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doi: 10.3866/PKU.WHXB201304021

www.whxb.pku.edu.cn

CH₃SO₃裂解反应的机理和热力学性质

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摘要: 在G3XMP2//B3LYP/6-311+G(3df,2p)水平上对CH₃SO₃裂解反应的机理进行了研究, 获得了6条通道(10条路径), 并构建了其势能剖面. 同时采用单分子反应理论计算了各个通道在温度200–3000 K区间的速率常数. 研究表明, 在计算温度范围内, CH₃SO₃裂解反应的主产物为P1(CH₃+SO₃), 产物P2(CH₃O+SO₂)和P3(HCHO+HOSO)仅在温度大于3000 K时对总产物有贡献, 而产物P4(CHSO₂+H₂O)、P5(CH₂SO₃+H)和P6(CHSO₃+H₂)贡献相对较少. 将裂解反应总的速率常数拟合为 $k_{\text{total}}=1.40 \times 10^{12} T^{0.15} \exp(-7831.58/T)$. 此外, 根据统计热力学原理, 预测了所有物种的生成焓($\Delta_f H_{298\text{ K}}^\circ$, $\Delta_f H_{0\text{ K}}^\circ$)、熵($S_{298\text{ K}}^\circ$)和热容(C_p , 298–2000 K), 计算的结果与实验值较接近.

关键词: CH₃SO₃; 裂解机理; 热力学性质; 速率常数

中图分类号: O641

Mechanism and Thermodynamic Properties of CH₃SO₃ Decomposition

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Abstract: The mechanism and kinetics of unimolecular decomposition of CH₃SO₃ are studied at the G3XMP2//B3LYP/6-311+G(3df,2p) level of theory. Six possible dissociation channels and potential energy surface for the CH₃SO₃ decomposition are investigated. Rate constants over the temperature range of 200–3000 K are calculated using Rice-Ramsperger-Kassel-Marcus (RRKM) theory. The results indicate that the product P1(CH₃+SO₃) is dominant between 200–3000 K. Products P2(CH₃O+SO₂) and P3(HCHO+HOSO) increase significantly at higher temperatures (>3000 K). Products P4(CHSO₂+H₂O), P5(CH₂SO₃+H), and P6(CHSO₃+H₂) show little formation in the temperature range (200–3000 K). The total rate constant can be expressed as $k_{\text{total}}=1.40 \times 10^{12} T^{0.15} \exp(-7831.58/T)$. Thermodynamic properties including enthalpies of formation ($\Delta_f H_{298\text{ K}}^\circ$, $\Delta_f H_{0\text{ K}}^\circ$), entropies ($S_{298\text{ K}}^\circ$), and heat capacities (C_p , 298–2000 K) of all the minima and transition states are predicted from statistical mechanics, and found to be in good agreement with the available experimental values.

Key Words: CH₃SO₃; Decomposition mechanism; Thermodynamic property; Rate constant

1 Introduction

Environmental problems such as the acid rain formation seriously affecting the health of human beings and animals, are becoming global issues.¹ Acid rain is primarily caused by sulfuric

acid,² whereas sulfur trioxide is the main precursor of sulfuric acid in Earth chemistry. Hence, numerous studies on the atmospheric reaction involving SO₃ have been reported.³

CH₃SO₃ is an important intermediate in the atmospheric oxi-

Received: December 17, 2012; Revised: April 1, 2013; Published on Web: April 2, 2013.

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The project was supported by the National Natural Science Foundation of China (21173139) and Foundation of Shaanxi Education Department (2013JK0667).

国家自然科学基金(21173139)和陕西省教育厅科学研究计划(2013JK0667)资助项目

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dation of CH_3SCH_3 . CH_3SCH_3 is considered as the largest source of natural sulfur to the atmosphere.⁴ The dissociation of CH_3SO_3 , leading to the formation of SO_3 , is a potential direct pathway to the formation of H_2SO_4 , reviewed by Barnes *et al.*⁵ Ray *et al.*⁶ confirmed the formation of CH_3SO_3 in the reaction of NO_2 with CH_3SO_2 using a discharge flow reactor, and the rate constant at 298 K was $(2.2 \pm 1.1) \times 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$. Barnes *et al.*^{7,8} found that CH_3SO_3 could be also produced through the reactions of $\text{CH}_3\text{S}(\text{O})_2\text{OO} + \text{NO}$ and $\text{CH}_3\text{SO}_2 + \text{NO}_2$. Salta *et al.*⁹ have investigated the geometry, formation enthalpy, and isomerization [$\text{CH}_3\text{S}(\text{O})\text{O}_2 \rightarrow \text{CH}_3\text{SO}_3$] of CH_3SO_3 . However, a detailed knowledge of the mechanism and kinetics for the decomposition of CH_3SO_3 is required to assess the environmental impact of CH_3SO_3 . To our regret, no other experimental and theoretical studies on the decomposition of CH_3SO_3 have been performed to date. Furthermore, knowledge on thermodynamic properties is a key element in understanding the rate and selectivity of modeling atmosphere sulfur cycle,¹⁰ whereas little information is available for the thermodynamic properties of CH_3SO_3 decomposition process.

