliest published works on the subject, Pak discussed how various types of nitrile oxides might be used as curing agents in an ADN-based propellant.[5] Belousov et al.[6] and Okhotnikov et al.[7] have both reported the use of different nitrile oxides as curing agents together with unsaturated polyester urethanes. Furthermore, it has been suggested by Manzara et al.[8] that multifunctional acrylates might function as curing agents together with the energetic polymer poly(glycidyl azide), GAP. The above-mentioned polymer systems are all cured via the 1,3-dipolar cycloaddition mechanism (see Figures 1 and 2). Unfortunately, preliminary studies suggests that unsaturated functionalities inherent in alkenes, acrylates and ethers are chemically unstable together with the ADN salt.[9] This is cause for concern, and it is imperative to find an explanation for the incompatibility.

It is clear that to design a binder matrix that is suitable for usage with ADN, one needs to understand the different pathways of decomposition. It has been suggested that decomposition of pure ADN mainly occurs via dinitraminic acid (HDN).[10,11] HDN, which is a very strong inorganic acid, can be formed from solid ADN after a proton transfer to a dinitramide anion. Aside from reacting with other species HDN is know to be prone to self-decomposition. The activation energy for ADN's (HDN's) self-decomposition has been investigated both experimentally and theoretically by several researchers and is reported to be in the vicinity of 35−40 kcal/mol.[11−15] HDN can react with surrounding polymers at the ADN−polymer interface. It is also possible that individual HDN molecules become "solvated" by the surrounding environment, which can facilitate decomposition.

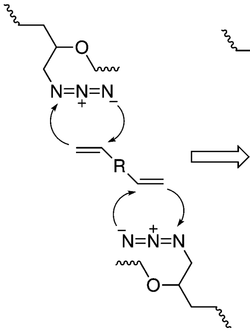

Figure 1. 1,3-Dipolar cycloaddition reaction between an azide group present in the GAP polymer and an arbitrary end-unsaturated linker molecule.

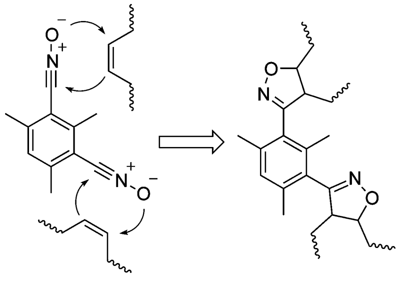

Figure 2. 1,3-Dipolar cycloaddition between a difunctional nitrile oxide (2,4,6-trimethylisophthalonitrile *N,N*′-dioxide) and *cis*-1,4-polybutadiene forming a isoxazoline cross-link.

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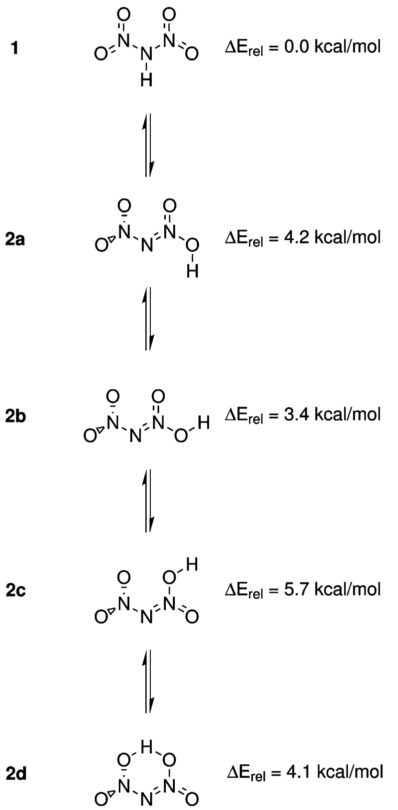

Figure 3. Zero-point corrected energies of the different conformers of **2** relative **1**. Energies are obtained at the CBS-QB3 level.

The HDN isomer **2** is formed as a result of intra or intermolecular proton transfers.[15] The proton transfer isomer exists in four different conformers, which are labeled **2a**, **2b**, **2c**, and **2d** (Figure 3). In the gas phase the conformers are all slightly higher in energy compared to the original HDN molecule. However, the relative energies may shift significantly depending on the local environment. Due to the repositioning of the proton from the center nitrogen to one of the oxygen, these species will react differently.

In this computational study it was discovered that **1** as well as its proton transfer isomer **2** can react with carbon−carbon double bonds via the 1,3-dipolar cycloaddition reaction. The question was raised how the kinetics of these reactions vary with different substitution on the double bond, and also how the rates of reaction compare to some experimentally known cycloadditions. As a ground for comparison, all calculated reactions with **1** and **2d** have also been performed with azide and nitrile oxide.

Shown in Figures 1 and 2 are the two curing reactions that have been modeled. The functionality of the GAP polymer lies with its azide group $-N{=}N^{+}{=}N^{-}$. This group has been simulated using a $C_2H_5{-}N_3$ unit. The nitrile oxide group was represented by a $H_3C{-}C{\equiv}N^{+}{-}O^{-}$ unit. These units were modeled together with methyl vinyl ether and methyl acrylate to simulate the reactivity toward ethers and acrylates, and with different alkenes such as ethene, 1-butene and *trans*-2-butene to simulate the reactivity toward olefins. 2-Propenal, dimethyl fumarate and methyl 2-cyanoacrylate were also used to investigate the effect of strong electron acceptors substituted on the carbon−carbon double bond. The corresponding 1,3-dipolar cycloadditions have been calculated. The barriers have been compared to possible side reactions between the same unsaturated molecules and **1** and **2**, thus determining if the functionalities are HDN/ADN compatible in this respect.

