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Theoretical study of initial reactions of amine $(\text{CH}_3)_n\text{NH}_{(3-n)}$ ($n = 1, 2, 3$) with ozone

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Keywords

Rate constants, Methyl amine and biradical O_3 reactions, H-abstraction, Reaction pathway search

ABSTRACT

We performed a systematic reaction path search for the initial reactions of methyl amine with ozone (O_3) in gas phase, by using a single-component artificial force induced reaction (SC-AFIR) method. The reaction rate constants calculated by UCCSD(T) energies and UM062X frequencies, agreed well with the experimental observation. This agreement could support the proposed reaction pathway for H-abstraction from amine as an initial step. The high rate constant for the reaction of trimethyl amine with O_3 could be explained by a formation of the cyclic transition state structure.

1. Introduction

Alkyl amines are hazardous chemical substances with an unpleasant smell, which are released into the atmosphere from a variety of sources, *e.g.* animal husbandry and biomass burning [1]. Recent use of organic amines as an absorption solvent in carbon capture and storage (CCS) technology [1, 2] is an additional source for aliphatic amines. For example, methyl amine (MA: CH_3NH_2) is a potential degradation product of monoethanol amine that is one of the proposed solvents [3]. Once alkyl amines are released into the atmosphere, they are removed by heterogeneous uptake into aerosols and water droplets, and also through the gas-phase reactions with atmospheric oxidants such as OH radical. Methyl amines were reported to react with OH radical where the observed reaction rate constants at 298 K were $1.9 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$ for MA, $6.3 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$ for dimethyl amine [DMA: $(\text{CH}_3)_2\text{NH}$], and $5.8 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$ for trimethyl amine [TMA: $(\text{CH}_3)_3\text{N}$] [4]. The experimentally observed kinetics was well reproduced by the highly-sophisticated theoretical computations at the CCSD(T*)-F12a/aug-cc-pVTZ//MP2/aug-cc-pVTZ level [4].

Ozone (O_3) is another important atmospheric oxidant and can initiate the oxidation of organic compounds containing a $\text{C}=\text{C}$ bond in the atmosphere. The reactions of alkene with O_3 are considered to proceed *via* Criegee mechanism (symmetric mechanism) efficiently [5]. Alkyl amines are also known to react with O_3 , although they do not contain a $\text{C}=\text{C}$ bond [6, 7]. In other words, for the reaction of amine with O_3 , the reaction by symmetric mechanism does not occur but a slow biradical reaction is considerable. One can get insight to the mechanism for the reaction of amine with O_3 through a comparison with the reaction of the olefin and O_3 which is one of the important reactions between organic compounds and O_3 [5]. For example, the rate constants for the reactions of MA, DMA, and TMA with O_3 at 298 K have been reported to be

7.4×10^{-21} , 1.7×10^{-18} , and $7.8 \times 10^{-18} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$, respectively [6]. First, we note that the rate constants increase in going from primary to tertiary methyl amines. The rate constant for the TMA reaction is larger than that for the DMA reaction, which is clearly contrast to the case of the reactions with OH radical. Second, although the symmetric mechanism is not considerable for the reaction between alkyl amine and O_3 , the rate constants for reactions of DMA and TMA with O_3 are comparable to those for reactions of ethene and propene with O_3 (1.6×10^{-18} and $1.0 \times 10^{-17} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$, respectively) [8]. Furthermore, the rate constant for the reaction of triethyl amine with O_3 was reported as $8.2 \times 10^{-17} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$. These rate constants indicate that the reaction with O_3 cannot be negligible as an atmospheric loss of triethyl amine [7].

As to the reaction of methyl amines with O_3 , Tuazon et al. [6] proposed that the reaction proceeds via energy-rich amine oxide intermediate to explain their observed reaction products. Their proposed mechanism is informative to explain the product distribution, but it is still difficult to understand the characteristics of the values and trend of the rate constant. Theoretically, quantum chemical calculations have been carried out for the reaction of MA with O_3 at the restricted (R)B3LYP level [9]. This computational study clarified the existence of six different products, but it did not investigate the processes involving (bi)radical electronic species. It is still required to investigate the reaction processes including molecular systems with a radical character to understand the experimentally observed feature in rate constants of the reactions of methyl amines with O_3 .