The purpose of this work is to investigate the mechanism and kinetics of the decomposition of CH_3SO_3 . Rate constants are calculated using Rice-Ramsperger-Kassel-Marcus (RRKM) theory. Moreover, the enthalpies of formation, entropies, and heat capacities for all the minima and transition states are predicted.

2 Computational methods

The geometries and frequencies of all the stationary points were calculated using B3LYP method with 6-311+(3df,2p) basis set.^{11–13} All the species were identified for minima (no imaginary frequency) or transition state (one imaginary frequency). Transition state geometries that linked the desired reactants and products along the reaction paths were checked by the intrinsic reaction coordinate (IRC) calculations at the same level. Besides, in order to obtain more reliable energies of each species on the potential energy surface, single point energies were computed by using G3XMP2 method.^{14,15} The total G3XMP2 energy, $E[\text{G3X}(\text{MP2})]$, was given follows:

$$E[\text{G3X}(\text{MP2})] = E[\text{QCISD}(\text{T})/6-31\text{G}(\text{d})\text{-MP2}/6-31\text{G}(\text{d})] + E(\text{MP2}/\text{G3MP2Large-HF}/\text{G3MP2Large}) + E(\text{HF}/\text{G3Xlarge}) + E(\text{HLC}) + E(\text{ZPE})$$

where, $E[\text{QCISD}(\text{T})/6-31\text{G}(\text{d})\text{-MP2}/6-31\text{G}(\text{d})]$ was the energy difference between the QCISD(T)/6-31G(d) and MP2/6-31G(d) methods. $E(\text{MP2}/\text{G3MP2Large-HF}/\text{G3MP2Large})$ was defined as the energy difference between the MP2/G3MP2Large and HF/G3MP2Large methods. $E(\text{HF}/\text{G3Xlarge})$ was the energy calculated by HF/G3Xlarge method. $E(\text{HLC})$ was the empirical higher-level correction energy, where $E(\text{HLC}) = -9.680n_{\text{p}} - 4.715(n_{\text{a}} - n_{\text{p}})$ for the molecules, $E(\text{HLC}) = -10.039n_{\text{p}} - 2.010(n_{\text{a}} - n_{\text{p}})$ for the atoms, n_{a} and n_{p} were the numbers of valence electrons, $n_{\text{a}} \geq n_{\text{p}}$. $E(\text{ZPE})$ was the zero vibrational energy (ZPE). A scaling factor of 0.9854 was used in the calculation

of zero-point energy.¹⁵ All the calculations were performed using the Gaussian 03 program.¹⁶

Theoretical rate constants were calculated with Rice-Ramsperger-Kassel-Marcus (RRKM) theory.^{17,18} Further details of the complete treatment have been described elsewhere. All of the rate constant calculation was employed by using VKLab version 1.0 program.^{19,20}

Standard formation enthalpies ($\Delta_f H_{298\text{K}}^\ominus$, $\Delta_f H_{0\text{K}}^\ominus$), entropies ($S_{298\text{K}}^\ominus$), and heat capacities (C_p) for all the studied species (CH_3SO_3 , intermediates, transition states, and products) were calculated. Enthalpies of formation^{21,22} were predicted based on atomization work reaction by using G3XMP2 method. For any molecule M, the enthalpies of formation ($\Delta_f H$) were given by equation,

$$\Delta_f H_{(\text{g},\text{M})} = \sum_{\text{atoms}} \Delta_f H_{(\text{g})} + H_{(\text{g})}(\text{M}) - \sum_{\text{atoms}} H_{(\text{g})}$$

where $\sum_{\text{atoms}} \Delta_f H_{(\text{g})}$ denotes experimental enthalpies of formation

for the corresponding atoms, with reference enthalpies of formation 221.09 (216.85), 713.50 (714.97), 247.76 (252.13), and 275.77 (280.18) $\text{kJ} \cdot \text{mol}^{-1}$ for H, C, O, and S atom at 298 K (0 K), respectively.²¹ $\sum_{\text{atoms}} H_{(\text{g})}$ stands for the calculated enthalpies

of the isolated atoms, $H_{(\text{g})}(\text{M})$ denotes calculated enthalpy of molecule M. Entropies ($S_{298\text{K}}^\ominus$) and heat capacities (C_p) were obtained according to the statistical mechanics principles in Mulltiwell program,^{23–25} using B3LYP/6-311+G(3df,2p) structures and vibrational frequencies.