2. 1,3-Dipolar Cycloaddition

This type of reaction is in many aspects similar to the well-known Diels−Alder reaction. The reaction enables the union of a 1,3-dipole with a dipolarophile. A 1,3-dipole is heterogeneous compound (or group) that is described by at least one zwitterionic resonance structure and reacts 1,3 in cycloadditions. A dipolarophile is usually an unsaturated hydrocarbon or a similar heteroatomic molecule.

Experimental studies have shown that the reaction results in retention of stereochemistry on the double bond and that the rate is relatively insensitive to solvent polarity.[16] This is accord with a concerted pericyclic reaction. The issue of whether the reaction is concerted or proceeds via a stepwise diradical transition has been thoroughly debated in the 1960s.[17,18] The possible diradical nature of 1,3-dipoles does not exclude a concerted mechanism, and this have also been the subject of some discussions.[19,20] In early computational work on the subject ab initio methods showed a preference for a concerted synchronous mechanism, and semiempirical methods provided more asynchronous transition state structures.[21] Today's modern methods include electron correlation to a larger degree and most such methods confirm the preference for a concerted synchronous mechanism.[22] The reaction exhibits second-order kinetics.

Concerted cycloaddition is possible when two π-systems interact. Two π-bonds are broken and two new σ-bonds are subsequently formed. The rate of reaction is known to be highly dependent on steric and electronic influences from neighboring groups. The dominating bonding interaction is usually of either **a** or **b** type.

a: HOMO(1,3-dipole)−LUMO(dipolarophile)

b: LUMO(1,3-dipole)−HOMO(dipolarophile)

The HOMO−LUMO energy gap for the corresponding cases generally determines which interaction is the most important. The lower the energy difference the greater is the orbital interaction. In most cases **a** is dominating. However, this changes as the electron donating ability of the 1,3-dipole decreases or the donating ability of the dipolarophile increases. The total orbital interaction is a summation over the overlaps between many orbitals. However, the HOMO and LUMO orbitals are usually the most important.

This approximative method to analyze reactions is referred to as the Frontier molecular orbital theory and was mainly developed by Fukui.[23] It was first applied to 1,3-dipoles by Sustmann.[24] Houk has also performed extensive work on the subject.[25,26] The Frontier molecular orbital theory has been used successfully in explaining the reactivities of many cycloaddition reactions. However, the theory is a simplification and there are cases were it fails.[27]

3. Theoretical Methods

All calculations were performed using Gaussian 03, revision C.02.[28] The default method has been density functional theory with Becke's[29] non local B3LYP hybrid Hartree−Fock approach, using a 6-31+G(d,p) basis set. No symmetry restrictions were applied during geometry optimizations. Harmonic frequencies, zero-point energies and thermodynamic corrections were obtained using analytical force constants.

Previous work on ADN and ammonium nitrate (AN) by Thompson et al. has shown that the B3LYP functional produces geometries of high quality when used together with sufficiently large basis sets, such as 6-311G(d,p).[30,31]

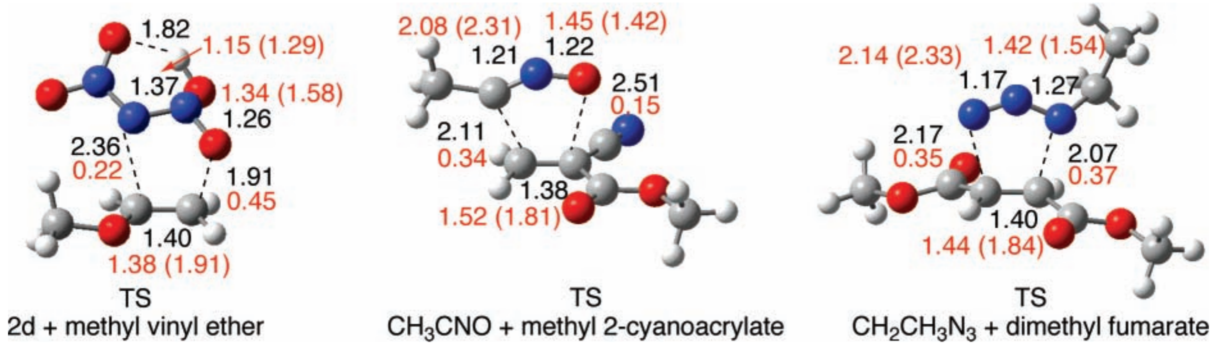

Figure 4. B3LYP/6-31+G(d,p) optimized transition state geometries of three relevant 1,3-dipolar cycloadditions. Bond lengths are given in Ångström (Å). Wiberg bond indices calculated from natural atomic orbitals (NAO) are shown in red. Values for reactants are in parentheses.

Ess and Houk has presented a thorough benchmark of the B3LYP-DFT method applied to 1,3-dipolar cycloadditions.[22] B3LYP/6-31G* was compared with two experimental activation energies. In both cases it provided an overestimation of the barriers by approximately 2 kcal/mol.

When the B3LYP/6-31+G(d,p) method was applied to the reaction barriers of eighteen different 1,3-dipolar cycloaddition reactions and compared to the high level CBS-QB3 method, it was reported to have a mean deviation (MD) of 2.7 kcal/mol and a mean absolute deviation (MAD) of 2.6 kcal/mol. The corresponding values for reaction enthalpies were reported to be 3.0 and 3.6 kcal/mol.