In this study, we investigate the initial steps of the reactions of the most basic primary, secondary and tertiary amines $[(\text{CH}_3)_n\text{NH}_{(3-n)} (n = 1, 2, 3)]$ with O_3 by theoretical calculations to reveal the mechanism of these reactions. We systematically explore the pathways for reactions between the amines and O_3 by using the single component artificial force induced reaction (SC-

AFIR) [10] method based on density functional theory (DFT) calculations with spin-unrestricted wave functions to examine the reactions involving (bi)radical electronic structures. By applying the SC-AFIR approach, we determine the transition state (TS) structures for structural transformations of a lot of minima including those of radical species, and discuss the reaction mechanism and the rate constant of the initial processes.

2. Computational details

First we performed reaction path searches for the reactions between the amine and O₃ by SC-AFIR at the UB3LYP [11] level with 6-31G* basis sets [12] (to save the computational cost), using Gaussian 09 program [13] and a developmental version of the Global Reaction Route Mapping (GRRM) program [14]. The model collision energy parameter γ of SC-AFIR was set to 100 kJ mol⁻¹. During the automated search, the molecular orbital stability check was done in a certain interval by giving the keyword "stable=opt" in Gaussian 09 inputs, to detect (bi)radical electronic characters. This treatment allowed for finding equilibrium (EQ) and TS structures having the biradical open-shell singlet character with $\langle S^2 \rangle$ more than zero. By employing a *NoBondRearrange* keyword in the GRRM program, the searches were carried out only from the structures which had the same bond connectivity as the initial geometry, i.e. the pre-reaction complexes between the amine and O₃.

After the SC-AFIR searches, we re-optimized the obtained EQ and TS structures at the level of UM062X [15] with aug-cc-pVDZ basis sets [16, 17] using the high-grid option Int(Grid=UltraFine) in Gaussian 09 [13] and *RePath* and *ReStruct* keywords in GRRM [14] for automatic re-optimization. Such a two-step procedure was adopted assuming that all paths at the

UM062X/aug-cc-pVDZ level also exist at the UB3LYP/6-31G* level, in order to accelerate the entire calculation significantly. The intrinsic reaction coordinate (IRC) calculations [18] were also performed to check the connectivity of EQs and TSs. Each of all initial (elementary) reactions obtained in this study was based on two EQs such as pre-reaction complex (amine...O₃ non-covalent bond formation) and intermediate (amine...O₃ covalent bond formation) connected by the IRC via one TS. All the energy values for EQ and TS were given as those relative to the dissociation limits of the amine (one of MA, DMA or TMA) and O₃.

Finally, we estimated the rate constants at 1 atm and 298.15 K, based on a transition state theory (TST) for bond-dissociation or migration reactions with the partition functions from harmonic frequencies at the UM062X/aug-cc-pVDZ level, with the relative energy estimated by high-level methods, UCCSD(T)/aug-cc-pVDZ, UCCSD/aug-cc-pVDZ, and UM06-2X/aug-cc-pVDZ. For UCCSD [19-21] and UCCSD(T) [22] energy calculations, we used the initial molecular orbital guess calculated at the UHF/aug-cc-pVDZ level with "stable=opt" option in Gaussian 09. We evaluated the total rate constant as a sum of the rate constants of all elementary reactions, including both bond-dissociation and migration reactions, in the initial step of the reactions.

