Ab Initio Study of Unimolecular Decomposition of Nitroethylene

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Four distinct pathways of unimolecular decomposition of nitroethylene, the C−NO_2 bond breaking, nitro-to-nitrite rearrangement, 1,2-elimination reaction and 1,1-elimination reaction, have been computationally investigated with ab initio, MP2, MP4, and G2 methods as well as with DFT methods. The nitro-to-nitrite rearrangement and 1,2-elimination reaction are found to give the lowest energy decomposition pathways for this molecule, about 15 kcal/mol lower than the cleavage of the nitro group.

Introduction

Decomposition of nitro-containing compounds is of special interest, partly because these reactions occur at relatively low temperatures and partly because of the role such reactions play in the detonation of explosives. The smallest organic compound containing a nitro group is nitromethane, which has been studied quite extensively. The initial step in thermal decomposition of nitro-containing compounds is often the cleavage of the C−NO_2 or N−NO_2 bond.[1] During the unimolecular decomposition of nitromethane, however, Wodtke et al.[2] observed not only the formation of CH_3 and NO_2 but also the formation of considerable amounts of CH_3O. They concluded that C−NO_2 bond rupture (eq 1) must compete with isomerization of nitromethane to methyl nitrite CH_3ONO (eq 2), which may further break into CH_3O and NO. This mechanism had also been predicted theoretically by Dewar et al.[3]

$$CH_3NO_2 \rightarrow CH_3 + NO_2 \qquad (1)$$

$$CH_3NO_2 \rightarrow CH_3ONO \rightarrow CH_3O + NO \qquad (2)$$

Recent experimental studies of possible nitromethane decomposition pathways include, in addition to C−NO_2 bond cleavage (eq 1) and nitro-to-nitrite rearrangement (eq 2), bimolecular[4,5] and ionic[6] decomposition. Theoretical studies concerning C−NO_2 bond dissociation via singlet and triplet electronic states and intersystem crossing of ground and excited-state potential energy surfaces have been carried out.[7,8] The mechanism for sensitizing nitromethane toward detonation by the addition of traces of amines has also been investigated theoretically.[9]

Nitroalkanes with more than one carbon atom are also known to undergo reactions different from (eq 2), viz., elimination reactions with the formation of corresponding alkenes and HONO. For instance, it is known from thermal decomposition studies[10] that elimination reaction 4 is a low energy decomposition pathway of nitroethane, and therefore it competes with the C−NO_2 bond rupture (eq 3).

$$C_2H_5NO_2 \rightarrow C_2H_5 + NO_2 \qquad (3)$$

$$C_2H_5NO_2 \rightarrow C_2H_4 + HONO \qquad (4)$$

Wodtke et al.[2] investigated both nitroethane and 2-nitropropane and reported that the decomposition mechanism for 2-nitropropane is analogous to that for the nitroethane system, i.e., the decomposition mechanism is described by reactions analogous to eqs 3 and 4. Furthermore, work has been reported which supports a concerted nitro-to-nitrite rearrangement in nitrobenzenes,[11−13] which is competitive with C−NO_2 bond breaking.

Less is known, however, about the unimolecular decomposition pathways of compounds which contain a nitro group adjacent to a carbon−carbon double bond. An example of a potentially important compound that falls under this category is 1,1-diamino-2,2-dinitro-ethylene (DADNE). DADNE has recently been synthesized and shows promise as an explosive.[14−16] As Politzer et al.[17] have pointed out, DADNE has the same molecular stoichiometry as RDX and HMX, compounds which are among the most effective currently used explosives and monopropellants, and because of the equivalent stoichiometries, it is evident that DADNE has a high ratio of moles of gaseous products per gram of compound, one of the key determinants of explosive and propellant performance. To the best of our knowledge, however, the decomposition mechanism of DADNE has not yet been reported. An understanding of the decomposition mechanism is useful for the evaluation of this compound as an explosive. A study has now been made and appears following this article.[18]

Before we attempted to address this rather complicated task, we decided to carry out a study of the unimolecular decomposition of a simpler, but related compound, nitroethylene. We considered the behavior of the nitro group in nitroethylene to be a possibly useful model for the behavior of nitro groups in DADNE, because the nitro group is adjacent to a carbon−carbon