3 Results and discussion

Zero point energies, electronic structure energies (E), relative energies (E_{R}) of the reactant, intermediates, transition states, products in the decomposition of CH_3SO_3 are shown in Table S1 (in Supporting Information). Potential energy diagram for the decomposition of CH_3SO_3 obtained at the G3XMP2//B3LYP/6-311+G(3df,2p) level is presented in Fig.1 and Fig.2. Optimized geometries of all the species at the B3LYP/6-311+G(3df,2p) level along with available experimental values are described in Fig.S1. For the molecules [CH_3 ,²⁶ SO_3 ,²⁶ HCHO ,²⁶ H_2O ,²⁷ H_2 ,²⁸ SO_2 ,²⁶ and $\text{CH}_3\text{O}^{\cdot}$], the average absolute deviations of bond lengths and bond angles between the calculated values at the B3LYP/6-311+G(3df,2p) level and the corresponding experiment ones are 0.0010 nm and 0.54° , respectively. So, the B3LYP/6-311+G(3df,2p) method is valid for the calculations of the bond lengths and angles.

3.1 Reaction mechanism

Six dissociation channels are investigated for the decomposition of CH_3SO_3 , which are listed in Scheme 1, where “TS” and “IM” denote transition state and intermediate of the corresponding reaction pathway, respectively.

3.1.1 $\text{CH}_3 + \text{SO}_3$ and $\text{CH}_3\text{O} + \text{SO}_2$ channels

As seen in Scheme 1 and Fig.1, $\text{P1}(\text{CH}_3 + \text{SO}_3)$ is mainly formed through two reaction pathways. One is *via* the direct cleavage of C—S bond and proceeds with a $64.55 \text{ kJ} \cdot \text{mol}^{-1}$ barrier at transition state TS1. The breaking C—S bond in TS1

Fig.1 Potential energy diagram for the formation of P1 and P2 products

The energies are calculated at the G3XMP2//B3LYP/6-311+G(3df,2p) level. The energies are in $\text{kJ}\cdot\text{mol}^{-1}$. Bond lengths are in nm and angles are in degree at the B3LYP/6-311+G(3df,2p) level of theory.

Fig.2 Potential energy diagram for the formation of P3, P4, and P5 products

The energies are calculated at the G3XMP2//B3LYP/6-311+G(3df,2p) level. The energies are in $\text{kJ}\cdot\text{mol}^{-1}$. Bond lengths are in nm and angles are in degree at the B3LYP/6-311+G(3df,2p) level of theory.

is elongated by 0.0163 nm, compared with that in CH_3SO_3 . This reaction is found to be endothermic by $63.54 \text{ kJ}\cdot\text{mol}^{-1}$.

The other pathway occurs *via* the CH_3 migration from S at-

om to the neighboring O atom firstly leading to the formation of CH_3OSO_2 (labeled as IM2), proceeding with a $155.03 \text{ kJ}\cdot\text{mol}^{-1}$ barrier at TS2. The energy of IM2 is $37.87 \text{ kJ}\cdot\text{mol}^{-1}$ low-

Scheme 1 Schematic diagram of proposed paths for the decomposition of CH_3SO_3

er than that of CH_3SO_3 . Subsequently, IM2 dissociates through TS3 producing $\text{P1}(\text{CH}_3 + \text{SO}_3)$ with a barrier of $157.33 \text{ kJ} \cdot \text{mol}^{-1}$. Meanwhile, IM2 can also decompose *via* TS4 producing $\text{P2}(\text{CH}_3\text{O} + \text{SO}_2)$, associating with a barrier height of $78.15 \text{ kJ} \cdot \text{mol}^{-1}$. The breaking S—O bond length is 0.2279 nm , which is 0.0657 nm larger than that in IM2.

In general, the formation of IM2 needs to overcome a high barrier height. Products $\text{P1}(\text{CH}_3 + \text{SO}_3)$ and $\text{P2}(\text{CH}_3\text{O} + \text{SO}_2)$ starting from IM2 are mainly controlled by the first step (the formation of IM2) and expected to be kinetically unfavorable. The direct decomposition of CH_3SO_3 *via* TS1 to product $\text{P1}(\text{CH}_3 + \text{SO}_3)$ is dominant.