3. Results and discussion

The present SC-AFIR calculations have clarified that the initial reactions of amine (MA, DMA, or TMA) with O₃ consist of (I) H-abstraction from methyl groups by O₃, (II) H-abstraction from an amino group by O₃, and (III) covalent N-O bond formation between amino group and O₃ with H-abstraction from an amino group. According to the present calculations, TS

structures were located for MA + O₃ (reaction I, II), for DMA + O₃ (reaction I, II, III), and for TMA + O₃ (reaction I). Figs. 1, 2, and 3 show the Gibbs free energy diagram of the reactions with the lowest and second lowest TSs in the initial reactions of MA + O₃, DMA + O₃, and TMA + O₃, respectively. As shown in these Figures, the energy levels of the pre-reaction complexes are higher than the respective dissociation limits in all cases, and thus, the pre-reaction complexes are not important from the viewpoint of kinetics.

In the initial H-abstraction reactions of MA with O₃, we located two TSs for the reaction I and three TSs for the reaction II at the UM062X/aug-cc-pVDZ level. Fig. 1 shows the Gibbs free energy diagram of the reaction I via TS1/4 and the reaction II via TS2/6 for MA + O₃, where TS*k*/*l* denotes a transition state that connects a pre-reaction complex EQ*k* and an intermediate EQ*l* through an IRC pathway. Fig. S1 complements equilibrium structures of three pre-reaction complexes (EQ1-3) and four intermediates (EQ4-7) as well as five TS structures. The pre-reaction complexes consist of amine and O₃ interacting with hydrogen bonds, and the previously reported four-membered ring structure consisting of one nitrogen atom in MA and three oxygen atoms in O₃ at the RB3LYP/6-311++G(3df,3pd) level [9] was not found in the present search. As intermediates, EQ4 and EQ5 are produced by H-abstraction from a methyl group (reaction I) while EQ6 and EQ7 are produced by H-abstraction from an amino group (reaction II). The diradical electronic state for O₃ leads to O₃H radical formation as an intermediate, which was not stable at the RB3LYP level [9]. The use of "stable=opt" option to describe (bi)radical electronic characters is a key approach for searching the reaction pathway with O₃ without using multi-reference wave functions. This point will be discussed later.

Fig. S1 also shows the free energies of the respective EQs and TSs, relative to the dissociation limit of MA + O₃, calculated with a condition of 1 atm and 298.15 K at the

UCCSD(T)//UM062X/aug-cc-pVDZ level (see Tables S1-S3 for the corresponding electronic and zero-point vibrational energies). The electronic energies of the pre-reaction complexes, EQ1, EQ2, and EQ3, relative to the dissociation limit, were calculated as -9.7, -11.7, and -8.2 kJ mol⁻¹, respectively, while the free energies were calculated as 29.9, 33.0, and 30.8 kJ mol⁻¹, respectively. The energies for EQ4 and EQ5 (CH₂NH₂...O₃H) are lower than those for EQ6 and EQ7 (CH₃NH...O₃H). The free energies at TS for H-abstraction from a methyl group are lower than those for H-abstraction from an amino group. The energy levels of the lowest TSs in Fig. 1 indicate that the reaction of MA with O₃ is very slow [2, 6]. In a previous theoretical study on the reaction of MA with O₃ at the RB3LYP/6-311++G(3df,3pd) level [9], two TSs were reported for the initial reactions. One TS has the nitrogen atom in CH₂NH₂ interacting with O₃H, while another TS is assigned to the reaction III. It is noted that RB3LYP calculations on the singlet states cannot describe a radical character of electronic structures for CH₂NH₂...O₃H and CH₃NH...O₃H, and does stabilize the electronic structures with covalent bonds for CH₃N(O₃H)H and HO₃CH₂NH₂ that are initial intermediate equilibrium structures.