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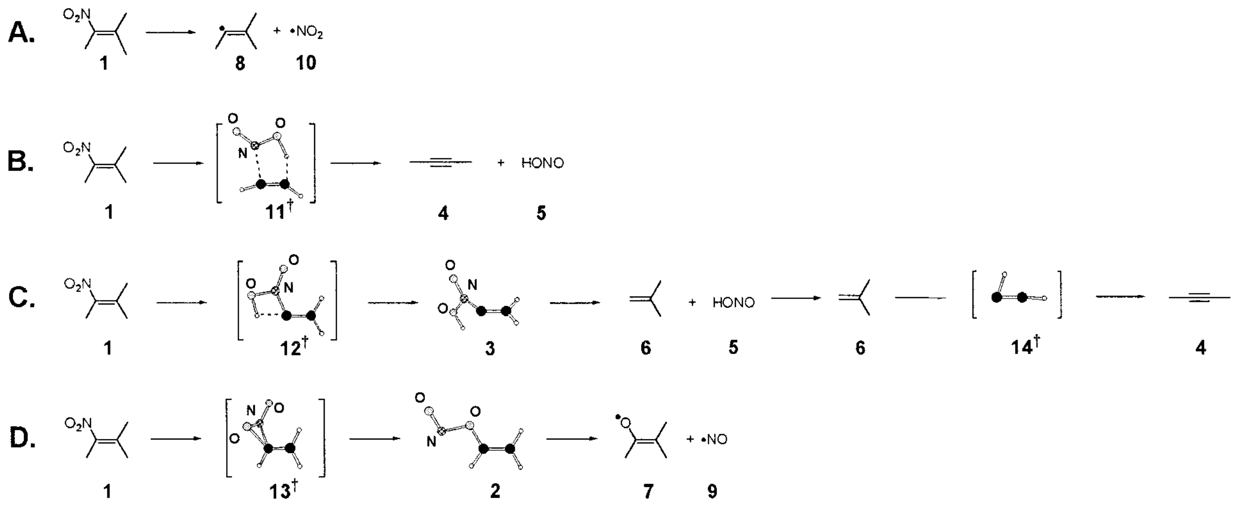


Figure 1. A scheme of pathways for the unimolecular decomposition of nitroethylene.

TABLE 1: Absolute Energies (a.u.), Imaginary Frequencies (cm^{-1}), and Zero-Point Vibrational Energies, ZPVE, (kcal/mol) of Species Involved in Nitroethylene Decomposition[a]

method	G2	MP2	ν_i	ZPVE	MP4(SP)	B3P86	ν_i	ZPVE	B3P86(SP)	B3LYP	ν_i	ZPVE	B3LYP(SP)
basis		6-31G (d,p)	cm^{-1}		6-311+G (d,p)	6-31+G (d,p)	cm^{-1}		6-311++G (3df,3pd)	6-31+G (d,p)	cm^{-1}		6-311++G (3df,3pd)
structure[b]													
1	−282.69591	−282.31631		35.21	−282.51309	−283.78047		34.69	−283.86998	−283.10901		34.45	−283.20001
2	−282.69888	−282.31291		33.34	−282.51316	−283.77755		33.24	−283.86751	−283.10888		32.97	−283.20053
3	−282.62841	−282.24032		33.97	−282.44345	−283.71362		33.24	−283.80553	−283.04285		32.88	−283.13631
4	−77.19046	−77.08167		15.33	−77.14184	−77.57956		15.81	−77.60319	−77.33714		15.73	−77.36200
5	−205.46450	−205.17608		12.67	−205.32286	−206.13464		12.91	−206.20479	−205.71501		12.69	−205.78618
6	−77.11922	−77.00116		15.18	−77.06963	−77.51296		14.88	−77.53278	−77.27235		14.90	−77.29315
7	−152.92519	−152.72129		27.66	−152.82762	−153.59043		26.80	−153.63623	−153.18635		26.70	−153.23331
8	−77.73968	−77.63802		24.53	−77.69446	−78.17703		23.04	−78.19795	−77.91304		22.93	−77.93496
9	−129.73657	−129.56321		5.60	−129.64886	−130.15256		2.88	−130.19593	−129.89548		2.83	−129.93958
10	−204.84048	−204.56420		6.29	−204.70102	−205.48464		5.65	−205.55477	−205.08389		5.51	−205.15489
[11]† [c]	−282.60489	−282.20996	1351i	29.86	−282.41622	−283.68259	987i	29.45	−283.77476	−283.01275	1231i	28.99	−283.10622
[12]†	−282.60360	−282.22247	692i	32.30	−282.42223	−283.68558	791i	32.20	−283.77579	−283.01377	802i	31.86	−283.10539
[13]†	−282.59746	−282.20806	1345i	31.56	−82.40993	−283.68188	1318i	31.13	−283.77196	−283.00869	1267i	30.68	−283.09987
[14]†	−77.11759	−76.99947	1070i	13.71	−77.06585	−77.50736	888i	14.88	−77.52986	−77.26385	879i	13.22	−77.28695