3.1.2 IM4 and IM5 channels

As described in Scheme 1 and Fig.2, CH_3SO_3 initially undergoes the H-migration from CH_3 group to O atom forming $\text{CH}_2\text{S}(\text{OH})\text{O}_2$ (labeled as IM4) *via* transition state TS5 with a $133.04 \text{ kJ} \cdot \text{mol}^{-1}$ barrier height. Starting from IM4, two routes are investigated. One takes place *via* transition state TS6 with $129.20 \text{ kJ} \cdot \text{mol}^{-1}$ barrier height producing IM4', which is the same substance as the IM4. The other occurs through TS7 overcoming $210.27 \text{ kJ} \cdot \text{mol}^{-1}$ barrier height forming the isomer $\text{CH}_2(\text{OH})\text{SO}_2$ (labeled as IM5). This process is found to be $-39.58 \text{ kJ} \cdot \text{mol}^{-1}$ exothermic. Once isomer IM5 is formed, four possible reaction pathways may occur. As shown in Fig.2: (1) the first pathway takes place *via* TS8 with a barrier height of $53.05 \text{ kJ} \cdot \text{mol}^{-1}$. In TS8, the breaking $\text{H}(1) - \text{O}(1)$ bond length and the forming $\text{H}(1) - \text{O}(2)$ bond length are 0.1119 and 0.1303 nm , respectively. This process is thermodynamically feasible, and exothermic by $46.06 \text{ kJ} \cdot \text{mol}^{-1}$, forming the most stable product $\text{P3}(\text{HCHO} + \text{HOSO})$ on the potential energy surface, however, kinetically, it is not easy to happen, compared to the path of yielding $\text{P1}(\text{CH}_3 + \text{SO}_3)$; (2) IM5 can be dissociated to $\text{P4}(\text{CHSO}_2 + \text{H}_2\text{O})$ *via* TS9 proceeding with a barrier height of $345.85 \text{ kJ} \cdot \text{mol}^{-1}$; (3) similarly, IM5 can be also decomposed to $\text{P4}(\text{CHSO}_2 + \text{H}_2\text{O})$ through TS10 with a barrier height of $298.47 \text{ kJ} \cdot \text{mol}^{-1}$; (4) IM5 undergoes H-elimination *via* transition state TS11 with $316.60 \text{ kJ} \cdot \text{mol}^{-1}$ barrier height, forming $\text{P5}(\text{CH}_2\text{SO}_3 + \text{H})$. Furthermore, $\text{P5}(\text{CH}_2\text{SO}_3 + \text{H})$ can be also formed by the direct C—H bond rupture of CH_3SO_3 . The reaction proceeds through TS12 associating with a barrier height of $256.87 \text{ kJ} \cdot \text{mol}^{-1}$.

Isomerization of CH_3SO_3 to IM4 is expected to be less im-

portant than the direct dissociation of CH_3SO_3 to $\text{P1}(\text{CH}_3 + \text{SO}_3)$, owing to the high energy transition state of TS5 ($133.04 \text{ kJ} \cdot \text{mol}^{-1}$).

3.1.3 $\text{CHSO}_3 + \text{H}_2$ channel

Product $\text{P6}(\text{CHSO}_3 + \text{H}_2)$ is formed by the H_2 elimination *via* transition state TS13 (in Supporting Information). In TS13, the breaking C—H bonds are elongated by $0.0439 [\text{C} - \text{H}(1)]$ and $0.0720 \text{ nm} [\text{C} - \text{H}(2)]$, and the forming $\text{H}(1) - \text{H}(2)$ bond is shortened by 0.0050 nm , compared with that in CH_3SO_3 . This reaction proceeds with a barrier height of $376.97 \text{ kJ} \cdot \text{mol}^{-1}$ and is endothermic by $231.15 \text{ kJ} \cdot \text{mol}^{-1}$. Compared to the $\text{CH}_3 + \text{SO}_3$ channel, $\text{CHSO}_3 + \text{H}_2$ channel is kinetically unfavorable.

3.2 Thermodynamic properties

Enthalpies of formation ($\Delta_f H_{298 \text{ K}}^\ominus$, $\Delta_f H_0^\ominus$), entropies ($S_{298 \text{ K}}^\ominus$), and heat capacities (C_p) for all the minima and transition states are listed in Table 1. Reliability of the employed methods is detected by comparing the formation enthalpies ($\Delta_f H_{298 \text{ K}}^\ominus$), entropies ($S_{298 \text{ K}}^\ominus$), and heat capacities (C_p , 298 K) of some studied species with available experimental values in Table 2. As listed in Table 2, the calculated $\Delta_f H_{298 \text{ K}}^\ominus$, $S_{298 \text{ K}}^\ominus$, and C_p for the species (CH_3 , SO_3 , HCHO , H_2O , SO_2 , CH_3O , and H_2) at the G3XMP2 level are in line with the corresponding experiment values.^{26,29,30} For example, the maximum deviation and the mean absolute deviation between the calculated $\Delta_f H_{298 \text{ K}}^\ominus$ using G3XMP2 method and the corresponding experimental ones are -5.50 and $3.02 \text{ kJ} \cdot \text{mol}^{-1}$, respectively. Also, the mean absolute deviations of $\Delta_f H_0^\ominus$, $S_{298 \text{ K}}^\ominus$, and C_p (298 K) are $2.27 \text{ kJ} \cdot \text{mol}^{-1}$, 6.89 and $0.71 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, respectively. Moreover, an experimental value for formation enthalpy of HOSO is unavailable, which has been calculated to be $-243.60 \text{ kJ} \cdot \text{mol}^{-1}$ at 0 K using CCSDT(Q) method,³¹ whereas our calculation provides a similar 0 K value of $-244.44 \text{ kJ} \cdot \text{mol}^{-1}$. Besides, our calculated $\Delta_f H_{298 \text{ K}}^\ominus$ (CH_3SO_3) of $-321.47 \text{ kJ} \cdot \text{mol}^{-1}$ is close to the latest theoretical value of $-316.26 \text{ kJ} \cdot \text{mol}^{-1}$ at CBS-QB3 level.⁸ These results can be used for atmosphere sulfur cycle modeling application.