As to the initial step of the reactions between DMA and O₃, we have located five, three and one TSs for H-abstractions from methyl groups (reaction I) and from an amino group (reaction II), and for the covalent bond formation (reaction III), respectively (Figs. 2 and S2). The free energies of the respective EQs and TSs are also shown in Fig. S2. The structures of TS2/8 in Fig. 2 and TS2/7 and TS3/8 in Fig. S2 suggest that energetically stable EQ8 and EQ7 with a C-O covalent bond are produced after H-abstraction from the pre-reaction complexes *via* one TS. This indicates that the less stable O₃H fragment is bound to a CH₂ moiety of the amine radical. The energy of TS4/10 (Fig. 2b) is the highest among nine TS structures shown in Fig. S2. The present results suggest that the contribution of reaction III seems small, although Tuazon

and co-workers [6] proposed that the reaction is initiated from the N-O covalent bond formation, similar with the reaction of alkylamines and triplet oxygen atom $O(P^3)$ [23]. The free energies of TSs for DMA and O_3 are lower than those for MA and O_3 (Figs. 2 and 1, respectively). The lower free energies at TSs mean the higher reactivity of DMA than MA for the reaction with O_3 [6].

As to the initial step of the reaction of TMA with O_3 , we located three pre-reaction complexes and four TS structures for the H-abstraction from methyl group (reaction I). The located EQ and TS structures and their free energies are shown in Figs. 3 and S3. The pre-reaction complexes EQ1-3 are connected to the structure having a C-O covalent bond (EQ5) *via* TSs by IRC. The pre-reaction complex EQ2 is also connected to the complex with O_3H substructure (EQ4) *via* one TS. Furthermore, as well as the DMA reaction with O_3 , the free energies of TSs for the reaction of TMA with O_3 are much lower than those for MA with O_3 (Figs. 3 and 1, respectively).

As discussed on the reaction mechanism of MA + O_3 above, RB3LYP cannot describe a radical character of electronic structure with singlet state, and the broken-symmetry treatment using spin-unrestricted wavefunctions is required for an open-shell singlet system. To show the significance of this broken-symmetry treatment, the expectation values of the spin-square operator, $\langle S^2 \rangle$, are given for all the stationary points of the reactions of MA + O_3 (Table S1), DMA + O_3 (Table S2), and TMA + O_3 (Table S3) in supporting information. In the ideal case, $\langle S^2 \rangle$ should be 0 for closed-shell singlet, while it can change to non-zero value for open-shell singlet (diradical). As shown in Tables S1-S3, most EQs and TSs show non-zero values of $\langle S^2 \rangle$ which is ranged from 0.4 to 1.0. Therefore, the broken-symmetry treatment is essential for describing the reaction pathways of the present amine-ozone reactions. The diradical electronic

state for O_3 leads to the formation of intermediates with the O_3H radical character. Note the experimental and theoretical study on *cis*- O_3H indicated the formation of OH radical and O_2 [24]. We also verified that the O_3 reactions with DMA and TMA lead to OH radical formations in a preliminary experiment: the reactions between alkylamine and O_3 may be related to OH radical formation.

The rate constants for the reactions of amines (MA, DMA, and TMA) with O_3 were estimated by TST with the TSs in Figs. S1, S2 and S3. The detailed components of the partition functions used for the rate constant calculation are given in Table S4. **Table 1** shows the calculated and available experimental rate constants at room temperature. Only the rate constants calculated at the UCCSD(T) level show the same order of magnitude as the experimental ones (see Table S5). In hydrogen transfer reaction, the tunneling effect plays a significant role. In a conventional scheme, the tunneling effect can be estimated by the Wigner correction based on the Eckart potential. The results are listed in **Table 1**, which were derived from the partition function in Table S7. The tunneling components of the partition functions were calculated in a range of 1.7 ~ 3.9 (MA + O_3), 1.1 ~ 2.9 (DMA + O_3), and 1.1 ~ 1.4 (TMA + O_3), and the reaction rate increases by a factor of 1.75 (MA + O_3), 1.93 (DMA + O_3), and 1.17 (TMA + O_3), as shown in Table 1. This information will be useful for the experimental observation of a kinetic isotope effect associated with isotopically substituted hydrogen atoms (H/D). Another factor to be considered is so-called "variational effect" (deviation of the free energy barrier from the saddle point) [25]. We have checked the free energy profile along the IRC pathways at the UM062X/aug-cc-pVDZ level for all the reactions of DMA + O_3 , since the DMA + O_3 system included reaction I, II, and III. To estimate the position of free energy maxima, normal mode analysis in the geometrical subspace perpendicular to the IRC path tangent was done at several

IRC path points near the corresponding saddle points. The maximum point of the free energy was deviated only one or two step ($<0.21 \text{ \AA u}^{1/2}$) from each respective saddle point, suggesting that the variational effect would not be so effective in the present reactions.

