

## Nitromethane - Methyl Nitrite Rearrangement: The Solving of Discrepancy between Theory and Experiment

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### ABSTRACT

The potential energy hyper surfaces (PES) of the unimolecular rearrangements of a) Nitromethane (1) to trans aci-nitromethane (2); b) nitromethane (1) to methyl nitrite (3) and c) nitromethane decomposition to methyl and nitrogen dioxide were searched using the *ab initio* MP2 method. Split valence 6-31G(d,p) basis set was used for geometry optimizations, frequency and IRC computations along each reaction path. The energy barrier for the decomposition path of nitromethane was found to be 87.8 kcal/mol via newly determined transition state. The nitromethane to methyl nitrite barrier height was previously determined to be the 70.5 kcal/mol, which is 17.3 kcal/mol less than that of the nitromethane decomposition path reported in this work. Using these data it was possible for the first time to explain the experimentally observed path of nitromethane decomposition.

**Key words:** Nitromethane; Methyl Nitrite; Potential Energy Surface; Rearrangement; Energetic Material

### INTRODUCTION

The ability to model energetic materials requires knowledge of the thermochemical properties of the initial energetic compound as well as those of the intermediates formed during the decomposition process. From the thermochemical properties one can determine the bond dissociation energies of a molecular compound and its subsequent reaction intermediates. Using theoretical approach, one can also determine reaction pathways and the activation energies involved in going from reactants to products.

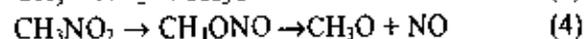
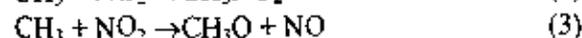
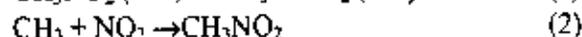
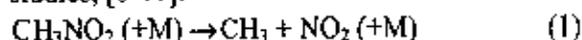
The concept of the reaction pathway has become important in the study of potential energy surfaces for chemical reactions. In general, the reaction path can be defined as the curve on the potential energy surface connecting the reactants and products through the transition state all in the same spin state. This curve can be found by following the steepest descent path or

minimum energy path (MEP) from the transition state toward reactants and products. When mass-weighted Cartesian coordinates are used, the path becomes the intrinsic reaction coordinate (IRC) [1].

Nitromethane,  $\text{CH}_3\text{NO}_2$ , is the simplest aliphatic nitro compound and a prototype for energetic materials that could be of use as high, pure solid explosives and propellant fuels [2]. As such, it is a model compound for experimental studies in ignition, combustion, and atmospheric pollution [3]. The rate constants for decomposition of nitromethane, referred to hereafter as NMT, were determined 35 years ago by Glaeser and Troc [4, 5] in shock tube experiments on the decomposition of highly diluted NMT (eq 1), and the reported values

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were largely supported by subsequent kinetic studies, [6-11].



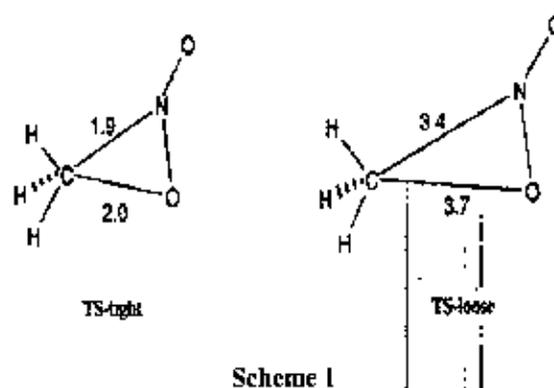
However, the more recent detailed kinetic modelings [6-10] also indicated that the NMT pyrolysis kinetics are much more complex than previously assumed with secondary reactions and the competition between different channels, e.g., simple bond cleavages, rearrangements, and molecular eliminations. It was also pointed out that significant deviations in the reported NMT thermochemistry from different sources led to a large uncertainty in the rate constants of eqs 1 and 2 [11-13].

In the reactions of hydrocarbons and nitric oxide (NO) that are the mutually sensitized oxidations, a key process is actually the one between the methyl radical and nitrogen dioxide (eq 3). The latter reaction is known to serve as a H-atom generator through the rapid dissociation of the methoxy radical and, thereby, to enhance the fuel oxidation process. Formation of NMT (eq 2) is expected to compete with eq 3. In this context, the NMT-MNT interconversion (eq 4) has been shown to play a pivotal role in the overall transformation.