3.3 Rate constant

The direct bond decomposition channels and rate-determining steps of multistep channels are considered for the rate constant calculations using the Rice-Ramsperger-Kassel-Marcus (RRKM) theory over the temperature range of $200\text{--}3000 \text{ K}$. The rate constant calculations of the selected channels are shown in Scheme 2, where k denotes the rate constant of the

Table 1 Enthalpies of formation ($\Delta_f H$), entropies ($S_{298\text{K}}$), and heat capacities (C_p) for the reactant, intermediates, transition states, products for the decomposition of CH₃SO₃

Species	$\Delta_f H/(\text{kJ}\cdot\text{mol}^{-1})$		$S_{298\text{K}}/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	$C_p/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$							
	298 K	0 K		298 K	400 K	600 K	800 K	1000 K	1200 K	1700 K	2000 K
CH ₃ SO ₃	-321.47	-308.45	327.73	87.99	103.11	125.03	139.15	148.97	156.16	167.16	171.02
IM1	-268.93	-257.04	335.87	94.46	108.49	128.18	140.99	150.02	156.74	167.29	171.07
IM2	-360.07	-346.46	328.06	83.62	98.15	120.67	135.95	146.66	154.43	166.24	170.35
IM3	-275.81	-266.95	379.68	95.05	106.68	126.21	139.99	149.86	157.04	167.92	171.65
IM4	-340.75	-327.81	327.94	93.74	109.66	129.95	142.09	150.44	156.74	166.87	170.60
IM5	-361.45	-348.18	329.62	87.11	101.89	123.69	137.80	147.55	154.73	165.94	169.97
IM6	-397.74	-388.29	369.52	96.31	107.73	126.13	139.27	148.89	156.03	167.12	170.98
IM7	-145.11	-137.89	381.78	110.88	121.84	136.12	145.28	152.00	157.33	166.57	170.18
IM8	-91.18	-80.85	368.72	97.15	112.94	134.48	147.50	156.03	162.04	170.86	173.88
TS1	-258.38	-243.64	314.79	82.19	97.02	118.02	131.59	141.08	148.05	158.89	162.71
TS2	-166.82	-152.80	324.32	82.99	97.44	118.15	131.59	140.99	147.92	158.72	162.54
TS3	-200.05	-188.54	353.39	91.39	104.41	122.51	134.27	142.76	149.10	159.26	162.92
TS4	-279.93	-268.00	346.63	84.88	96.68	116.59	130.70	140.78	148.09	159.22	163.00
TS5	-190.68	-174.89	306.10	81.73	98.91	121.97	136.08	145.40	151.91	161.53	164.81
TS6	-212.69	-198.11	316.18	85.05	101.39	123.02	136.29	145.24	151.62	161.24	164.56
TS7	-129.86	-116.76	328.44	90.30	104.83	123.61	134.95	142.93	148.93	158.76	162.41
TS8	-307.57	-294.92	339.40	86.18	99.50	120.46	134.57	144.23	151.03	161.11	164.51
TS9	-12.94	-1.01	344.61	93.32	107.23	125.92	137.63	145.74	151.62	160.86	164.14
TS10	-62.45	-48.55	318.28	90.30	105.84	126.08	138.31	146.50	152.33	161.32	164.51
TS11	-44.94	-30.37	312.69	88.54	105.80	127.64	140.28	148.47	154.18	162.75	165.69
TS12	-65.65	-50.57	309.58	86.23	103.53	125.96	139.15	147.71	153.64	162.50	165.52
TS13	56.91	69.97	323.27	96.31	113.02	132.76	143.60	150.53	155.48	163.17	165.90
CH ₃	144.44	147.76	200.89	39.14	42.34	48.30	53.72	58.63	62.87	70.39	73.25
SO ₃	-398.16	-392.41	272.58	50.86	57.88	67.45	72.95	76.19	78.20	80.68	81.44
HOSO	-248.72	-244.44	281.82	53.05	58.38	65.35	69.34	72.03	74.00	77.41	78.67
HCHO	-114.11	-110.25	225.08	35.32	38.98	47.67	55.36	61.40	65.98	73.08	75.56
CHSO ₂	114.70	119.11	290.98	65.18	73.79	84.59	90.89	94.96	97.82	102.14	103.61
H ₂ O	-241.84	-238.90	189.29	33.60	34.23	36.20	38.43	40.74	43.05	47.84	49.90
CH ₂ SO ₃	-303.37	-290.56	292.45	72.20	87.95	109.45	122.47	131.00	137.00	145.82	148.85
SO ₂	-302.27	-299.71	254.86	39.86	43.39	48.80	52.08	54.05	55.23	56.74	57.20
CH ₃ O	17.77	25.45	237.89	41.16	48.59	61.78	71.90	79.63	85.47	94.67	97.94
CHSO ₃	-79.72	-71.44	299.25	72.74	85.64	101.89	111.09	116.80	120.62	126.08	127.89
H ₂	-5.00	-4.96	130.75	29.23	29.23	29.23	29.40	29.57	30.41	32.13	33.01

