Nitromethane−Methyl Nitrite Rearrangement: A Persistent Discrepancy between Theory and Experiment

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Received: November 22, 2002; In Final Form: February 28, 2003

We reexamined the mechanism of the unimolecular rearrangement connecting both nitromethane and methyl nitrite isomers. The CH_3NO_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. A particular attention has been paid to the two following questions left open by earlier experimental and theoretical studies: (a) does the interconversion between nitromethane and methyl nitrite by a 1,2-CH_3 migration occur via a "loose" or "tight" transition structure (TS)? and (b) is the energy barrier associated with methyl migration actually smaller or larger than the C−N bond dissociation energy? The C−N bond dissociation energy was evaluated with BDE(CH_3-NO_2) $= 60 \pm 2$ kcal/mol in line with available results. In contrast to earlier studies (McKee, M. L. *J. Phys. Chem.* **1989**, *93*, 7365, and Saxon, R. P.; Yoshimine, M. *Can. J. Chem.* **1992**, *70*, 572) but partly in agreement with a recent G2MP2 study (Hu, W. F.; He, T. J.; Chen, D. M.; Liu, F. C. *J. Phys. Chem. A* **2002**, *106*, 7294), our multiconfigurational CASSCF computations demonstrated that the methyl migration involves a "tight" TS whose electronic wave function is dominated by the Hartree−Fock configuration. Calculations are thus internally consistent indicating that the energy of the TS for 1,2-CH_3 shift is at least 6 kcal/mol above the $CH_3 + NO_2$ asymptote. Thus, a discrepancy with a previous evaluation of experimental findings (Wodtke, A. M.; Hintsa, E. J.; Lee, Y. T. *J. Phys. Chem.* **1986**, *90*, 3549), which placed the $CH_3 + NO_2$ limit by 5 kcal/mol above the rearrangement TS, appears to persist.

1. Introduction

Nitromethane, CH_3NO_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.[1] As such, it is a model compound for experimental studies in ignition, combustion, and atmospheric pollution.[2] The rate constants for decomposition of nitromethane, referred to hereafter as NMT, were determined 30 years ago by Glanzer and Troe[3,4] in shock tube experiments on the decomposition of highly diluted NMT (eq 1), and the reported values were largely supported by subsequent kinetic studies,[5−10] including that by one of us.[6]

$$CH_3NO_2(+M) \rightarrow CH_3 + NO_2(+M) \tag{1}$$

$$CH_3 + NO_2 \rightarrow CH_3NO_2 \tag{-1}$$

$$CH_3 + NO_2 \rightarrow CH_3O + NO \tag{2}$$

$$CH_3NO_2 \rightarrow CH_3ONO \rightarrow CH_3O + NO \tag{3}$$

However, the more recent detailed kinetic modelings[5−10] 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 −1.[10−12]

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 2). 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 and/or its methyl nitrite isomer (MNT, eq −1) is expected to compete with eq 2. In this context, the NMT−MNT interconversion (eq 3) has been shown to play a pivotal role in the overall transformation. However, the corresponding step forming MNT[10] remains a subject of some continuing debate.

(A) Brief Summary of Previous Results. In 1985, Dewar et al.[13] theoretically studied the decomposition of NMT using their semiempirical MINDO/3 method and obtained the energy barriers of 47.0 and 32.4 kcal/mol for the conversion of NMT to MNT and fragmentation of MNT to $H_2CO + HNO$, respectively. These authors[13] estimated the kinetic frequency factors of various elementary processes and suggested that NMT decomposes via an initial rearrangement to MNT.

McKee[14] reported in 1986 a detailed description of the CH_3NO_2 potential energy surface (PES) using ab initio molecular orbital calculations at both Hartree−Fock (HF) and

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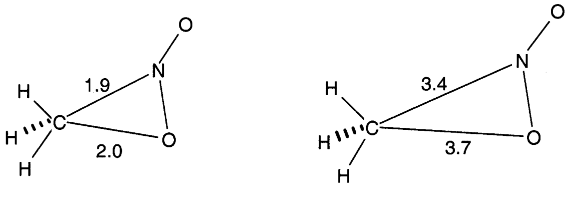
10.1021/jp027532h CCC: $25.00

SCHEME 1



second-order perturbation theory (MP2) levels with the 6-31G-(d) basis set. The PES included NMT, MNT, nitrosomethanol, *aci*-nitromethane isomers, and a number of dissociation limits. According to this author, the rearrangement of NMT to MNT 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 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[14] concluded that fragmentations are less energy-demanding and that a concerted rearrangement on the CH_3NO_2 PES is not to be observed.

