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A Density Functional Analysis of a Decomposition of 4-Nitro-1,2,3-Triazole through the Evolution of N2

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A density functional computational study shows that 4-nitro-1,2,3-triazole, which is highly impact sensitive, can decompose through ring opening and subsequent N_2 evolution, with the net release of 12 kcal/mole. An input of 52 kcal/mole is required to initiate the process.

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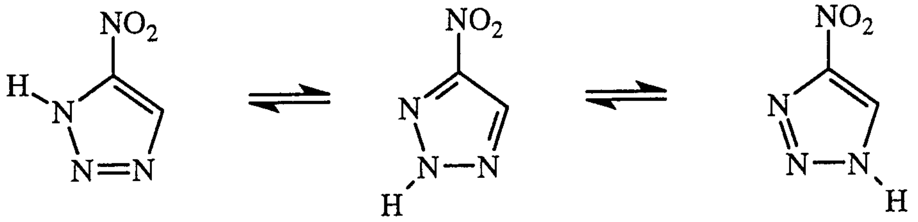
Introduction

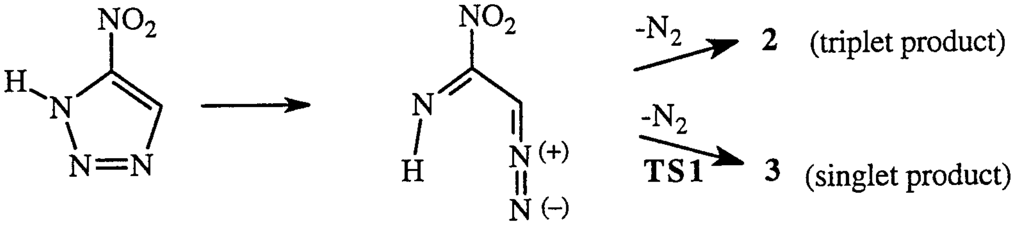
There is currently considerable interest in high-nitrogen-content molecules as energetic materials.[1-17] A matter for potential concern, however, is the instability or sensitivity toward shock and/or impact that is frequently associated with the presence of several linked nitrogens.[18] In some instances, for example certain picryl triazoles, it has been suggested that this instability is due to the availability of a relatively facile decomposition pathway involving the loss of N_2.[19]

We have accordingly investigated computationally the energetics of an N_2 evolution process in the case of the nitrotriazole **1**, which is known experimentally to be highly sensitive toward impact.[20] It has several tautomeric forms, as shown.



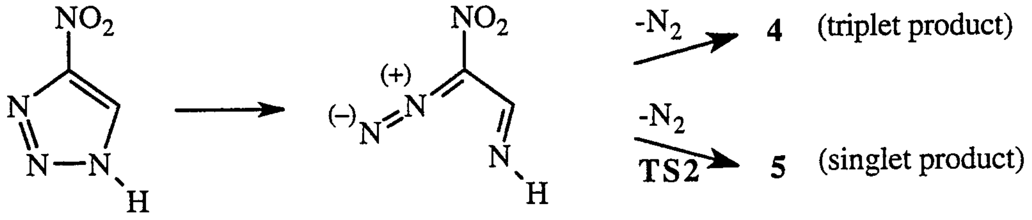
1A **1B** **1C**

For **1A** and **1C**, one can envision decomposition routes through ring opening to give the intermediates **1A*** and **1C***,[21] followed by the loss of N_2. This could leave either a singlet or a triplet product, and we have examined both possibilities in each case. The formation of the singlet products was found to involve transition states **TS1** and **TS2**.



(1)

1A **1A***



(2)

1C **1C***

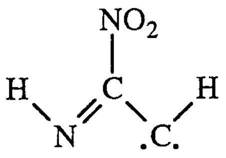
Method

We have computed optimized geometries and energies for **1A, 1B, 1C, 1A*, 1C*, 2, 3, 4, 5, TS1** and **TS2** with the density functional option of the code Gaussian 92/DFT, revision G.2,[22] using the Becke exchange[23] and the Perdew correlation[24] functionals and a 6-31G (d,p) basis set. The effectiveness of these functionals has been established through extensive comparisons with experimental and *ab initio* correlated studies.[25-34] Zero-point energies were also determined. It was verified, by the absence of imaginary vibrational frequencies, that **1A**, **1B**, **1C**, **1A***, **1C*** and **2** - **5** all correspond to energy minima. **TS1** and **TS2** each have one imaginary frequency, confirming that they are transition states.

Results and Discussion

The resulting total and zero-point energies are given in Table 1, and the ΔE values for the individual steps in eqs. (1) and (2) are in Table 2. The energies of the tautomeric pair **1A** and **1C** are virtually equal (differing by only 0.6 kcal/mole) as are those of **1A*** and **1C*** (difference = 0.006 kcal/mole). Accordingly the energetics of the initial steps in eqs. (1) and (2), opening the triazole ring, are essentially identical, requiring an energy input of approximately 16 kcal/mole (Table 2).

The loss of N_2 from either **1A*** or **1C*** to form the triplet product **2** or **4** is simply a bond-breaking process; $\Delta E = +32.4$ and $+39.5$ kcal/mole, respectively (Table 2).