[a] SP denotes that a single-point calculation has been performed on a structure optimized at a lower level of theory (presented to the left of a column in question). [b] See figures 1 and 2. [c] Symbols such as [11]† refer to a transition state.

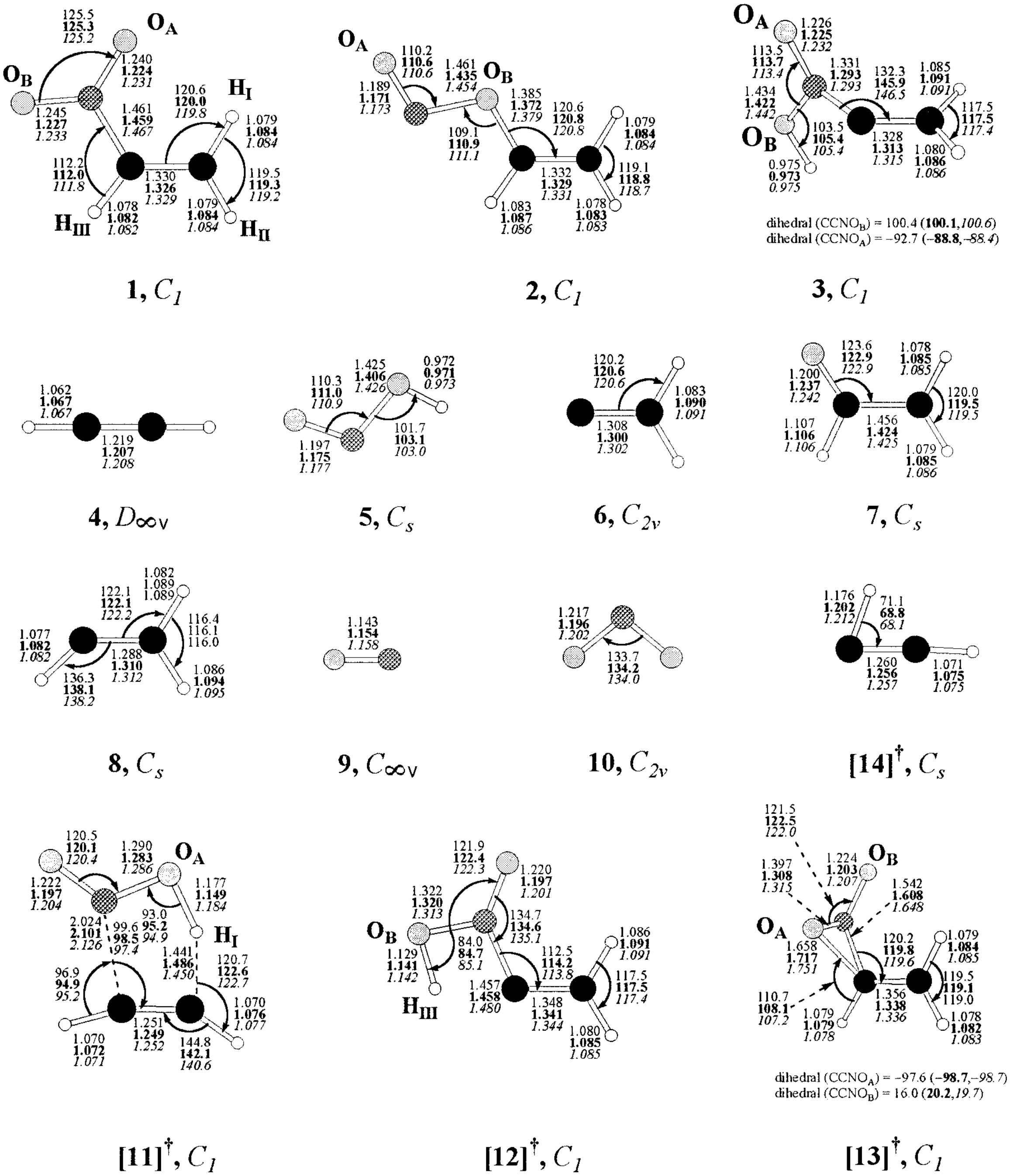
double bond. One of our objectives in this study was to compare the results for nitroethylene decomposition obtained with *ab initio*, MP2, MP4, and G2 methods to the less computationally intensive DFT methods. If DFT methods performed well as compared to the ab initio ones for the case of nitroethylene, this would suggest that it may be possible to apply DFT methods to the study of the decomposition of DADNE at a smaller computational expense. At the same time, the study of the decomposition mechanism for nitroethylene has its own inherent interest.