At about the same time, Wodtke, Hintsa, and Lee (WHL)[15,16] reported the first experimental evidence for a primary production of CH_3O from CH_3NO_2. Using a molecular beam in conjunction with infrared multiphoton dissociation technique, WHL[15,16] suggested an initial isomerization of NMT to MNT when detecting the CH_3O and NO fragments presumably from the dissociation of the internally very hot, but collision-free, isomerized NMT (cf. eq 3). 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[16] subsequently carried out a RRKM theory treatment in taking some numerical kinetic parameters from ref 13, and overall they reported the following findings: (i) a branching ratio between NO/NO_2 production is about 0.6 in favor of 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 13), a fitting of the obtained data within an RRKM framework led to a barrier height to the NMT−MNT isomerization of about 55.5 kcal/mol, relative to NMT. 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 NMT−MNT is actually smaller than the C−N bond energy of NMT known to be in the range from 58.5[12] or 59.4[17a]−60.1 kcal/mol.[17b]

WHL's evaluations of their experimental results were thus in sharp contrast, both quantitatively and qualitatively, to the ab initio MO results of McKee[14] 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[18] reinvestigated the NMT−MNT 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[18] was that the transition structure (TS) for 1,2-methyl migration turned out to be a loose form between both CH_3 and 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 NO_2 are distributed in the nitrogen lone pair orbital (a′) and the two π 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 CH_3 and NO_2 radicals energies.[18]

In a following theoretical study, Saxon and Yoshimine (SM)[19] reexamined the TS for NMT−MNT interconversion making use of a multconfigurational 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.

In the most recent theoretical article, Hu et al.[20] reported the results of an extensive exploration of the CH_3NO_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[20] found that the C−N bond dissociation energy for NMT is 61.9 kcal/mol, which is lower than the barriers for NMT−MNT and NMT−*aci*-nitromethane isomerizations by 2.7 and 2.1 kcal/mol, respectively. Therefore, it has been suggested on one hand that the NMT 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 NMT decomposition seems to occur either via the C−N bond rupture or via concerted molecular elimination. In other words, the latest results[20] substantiated the discrepancy not only between experimental and theoretical analyses but also between theoretical results reported in earlier papers.[13−19] Nevertheless, the nature of the TS for rearrangement, tight versus loose, has not been examined by an appropriate treatment.

As a matter of fact, a rapid analysis of the possible reasons for the discrepancy points toward, on one hand, the usual shortcomings of quantum chemical treatments, namely, the rather small basis sets employed and noncomplete incorporation of electron correlation, and on the other hand, the use of empirical frequency factors reported in ref 13 in the experimental fittings of WHL in ref 16. In particular, the shape of the migration TS, tight versus loose, might have a direct consequence on the frequency factors (via entropic terms) and thereby the kinetic fittings. In a recent reevaluation of the gas-phase decomposition mechanisms of nitro compounds, Zhang and Bauer[12] stated that "...more rigorous theoretical investigations are needed to resolve this problem" (ref 12, page 662).

In this context, we set out to perform computations using more appropriate levels of ab initio quantum chemical theory with the primary aims to probe again the shape of the TS for

