DFT/Ab initio Study on the Pathways for the Reaction of CH_3SH with NO_3 Radical

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Pathways for hydrogen abstraction (H-abstraction) by the NO_3 radical from the SH and the CH sites of the CH_3SH molecule have been found for the reaction of $CH_3SH + NO_3$. Energy evaluations of the stationary points indicate that H-abstraction exclusively occurs from the SH site via a reactant complex [$CH_3S(H)–ONO_2$] possessing a two-center three-electron (2c–3e) S–O bond. Two oxygen atoms of the NO_3 radical are involved separately in the 2c–3e S–O bond and in H-abstraction from the SH site.

Methanethiol (CH_3SH) is one of the most abundant natural sources of reduced sulfur species in the atmosphere.[1,2] It is widely accepted that the reactions with OH and NO_3 radicals are both highly important for the tropospheric degradation of CH_3SH.[3] For the reaction of $CH_3SH + OH$, computational studies have been reported by several research groups.[4–7] Meanwhile, reports on theoretical evaluations of the reaction of CH_3SH with NO_3 radical are quite few. Very recently, Jee and Tao have reported computational investigation on the reactions of the three major reduced sulfur compounds (CH_3SH, CH_3SCH_3, and CH_3SSCH_3) with the NO_3 radical.[8] After geometry optimizations at the DFT and MP2 levels, they carried out CCSD(T) energy evaluations. For the reaction of $CH_3SH + NO_3$, they reported reaction pathway and energy profile for hydrogen abstraction (H-abstraction) by the NO_3 radical form the SH site of CH_3SH molecule (R1).

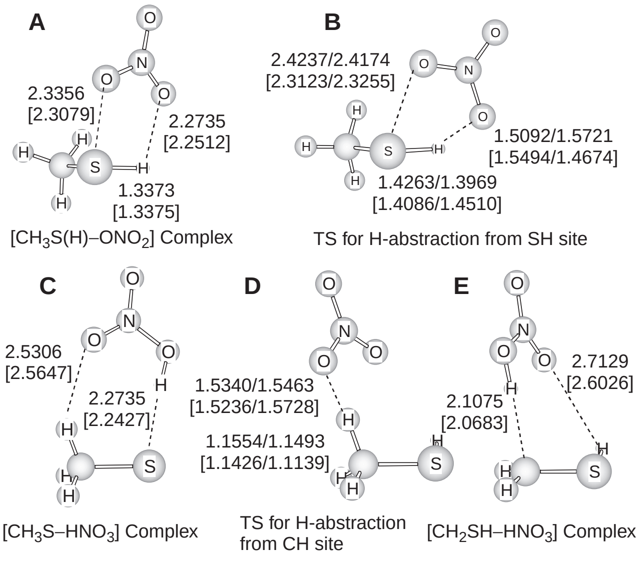
In the present study we examined the potential energy surface for the reaction of $CH_3SH + NO_3$.[9] We found reaction pathways for NO_3 radical H-abstraction not only from the SH site of CH_3SH molecule (R1) but also from the CH site of CH_3SH molecule (R2).

$$CH_3SH + NO_3 \rightarrow CH_3S + HNO_3 \qquad (R1)$$

$$CH_3SH + NO_3 \rightarrow CH_2SH + HNO_3 \qquad (R2)$$

Structures of the stationary points were optimized with BHandHLYP[10,11] and MP2[12] calculations using the 6-311++G(d,p) basis set (Figure 1). IRC calculations suggested that H-abstraction from the SH site (R1) will proceed via reactant complex [$CH_3S(H)–ONO_2$] (Figure 1A) and the transition state (Figure 1B), leading to the product complex [$CH_3S–HNO_3$] (Figure 1C). The structure and the electronic configuration of the reactant complex [$CH_3S(H)–ONO_2$] suggest a two-center three-electron (2c–3e) bond between the sulfur atom of CH_3SH and one of the oxygen atoms of the NO_3 radical.[13] Product complex [$CH_2SH–HNO_3$] (Figure 1E) was located along the reaction coordinate for H-abstraction from the CH site (R2).

In addition to CCSD(T) energy evaluations, we carried out (i) extrapolations of the CCSD(T) energies of the stationary points at the basis set limit, (ii) corrections for basis set superposition errors (BSSEs)[14] for the reactant complex, and (iii) IRC-max[15] calculations. After taking these results into account, we compared the energetics for the H-abstraction pathways (R1) and (R2).



[$CH_3S(H)–ONO_2$] Complex TS for H-abstraction from SH site

[$CH_3S–HNO_3$] Complex TS for H-abstraction from CH site [$CH_2SH–HNO_3$] Complex

Figure 1. Optimized structures of the transition states and the reactant/product complexes for the H-abstraction reaction of CH_3SH and NO_3 radical. The BHandHLYP/6-311++G(d,p)- and MP2/6-311++G(d,p)-optimized (in square brackets) values of the selected bond lengths are given in Å. The second values of the bond lengths for the transition states are those obtained with the IRC-max calculations.