Computational Details

All quantum mechanical calculations were carried out with the *Gaussian 98* program package.[19] The reader is referred to ref 20 for definitions of technical symbols. The geometries of all reactants, products, and transition states have been optimized at the MP2(FC)/6-31G(d,p) level of theory, where FC denotes the frozen core. When calculating the relative energies for the systems where radicals were involved, PMP2 (spin-projected MP2) rather than MP2 energies were used. Vibrational frequencies have been calculated using the same approximation for the characterization of the nature of stationary points and the determination of zero-point vibrational energy (ZPVE) corrections. To obtain more reliable energies for all of the structures involved, we performed single-point calculations at MP4(SDTQ)/6-311+G(d,p) level of theory. All of the stationary points have been positively identified for minimum energy with no imaginary frequencies and the transition states with one imaginary frequency. For anharmonicity correction,[21] the calculated ZPVE values were scaled by 0.9608. Intrinsic reaction coordinate (IRC) analysis was carried out for each transition state to make sure that it is the transition structure connecting the desired reactants and products. The calculated values of the vibrational frequencies are given as Supporting Information.

We also performed a G2 procedure as implemented in the *Gaussian* code for all of the structures involved. Differently from the standard G2 procedure, we used the ZPVE values obtained with MP2 rather than HF for anharmonicity corrections.

The same analysis as described for MP2 above was also carried out with two DFT methods. The Becke three-parameter hybrid (B3)[22] was used in conjunction with two correlation functionals, Perdew-86 (P86)[23] and Lee−Yang−Parr (LYP).[24] The geometries of all reactants, products, and transition states have been optimized using B3P86/6-31+G(d,p) and B3LYP/6-31+G(d,p). For anharmonicity correction,[21] the calculated ZPVE values were scaled by 0.9759 and 0.9806 for B3P86 and



1, C_1 **2**, C_1 **3**, C_1

4, $D_{\infty v}$ **5**, C_s **6**, C_{2v} **7**, C_s

8, C_s **9**, $C_{\infty v}$ **10**, C_{2v} **[14]**†, C_s

[11]†, C_1 **[12]**†, C_1 **[13]**†, C_1

Figure 2. Geometrical parameters for all of the species involved in the unimolecular decomposition of nitroethylene. The regular font indicates use of the MP2(FC)/6-31G(d,p) method, while bold and italic fonts indicate use of the B3P86/6-31+G(d,p) and the B3LYP/6-31+G(d,p) methods, respectively.

B3LYP, respectively. To obtain more reliable energies for all of the structures involved, we performed single point calculations at B3P86/6-311++G(3df,3pd) and B3LYP/6-311++G-(3df,3pd) levels of theory, respectively.