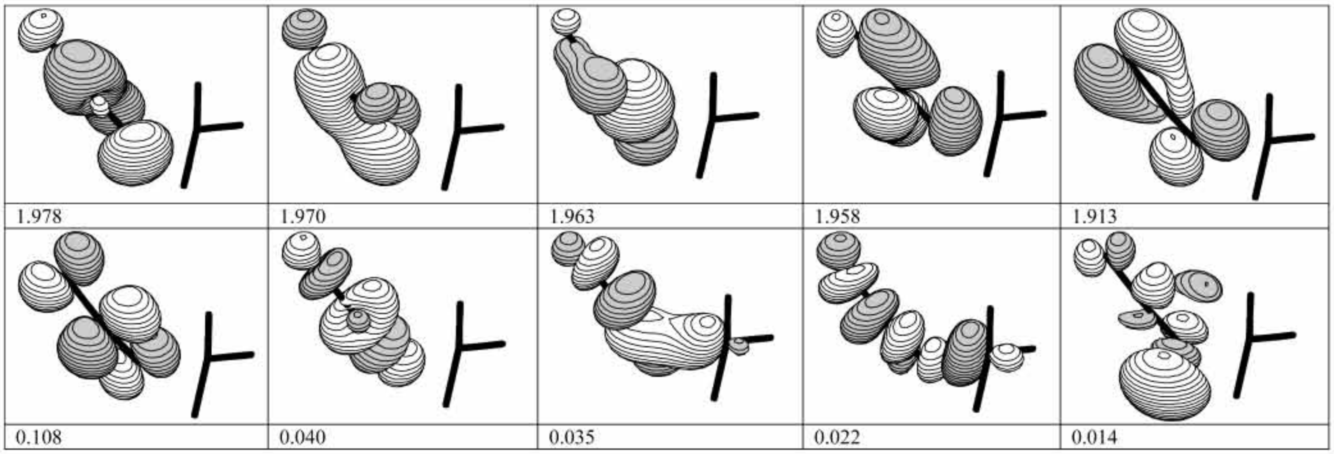


Figure 1. The shape of the 10 natural orbitals included in the active space of CASSCF(10,10) calculations on the TS for 1,2-methyl migration connecting nitromethane and methyl nitrite. The values given are the occupation numbers of the corresponding natural orbitals.

1,2-methyl migration in the nitro-nitrite rearrangement and to determine the associated energy barrier and C−N bond dissociation energy. For the sake of completeness, a comparison with the results of Hu et al.[20] for other relevant pathways on the CH_3NO_2 PES has also been made for an understanding of the reactivity of related species. 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. We however note that the dynamics and mechanisms of the NMT and MNT decomposition have recently been the subjects of numerous experimental investigations in various media[21−23] and theoretical studies.[24−28]

2. Results and Discussion

All calculations were carried out using the GAUSSIAN 98[29] and MOLPRO[30] sets of programs. In the construction of the lowest singlet state PES of the CH_3NO_2 system related to the NMT and MNT exit channels, various isomeric intermediates, and the TSs connecting them, were located by geometry optimizations using density functional theory with the B3LYP hybrid functional,[31] and molecular orbital theory with the coupled-cluster CCSD(T) method.[32] The correlation-consistent cc-pVDZ basis set[33] was used. While geometry optimizations at the B3LYP were carried out using analytical energy gradients and Hessians, those at the CCSD(T) level made use of numerical gradients and Hessians in conjunction with the eigenvector following (EF) optimization technique. Vibrational frequencies were calculated at the B3LYP/cc-pVDZ level for characterization of stationary points (number of imaginary frequencies NIMAG = 0 and 1 for local minima and TSs, respectively) and to obtain zero-point energy (ZPE) corrections. In the electron correlation calculations, the core orbitals were kept frozen.

(A) Transition Structure and Energy Barrier for 1,2-Methyl Migration. Let us first consider the transition structure of interest involving the methyl migration from nitrogen to oxygen and thus connecting NMT to MNT. In attempts to locate both TS-tight and TS-loose structures depicted in Scheme 1, along with the single-reference molecular orbital HF, MP2, and CCSD(T) methods, and the density functional B3LYP technique, we additionally performed geometry optimizations using multiconfigurational wave functions.

In the complete active space self-consistent field (CASSCF)[35] method, a modified (aug)-cc-pVTZ basis set was employed in which diffuse functions were not added to hydrogen atoms but were on heavier C, N, and O atoms. The active space used in CASSCF calculations comprises 10 electrons distributed over 10 orbitals. The latter have been selected in considering the most relevant orbitals of both nitrogen dioxide and methyl radicals and the interacting orbitals between them as well. The shape of the 10 active orbitals employed is similar to those displayed in Figure 1, which are the natural orbitals (NO) obtained from a CASSCF calculation. Note that, in previous studies,[18,19] only an active space of four-electron-in-four-orbital was used in MCSCF computations.