Note that the final computational level chosen in this study is denoted as UCCSD(T)/aug-cc-pVDZ//UM062X/aug-cc-pVDZ. Use of the M062X functional has been justified in previous benchmark studies on atmospheric reactions [26-29]. As shown above, the present computational level was well enough in reproducing the order among the three amines, regarding rate constants of their reactions with O_3 . Furthermore, the present results reproduced fairly well even absolute values of the rate constants. Further improving the accuracy, an investigation with higher computational levels such as CCSD(T*)-F12a/aug-cc-pVTZ//MP2/aug-cc-pVTZ is required [4]. Such a highly accurate calculation is beyond the scope of this study aiming at revealing the origin of the order among the three amines in their reactivity with O_3 .

As well as the low activation barriers for TS listed in Tables S1-S3, the cyclic structural features of TS, as shown in Figs. 2a and 3, play a significant role in accelerating H-abstraction reactions between amines and O_3 . The contributions of multiple structures were discussed by Truhlar's group using the MS-VTST method [30] for H-abstraction reaction by the hydroperoxyl radical (i.e. oxidant) [31]. In addition, the percentage of the contribution for the rate constant in **Table 2** reflects both low activation barriers and the partition functions (Table S4) of which the cyclic TS structure is effective: Cyclic hydrogen bond formations might be also effective to stabilize the TS and to reproduce the experimental results at the UCCSD(T) level, compared with the calculations at the UM062X and UCCSD levels (see Table S6 for further comparisons). Three cyclic TS structures generating from the TMA and O_3 pre-reaction complexes (Fig. S3) had the lower free energies than those for the TS structures from the DMA and O_3 pre-reaction

complexes (Figs. 2a and S2). This corresponds to the larger rate constant for the TMA + O₃ reaction than for the DMA + O₃ reaction, in contrast to the case of the OH radical reactions [4]. The trend of the rate constant between DMA or TMA with O₃ is qualitatively favorable for H-abstraction reactions rather than the reaction mechanism starting from the energy rich N-O covalent bond formation proposed by Tuazon and co-workers [6].

From the calculated results and analyses, we can propose two reaction pathways initiated by H-abstraction from methyl group, which is connected to EQs such as (CH₃)_(n-1)NH_(3-n)(CH₂)...O₃H ($n = 2, 3$) at secondary and tertiary amines. The (bi)radical electronic state for the O₃ is the key of the initial reaction for the H-abstraction reaction as well as the alkyl amine reaction with OH radical [2]. Finally we mention that our preliminary experiments indicate that OH radical is formed in DMA + O₃ and TMA + O₃ reactions.

4. Conclusions

We performed a systematic reaction path search for the initial step of the gas phase reaction of methyl amine with O₃ by using the SC-AFIR method. In quantum chemical calculations, we employed the methodology to treat the biradical electronic character appropriately. Because the Gibbs free energy for the pre-reaction complexes are higher than the dissociation limits, the pre-reaction complexes are not important in determining the rate constant of the initial reactions. The calculated results indicate that the tunneling effect works to increase the rate constant by a factor of 1.75 (MA + O₃), 1.93 (DMA + O₃), and 1.17 (TMA + O₃), while the variational effect seems not so effective and not included in the present evaluation of the reaction rate. The total reaction rate, estimated as the sum of the reaction rates for elementary

processes based on the UCCSD(T) energies and UM062X frequencies for the TSs agrees well with the experimental observations. The faster rate constant for the trimethyl amine reaction with O₃ can be explained by the cyclic TS formations at the initial step of the reactions. This agreement supports the proposed reaction mechanism based on the H-abstraction with biradical O₃ from amine as an initial step rather than the formation of energy-rich amine oxide.