In 1985, Dewar *et al.* [14] theoretically studied the decomposition of nitromethane using their semiempirical MINDO/3 method and obtained the energy barriers of 47.0 and 32.4 kcal/mol for the conversion of nitromethane to methyl nitrite and fragmentation of methyl nitrite to  $\text{H}_2\text{CO} + \text{HNO}$ , respectively. These authors [14] estimated the kinetic frequency factors of various elementary processes and suggested that nitromethane decomposes via an initial rearrangement to methyl nitrite.

McKee [15] reported in 1986 a detailed description of the  $\text{CH}_3\text{NO}_2$  potential energy surface (PES) using ab initio molecular orbital calculations at both Hartree-Fock (HF) and second-order perturbation theory (MP2) levels with the 6-31G(d) basis set. The PES included nitromethane, methyl nitrite, nitrosomethanol, *aci*-nitromethane isomers, and a number of dissociation limits. According to this author, the rearrangement of nitromethane to methyl nitrite

corresponds to the lowest energy pathway but is associated with a rather large energy barrier of 73.5 kcal/mol. Such a barrier arises from, on one hand, a distortion of  $\text{NO}_2$ , and on the other hand, a strongly antibonding interaction in the compact transition structure (TS-tight, Scheme 1) between a lone pair on oxygen and the migrating methyl group. In a sense, this is equivalent to the four-electron-two-orbital destabilizing interaction, and the migration is thus orbital forbidden. Note that both reported interfragment distances C-N (1.93 Å) and C-O (2.01 Å) in TS-tight are rather short. Elimination of formaldehyde from MNT was found to have a lower barrier height of 44.1 kcal/mol. This author [15] concluded that fragmentations are less energy demanding and that a concerted rearrangement on the  $\text{CH}_3\text{NO}_2$  PES is not to be observed.



Scheme 1

At about the same time, Wodtke, Hintska, and Lee (WHL) [16, 17] reported the first experimental evidence for a primary production of  $\text{CH}_3\text{O}$  from  $\text{CH}_3\text{NO}_2$ . Using a molecular beam in conjunction with infrared multiphoton dissociation technique, WHL [16, 17] suggested an initial isomerization of nitromethane to methyl nitrite when detecting the  $\text{CH}_3\text{O}$  and NO fragments presumably from the dissociation of the internally very hot, but collision-free, isomerized nitromethane (cf. eq 4). In these experiments, the presence of an exit barrier on the PES could be determined by a direct measurement of the product translational energy distribution. To relate their spectroscopic results to pyrolysis experiments, WHL [17] subsequently carried out a RRKM theory treatment in taking some numerical kinetic parameters from ref 43, and overall they reported the following findings: (i) a branching ratio between  $\text{NO}/\text{NO}_2$  production is

about 0.6 in favor of  $\text{NO}_2$ ; (ii) but when using the previously estimated frequency factors for both C-N bond cleavage ( $A = 10^{15.6}$ ) and isomerization processes ( $A = 10^{13.3}$ , value taken from ref 14), a fitting of the obtained data within an RRKM framework led to a barrier height to the nitromethane - methyl nitrite isomerization of about 55.5 kcal/mol, relative to nitromethane. In taking the major sources of error into account, WHL evaluated the maximum barrier height at 57.0 kcal/mol and the minimum barrier at 51.5 kcal/mol; and (iii) an energy barrier of 55.5 kcal/mol for nitromethane - methyl nitrite is actually smaller than the C-N bond energy of nitromethane known to be in the range from 58.5 [13] or 59.4 [18a] - 60.1 [18b] kcal/mol.