All the single-reference MO methods employed, either HF or correlated MP2 and CCSD(T), invariably led to a TS-tight. Similarly, the DFT/B3LYP methods also gives rise to a tight TS and, thus, concur with the results of Hu et al.[20] To locate the TS-loose, we have been using different geometry optimization techniques, together with various guess starting points and/or Hessians. However, despite extensive attempts, we were not able to reproduce a TS-loose when using CASSCSF(10,10)/(aug)-cc-pVTZ wave functions. At relatively long interfragment distances (>3.5 Å), some first-order saddle points could be found, but they do not correspond at all to a methyl migration but rather to methyl configurational changes. We also carried out CASSCF calculations employing smaller active spaces, having a (4,4) size and being similar to those employed in refs 18 and 19. Smaller sets of basis functions were equally taken, namely, the 4-31G (used in ref 19) and 6-31G(d,p) (used in ref 18), but again, despite our intensive and careful searching, we failed to locate a TS-loose.

There has been a suggestion by a reviewer that a loose-TS could resemble a TS for the $CH_3 + NO_2 \rightarrow CH_3ONO$ recombination. Despite extensive searches for such a TS, again no relevant saddle point(s) could be found. In view of its nonexistence, the eventual question on the identity of a loose-TS could not be posed.

Geometrical parameters of the TS-tight are shown in Figure 2, including the values obtained at the CCSD(T)/cc-pVDZ, B3LYP/cc-pVDZ, and CASSCF(10,10)/(aug)-cc-pVTZ levels. For the sake of simplicity, the HF and MP2 values are omitted. In general, the values are in the same order of magnitude, and consistent with each other. The most sensitive parameters are, as expected, the interdistances C−N and CO. In going from one level to another, the variations on these distances are relatively small, amounting up to 0.05−0.06 Å.

TABLE 1: Relative Energies of Species Included in the Potential Energy Surface of $CH_3 + NO_2$

	relative energies (kcal/mol)									
species	B3LYP/ 6-311G(d,p)	MP4/ 6-311G(d,p)	MP4/ 6-311+G(d,p)	MP4/ 6-311G(2df,p)	CCSD(T)/ 6-311G(d,p)	MP2/ 6-11G(3df,2p)	G2M[a]	B3LYP[b,c] cc-pVDZ	CCSD(T)[b,b] cc-pVDZ	CCSD(T)[b,d] cc-pVTZ
$CH_3O + NO$	−15.1	−12.6	−12.4	−10.5	−19.5	−5.5	−17.3	−14	−19	−19
$CH_2O + HNO$	−35.7	−36.4	−37	−35.8	−43.8	−40	−47.7	−34	−43	−45
$CH_3 + NO_2$	0	0	0	0	0	0	0	0	0	0
$HCNO + H_2O$	−51	−49.7	−53.2	−52	−51.8	−65	−62	−46	−48	−58
CH_3ONO	−50.4	−48.2	−48.8	−50.7	−53.4	−53.7	−59.9	−51	−52	−61
CH_3NO_2	−52.7	−50.2	−51.3	−53.6	−53.8	−61	−62.3	−53	−52	−63
$CH_3N(O)OH$	−38.5	−31.1	−32.7	−36.3	−36.7	−44	−47.3	−38	−34	−48
CH_2ONOH								−24	−26	−39
CH_2OHNO								−50	−55	−65
TS_2	13.3	18.7	15.2	14.3	15.1	11.9	3.9	13	16	6
TS_3	−12	−12.3	−13.6	−13.5	−12.7	−16.5	−18.7	−13	−13	−15
TS_4	8.9	14.3	13.6	9.8	10.3	3.6	1.9	6	11	3
TS_5								9	16	9
TS_6								21	17	11
TS_7								−17	−16	−24
TS_8								24	21	11

[a] G2M calculations were performed by Eva Riihimaki (ref 37). [b] ZPE values derived from B3LYP/cc-pVDZ. [c] Using optimized geometries at the indicated level. [d] Single-point energy calculations using the CCSD(T)/cc-pVDZ geometries.