Results and Discussion

We investigated four distinct pathways (A−D) of nitroethylene decomposition, shown in Figure 1. The structures and optimized geometrical parameters of all the species involved are depicted in Figure 2, and their absolute energies presented in Table 1. The relative (to nitroethylene) energies of all species are tabulated in Table 2. The reaction diagram is displayed in Figure 3.

Pathway A. Pathway A is a C−NO_2 bond rupture. The experimental C−NO_2 bond dissociation energy (BDE) in nitroethylene is not known. The value theoretically predicted by McKee[25] using HF/3-21G//MP4/6-31G(d,p) level of theory is 71.0 kcal/mol. Our G2 result is 72.6 kcal/mol, while the MP4-(SDTQ)/6-311+G(d,p) calculated value with the use of MP2/6-31G(d,p) optimized geometries is 69.4 kcal/mol. While B3P86 and B3LYP both underestimate this value, the B3P86/6-31+G-(d,p) result of 68.7 kcal/mol is somewhat closer to the ab initio results than that of B3LYP at 64.4 kcal/mol.

Pathway B. Pathway B is an elimination reaction with formation of acetylene and HONO, which proceeds through a planar five-membered cyclic transition state [**11**]† with an activation energy of 57.1 kcal/mol as calculated with the G2 method. The values obtained with all of the other methods used are reasonably close (within a few kcal/mol) to the G2 result. The formation of acetylene and HONO may be viewed as an

TABLE 2: Relative (to Nitroethylene) Energies in kcal/mol of Species Along the Nitroethylene Decomposition Pathways[a]

method basis set ZPVE scale factor		G2	MP2/ 6-31G(d,p) 0.9608	MP4/ 6-311+G(d,p)	B3LYP/ 6-31+G(d,p) 0.9806	B3LYP(SP)/ 6-311++G (3df,3pd)	B3P86/ 6-31+G(d,p) 0.9759	B3P86(SP)/ 6-311++G (3df,3pd)
Path A	8+10	72.6	67.4	69.6	64.4	63.2	68.7	67.7
Path B	$[11]^\dagger$	57.1	61.6	55.6	55.0	53.5	56.3	54.6
	4+5	25.7	29.8	23.4	29.8	26.6	35.8	33.1
Path C	$[12]^\dagger$	61.8	64.4	61.2	59.2	59.1	58.4	58.0
	3	42.4	46.5	42.5	40.0	38.4	40.5	39.0
	6+5	70.4	80.2	68.6	69.6	69.0	76.6	76.3
	$[14]^\dagger$+5	71.4	79.8	69.6	73.3	71.2	80.2	78.2
	4+5	25.7	29.8	23.4	29.8	26.6	35.8	33.1
Path D	$[13]^\dagger$	57.9	56.1	54.2	57.2	56.8	57.1	56.7
	2	−1.9	0.3	−1.8	−1.4	−1.8	0.4	0.1
	7+9	21.4	18.1	21.1	12.2	12.2	18.6	18.8

[a] The relative energies were corrected for scaled zero-point vibrational energies.