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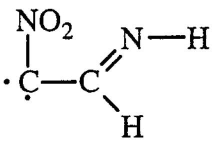

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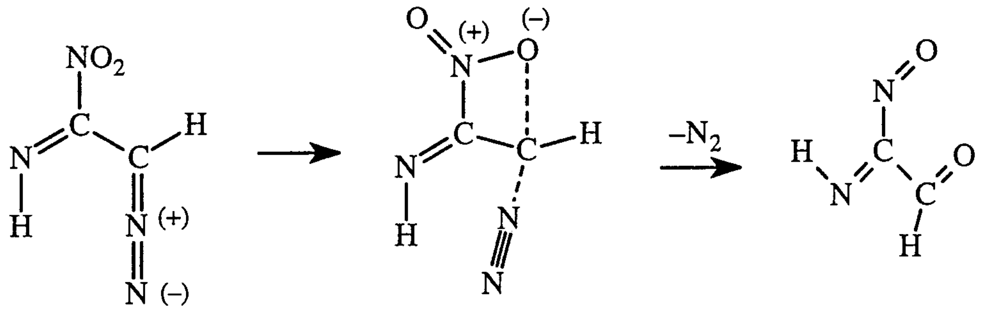
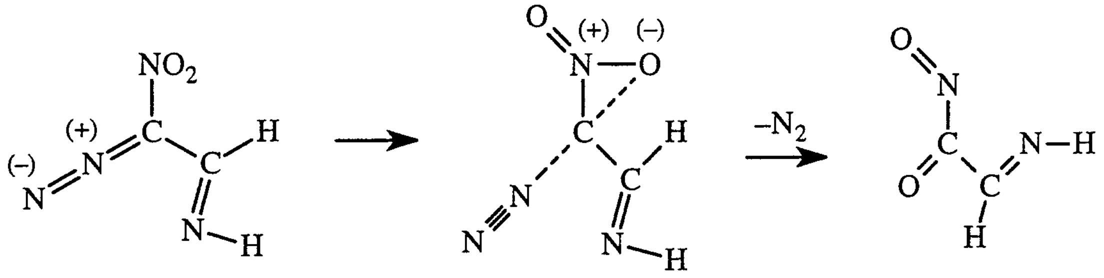
The formation of the singlet products **3** and **5**, on the other hand, involves structural rearrangements in which one of the oxygens of the nitro group migrates to the carbon from which the N_2 is leaving. This was found to proceed through the transition states **TS1** and **TS2**, as shown in eqs. (3) and (4). Table 2 shows that the energy barriers to these transition states, **1A*** → **TS1** and **1C*** → **TS2**, are +38.0 and +32.4 kcal/mole, respectively. Overall, however, the reactions represented by eqs. (3) and (4) release energy; for **1A***→ **3** + N_2, $\Delta E = -31.6$ kcal/mole, and for **1C*** → **5** + N_2, $\Delta E = -31.3$ kcal/mole.



(3)

1A* **TS1** **3**



(4)

1C* **TS2** **5**

An additional factor to be considered is the third tautomer, **1B**. It is prevented, for structural reasons, from forming an analog of **1A*** (and **1C***). However Table 2 shows that **1B** is about 3 kcal/mole more stable than **1A** and **1C**. We must therefore assume that there is a preference for the nitrotriazole **1** to exist as the tautomer **1B**.

Conclusion

On the basis of this study, we suggest that one plausible decomposition route for **1**, which could for example follow shock or impact, is that represented by eq. (5):

$$\mathbf{1B} \longrightarrow \mathbf{1C} \longrightarrow \mathbf{1C^*} \longrightarrow \mathbf{TS2} \xrightarrow{-N_2} \mathbf{5} \qquad (5)$$

The first three steps in eq. (5) require 2.8 + 16.4 + 32.4 = 51.6 kcal/mole of energy; however the overall ΔE is -12.1 kcal per mole of **1B**. The energy that must be provided to initiate this process is less than that typically needed to rupture a C–NO_2 linkage,[35-38] which is believed to be the first step in the decomposition of many energetic materials.[35,39-45] Furthermore, the reaction in eq. (5) results in the release of a significant amount of energy which can be used to promote further decomposition. This appears, therefore, to be a reasonable interpretation of the high sensitivity that has been observed for the nitrotriazole **1**.[20]

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Table 1. Calculated DFT energies, in hartrees.

System	Total energy, E	Zero-point energy, ZPE	E + ZPE
1A	–446.75903	+0.05933	–446.69970
1B	–446.76541	+0.06019	–446.70522
1C	–446.76004	+0.05933	–446.70071
1A*	–446.73015	+0.05563	–446.67452
1C*	–446.73074	+0.05623	–446.67451
2	–337.14470	+0.04314	–337.10156
3	–337.24779	+0.04418	–337.20361
4	–337.13425	+0.04405	–337.09020
5	–337.24743	+0.04433	–337.20310
N_2	–109.52670	+0.00536	–109.52134
TS1	–446.66559	+0.05158	–446.61401
TS2	–446.67360	+0.05078	–446.62282

Table 2. Energy changes corresponding to individual steps in reactions. Differences in zero-point energies are taken into account.

Process	ΔE, kcal/mole
1B → **1A**	+3.5
1A → **1A***	+15.8
1A* → **2** + N_2	+32.4
1A* → **TS1**	+38.0
1A* → **3** + N_2	−31.6
1A → **3** + N_2	−15.8
1B → **1C**	+2.8
1C → **1C***	+16.4
1C* → **4** + N_2	+39.5
1C* → **TS2**	+32.4
1C* → **5** + N_2	−31.3
1C → **5** + N_2	−14.9