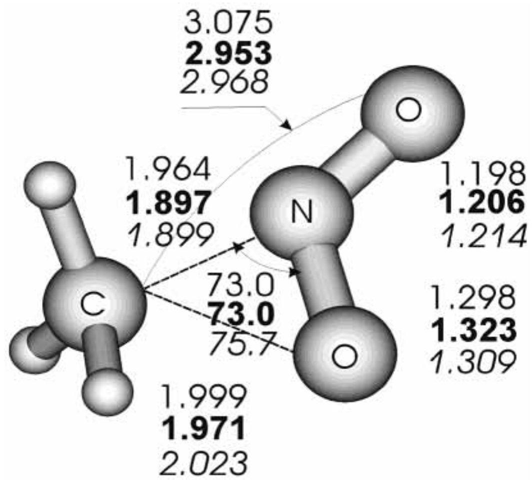


Figure 2. Selected geometrical parameters of the TS for 1,2-methyl migration connecting nitromethane and methyl nitrite optimized using three distinct levels of theory. The entries of values are upper (normal type), B3LYP/cc-pVDZ; middle (boldface), CCSD(T)/cc-pVDZ; and lower (italic), CASSCF(10,10)/(aug)-cc-pVTZ (cc-pVTZ for H and aug-cc-pVTZ for C, N, and O). Bond lengths are given in angstroms and bond angles in degrees.

It is important to stress that the CASSCF wave function of the TS-tight is effectively dominated by the HF configuration whose coefficient of C_0 is larger than 0.93. This is also reflected in the occupation numbers of the resulting natural orbitals, seen in Figure 1, that are larger than 1.9 electrons in all occupied orbitals.

At this stage of the study, we ought to conclude that, when using available quantum chemical methods, we can locate only a TS-tight for methyl migration linking NMT and MNT. We are thus not able to confirm the existence of a TS-loose as previously reported from MCSCF(4,4) computations.[18,19]

When evaluating the difference between the energy barrier via TS-tight and the C−N bond dissociation of NMT, we have considered various levels of theory, namely, the perturbation theory MPn and the coupled-cluster theory CCSD(T), with different basis sets ranging from 6 to 311G(d,p) to 6-311G-(3df,2p). A modified G2M[34] method was also applied. As shown by the results summarized in Table 1 (TS-tight becoming here TS_2), the *TS for 1,2-methyl migration is consistently higher in energy than the $CH_3 + NO_2$ dissociation limit*, irrespective of the level employed. Nevertheless, it is worth noting that the lower levels provide, on one hand, larger difference for both quantities, up to 15−18 kcal/mol, and on the other hand, significantly smaller C−N bond dissociation energy. For the relative position between the TS and the limit, the smallest value of 3.9 kcal/mol, obtained here from a G2M approach, is comparable to that of 2.7 kcal/mol derived from a G2MP2 level by Hu et al.[20]

As far as the C−N bond dissociation energy is concerned, the values of 62.3 kcal/mol suggested by G2M and 63.0 kcal/mol by CCSD(T)/cc-pVTZ (Table 1) are equally in line with that of 61.9 kcal/mol obtained by a G2MP2 method.[20] In both cases, the small deviation of about 1 kcal/mol arises no doubt from the use of different geometries and, in part, from zero-point energies in two modified G2 procedures.

To evaluate further both quantities, we also carried out single-point electronic energy calculations making use of an internally contracted multireference configuration interaction method (MRCI),[36] which included all the single and double excitations as well as the quadruple corrections, that is, the MRCISD-(10,10)+Q/(aug)-cc-pVTZ//CASSCF(10,10)/cc-pVDZ + ZPE level, where "Q" stands for the Davidson corrections for quadruple substitutions. The active space selected for the MRCI treatment was the same as that for the resulting CASSCF wave functions that, in addition, were used as references for generating electronic configurations. At this level of theory, the energy difference between TS-tight and $CH_3 + NO_2$ turns out to be 10.5 kcal/mol, whereas the C−N bond energy is evaluated to be 59.2 kcal/mol. Note that, for the latter quantity, the CASSCF-(10,10), CASPT2(10,10), and MRCISD methods result in the values of 68.0, 51.8, and 59.9 kcal/mol, respectively. Thus, the corresponding quadruple correction is rather small.

When all the calculated values available in the present study and in ref 20 are taken into account, it seems reasonable to suggest that the C−N bond dissociation energy in NMT amounts to $BDE(CH_3{-}NO_2) = 60$ kcal/mol, with a probable error of ±2 kcal/mol, whereas the energy barrier for methyl migration via a tight TS is larger than the latter by, at least, 6 kcal/mol. The calculated BDE value is consistent with the evaluation of Benson et al.[17] (see above).