WHL's evaluations of their experimental results were thus in sharp contrast, both quantitatively and qualitatively, to the ab initio MO results of McKee [15] mentioned above in which the barrier of 73.5 kcal/mol was found to be 16.1 kcal/mol higher than the C-N bond asymptote. In view of the discrepancy, the latter author [19] reinvestigated the nitromethane - methyl nitrite rearrangement in constructing multiconfiguration wave functions including four-electron-in-four-orbitals in the active space (MCSCF(4,4)/6-31G(d)). The most striking result in this paper [19] was that the transition structure (TS) for 1,2-methyl migration turned out to be a loose form between both  $\text{CH}_3$  and  $\text{NO}_2$  radicals, with long interfragment distances (longer than 3.6 Å), as seen in TS-loose depicted in Scheme 1. The latter was characterized as a biradical essentially keeping the two unpaired electrons of both radical partners well separated from each other. The predominant contributing configuration is the one in which the three unpaired electrons of  $\text{NO}_2$  are distributed in the nitrogen lone pair orbital (a') and the two combinations of oxygen lone pairs (a"). Subsequent truncated multireference configuration interaction (MRCI) computations confirmed that, considering the new TS-loose, the unimolecular barrier remains 10 kcal/mol above the sum of  $\text{CH}_3$  and  $\text{NO}_2$  radicals energies. [19]

In a following theoretical study, Saxno and Yoshimine (SM) [20] reexamined the TS for nitromethane - methyl nitrite interconversion making use of a multiconfigurational method: that was a similar MCSCF-(4,4) treatment but instead with a smaller 4-31G basis set without

polarization d-functions. In line with previous results of McKee, geometry optimizations by SM invariably led to the TS-loose, with the C-N and C-O distances of 3.4 and 3.7 Å, respectively (cf. Scheme 1). Further single-point electronic energy calculations at the MCSCF-CI(7)/6-31G(d) level, with zero-point energy corrections, yielded an energy barrier of 56.7 kcal/mol for 1,2-methyl shift and a C-N bond dissociation energy of 57.1 kcal/mol. In other words, although a better agreement with experimental data was obtained by SM, the loose character of the TS for rearrangement remains striking.

Lammertsma and Prasad [21] in 1993 studied nitromethane - *aci*-nitromethane tautomerism by high-level ab initio methods. The MP2/6-31G\* geometry of nitromethane compares well with that determined experimentally. In this paper the G1 energy difference between the two tautomers amounts to 14.1 kcal/mol in favor of nitromethane and the calculated heat of formation of -570.7 kcal/mol for nitromethane differs by only 2.4 kcal/mol from the experimental value.

In the theoretical article, Hu *et al.* [22] reported the results of an extensive exploration of the  $\text{CH}_3\text{NO}_2$  PES which included no less than 10 isomers, 46 transition structures, and 16 dissociation product limits. The energies were obtained at a G2MP2 level on the basis of geometries optimized using density functional theory with the popular B3LYP functional. It is remarkable that the B3LYP/6-311++G(2d,2p) provides a TS-tight for the methyl migration. In addition, these authors [22] found that the C-N bond dissociation energy for nitromethane is 61.9 kcal/mol, which is lower than the barriers for nitromethane - methyl nitrite and nitromethane - *aci*-nitromethane isomerizations by 2.7 and 2.1 kcal/mol, respectively. Therefore, it has been suggested no one had that the nitromethane isomerization pathways are kinetically disfavored in view of the relatively higher energy barriers, which are in excess of 60 kcal/mol. On the other hand, the nitromethane decomposition seems to occur either via the C-N bond rupture or via concerted molecular elimination. In other words, the latest results [22] substantiated the discrepancy not only between experimental and theoretical analyses but also between theoretical

results reported in earlier papers [14-20]. Nevertheless, the nature of the TS for rearrangement, tight versus loose, has not been examined by an appropriate treatment.

Nguyen and *et al.* [23] in 2003 reexamined the mechanism of the unimolecular rearrangement connecting both nitromethane and methyl nitrite isomers. The  $\text{CH}_3\text{NO}_2$  potential energy surface was constructed using different molecular orbital [CCSD(T) and CASSCF] and density functional theory (B3LYP) methods including a few lower lying isomeric intermediates. Calculations are thus internally consistent indicating that the energy of the TS for 1,2- $\text{CH}_3$  shift is at least 6 kcal/mol above the  $\text{CH}_3 + \text{NO}_2$  asymptote.