The benchmark study found that the accuracy of B3LYP was seen to decreases with an increased size of the basis set. When the 6-311+G(2d,p) basis was applied on activation energies and reaction enthalpies the MAD values were increased to 3.9 and 6.3 kcal/mol, respectively. When B3LYP was used on the HDN reactions, single point calculations at the DFT-B3LYP/6-311+G(3df,2p) level generally provided barriers 3−5 kcal/mol higher than the 6-31+G(d,p) basis.

In the same paper, Ess and Houk found that the modified Perdew−Wang one-parameter model for kinetics (MPW1K)[32] is better suited than B3LYP for acquiring reaction barriers of 1,3-dipolar cycloaddition reactions. The MPW1K energies was reported to correlate more correctly with barriers obtained with the CBS-QB3 method. At the level of MPW1K/6-31+G(d,p), it was found to have a MD and a MAD value both of 1.7 kcal/mol.

However, in this work a different behavior for the reactions involving HDN and its isomers was observed. The reaction barriers calculated with MPW1K differed very little when compared to B3LYP calculations using the same basis set and provided no improvement when compared to the CBS-QB3 results. The MPW1K method is optimized for barrier heights but is also as a consequence particularly bad at reproducing reaction enthalpies. At the 6-31+G(d,p) basis the benchmark provided MD and MAD values of −14.4 and +14.4 kcal/mol, respectively.

To obtain very accurate decomposition kinetics, the high level complete basis set (CBS-QB3) method of Montgomery, Ochterski and Peterson was implemented.[33,34] CBS-QB3 applies B3LYP/6-311G(d,p) optimized geometries and frequencies to calculate zero-point vibrations and thermodynamic corrections. Coupled cluster (CCSD(T)) calculations are combined with basis set extrapolation using Møller−Plesset perturbation theory (MP2 and MP4) and empirical corrections to obtain reliable energies. The CBS-QB3 method was used as the reference method by Ess and Houk in the above-mentioned benchmark.[22] When compared to experimental energies of activation for hydrocarbon pericyclic reactions, it was found to have a MD value of −1.8 kcal/mol and a MAD value of 2.3 kcal/mol. CBS-QB3 has also been used by Guner et al. on the same type of reactions.[35,36] When compared to experimental reaction enthalpies, it was found to have MD value of −1.4 kcal/mol and a MAD value of 1.9 kcal/mol.

4. Results

As mentioned in the introductory section, much effort has been put into understanding the self-decomposition of the ADN salt. Previous experimental and theoretical research points to a decomposition barrier of approximately 35 kcal/mol.[10−15] It should be noted that the barrier height of 35 kcal/mol exceeds most of the barriers observed in this study (20−35 kcal/mol). Thus, intramolecular self-decomposition of HDN is less likely to occur than the reactions that have been investigated here.

All investigated reactions have been shown to proceed via the same type of pathway, the 1,3-dipolar cycloaddition mechanism. Frequency analysis on identified transition states confirms that all reactions are concerted, in full agreement with modern computational studies.[22] The extent of synchronicity was analyzed from the transition state bond lengths and Wiberg bond indices[37] calculated from natural atomic orbitals (NAOs).[38] It was found to be highly dependent on the level of symmetry of the corresponding dipolarophile. When the 1,3-dipoles are made to react with dipolarophiles such as ethene or *trans*-2-butene, the transition states are highly synchronous with a difference in bond length of 0.01−0.2 Å. However, when less symmetric species such as methyl vinyl ether or 1-butene are used, the transition state structures become more asynchronous. One of the least synchronous structures is the one between **2d** and methyl vinyl ether. This structure is depicted in Figure 4, together with two other relevant transition state structures. The bond lengths and bond indices are in all cases indicative of an early transition state. This is in agreement with exothermic nature of the reactions. It should be noted that the type of 1,3-dipole found in **2d** has never been previously investigated, contrasting the well-known reactions of 1,3-dipoles such as the nitro, nitrile oxide and azide groups. The synchronous-like nature of most transition states is in agreement with the recent quantum chemical studies by Ess and Houk.[22]

4.1. Reactions with Dinitraminic Acid (1 and 2d). Depicted in Figure 5 are the frontier orbitals of a typical reaction between **1** and an olefin chain, here modeled as *trans*-2-butene. The orbital energies are shown in Figure 6. It is clear that the difference in energy between **1**’s LUMO and *trans*-2-butene’s HOMO is by far smaller than that of the opposite HOMO−LUMO combination. The energy differences calculated from B3LYP orbital energies are 0.113 and 0.367 hartree, respectively. The dominating orbital interaction is hence that of the

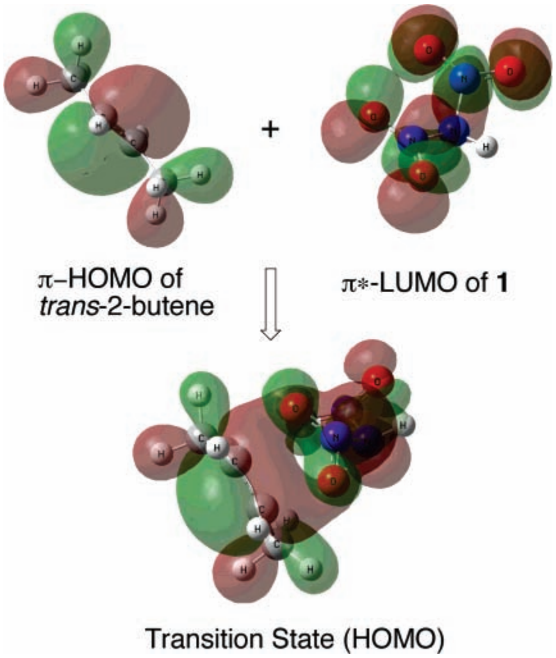

Figure 5. HOMO orbital of *trans*-2-butene interacting with the LUMO orbital of **1** in a 1,3-dipolar cycloaddition.