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Table 1. The rate constants ($\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$) calculated for the initial reactions of amine with O_3 based on the UCCSD(T)//UM062X/aug-cc-pVDZ energy with harmonic frequencies at the UM062X/aug-cc-pVDZ level with a condition of 298.15 K.

	Present calculation	With tunneling effect ^a	Expt. ^b
MA + O_3	3.26×10^{-21}	5.70×10^{-21}	$(7.4 \pm 2.4) \times 10^{-21}$
DMA + O_3	3.21×10^{-18}	6.18×10^{-18}	$(1.67 \pm 0.20) \times 10^{-18}$
TMA + O_3	8.78×10^{-18}	1.03×10^{-17}	$(7.84 \pm 0.87) \times 10^{-18}$

^a Table S7 indicates the distribution functions for the Wigner correction based on the Eckart potential and a formula to estimate the tunneling effect. ^b Tuazon et al. [6] at 298 ± 2 K.

Table 2. The ratio of contributions from the respective elementary reactions to the total reaction rate, for the initial reactions of amine with O₃.^a

	TS ^b	ratio (%)
MA + O ₃	TS1/4 (Reaction I)	78.3
	TS2/5 (Reaction I)	19.6
	TS2/6 (Reaction II)	1.3
	TS2/7 (Reaction II)	0.4
	TS3/7 (Reaction II)	0.5
DMA + O ₃	TS1/5 (Reaction I)	0.5
	TS2/7 (Reaction I)	3.2
	TS2/8 ^c (Reaction I)	37.7
	TS3/6 ^c (Reaction I)	13.6
	TS3/8 (Reaction I)	0.3
	TS1/9-1 (Reaction II)	19.2
	TS1/9-2 (Reaction II)	15.2
	TS4/9 (Reaction II)	10.2
	TS4/10 (Reaction III)	0.0
TMA + O ₃	TS1/5 ^c (Reaction I)	21.5
	TS2/5 ^c (Reaction I)	51.6
	TS2/4 ^c (Reaction I)	25.9
	TS3/5 (Reaction I)	1.0

^a The reaction rate constants are available at **Table 1**.

^b The initial reactions of amine with O₃ consist of (I) H-abstraction from methyl groups by O₃, (II) H-abstraction from an amino group by O₃, and (III) covalent N-O bond formation between amino group and O₃ with H-abstraction from an amino group.

^c A cyclic structure is formed *via* hydrogen bonds between oxygen and hydrogen atoms.

Figure captions

Fig. 1. The Gibbs free energy diagram for the MA...O₃ system. EQs include pre-reaction complexes and intermediates connected to the pre-reaction complexes *via* one TS; TS k/l is a transition state that connects EQ k and EQ l by IRC. The free energies of each EQ and TS, relative to the dissociation limit of MA and O₃ (in kJ mol⁻¹), calculated with UCCSD(T)/aug-cc-pVDZ energies and UM062X/aug-cc-pVDZ harmonic frequencies are also shown. Other TSs and EQs are given in Fig. S1.

Fig. 2. The Gibbs free energy diagram for the DMA...O₃ system: (a) reaction I and (b) reactions II and III. The free energies of each EQ and TS, relative to the dissociation limit of DMA and O₃ (in kJ mol⁻¹), calculated with UCCSD(T)/aug-cc-pVDZ energies and UM062X/aug-cc-pVDZ harmonic frequencies are also shown. Other TSs and EQs are given in Fig. S2. TS1/9-1 denotes a transition state between EQ1 and EQ9 with the lowest energy (see Fig. S2).