In this context, we set out to perform computations using appropriate levels of *ab initio* quantum chemical theory with aim to probe again the shapes of the TS for unimolecular and 1,2-methyl migration in the nitro-nitrite rearrangement. For the sake of completeness, a comparison with the results of Nguyen and *et al.* [23] on the  $\text{CH}_3\text{NO}_2$  PES has also been made. It should be stressed that a reinvestigation of the detailed kinetics of the processes considered goes beyond the scope of the present work. An accurate and consistent determination of the frequency factors for different barrierless reactions involving radical recombinations and bond cleavages, that are necessary for kinetic RRKM treatments, in fact, requires appropriate quantum chemical calculations and much effort

## CALCULATIONS

All calculations were carried out using the PC GAMESS 7.1.5 [24] Spartan'06 [25] programs. In the construction of the lowest singlet state PES of the  $\text{CH}_3\text{NO}_2$  system, various isomeric intermediates, and the TSs connecting them, were located by geometry optimizations as relax using MP2 (Møller-Plesset second-order perturbation theory) quantum chemical procedure with a 6-31G(d,p) basis set. The excellent results of MP2 in conjunction with Pople type basis set has been well documented for studying the molecular properties of large number of organic molecules. Vibrational frequencies were calculated at the

MP2/6-31G(d,p) level for characterization of stationary points (number of imaginary frequencies NIMAG) 0 and 1 for local minima and TSs, respectively. Intrinsic reaction coordinate (IRC) calculations [26, 27] are carried out using the same basis sets to make sure the transition states connect the expected stationary points on the energy surface.

## RESULTS AND DISCUSSION

Total energies and equilibrium geometries in searching of PES at the MP2/6-31G(d,p) basis set are presented in Table 1 and Figure 1. Their PES diagram is shown in Figure 2. In this shape the energy of nitromethane is zero and energies of the other geometries are given relative to nitromethane in kcal/mol.

**Table 1.** Total energy and ZPE of substrates, products and transition states with MP2/6-31G(d,p)

Compound	Total energy (a.u.)	ZPE (kcal/mol)
$\text{CH}_3\text{NO}_2$ (1)	-244.35506	32.315
$\text{CH}_2\text{N}(\text{O})\text{OH}$ (2)	-244.31031	30.642
$\text{CH}_3\text{ONO}$ (3)	-244.34601	30.846
$^2\text{CH}_3 + ^2\text{NO}_2$	-244.25269	25.569
TS1	-244.24234	28.754
TS2 -tight	-244.23831	29.546
TS3	-244.20569	26.424

For comparing to previous reported computations the relative energies of species included in the potential energy surface of nitromethane with perturbation theory MPn and the coupled-cluster theory CCSD(T), with different basis sets ranging from 6-31G\* to 6-311G(3df,2p) are summarized in Table 2. Coupled-cluster CCSD(T) with cc-pVDZ and cc-pVTZ basis sets, DFT method including B3LYP with 6-311G(d,p) and cc-pVDZ basis sets and modified G2M [28] method are also included. As Table 2 shows the present computations are in good agreement with all other entries. The new species TS3 is reported for the first time. To have a complete picture of the paths on the PES, the two sides around each TS geometry on PES were searched via Intrinsic Reaction Coordinate(IRC) method.

