

Theoretical Studies of the Reaction Mechanisms of CH₃S + NO₂

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Abstract: The potential energy surface for the CH₃S + NO₂ reaction has been studied using the *ab initio* G3 (MP2) method. A variety of possible complexes and saddle points along the minimum energy reaction paths have been characterized at UMP2 (full)/6-31G(d) level. The calculations reveal dominating reaction mechanisms of the title reaction: CH₃S + NO₂ firstly produce intermediate CH₃SONO, then break up into CH₃SO + NO. The results are valuable to understand the atmospheric sulfur compounds oxidation mechanism.

Keywords: *Ab initio*, reaction mechanism, methylthiyl radical (CH₃S).

The low valence sulfur compounds such as CH₃SCH₃, CH₃SH, and CH₃SSCH₃ play an important role in atmospheric chemistry. These compounds are produced biogenically and released into the atmosphere at a rate comparable with emission of SO₂ from human activity. Oxidation of these low valence sulfur compounds is initiated primarily through the reactions with OH•, NO₃ or halogen atoms. The CH₃S radical is believed to be the key intermediate in these oxidative processes in the atmosphere, and it is necessary to understand the reactions of CH₃S with its most likely atmospheric oxidants, such as O₂, O₃, and NO₂.

Although previous experimental studies¹⁻⁶ had reported reaction of CH₃S with NO₂, and confirmed that CH₃SO and NO are the main products, but the reactive mechanism was still unclear. The theoretical study of this reaction also has not appeared. Using the *ab initio* G3 (MP2),⁷ we firstly report almost all the possible reaction pathways of CH₃S with NO₂.

Computations

The geometries of the reactants, products, and transition states were optimized at the MP2(full)/6-31G(d) level. The vibrational frequencies were obtained at the same level. All transition states were subjected to intrinsic reaction coordinate (IRC) calculations. The energetics were obtained *via* the G3(MP2) method, which performs well for both

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reaction heat and barrier height^{7,8} with an accuracy of ± 2 kcal/mol.

Results and Discussion

The reaction of CH₃S with NO₂ can proceed *via* singlet-state (ground-state) PES or *via* triplet-state (excited-state) PES. No matter which PES the reaction occurs, the intermediates (CH₃SNO₂ and CH₃SONO) are produced. Because the calculational triplet-state energies of CH₃SNO₂ and CH₃SONO all are higher 320 kJ/mol than that of singlet-state, NO₂ and CH₃S react mainly on singlet-state PES at room temperature.

G3 (MP2) total energies and the relative energies of various species for reaction of CH₃S with NO₂ are given in **Table 1**. The calculated reaction potential energy surface (PES) of singlet-state is shown in **Figure 1**. The reaction of NO₂ with CH₃S produces directly abundant energetic CH₃SNO₂ and CH₃SONO. Compared with NO₂ and CH₃S, CH₃SNO₂ and CH₃SONO have 167.9 and 157.0 kJ/mol energies respectively, it is possible that they take place unimolecular decomposition and isomerization.

Unimolecular decomposition of CH₃SNO₂

The highly endothermic C—S, N—O, and C—H simple bond scissions of CH₃SNO₂ proceed without transition state and are less important. The five-center decomposition of CH₃SNO₂ produces CH₂S + HONO *via* transition state TS1. The breaking S—N and C—H bonds are elongated 0.024 nm and 0.044 nm, respectively. The forming H—O bond is 0.114 nm and 0.016 nm longer than the equilibrium distance of HONO. As **Figure 1** shown, the channel of CH₂S + HONO not only possesses the lowest barrier, but is the lower endothermic (31.4 KJ/mol) in all decomposition channels of CH₃SNO₂, thus this channel is the most possible reaction pathway from CH₃SNO₂. However this barrier is still much high (145.5 kJ/mol), so this channel does not occur easily. Experiments² had inspected CH₃SNO₂ with a minor product, but without CH₂S or HONO product in smog chamber.

