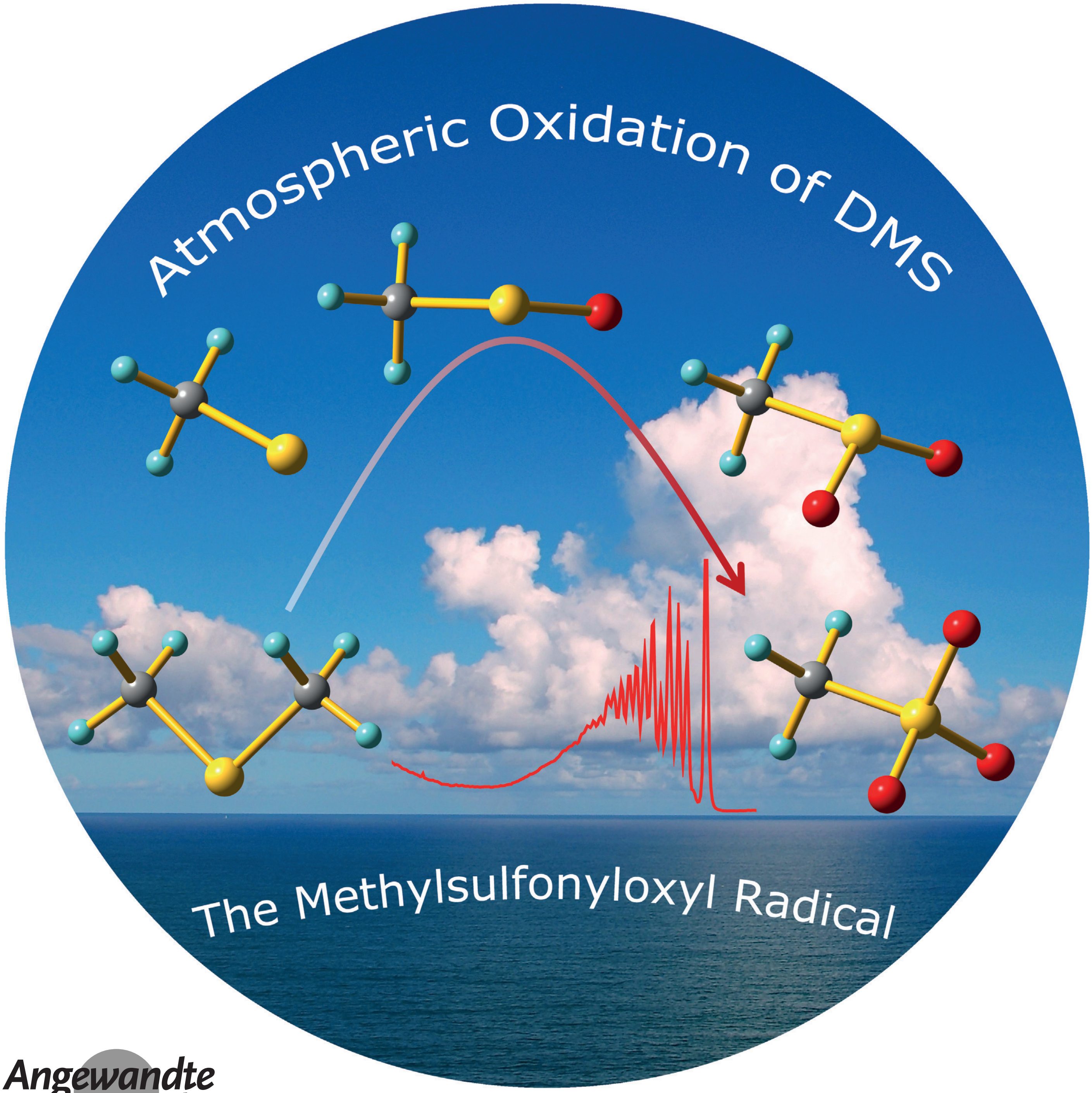
Key Intermediates | Hot Paper

International Edition: DOI: 10.1002/anie.201503776
German Edition: DOI: 10.1002/ange.201503776

The Methylsulfonyloxyl Radical, CH_3SO_3**

Bifeng Zhu, Xiaoqing Zeng, Helmut Beckers,* Joseph S. Francisco,* and Helge Willner*



Angewandte Chemie International Edition

***Abstract:** The methylsulfonyloxyl radical, CH_3SO_3, one of the key intermediates in the atmospheric oxidation of dimethyl sulfide (DMS), was generated by flash pyrolysis of $CH_3SO_2OOSO_2CH_3$ and subsequently isolated in solid noble-gas matrices. The radical has been characterized by UV/Vis and IR spectroscopy and its tautomerization to CH_2SO_3H observed upon irradiation with light of $\lambda \geq 360$ nm.*

Volatile organic sulfur compounds (VOSCs), formed by anthropogenic, geochemical, and biological processes, have been known to play important roles in global warming, acid rain, and cloud formation.[1] Dimethyl sulfide (DMS), one of the most abundant biogenic VOSCs, is emitted from the oceans.[2] Its photooxidation, initiated by HO and NO_3 radicals in the atmosphere, was found to eventually produce CH_3SO_3H (MSA) and H_2SO_4, both of which are key contributors to cloud condensation nuclei (CCN).[3]