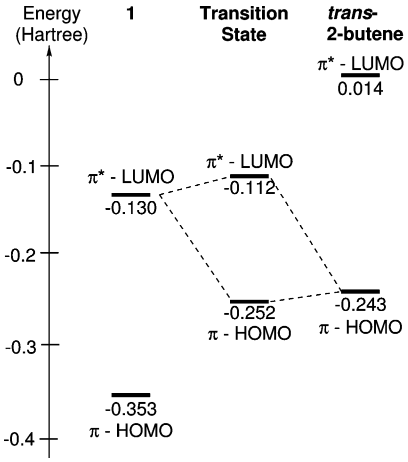

Figure 6. Energies of the frontier orbitals of **1**, *trans*-2-butene, and the corresponding transition state obtained at the B3LYP/6-31+(d,p) level.

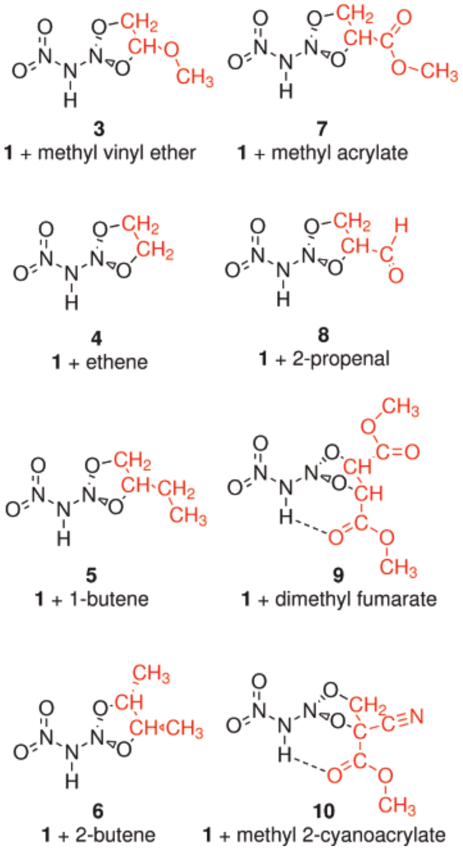

Figure 7. Kinetically most favored products for 1,3-dipolar cycloaddition reactions between **1** and unsaturated model compounds.

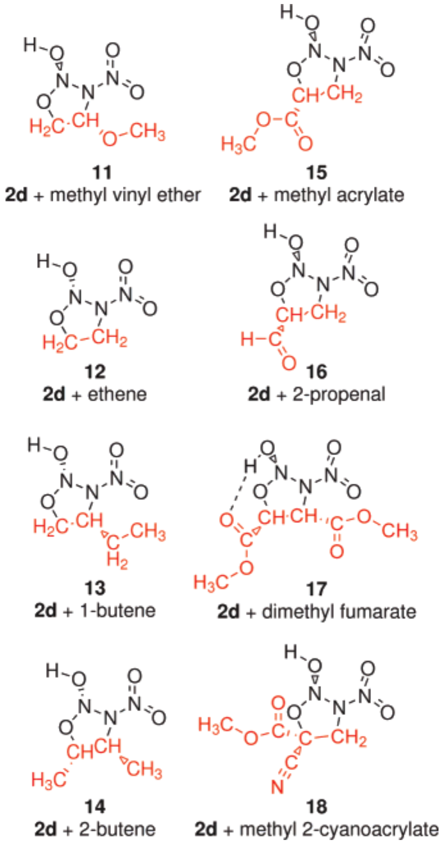

Figure 8. Kinetically most favored products for 1,3-dipolar cycloaddition reactions between **2d** and unsaturated model compounds.

HOMO orbital of the carbon π-system with the LUMO of **1**. This corresponds to interaction **b** described in the previous section on 1,3-dipolar cycloaddition.

The only possible way for **1** to react directly with a double bond is at its NO_2 group. The most reactive of HDN's proton transfer isomers was found to be **2d**. The reaction pathways via the **2d** conformer were often found to have the lowest barriers also after correcting for the higher ground state energy relative **1**. In **2d** the proton is positioned on an oxygen, forming an hydroxy group. The hydroxy group is turned in such a way that a hydrogen bond to the adjacent NO_2 group helps to stabilize the structure. This leaves the center nitrogen bonded only to its two neighboring nitrogens. The nitrogen−nitrogen bonds are stabilized by resonance. There are two possible reaction sites at **2d**, either on the NO_2 group or at the $^{-}O{-}N^{+}{=}N{-}$ position. The latter being the most favorable one. Out of the four conformers of **2** only **2c** and **2d** can react over the $^{-}O{-}N^{+}{=}N{-}$ position. **2c** was found to consequently result in higher reaction barriers than **2d** or to transform into **2d** during optimization of the transition state. The energy gap between **2d**'s LUMO orbital and *trans*-2-butene's HOMO orbital is 0.084 hartree. This is a considerably smaller gap than the 0.352 hartree

TABLE 1: Relative Energies of Reaction Together with the Corresponding Transition State Barriers for the Reactions Shown in Figures 7 and 8. All Energies are in kcal/mol.