It is known that, in transfer reactions, a heavy atom tunneling could occur, which in turns might accelerate the migration and

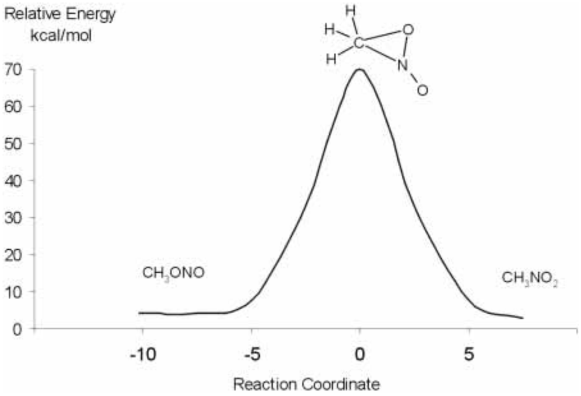


Figure 3. The potential energy profile of the methyl migration connecting nitromethane and methylnitrite along the intrinsic reaction coordinate. Geometries and energies are obtained from B3LYP/cc-pVDZ calculations.

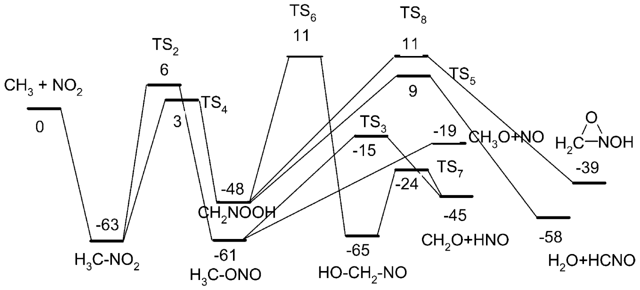


Figure 4. The shape of a portion of the CH_3NO_2 potential energy surface including some lower lying isomers computed at the CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVDZ + ZPE level. Relative energies are given in kcal/mol.

thereby affect the branching ratio for the competing dissociations. To probe such a possibility, Figure 3 displays the intrinsic reaction coordinate pathway of the methyl migration connecting both NMT and MTN isomers using the B3LYP/cc-pvDZ level. At the middle position of the barrier, the barrier width amounts to about five (5) units of the reaction coordinate which is rather sharp. However, without a detailed and appropriate kinetic analysis using a RRKM-type method, it is rather hard to quantitatively evaluate any possible tunneling effect. We point out that such a methyl tunneling needs to be included in any future kinetic treatment.

(B) CH_3NO_2 Potential Energy Surface. As mentioned above, Hu et al.[20] described in much detail this PES. It is not our intention to reexplore here the whole surface but rather a relevant portion of it surrounding the NMT's potential well. The purpose is to verify once more if there is any energetically lower lying exit channel for NMT.

The relative energies of the stationary points on the surface considered were refined by single-point electronic energy computations using the second-order MP2 and fourth-order MP4 perturbation theory,[29] coupled-cluster theory CCSD(T), and also a modified G2M[34] method. The results are listed in Table 1. In general, the relative energy ordering remains internally consistent, even though there are, as expected, various deviations in going from one level to another. Our best estimates for relative energies were thus determined at the level of CCSD(T)/cc-pvTZ//CCSD(T)/cc-pVDZ + ZPE[B3LYP/cc-pVDZ]. The corresponding potential energy profile is schematically displayed in Figure 4. The following points are again worth noting:

(i) In an attempt to search for possible transition structures for recombination reactions of both CH_3 and NO radicals leading to either NMT or MNT, calculations along the C···N and N···O reaction coordinates, respectively, using the CCSD(T) method have been carried out. So far, no such TS could be located, in agreement with earlier studies.[18−20] Thus, it is confirmed that the C−N bond cleavage of NMT corresponds overall to its most favored decomposition channel.

(ii) MNT is estimated to be about 2 kcal/mol *higher* in energy than NMT. In this region of the PES, nitrosomethanol (HO−CH_2−NO) constitutes the lowest lying isomer, being 2 kcal/mol below NMT.

(iii) The formation of NO is possible through an initial NMT−MNT rearrangement followed by a N−O bond cleavage of MNT. Relative to the C−N bond cleavage, this process requires an additional activation energy of about 6 kcal/mol via TS_2 (which is actually the TS-tight seen in Scheme 1).