Fig. 3. The Gibbs free energy diagram for the TMA...O₃ system. The free energies of each EQ and TS, relative to the dissociation limit of TMA and O₃ (in kJ mol⁻¹), calculated with UCCSD(T)/aug-cc-pVDZ energies and UM062X/aug-cc-pVDZ harmonic frequencies are also shown. Other TSs and EQs are given in Fig. S2.

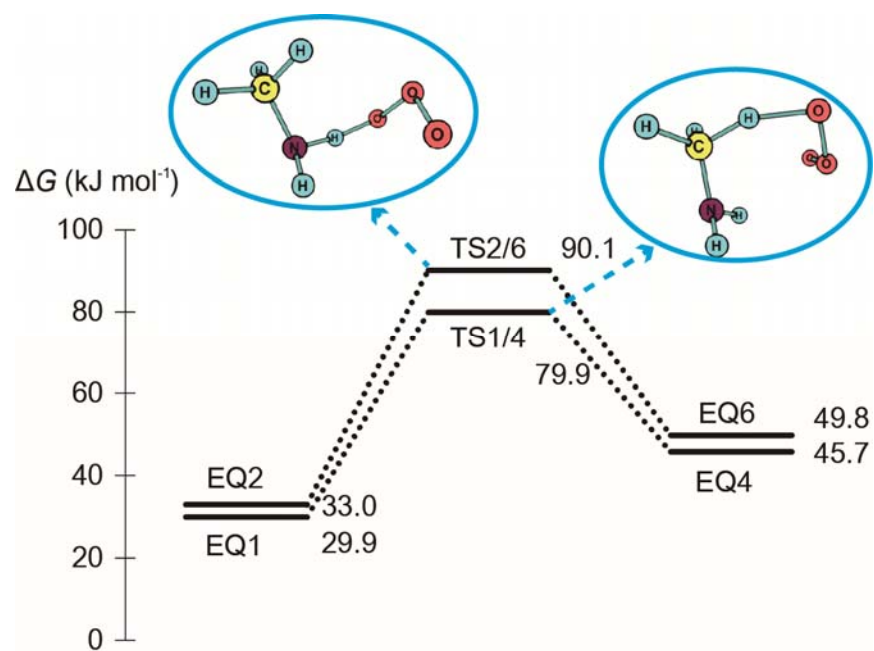


Fig. 1

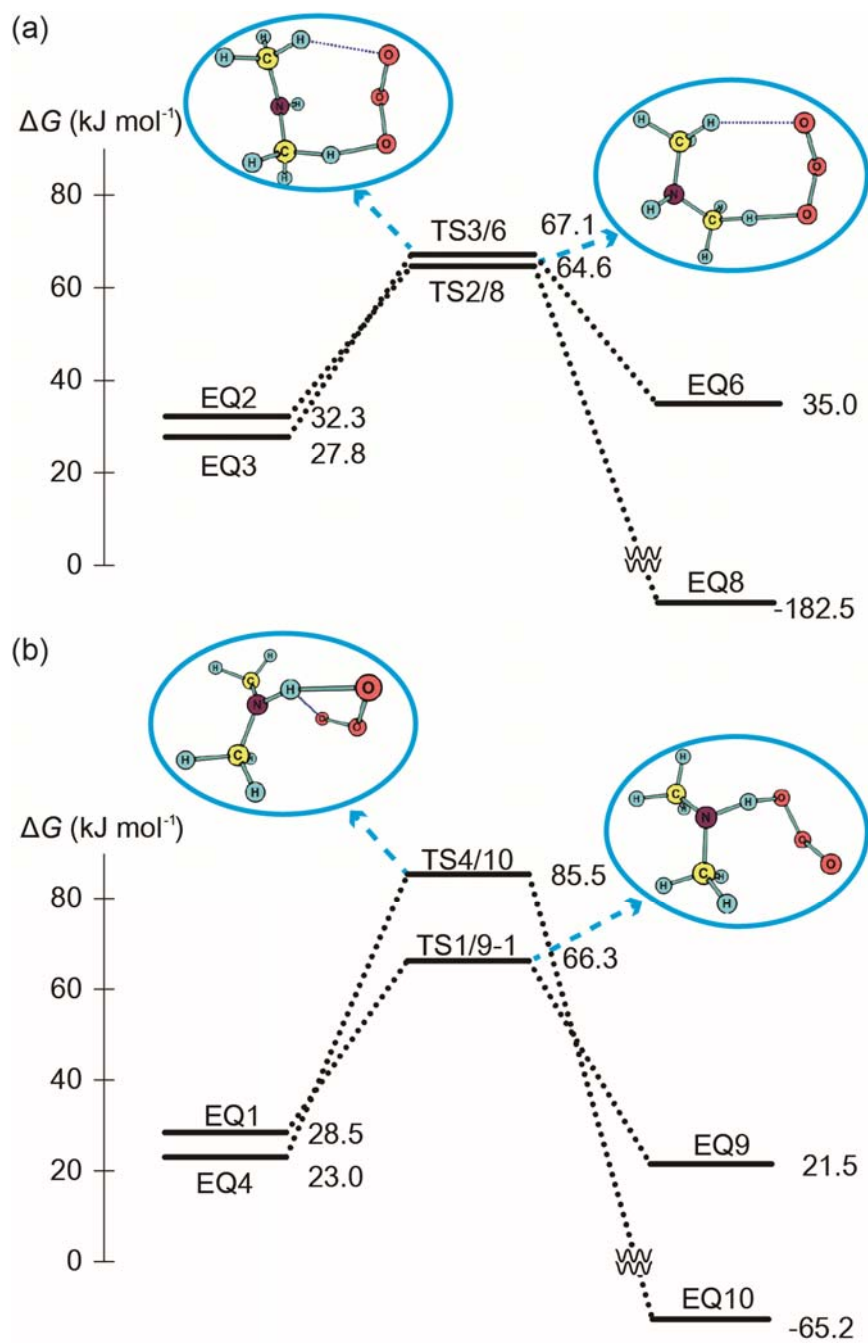


Fig. 2

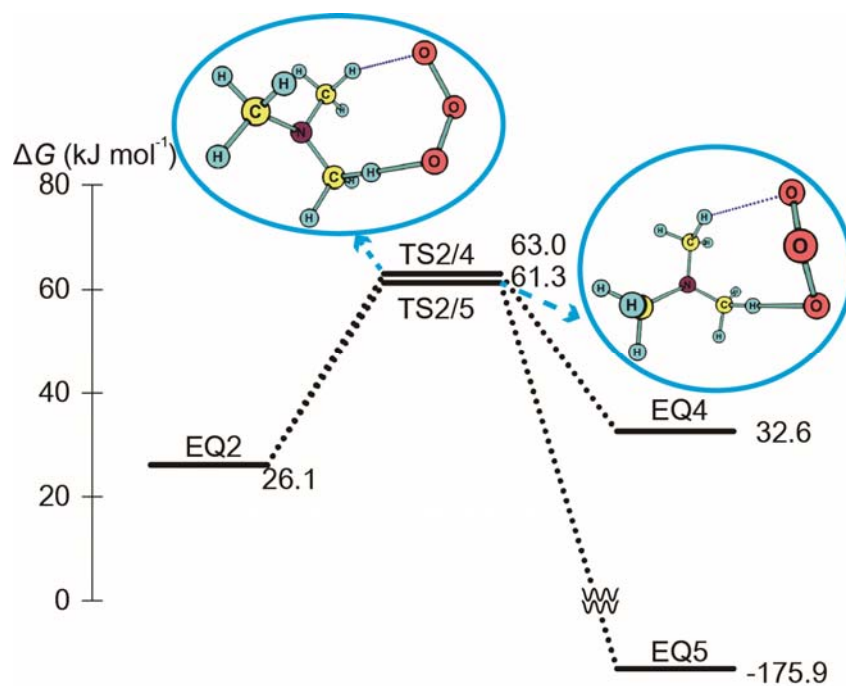


Fig. 3