corresponding reaction pathway. The total rate constant k_{total} is given by $k_{\text{total}}=k_1+k_2+k_3+k_4+k_5$. The energies, vibrational frequencies, and moments of inertia used in the rate constant calculations are listed in Tables S1, and S2.

Calculated results in Fig.3 show that the rate constants k_1 , k_2 ,

Table 2 Deviations from experiment in the calculated enthalpies of formation ($\Delta_f H$), entropies ($S_{298\text{K}}$), and heat capacities (C_p) of some studied species using G3MP2 method

Species	Deviation			
	$\Delta_f H_{298\text{K}}^{\text{cal}}$ (kJ·mol ⁻¹)	$\Delta_f H_{0\text{K}}^{\text{cal}}$ (kJ·mol ⁻¹)	$S_{298\text{K}}^{\text{cal}}$ (J·mol ⁻¹ ·K ⁻¹)	C_p (298 K) (J·mol ⁻¹ ·K ⁻¹)
CH ₃	-2.18	2.27	6.89	0.71
SO ₃	-2.44	2.14	16.04	0.25
HCHO	-5.50	5.38	14.70	-0.08
H ₂ O	0.00	0.00	0.46	0.00
SO ₂	-5.46	5.42	6.64	0.00
CH ₃ O	0.59	2.94	3.61	-1.39
H ₂	-5.00	4.96	0.04	0.38
MAD	3.02	2.27	6.89	0.71

MAD denotes mean absolute deviation.

k_3 , k_4 , and k_5 increase with the temperature (200–3000 K), which are qualitatively in consistent with their positive barrier heights. As seen in Fig.4, the branching ratio of k_1/k_{total} decreases gradually from 98.8% at 2000 K to 91.7% at 3000 K, while k_2/k_{total} (1.14% at 2000 K) and k_3/k_{total} (0.10% at 2000 K) increase to 6.55% and 1.69% at 3000 K, respectively. The above results indicate that P1(CH₃+SO₃) is main product for all temperatures, products starting from IM2 and IM4 are relatively unimportant at temperatures of 200–2000 K but increase in significance at temperatures of 2000–3000 K. Formations of P5(CH₂SO₃+H) and P6(CHSO₃+H₂) are not significant and the branching ratios of two channels (k_4/k_{total} , 0.06%,

Scheme 2 Selected reaction channels in rate constant calculations

Fig.3 Rate constants plotted as a function of temperature at 200–3000 K

Fig.4 Branching ratios as a function of temperature at 200–3000 K

k_5/k_{total} , 0.006%, 3000 K) are lower than 1% in the whole temperature range.

The calculated rate constants are given over the temperature range of 200–3000 K in the Arrhenius express in unit of s^{-1} as follows:

$$\begin{aligned} k_1 &= 2.03 \times 10^{12} T^{0.09} \exp(-7854.93/T) \\ k_2 &= 4.90 \times 10^{12} T^{0.11} \exp(-18818.00/T) \\ k_3 &= 7.31 \times 10^{12} T^{0.15} \exp(-25031.50/T) \\ k_4 &= 1.10 \times 10^{10} T^{0.80} \exp(-30765.90/T) \\ k_5 &= 8.59 \times 10^8 T^{4.45} \exp(-45249.30/T) \\ k_{\text{total}} &= 1.40 \times 10^{12} T^{0.15} \exp(-7831.58/T) \end{aligned}$$

The above theoretical rate constants are the essential kinetic parameter to estimate the relative importance of the reaction.

4 Conclusions

Reaction mechanism and kinetics of the decomposition of CH_3SO_3 have been investigated at the G3XMP2//B3LYP/6-311+G(3df,2p) level. The main conclusions are summarized as follows.

(1) Ten possible channels are found. Among them, the direct dissociation leading to $\text{CH}_3 + \text{SO}_3$ by direct C—S bond breaking is the most feasible channel. All the other pathways may be less important because of their high barrier heights.