(iv) The rearrangement of NMT to CH_2NOOH is now associated with the TS_4 which lies marginally below TS_2 (by 3 kcal/mol). The latter isomer is shown to contribute to the formation of water and formaldehyde through slightly more energy-demanding eliminative processes (via TS_5 and TS_6).

(v) In comparing the following pathways: (a) NMT (−63) → TS_2 (6) → MNT (−61) → TS_3 (−15) → $CH_2O + H_2O$ (−45), (b) NMT (−63) → TS_2 (6) → MNT (−61) → CH_3O + NO (−19), and (c) NMT (−63) → TS_4 (3) → CH_2NOOH (−48) → TS_5 (9) → H_2O + HCNO (−58), we could note that both processes a and b involving an initial NMT−MTN isomerization, remain more favored than process c. The position of the TS_5 which is found here to be 3 kcal/mol higher than TS_2, is thus at variance with the results obtained by Hu et al.,[20] which placed TS_5 about 1.7 kcal/mol below TS_2. Note that the latter finding allowed these authors to conclude that the concerted molecular elimination is open, whereas the NMT−MNT isomerization is not. In view of the expected but significant fluctuations of relative energies with respect to the levels of theory, it is apparently not meaningful to make a firm conclusion on the basis of an energy difference of 1−2 kcal/mol calculated at a certain level. It is likely that both channels passing through TS_2 and TS_5 are open and competitive.

3. Concluding Remarks

In the present theoretical study, we have reinvestigated the PES related to the nitromethane−methyl nitrite rearrangement. We found that the 1,2-methyl shift connecting both isomers occurs through a tight transition structure (TS),[14,20] and after careful and intensive attempts, we were not successful in reproducing a loose TS for this process using CASSCF(10,10) wave functions, a clear discrepancy with two earlier theoretical studies.[18,19] The reason for this variance seemingly resides in the selection of the active space(s) for multiconfigurational treatments. However the detailed difference is not clear to us yet.

Regarding the energetic aspect, we should first stress that the C−N bond dissociation of nitromethane is evaluated to be 60 ± 2 kcal/mol, in good agreement with previous experimental and theoretical results.[16,17,20] For the relative energy position between the TS for nitromethane−methyl nitrite isomerization and the $CH_3 + NO_2$ dissociation limit, we have again found that the latter (limit) lies at least 6 kcal/mol below the former (TS).[18,20] This result is in sharp contrast with that of a previous kinetic analysis of experimental data,[15,16] which placed in fact the TS at 5 kcal/mol below the limit (the TS being 55 kcal/mol above nitromethane). We are convinced that such discrepancy came from the fact that, in ref 16, the authors took, for their RRKM analysis, the frequency factors of both the barrier-free C−N bond cleavage and NMT−MNT isomerization channels from the semiempirical MINDO/3 results of ref 13. It appears to be obvious that the latter are not reliable for such purpose.

Thus, the present study does not yet solve the discrepancy which appears to persist but rather puts it in a clearer perspective. Indeed, much effort needs to be invested in both experimental and theoretical sides to reconcile the interpretations. It is also confirmed that both radical recombination reactions are barrierless processes. From the computational point of view, an accurate and consistent evaluation of the frequency factors for simple bond cleavage channels of both isomers, namely, $CH_3NO_2 \rightarrow CH_3 + NO_2$ and $CH_3ONO \rightarrow CH_3O + NO$, that are to be used in any advanced kinetic treatment of the whole process starting from either NMT or MNT, or the reverse process, represents a formidable challenging task, due to the nonexistence of the energy barriers or free energies of activation for relevant processes.[37] Finally, the barrier width of the methyl migration connecting both isomers is relatively small amounting to about five units of the intrinsic reaction coordinate, suggesting a possible heavy atom tunneling.

Acknowledgment. The Leuven and Budapest groups thank the Governments of the Flemish Community of Belgium and Hungary for financial support within their Bilateral Cooperation Agreement (Projects BIL-01/17 and OTKA T034768). M.T.N. was an Emerson fellow of the Emory University, Atlanta, where this work was initiated. M.C.L. acknowledges the support from the U.S. Office of Naval Research under Contract N00014-020C-0292.

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