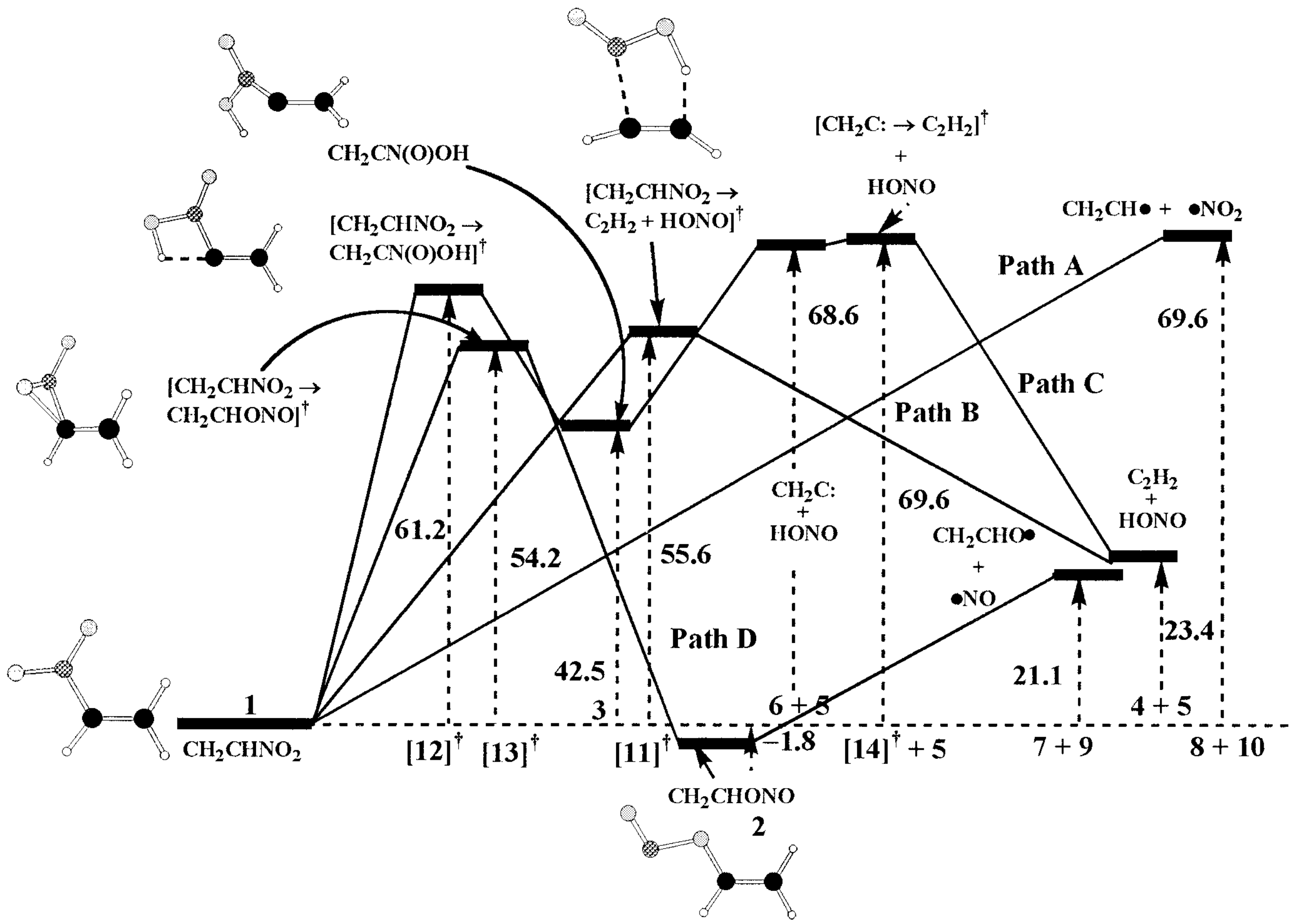


Figure 3. Energy diagram of nitroethylene decomposition pathways. The energy values are in units of kcal/mol and have been calculated by performing single-point energy calculations with the MP4/6-311+G(d,p) method and the use of optimized geometries obtained from the MP2-(FC)/6-31G(d,p) calculations. The energy values were corrected for ZPVE obtained from the MP2(FC)/6-31G(d,p) calculations.

analogue of reaction 4 for nitromethane. Upon examination of the transition structure, one may conclude that, as the C−N bond distance increases, the formation of a new bond between O_A and H_I is energetically favored. Note that the products of this reaction are two stable closed shell molecules, which are separated from the reactant, nitroethylene, by a clearly pronounced maximum on the potential energy curve. These products energetically lie above nitroethylene by 27.6 kcal/mol as calculated with the G2 method. Again, the other methods agree reasonably well with the G2 results, except for B3P86 which seems to overestimate this value by more than 6 kcal/mol.