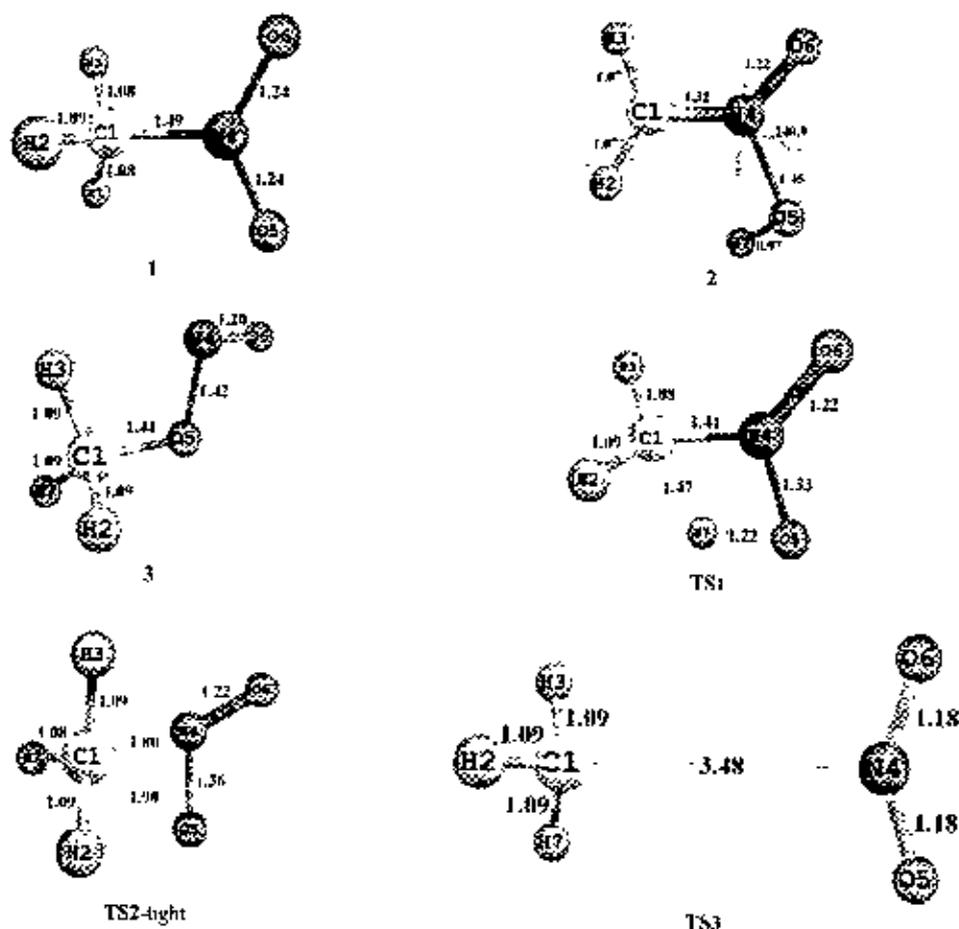


Fig. 1. Geometries of substrates, products and transition states with selected geometric distances (Å).

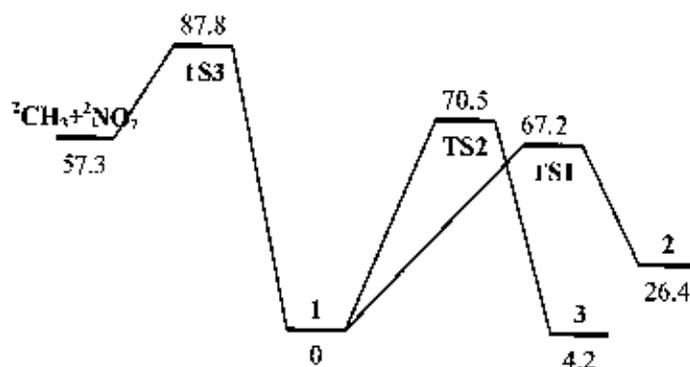


Fig. 2. The shape of a portion of the nitromethane potential energy surface with MP2/6-31G(d,p). Relative energies are given in kcal/mol.

The first path searched with IRC on nitromethane PES, is the migration of hydrogen atom (H7) in nitromethane **1** from carbon atom (C1) to O5 in trans-aci-nitromethane (**2**) via TS1 (Figure 1). By implementing the ZPE the barrier height of 67.2 kcal/mol was obtained for this unimolecular path which is the rearrangement of

nitromethane to trans-aci-nitromethane. As Figure 1 shows the major changes in bond distances in reactant-TS path, are due to the C1-H7 distance (1.08 Å to 1.47 Å) and the O5-H7 (2.45 Å to 1.22 Å) (Figure 1). In TS-product path, the C1-N4, N4-O5 and H7-O5 bond distances undergo larger changes (1.41 Å to 1.32 Å), (1.33 Å to 1.45 Å) and (1.22 Å

to 0.97 Å) which can be attributed to the change of hybridization of C and O atoms (in context of VB).

Starting from the nitromethane (1), another path was found. This path was determined via IRC computations to be the rearrangements of nitromethane (1) to methyl nitrite (3) via TS2-tight with the barrier height of 70.5 kcal/mol. The large increase in C-N bond length by 0.31 Å is the one of the characteristics of TS2-tight. As the geometry of this TS implies this path can be attributed to the rearrangement of the whole NO<sub>2</sub> group in space. Flipping the NO<sub>2</sub> group in (1) in the plane which approximately bisects the two Hs (H2,H3) of methyl group, would be the classical description for breaking the C-N bond and formation the C-O5 bond. TS2-loose with the relative energy of 74.4 kcal/mol at CAS/6-31G\* level [19] was not observed.