The BHandHLYP and MP2 structures do not differ significantly (Figure 1), and thus we will hereafter refer to the energies obtained for the BHandHLYP-optimized structures. We obtained estimates for the basis set limit energies at the CCSD(T) level[16] [$E_{\text{CCSD(T) basis set limit}}$] in the following manner. By using the results of energy evaluations at the MP2 level with the correlation consistent basis sets, aug-cc-pVXZ; X = T and Q,[17–19] we estimated MP2 correlation energies at the basis set limit [$E^{\text{cor}}_{\text{MP2 basis set limit}}$]. According to the procedure prescribed by Helgaker et al.,[20] the MP2 correlation energies were fitted to the form $a + bX^{-3}$ [$X = 3$ for aug-cc-pVTZ and $X = 4$ for aug-cc-pVQZ] to extrapolate the correlation energies to the MP2 basis set limit. Furthermore, we took the difference between the CCSD(T) and the MP2 energies [$\Delta_{\text{CCSD(T)}}$] calculated with the 6-311++G(2df,p) basis set into account. The estimates for $E_{\text{CCSD(T) basis set limit}}$ were obtained by adding $E^{\text{cor}}_{\text{MP2 basis set limit}}$ and $\Delta_{\text{CCSD(T)}}$ to the HF energy calculated with aug-cc-pVQZ basis set, $E_{\text{HF/aug-cc-pVQZ}}$, i.e., $E_{\text{CCSD(T) basis set limit}} = E_{\text{HF/aug-cc-pVQZ}} + E^{\text{cor}}_{\text{MP2 basis set limit}} + \Delta_{\text{CCSD(T)}}$, (see Table S3).[26]

The counterpoise calculations[14] suggested BSSE of

Table 1. Relative energies of the stationary points[a,b]

	CCSD(T)/6-311++G(2df,p)	$E_{\text{CCSD(T) basis set limit}}$
Reactant[c]	0.00	0.00
$S[CH_3S(H)–ONO_2]$	−6.46	−6.75
	−3.73[d]	−6.31[d]
TS (SH site)	−6.51	−7.29
	−6.31[e]	−7.11[e]
TS (CH site)	2.86	2.67
	2.81[e]	2.62[e]
$[CH_3S–HNO_3]$	−24.41	−24.32
$[CH_2SH–HNO_3]$	−13.60	−13.85
$CH_3S + HNO_3$	−18.07	−17.82
$CH_2SH + HNO_3$	−8.60	−9.97

[a]In kcal/mol, 1 kcal = 4.184 kJ. [b]Relative energy (including zero point energies) were calculated at the BHandHLYP/6-311++G(d,p)-optimized geometries. [c]The electronic and the zero-point energies of the NO_3 radical were calculated at the D_{3h} and the 1S2L C_{2v} geometries, respectively (see Ref. 13). [d]BSSE corrected energy. [e]The energy of the IRC-max point.

ca. 3 kcal/mol for the reactant complex $[CH_3S(H)–ONO_2]$ at CCSD(T)/6-311++G(2df,p) level (Table 1). Meanwhile, the BSSE-corrected and uncorrected CCSD(T) relative energies at the basis set limit for the reactant complex are almost identical to each other, −6.31 and −6.75 kcal/mol, respectively, and hence BSSEs are negligible at the basis set limit (Table 1). In addition, IRC-max[15] calculations at the CCSD(T)/6-311++G(d,p) level were carried out along the BHandHLYP and the MP2 reaction coordinates. The structures of the IRC max points did not differ from those of the transition states (Figures 1B and 1D), and the differences in energy between the transition states and the corresponding IRC-max points were quite small, less than 0.2 kcal/mol (Table 1).

Considering these results, we conclude that the transition state for H-abstraction from the SH site and that for H-abstraction from the CH site are 6–7 kcal/mol lower and ca. 3 kcal/mol higher in energy than the reactants ($CH_3SH + NO_3$), respectively. In addition, the SH site transition state is found to be quite close in energy to the reactant complex $[CH_3S(H)–ONO_2]$ (Table 1 and Figure S1).[26] Accordingly, H-abstraction by NO_3 radical from CH_3SH molecule is energetically much more preferable at the SH site (R1) than at the CH site (R2), which should be closely related with the fact that the $CH_3S–H$ bond is significantly weaker than $H–CH_2SH$ bond (87.4 ± 0.5 vs 93.9 ± 2.0 kcal/mol).[21] In addition, our calculations suggest that two oxygen atoms of the NO_3 radical will be involved separately in the 2c–3e bond and in H-abstraction in the reactant complex $[CH_3S(H)–ONO_2]$, and we can thus consider that H-abstraction from the SH site proceeds in an intramolecular manner (see Figure 1).

Experimental measurements of the kinetics for the $CH_3SH + NO_3$ reaction were carried out several groups. Wallington et al. reported slightly negative temperature dependence of the rate constant ($E/R = 600\,\text{K}$ over the temperature range 280–350 K),[22] while Dlugokencky and Howard reported temperature independence of the rate constant over the temperature range 254–367 K.[23] Mac Leod et al.[24] and Jensen et al.[25] carried out product studies on the $CH_3SH + NO_3$ reaction. They identified CH_3SO_3H, SO_2, HCHO, CH_3ONO_2, and HNO_3 as the reaction products. These experimental results suggest that the reaction of $CH_3SH + NO_3$ should proceed via formation of an initial adduct, followed by H-abstraction from the SH site to form the CH_3S radical. The reaction energy profiles obtained in the present work qualitatively support this mechanism.

In summary, reaction pathways for H-abstraction from the SH and CH sites of the CH_3SH molecule have been found. Energy evaluations of the stationary points suggest that H-abstraction from the CH site is energetically unfavorable and that H-abstraction exclusively occurs at the SH site via a reactant complex. Our calculation results are qualitatively consistent with previously reported experimental results.

This paper is dedicated to Professor Teruaki Mukaiyama on the occasion of his 80th birthday.

References and Notes

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