(2) Enthalpies of formation, entropies, and heat capacities

of all the studied species are predicted. The overall agreement between the theoretical values and experimental data is good.

(3) The rate constants are evaluated in the temperature range of 200–3000 K. The formation of $\text{P1}(\text{CH}_3 + \text{SO}_3)$ is dominant through the whole temperature range. Products starting from $\text{IM2}(\text{CH}_3\text{OSO}_2)$ and $\text{IM4}[\text{CH}_2\text{S}(\text{OH})\text{O}_2]$ increase gradually with the temperature and branching ratios reach to 6.55% (k_2/k_{total}) and 1.69% (k_3/k_{total}) at 3000 K, respectively. The contribution of products $\text{P5}(\text{CH}_2\text{SO}_3 + \text{H})$ and $\text{P6}(\text{CHSO}_3 + \text{H}_2)$ to the total reaction is small in the studied temperature range.

Supporting Information: Zero point energies, electronic energies, relative energies (E_R) of all the species at the G3XMP2//B3LYP/6-311+G(3df,2p) level of theory have been listed. The optimized geometries, frequencies, and moments of inertia for all the species at the B3LYP/6-311+G(3df,2p) level of theory have been included. This information is available free of charge via the internet at <http://www.whxb.pku.edu.cn>.

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CH₃SO₃ 裂解反应的机理和热力学性质

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Mechanism and Thermodynamic Properties of CH₃SO₃ Decomposition

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Table S1 Zero point energies (ZPE, Hartrees), electronic energies (E , Hartrees), relative energies (E_R , $\text{kJ}\cdot\text{mol}^{-1}$) of the reactant, intermediates, transition states, products for the decomposition of CH_3SO_3

Species	ZPE ^a	E^b	E_R^b
CH_3SO_3	0.048072	-662.953550	0.00
IM1	0.046720	-662.934059	51.17
IM2	0.050328	-662.967974	-37.87
IM3	0.045005	-662.937810	41.33
IM4	0.047562	-662.960908	-19.32
IM5	0.050143	-662.968629	-39.58
IM6	0.046280	-662.983849	-79.55
IM7	0.044302	-662.888840	169.90
IM8	0.040396	-662.867206	226.70
TS1	0.047387	-662.928966	64.55
TS2	0.047265	-662.894501	155.03
TS3	0.044627	-662.908052	119.46
TS4	0.045991	-662.938207	40.28
TS5	0.043718	-662.902877	133.04
TS6	0.043363	-662.911694	109.89
TS7	0.045855	-662.880819	190.96
TS8	0.043174	-662.948420	13.47
TS9	0.042199	-662.836900	306.27
TS10	0.042442	-662.854946	258.89
TS11	0.040541	-662.848040	277.02
TS12	0.041424	-662.855712	256.87
TS13	0.038407	-662.809969	376.97
P1(CH_3+SO_3)	0.042028	-662.929351	63.53
P2($\text{CH}_3\text{O}+\text{SO}_2$)	0.043106	-662.940592	34.02
P3($\text{HCHO}+\text{HOSO}$)	0.043026	-662.971094	-46.06
P4($\text{CHSO}_2+\text{H}_2\text{O}$)	0.047958	-662.881980	187.91
P5($\text{CH}_2\text{SO}_3+\text{H}$)	0.040110	-662.864484	233.84
P6(CHSO_3+H_2)	0.036663	-662.865509	231.15

^a at the B3LYP/6-311+G(3df,2p) level.

^b at the G3XMP2//B3LYP/6-311+G(3df,2p).

Table S2 Moments of inertia and vibrational frequencies for the reactant, complexes and transition states computed at the B3LYP/6-311+G(3df,2p) level of theory