The IRC computations around the PES position of TS3 led to the new path. This path which is reported for the first time connects the new TS3 geometry to nitromethane (1) and the

supramolecule complex composed of CH<sub>3</sub> and NO<sub>2</sub> parts and can be attributed to unimolecular thermal decomposition of nitromethane at singlet electronic state. The barrier height is 87.8 kcal/mol relative to nitromethane energy level. This new path provides the acceptable explanation for this experimental that the nitromethane does not readily undergo the thermal decomposition and prefers the paths of rearrangement to compounds 2 and 3.

## CONCLUSIONS

The experimental result by Wodtke, Hintsa, and Lee (WHL) [16,17] with an RRKM framework led to the barrier height of nitromethane - methyl nitrite isomerization about 55.5 kcal/mol. This energy barrier is actually smaller than the C-N bond energy in nitromethane with the estimated values of 58.5 kcal/mol [13], 59.4 kcal/mol [18a] and 60.1 kcal/mol [18b].

Table 2. Relative energies of species included in the potential energy surface of nitromethane with ZPE

species	Relative energies (kcal/mol)						CCSD(T)/ 6-311G(d,p) <sup>b</sup>
	MP2/ 6-31G(d) <sup>a</sup>	MP2/ 6-31G(d,p) <sup>a</sup>	B3LYP/ 6-311G(d,p) <sup>a</sup>	MP4/ 6-311G(d,p) <sup>a</sup>	MP4/ 6-311+G(d,p) <sup>a</sup>	MP4/ 6-311G(2df,p) <sup>a</sup>	
CH <sub>3</sub> NO <sub>2</sub> (1)	0	0	0	0	0	0	0
CH <sub>2</sub> N(O)OH (2)	29.5	26.4	14.2	19.1	18.6	17.3	17.1
CH <sub>3</sub> ONO (3)	5.6	4.2	2.3	2.0	2.5	2.9	0.4
<sup>2</sup> CH <sub>3</sub> + <sup>2</sup> NO <sub>2</sub>	57.5	57.3	52.7	50.2	51.3	53.6	53.8
TS1	75.0	67.2	61.6	64.5	64.9	63.4	64.1
TS2-tight	73.5	70.5	66.0	68.9	66.5	67.9	68.9
TS3		87.8					
	MP2/ 6-311+G(3df,2p) <sup>†</sup>	G2M <sup>b</sup>	B3LYP/ cc-pVDZ <sup>c,d,e</sup>	CCSD(T)/ cc-pVDZ <sup>c,e</sup>	CCSD(T)/ cc-pVTZ <sup>c,e</sup>	G2MP2/ B3LYP/ 6-311++G(2d,2p) <sup>f</sup>	exp <sup>g</sup>
CH <sub>3</sub> NO <sub>2</sub> (1)	0	0	0	0	0	0	
CH <sub>2</sub> N(O)OH (2)	17	15	15	18	15	21.4	
CH <sub>3</sub> ONO (3)	7.3	2.4	2	0	2	2	
<sup>2</sup> CH <sub>3</sub> + <sup>2</sup> NO <sub>2</sub>	61	62.3	53	52	63	61.9	60.1 <sup>g</sup> 58.5 <sup>h</sup>
TS1	64.6	64.2	59	63	66	64.0	
TS2-tight	72.9	66.2	66	68	69	64.6	55.5 <sup>i</sup>

† This work.

a) Ref. [15] b) Ref. [23] c) ZPE values derived from B3LYP/cc-pVDZ. d) Using optimized geometries at the indicated level. e) Single-point energy calculations using the CCSD(T)/cc-pVDZ geometries. [23] f) ref. [22] g) Ref. [18b] h) Ref. [13] i) Refs. [16, 17].

In sharp contrast the theoretical results were shown that the C-N bond dissociation energy for nitromethane is lower than the barriers for nitromethane - methyl nitrite and oitromethane - aci-nitromethane isomerizations which implied that the nitromethane molecule is decomposed before isomerization.

Our computations show that the decomposition of nitromethane can occur thermally by passing

through the new structure TS3 with the barrier height of 87.8 kcal/mol, which is much higher than the barrier heights of isomerization paths. This result which is in agreement with experiment results of WHL, removes the discrepancy in previous theoretical explanations based on photodissociation of C-N bond in nitromethane.

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