Isomerization of CH₃SNO₂

CH₃SNO₂ rearranges to CH₃SONO or CH₃ON(O)S *via* the concerted O migration from N to another O, or *via* the concerted O,S-migration, but against the barrier (TS3, TS4) exceed 214 kJ/mol. Thus the reaction cannot occur despite many open channels of the isomers.

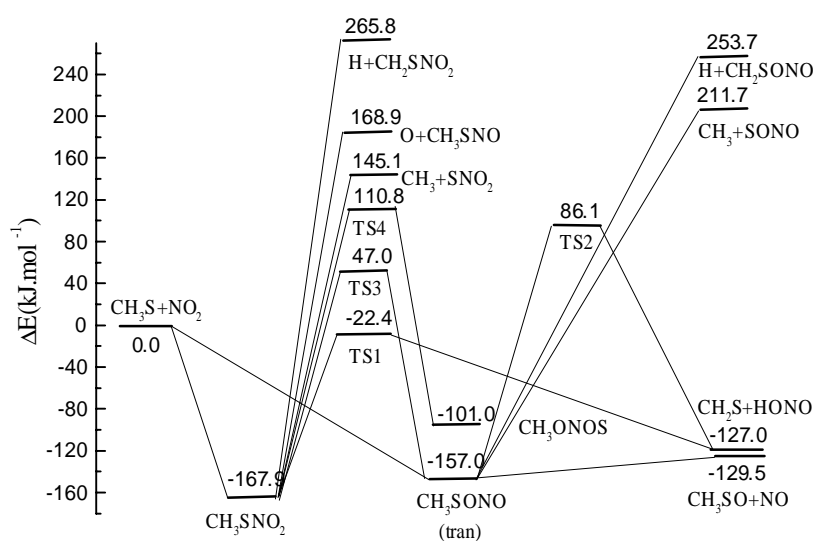
Unimolecular decomposition of CH₃SONO

Three single bond scissions (C—S, C—H, O—N) of CH₃SONO proceed without transition states. The channels of the C—S and C—H bond scissions are less important

Table 1 G3 (MP2) total energies (E_0 , in Hartree) and the relative energies (ΔE , in KJ/mol) of various species for reaction of CH₃S+NO₂

Species	E_0 [G3(MP2)] ^a	ΔE^a
CH ₃ S+NO ₂	-642.38848	0.0
CH ₃ SNO ₂	-642.45242	-167.9
CH ₃ SONO(cis)	-642.44627	-151.7
CH ₃ SONO(tran)	-642.44828	-157.0
CH ₃ ONOS	-642.42694	-101.0
TS1	-642.39700	-22.4
TS2	-642.35567	86.1
TS3	-642.37059	47.0
TS4	-642.34629	110.8
CH ₃ SO +NO	-642.43782	-129.5
CH ₃ +SONO	-642.30783	211.7
CH ₂ S+HONO	-642.43684	-127.0
CH ₃ +SNO ₂	-642.33322	145.1
CH ₃ SNO+O	-642.32415	168.9
CH ₂ SNO ₂ +H	-642.28723	265.8
CH ₂ SONO+H	-642.29187	253.7

^a Both E_0 [G3(MP2)] and ΔE have included the ZPE corrections. ΔE is the difference between the E_0 [G3(MP2)] of various species and the E_0 [G3(MP2)] of the CH₃S + NO₂

Figure 1 The overall profile of the PES (in kJ/mol) for CH₃S+NO₂ system.

because of their high dissociation energies. Only the O—N bond dissociation is valuable. The O—N bond scission channel not only possesses the lower dissociation energy, but also is the least endothermic (27.5 kJ/mol), so this channel occurs easily. The conclusion is consistent with the experimental result. According to the previous works^{3,4}, CH₃SO and NO are the primary products of reaction (CH₃S + NO₂). Calculations show that CH₃SONO possesses abundant energy, which is useful to interpret experimental phenomenon that the title reaction has a weak negative temperature dependence.

CH₃SONO can produce HONO + CH₂S *via* four-center transition state TS2. The barrier of TS2 is 243.1 kJ/mol. In thermodynamic, although this channel is not much endothermic (30.0 KJ/mol), compared with TS1 channel, this reaction pathway is difficult to occur.

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