	B3LYP-DFT/6-31+G(d,p)				CBS-QB3			
reaction	$\Delta E^{TS\ a}$	$\Delta E_{reac}{}^{a}$	$\Delta G^{TS\ b}$	$\Delta G_{reac}{}^{b}$	$\Delta E^{TS\ a}$	$\Delta G^{TS\ b}$	reaction	$\Delta E^{TS\ a}$
Modeled Reactions with **1**								
1 + methyl vinyl ether → **3**	20.4	−11.6	33.8	2.7	16.9	−20.9	29.6	−7.7
1 + ethene → **4**	25.5	−8.4	38.0	4.0	21.8	−14.4	34.1	−2.3
1 + 1-butene → **5**	24.6	−10.0	37.9	3.4	21.6	−18.1	34.6	−5.0
1 + *trans*-2-butene → **6**	24.6	−10.8	37.7	2.6	18.8	−20.3	32.0	−7.3
1 + methyl acrylate → **7**	23.1	−5.3	36.4	8.4				
1 + 2-propenal → **8**	25.1	−0.9	38.0	12.0	19.5	−10.8	32.3	2.1
1 + dimethyl fumarate → **9**	25.6	0.2	39.4	13.9				
1 + methyl 2-cyanoacrylate → **10**	25.8	3.3	39.2	17.3				
Modeled Reactions with **2d**								
2d + methyl vinyl ether → **11**	16.1	−14.2	29.6	−0.2	11.9	−27.0	24.3	−14.1
2d + ethene → **12**	20.5	−17.6	32.6	−5.4	14.6	−26.3	26.7	−14.3
2d + 1-butene → **13**	21.5	−14.0	34.1	−0.7	13.8	−26.0	26.6	−12.7
2d + *trans*-2-butene → **14**	20.9	−14.3	33.8	−0.7	12.2	−27.5	25.2	−14.0
2d + methyl acrylate → **15**	21.9	−10.0	34.7	2.5				
2d + 2-propenal → **16**	22.9	−9.0	35.6	3.3	14.4	−21.3	27.0	−8.9
2d + dimethyl fumarate → **17**	26.1	0.2	39.6	13.9				
2d + methyl 2-cyanoacrylate → **18**	24.3	−1.9	37.5	11.4				

[a] Relative energy corrected for zero point vibrations. [b] Relative gas-phase free energy.

of the opposite HOMO−LUMO combination. Hence, the reaction is also in this case dominated by interaction **b**.

Some of the more important reactions that were modeled between **1** and unsaturated molecules are depicted in Figure 7. Zero point corrected energies of reaction and activation and corresponding free energies are presented in Table 1. Structures **3**−**10** are the resulting products of **1** reacting with methyl vinyl ether, ethene, 1-butene, *trans*-2-butene, methyl acrylate, 2-propenal, dimethylfumarate and methyl 2-cyanoacrylate, respectively. The corresponding products of **2d** are shown in Figure 8, which are labeled **11**−**18**. For clarity only the fastest *cis*/*trans*-isomer reactions are presented.

When one considers the enthaplic and entropic contributions to the free energies of activation and reaction for **1** and **2d** (as well as for azide and nitrile oxide), the entropy contributions are in all cases dominating over enthalpy. This is expected for bimolecular reactions, where the translational entropy loss due to fusion of two molecular entities into one leads to a large increase in free energy. ΔG values of activation are typically 12−13 kcal/mol higher than the relative SCF energies. The corresponding ΔH values are no more than 1.5 kcal/mol higher. This behavior is consistent for all investigated reactions, and does not appear to be influenced by the bulkiness of the dipolarophile. However, the enthalpy correction is somewhat reduced for the smaller dipoles, azide and nitrile oxide (<0.7 kcal/mol).

In initial calculations the larger ethyl vinyl ether was used to model an ether containing molecule. This molecule was later changed to the smaller methyl vinyl ether due to computational limitations when applying the expensive CBS-QB3 method. The removal of the CH_2 group resulted in only minor changes in the barrier heights (0.05−0.4 kcal/mol). Calculations on methyl acrylate, dimethyl fumarate and methyl 2-cyanoacrylate reactions are too expensive with the CBS-QB3 method and were hence not attempted at that level.

It is indicated from the calculations that the reactivity of the carbon−carbon double bond increases with the electron donating abilities of its neighboring group, ether > alkane > ester > aldehyde. As can be seen in Table 1, the free energy of activation, ΔG^{TS}, for reactions with **2d** is generally decreasing when going from more electron poor double bonds to more electron rich ones. At the highest level of calculation, CBS-QB3, the free energy of activation decreases from 27.0 to 26.7 to 26.6 and finally 24.3 kcal/mol in going from **2d**−2-propenal to **2d**−ethene via **2d**−1-butene and **2d**−methyl vinyl ether. The *trans*-2-butene is slightly faster than the 1-butene in all observed cases. This is most likely due to inductive electron donation from the extra methyl group. The acrylate group behaves as expected and gives high reaction barriers. The exception is in the case of reaction with **1**, where a H-bond between the hydrogen of **1** and the carbonyl group of the acrylate acts to stabilize the transition state and lowers the reaction barrier.

In an attempt to see if the trend of decreased reactivity with decreased electron density continues, the more heavily substituted dimethyl fumarate and methyl 2-cyanoacrylate were also studied. These two species proved more reactive toward the NO_2 group in **1** than the −N−N═O position of **2d**, when one considers the lower ground state energy of **1**. Compared to the other less electron-deficient double bonds, a large increase in barrier height is seen. This is clear from the transition state energies at the B3LYP level. ΔG^{TS} increases from 33.8 kcal/mol for methyl vinyl ether and **1** to 37.9 kcal/mol for **1** and 1-butene, and onward to 38.0, 39.2 and 39.4 kcal/mol for **1** with 2-propanol, methyl 2-cyanoacrylate and dimethyl fumarate, respectively. These values are all somewhat overestimated as seen when they are compared with the more accurate CBS-QB3 energies.