Species	$I_A, I_B, I_C/\text{a.u.}$	Frequencies (cm^{-1})
CH ₃ SO ₃	342.7, 387.9, 388.06	137, 141, 206, 327, 327, 523, 754, 968, 970, 997, 999, 1082, 1368, 1461, 1461, 3063, 3160, 3160
IM1	362.5, 436.4, 436.5	140, 157, 175, 175, 488, 507, 508, 587, 590, 1026, 1087, 1306, 1307, 1418, 1419, 3092, 3263, 3264
IM2	208.5, 494.6, 667.6	82, 133, 244, 406, 469, 526, 689, 993, 1101, 1174, 1183, 1296, 1468, 1489, 1502, 3050, 3132, 3155
IM3	248.4, 782.2, 912.6	36, 60, 89, 104, 161, 190, 526, 841, 1011, 1110, 1172, 1344, 1357, 1375, 1501, 2877, 2971, 3031
IM4	362.9, 375.8, 389.1	71, 274, 285, 355, 445, 482, 537, 553, 768, 827, 928, 1130, 1186, 1388, 1411, 3160, 3301, 3779
IM5	260.6, 535.7, 656.5	77, 198, 244, 347, 442, 478, 554, 888, 1068, 1126, 1168, 1261, 1275, 1394, 1487, 3048, 3161, 3796
IM6	233.7, 858.5, 1083.5	44, 69, 118, 156, 225, 242, 430, 740, 823, 1138, 1228, 1260, 1287, 1526, 1784, 2937, 3034, 3274
IM7	183.6, 841.3, 1016.5	44, 65, 96, 116, 227, 295, 365, 370, 486, 517, 701, 995, 1242, 1349, 1631, 3254, 3788, 3909
IM8	305.9, 400.8, 461.2	25, 25, 77, 295, 412, 452, 480, 635, 784, 888, 969, 1064, 1163, 1250, 1403, 1463, 3118, 3230
TS1	343.6, 396.0, 413.9	241i, 174, 228, 297, 464, 471, 514, 849, 863, 865, 1156, 1261, 1329, 1399, 1451, 3053, 3189, 3238
TS2	272.3, 458.1, 553.8	675i, 92, 145, 300, 439, 478, 532, 822, 831, 929, 1159, 1225, 1331, 1422, 1457, 3094, 3245, 3246
TS3	246.6, 645.4, 764.9	411i, 42, 64, 98, 417, 470, 487, 521, 524, 852, 963, 1257, 1344, 1417, 1421, 3118, 3294, 3301
TS4	222.3, 685.5, 857.8	192i, 63, 117, 126, 224, 242, 517, 978, 1058, 1118, 1167, 1356, 1368, 1384, 1506, 2915, 2995, 3057
TS5	323.1, 378.5, 420.5	269, 359, 422, 436, 487, 581, 733, 803, 919, 975, 1058, 1203, 1373, 1399, 1813, 3117, 3243
TS6	325.9, 369.2, 418.6	114, 281, 336, 462, 489, 558, 665, 805, 937, 959, 1019, 1067, 1351, 1390, 2130, 3164, 3306
TS7	304.4, 515.1, 594.1	129, 146, 303, 324, 390, 487, 663, 737, 778, 929, 946, 1221, 1389, 1412, 3189, 3324, 3763
TS8	211.7, 777.3, 846.0	1186i, 68, 121, 157, 328, 443, 479, 619, 950, 1057, 1181, 1211, 1315, 1440, 1592, 1724, 3077, 3191
TS9	274.2, 580.8, 686.4	1343i, 36, 114, 297, 313, 376, 440, 450, 639, 824, 959, 1077, 1137, 1272, 1420, 2238, 3128, 3784
TS10	346.4, 424.8, 440.0	1364i, 210, 284, 305, 315, 462, 512, 525, 677, 775, 860, 1013, 1192, 1307, 1398, 1865, 3155, 3775
TS11	287.4, 369.9, 447.6	1130i, 222, 317, 329, 428, 448, 496, 612, 772, 818,

		894, 925, 1028, 1236, 1409, 1418, 3155, 3288
TS12	280.8, 370.2, 453.9	874i, 264, 339, 359, 452, 453, 498, 582, 784, 869, 913, 1053, 1145, 1237, 1404, 1420, 3142, 3269
TS13	338.8, 382.7, 399.6	638i, 135, 263, 278, 406, 467, 491, 517, 563, 703, 728, 774, 1030, 1108, 1212, 1346, 3189, 3648
CH ₃	6.3, 6.3, 12.6	539, 1407, 1407, 3108, 3284, 3284
SO ₃	174.0, 174.1, 348.1	495, 524, 525, 1076, 1399, 1400
HOSO	51.9, 191.6, 242.6	97, 394, 759, 1066, 1178, 3748
HCHO	6.34, 45.9, 52.3	1198, 1266, 1531, 1820, 2886, 2944
CHSO ₂	177.8, 185.2, 361.5	229, 358, 471, 492, 634, 996, 1240, 1360, 3276
H ₂ O	2.2, 4.2, 6.4	1626, 3825, 3929
CH ₂ SO ₃	249.6, 343.7, 460.5	295, 412, 456, 480, 636, 784, 888, 969, 1064, 1164, 1251, 1403, 1463, 3117, 3229
SO ₂	30.1, 175.5, 205.6	519, 1179, 1377
CH ₃ O	11.4, 64.1, 64.5	695, 960, 1109, 1355, 1365, 1512, 2883, 2962, 3006
CHSO ₃	235.3, 336.4, 457.7	304, 391, 442, 448, 527, 713, 802, 1081, 1122, 1255, 1405, 3183
H ₂	1.0, 1.0	4422

Fig.S1 Optimized geometries of all the species at the B3LYP/6-311+G(3df,2p) level of theory. Bond lengths are in nm and angles are in degrees. ^{a-g} are the experimental values [26-29]