Pathway C. Pathway C might be an elimination reaction similar to pathway B. A bond between O_B and H_{III} would be formed, while the C−N bond would break, and the products would be two closed shell fragments, CH_2C and HONO. However, no transition state was found to connect nitroethylene with the products mentioned above. We reasoned that if the O_B-H_{III} bond forms while the C−N bond still exists, both the $C-H_{III}$ bond and the $N-O_B$ π bond would have to be broken, leaving one unpaired electron on both N and C. Therefore, the O_B-H_{III} bond would be stabilized by a π bond formation between C and N. However, the only way that such an interaction could take place would be if the NO_2 plane rotates about 90° with respect to the $C{=}CH_2$ plane to avoid the π orbital repulsion from the carbon−carbon double bond. In fact, there exists a transition state $[\mathbf{12}]^\dagger$, in which an O_B-H_{III} bond forms and the NO_2 plane is rotated 90° with respect to the $C{=}CH_2$ plane. It lies 61.8 kcal/mol (G2 result) above nitroethylene, and, again, all of the other methods agree closely for this step. The IRC analysis leads to a structure **3**, which has no imaginary frequencies, an indication that it is stable. We were not able to locate the transition state for HONO elimination from **3**. We thus obtained a PES by optimizing the geometry at a series of fixed C−N bond lengths in **3**. The energy of the system increases with an increasing bond length at first and then reaches the plateau. Therefore, the barrier for this process is approximately equal to the differences in energy between the reactant, **3**, and the two products, vinylidene, **6**, and HONO, **5**. We calculated this barrier to be 28.0 kcal/mol using the G2 method. The MP2 (33.7 kcal/mol) and B3P86 (36.1 kcal/mol) calculations overestimate the value of this barrier, while the MP4 (26.1 kcal/mol) and B3LYP (29.6 kcal/mol) calculations agree well with the G2 result. Vinylidene could further rearrange into acetylene through a transition state, which lies only 1.0 kcal/mol higher (G2). Schaefer et al.[26] have estimated this barrier to be ∼3 kcal/mol using coupled cluster energies (CCSDT-1), indicating that vinylidene is indeed a stable intermediate.

Pathway D. Pathway D is a nitro-to-nitrite rearrangement reaction and may be considered an analogue of reaction 2 of nitromethane. It proceeds through a triangular transition state $[\mathbf{13}]^\dagger$ in which the $C{-}O_B$ bond is created and the C−N bond is elongated, while the NO_2 group is bent out from the $C{=}CH_2$ plane. The barrier is 57.9 kcal/mol as calculated with the G2 method, and the values obtained with other methods are very similar. The product is isonitrite, **2**. To avoid confusion, we mention in passing that it is likely both O_A and O_B are equally capable of forming the bond with C. IRC analysis of $[\mathbf{13}]^\dagger$ led to a reactant with the NO_2 group rotated perpendicularly to the C−C−N plane, and this group can then rotate either way.

While there are a few rotational isomers of the product, **2**, resulting from rotations around $C{-}O_B$ and $N{-}O_A$ bonds, the one that is depicted in Figure 1 was obtained by optimizing the final structure from an IRC calculation and was calculated to be the most stable. Product **2** may further decompose into NO and CH_2CHO radicals via the $O_B{-}N$ bond dissociation. The BDE for this bond is rather low, 23.3 kcal/mol as calculated with the G2 method. B3LYP underestimates this value by almost 10 kcal/mol, while B3P86 performs somewhat better, underestimating this value by 3.3 kcal/mol.

Concluding Remarks

We conclude that the HONO elimination reaction B and nitro-to-nitrite rearrangement D are the lowest energy decomposition channels for nitroethylene with the G2 calculated activation barriers of 57.3 and 57.9 kcal/mol, respectively. This is ∼15 kcal/mol lower than the amount of energy required for the $C{-}NO_2$ bond cleavage.

We found that the DFT methods used, B3LYP and B3P86, were able to provide a realistic description of nitroethylene decomposition. While there are some quantitative differences between DFT and ab initio results, the qualitative trends are the same. It is known that DFT methods (especially those based upon the Becke three-parameter hybrid (B3) exchange functional) with a moderate basis set yield good geometries. It is often suggested that for a given geometry an efficient way to obtain more accurate evaluation of energy values is to carry out a single point calculation with a larger basis set. We found, however, that, in the case of nitroethylene, larger basis sets did not significantly improve the energy values obtained with the moderate basis set. In most decomposition steps B3LYP performed better than B3P86, except for estimations of BDE values, as judged by comparison to ab initio results.

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Supporting Information Available: Table of calculated values of the vibrational frequencies for each structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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