4.2. Reactions with Azide and Nitrile Oxide. The discussed reactions of the azide and nitrile oxide species were modeled with the same unsaturated molecules that were used together with **1** and **2d**. The most relevant of these calculations are shown in Figures 9 and 10, where the azide species are named **19**−**26**, and the nitrile oxides species **27**−**34**. The corresponding energies of reaction and activation are shown in Table 2.

It has been found that neither of the orbital interactions **a** nor **b** is in clear dominance when the nitrile oxide or the azide group reacts with ordinary olefins. The difference between the two HOMO−LUMO combinations are much smaller than for the reactions of **1** and **2d**. To clarify this, it can be mentioned that the energy gap between the nitrile oxide LUMO orbital and the HOMO orbital of *trans*-2-butene is 0.229 hartree. The opposite combination gives a gap of 0.274 hartree; i.e., the difference between the two gaps is only 0.045 hartree. The corresponding difference between the azide group and *trans*-

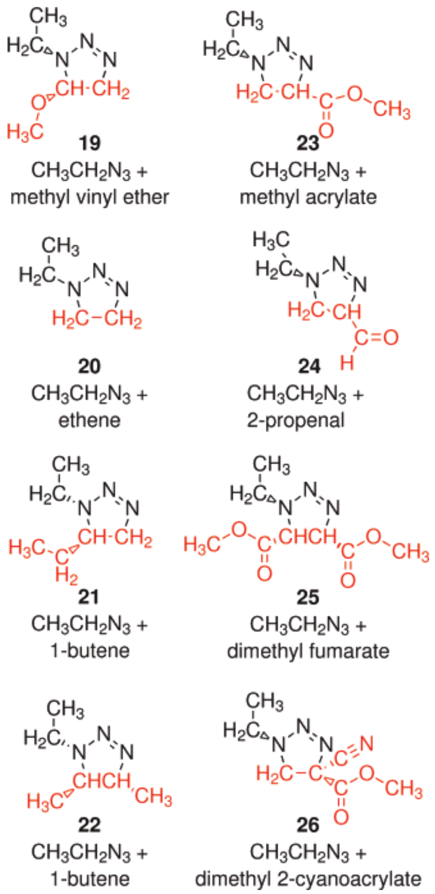

Figure 9. Kinetically most favored products for 1,3-dipolar cycloaddition reactions between the azide unit and unsaturated model compounds.

2-butene is 0.077 hartree. For comparison, **1** and **2d** each have a gap difference of 0.254 and 0.283 hartree, respectively, i.e., a much clearer dominance of **b**.

When the graphical representations of the molecular orbitals for the transition states and ground states of nitrile oxide and azide are observed, it is not obvious which type of interaction (**a** or **b**) is dominating. The reaction might be an almost equal mix of the two interaction types. Lower lying orbitals might also play a larger role, and it appears that the differences in reactivity between different dipolarophiles is difficult to explain purely based on the frontier orbital approach.

The fastest way that the GAP polymer, i.e., the azide group, can react with 1-butene is in the *cis* fashion. This reaction has a free energy barrier of 29.8 kcal/mol (CBS-QB3). The modeled nitrile oxide unit has a corresponding barrier of 23.5 kcal/mol. These values should be compared to the one were the reaction instead happens between **2d** and 1-butene, in which case it is 26.6 kcal/mol. Due to the large similarity of the barriers of **2d** and the azide unit, it can be argued that unsaturated molecules of this type might react with **2d** rather than with the desired polymer or cross-binder. It should be noted that the nitrile oxide unit consequently corresponds to the lowest energies of activation, as well as the most thermodynamically favorable reactions. Polymer curing with nitrile oxide as a constituent is known to proceed fast.[39] This in full agreement with the presented calculations. Indeed, if nitrile oxides can be used together with a carbon−carbon bond that is unreactive toward ADN a feasible system can be realized. However, this assumes that nitrile oxides are by themselves ADN compatible.

The most important realization resulting from this work can be understood when comparing the energetics of all modeled reactions of the azide unit with **1** and **2d**. A trend can be seen that is different from that observed for the reactions of **1** and **2d**. The dominating orbital overlap between the azide unit and its reacting counterpart appears to shift when varying the electron density of the carbon−carbon double bond. In the terms of frontier molecular orbital theory, from a **b**-type to a **a**-type interaction. The addition of a more electron withdrawing substituent lowers the frontier orbitals of the double bond so that the “gap difference” discussed earlier shifts in favor of **a**. This means that for an increasingly electron poor double bond the reactivity toward **1** and **2d** decreases, and the reactivity toward the azide increases.

Thus, it should be possible to optimize the reactive properties of the double bond by introducing strongly electron withdrawing substituents. This was attempted by investigating the reactions

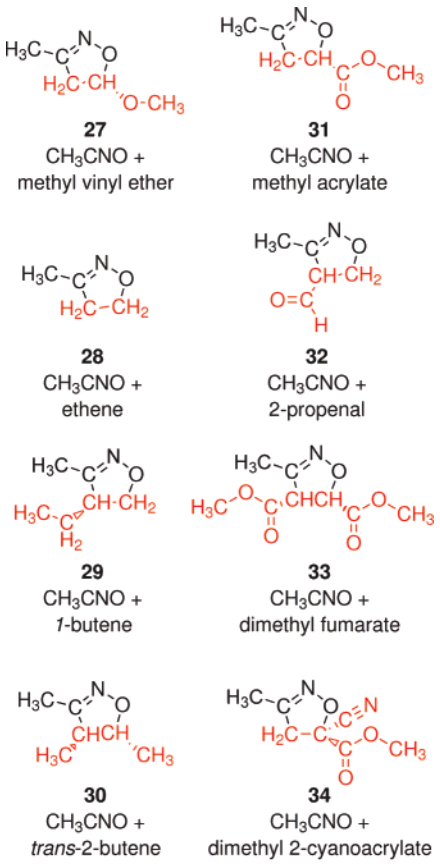

Figure 10. Kinetically most favored products for 1,3-dipolar cycloaddition reactions between the nitrile oxide unit and unsaturated model compounds.

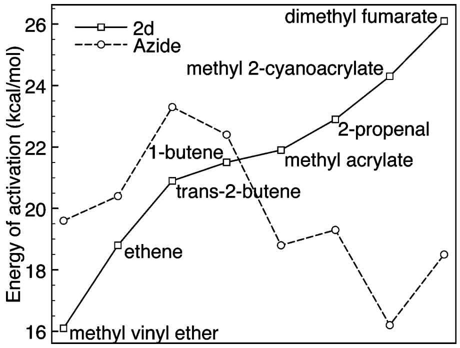

Figure 11. Zero-point corrected energies of activation for the reactions of different dipolarophiles with **2d** and with the azide unit. The observed shift in reactivity for the azide with the more electron deficient 1,3-dipolarophiles is explained by an increased **a**-type orbital interaction.

TABLE 2: Relative Energies (kcal/mol) of Reaction Together with the Corresponding Transition State Barriers for the Reactions Shown in Figures 9 and 10

reaction	B3LYP-DFT/6-31+G(d,p)			CBS-QB3		
	$\Delta E^{TS\ a}$	$\Delta E_{reac}{}^{a}$	$\Delta G^{TS\ b}$	$\Delta G_{reac}{}^{b}$	$\Delta E^{TS\ a}$	$\Delta G^{TS\ b}$
Modeled Reactions with Azide						
$CH_3CH_2N_3$ + methyl vinyl ether → **19**	19.6	−18.5	32.3	−4.4	18.2	29.9
$CH_3CH_2N_3$ + ethene → **20**	20.4	−18.7	31.9	−6.1	18.0	29.7
$CH_3CH_2N_3$ + 1-butene → **21**	22.4	−16.0	34.6	−2.7	17.5	29.8
$CH_3CH_2N_3$ + *trans*-2-butene → **22**	23.3	−17.6	35.5	−4.1	17.9	30.2
$CH_3CH_2N_3$ + methyl acrylate → **23**	18.8	−14.1	31.1	−1.1		
$CH_3CH_2N_3$ + 2-propenal → **24**	19.3	−13.7	31.5	−0.8	15.8	28.0
$CH_3CH_2N_3$ + dimethyl fumarate → **25**	18.5	−11.2	31.5	2.0		
$CH_3CH_2N_3$ + methyl 2-cyanoacrylate → **26**	16.2	−9.7	28.8	3.5		
Modeled Reactions with Nitrile Oxide						
CH_3CNO + methyl vinyl ether → **27**	12.5	−40.0	24.6	−26.4	9.9	21.1
CH_3CNO + ethene → **28**	15.4	−34.9	26.3	−22.8	12.8	23.9
CH_3CNO + 1-butene → **29**	15.8	−35.1	27.1	−22.5	11.8	23.5
CH_3CNO + *trans*-2-butene → **30**	18.7	−36.5	30.1	−23.5	13.0	24.7
CH_3CNO + methyl acrylate → **31**	13.5	−31.1	25.2	−18.8		
CH_3CNO + 2-propenal → **32**	13.3	−28.4	25.4	−16.3	8.8	21.0
CH_3CNO + dimethyl fumarate → **33**	13.9	−27.0	25.8	−14.3		
CH_3CNO + methyl 2-cyanoacrylate → **34**	12.1	−26.4	24.0	−13.6		

[a] Relative energies corrected for zero point vibrations. [b] Relative gas-phase free energy.

of dimethyl fumarate and methyl 2-cyanoacrylate. The promising results show a 7.9 kcal/mol difference in energies of activation when comparing dimethyl fumarate reacting with azide and with **1**. The corresponding difference for methyl 2-cyanoacrylate is even larger, 10.4 kcal/mol. In addition to the high activation energies between **1** and the substituted double bond ($\Delta G^{TS} >$ 39 kcal/mol), these reactions have been shown to be highly endothermic. Hence, they are neither kinetically nor thermodynamically viable. The obtained trends are clearly seen in Figure 11. The discussed shifts of frontier molecular orbital overlap (**a** vs **b**) that are believed to be the reason for the altered kinetics are shown in Figure 12. In this illustration 1-butene is compared to methyl 2-cyanoacrylate for the reactions with the two 1,3-dipoles, **2d** and azide.

The computational results correspond well with preliminary experimental data.[9] Both polyfunctional nitrile oxide cross-linkers together with different unsaturated polymers and the GAP polymer reacting together with different vinyl ethers and acrylates have been investigated. Among other things it has been observed by heat flow calorimetry that mixtures of ADN with ethers and acrylates are unstable. In particular vinyl ethers were extraordinary incompatible. At some instances the test vials were even reported to overheat and explode. Indeed the vinyl ether group is the one suggested by this work to be the most reactive of the investigated functionalities.

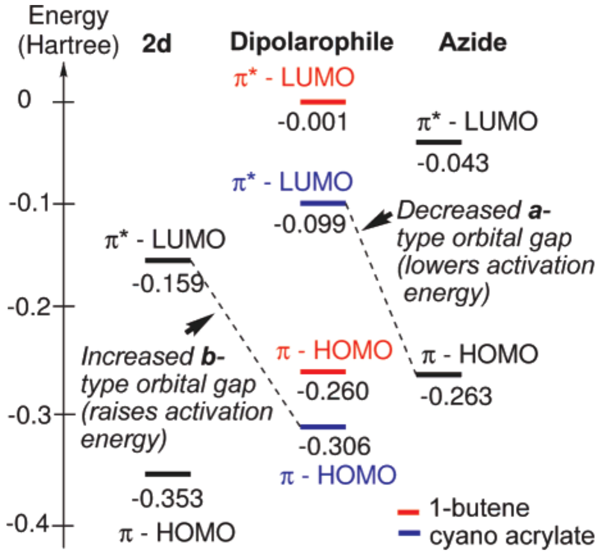

Figure 12. Energies of the frontier orbitals of **2d**, 1-butene, methyl 2-cyanoacrylate, and the azide unit obtained at the B3LYP/6-31+(d,p) level. The effects of a more electron deficient carbon−carbon double bond are shown in blue.

5. Discussion

The high reactivity of dinitraminic acid (HDN) in 1,3-dipolar cycloaddition reactions has important consequences for the design of an ADN based propellant. The apparent problems with using most carbon−carbon double bonds in such a system severely limits synthetic possibilities, and is believed to be the prime reason why no suitable system has been found thus far. Carbon−carbon double bonds present in any of the constituents of a binder formulation, such as unreacted vinyl monomers, oligomers or cross-linkers will come into contact with the ADN salt, aiding the decomposition. Vinyl monomers are frequently used in many methods such as radical or anionic polymerization. The need for carbon−carbon double bonds (or triple bonds) in the binder formulation is a necessity if the concept of cross-linking via cycloaddition is to be pursued. The reactivity of triple bonds is outside the scope of the current work. However, it is not unlikely that a similar behavior, and a subsequent need for substituent design, can be found here. After reaction with the azide or nitrile oxide, triple bonds will result in aromatic five membered rings. These reactions are very exothermic due to the lower energy of the aromatic system, and this may limit the applicability for binder formulation.

The concept of carbon−carbon double bond substituent design might prove valuable not only in the pursuit of a feasible ADN rocket propellant but also for other applications of 1,3-dipolar cycloaddition reactions. By explicitly considering the HOMO and LUMO energies, and the discussed gap difference between interacting molecular frontier orbitals ($\Delta\Delta E$), we can understand and control the behavior of similar cycloaddition systems. Not only can this be applied in manipulating the kinetics of two competing reactions (such as azide vs HDN), but it might also be used to fine-tune the thermodynamics of a system.

In returning to the issue of a feasible ADN system, experimental trials will have to determine if the suggested functionalities, methyl 2-cyanoacrylate and dimethyl fumarate, are indeed ADN compatible. In the case that either of the two is shown to aid degradation of the ADN salt, the reason is likely to be different from that of a cycloaddition reaction. Highly electron deficient double bonds like the ones suggested will be prone to react with nucleophiles, e.g., via 1,4-conjugate addition. To what extent unwanted side-reactions of this type will occur will depend on various effects, such as electronics, sterics and reaction conditions. Other types of electron withdrawing groups attached to the double bond should also be considered. Furthermore, the 1,3-dipolar cycloaddition is known to be sensitive to steric effects. This could be exploited by attaching bulky side chains near the double bond. Compared to the larger HDN molecule, the smaller azide (or nitrile oxide) groups might be less disfavored by this. The combination of sterics via the addition of aromatics or other bulky groups, and electron withdrawing effects via addition of nitro, aldehyde, ester, cyano and similar groups may enable the successful design of a ADN compatible binder formulation.

6. Summary and Conclusion

An important reason for the noncompatibility of ADN with many polymer binders is now believed to be understood. Dinitraminic acid (HDN), which can be formed from the ADN salt, has been shown to react readily with olefinic bonds via the 1,3-dipolar cycloaddition mechanism.

The activation energies of **1** and **2d** were found to increase when they react with double bonds of decreasing electron density. The rate of reaction decreases with substitution adjacent to the double bond in the order aldehyde < ester < alkene < ether. Very high activation energies were obtained with the electron deficient double bonds of methyl 2-cyanoacrylate and dimethyl fumarate. The decrease in reactivity is explained by an increased HOMO(dipolarophile)−LUMO(1,3-dipole) gap. The increase in the gap is caused by the lowering of the HOMO orbital due to the electron withdrawing effect of the substituents on the double bond.

The observed reactivity patterns for the azide and nitrile oxide reactions are different from the reactions of **1** and **2d**. The reactivity follows the behavior of **1** and **2d** for electron rich double bonds, and decreases with decreasing electron donating ability of the substituents. However, there is a shift in the reactivity trend with the introduction of electron withdrawing substituents; the reactivity starts to increase with increasing electron withdrawing power. The shift is due to a switch of the relevant orbital overlaps for the reaction, from HOMO(dipolarophile)−LUMO(1,3-dipole) to HOMO(1,3-dipole)−LUMO(dipolarophile). This discovery can enable the design of a double bond that is reactive toward azide, yet nonreactive toward ADN/HDN. Two investigated molecules with this function are methyl 2-cyanoacrylate and dimethyl fumarate, but other electron poor double bonds with preferable sterics should also be considered.

To conclude this work, it can be stated that from the viewpoint of the 1,3-dipolar cycloaddition mechanism that compounds containing the required carbon−carbon double bonds can be modified to minimize reactions with HDN. Future experimental trials will show whether the suggested design is sufficient to create an ADN compatible binder matrix, or if additional side reactions need to be considered.

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