Despite there being many laboratory simulations of DMS oxidation, the underlying mechanism remains largely unknown because of the complexity of many reaction channels involving short-lived radical species, and a large discrepancy still exits between the experimental measurements and simulation results.[4] According to the frequently applied kinetic model, the oxidation of DMS in the gas phase occurs through a stepwise formation of radical species CH_3SO_x ($x = 0$–3).[5] The final radical species, CH_3SO_3, can either dissociate into CH_3 and SO_3 followed by H_2SO_4 formation, abstract hydrogen from atmospheric volatile organic compounds R-H to produce MSA, or react with NO_2 to give methylsulfonyl nitrate, $CH_3SO_3NO_2$.[5] In addition to its atmospheric importance, CH_3SO_3 has also been proposed as the key intermediate in the industrial production of MSA from CH_4 and SO_3.[6]

Despite the importance of CH_3SO_3, knowledge about its properties and reactivity is limited. The first spectroscopic evidence for CH_3SO_3 was obtained by laser flash photolysis ($\lambda = 308$ nm) of methylsulfonyl peroxide ($CH_3SO_2OOSO_2CH_3$) in CH_3CN solution.[7] A transient structureless absorption band at $\lambda_{max} \approx 450$ nm with a lifetime of 7–20 μs was assigned to this radical, and its photoinduced ($\lambda_{max} = 480$ nm) dissociation into CH_3 and SO_3 was proposed.[7] A similar transient absorption band was also observed for the putative *p*-toluenesulfonyloxyl radical ($\lambda_{max} = 540$ nm) in CH_3CN solution during laser ($\lambda = 266$ nm) photolysis of iminosulfonates.[8] The formation of CH_3SO_3 was reported by electron beam irradiation (3 MeV) of the $CH_3SO_3^-$ ion in ionic liquids at 77 K,[9] and very recently by the reaction of methylsulfinyl radicals (CH_3SO) and molecular oxygen ($^3O_2$) in solid argon.[10]

The molecular structures and the thermodynamic properties of CH_3SO_3 and various isomers have been calculated at different theoretical levels.[11] According to these calculations, CH_3SO_3 is highly unstable in the gas phase due to the low dissociation barrier for cleavage of the weak C–S bond ($64.6\ kJ\,mol^{-1}$, G3XMP2//B3LYP/6-311+G(3df,2p)). An activation barrier of $133.0\ kJ\,mol^{-1}$ exists for rearrangement by an intramolecular hydrogen shift to the carbon-centered radical CH_2SO_3H, and the barrier for the rearrangement to CH_3OSO_2 through a CH_3 shift is $155.0\ kJ\,mol^{-1}$.[11a]

The key role of CH_3SO_3 in the atmospheric DMS chemistry of the Earth's sulfur cycle prompted us to generate this radical in the gas phase and to explore its spectroscopic properties as well as its photochemistry. As a continuation of our interest in sulfur-containing radicals (e.g. FSO_2[12] and NSO_2[13]), we report herein on the UV/Vis and IR spectra of CH_3SO_3, and its photoinduced tautomerization to CH_2SO_3H in solid noble-gas matrices.

For the flash pyrolysis experiment, freshly sublimed solid $CH_3SO_2OOSO_2CH_3$[14] was placed in a small U-trap and warmed to 50 °C in an Ar gas stream at low pressure. The resulting mixture (peroxide/Ar, ca. 1:1000) was subjected to flash pyrolysis at about 400 °C. The decomposition products were subsequently quenched as a solid Ar matrix at 16 K, and the IR spectrum of the deposit was recorded (see Figure S1 in the Supporting Information). In addition to the known IR bands of the peroxide precursor, the asymmetric stretching band of matrix-isolated SO_3 at $1385.2\ cm^{-1}$ can be easily assigned by comparison with the reported values of 1385.1 and 1388.8 (matrix-site splitting).[15]

Some new weak bands occurred in the region 1500–$700\ cm^{-1}$. To aid their assignments, the pyrolysis of $CH_3SO_2OOSO_2CH_3$ diluted in Ne (ca. 1:1000) was also performed, and all these weak IR bands were reproduced. The transparent Ne matrix enables the observation of a distinct visible absorption band in the region 400–550 nm characteristic of an RSO_3 chromophore (Figure 1). A comparison of this characteristic visible band with those of the analogous species FSO_3[16] and CF_3OSO_3[17] (Figure 1) suggests that the title radical species, CH_3SO_3, was formed by homoleptic fission of the peroxide.

Similar to the visible spectra of FSO_3 and CF_3OSO_3, the strong absorption band of CH_3SO_3 exhibits a well-resolved fine-structure. The $0 \leftarrow 0$ transition (τ_{00}) of the CH_3SO_3 radical (511.2 nm, $19584\ cm^{-1}$) is slightly blue-shifted compared to the UV spectra of FSO_3 ($\tau_{00} = 519.7$ nm, $19246\ cm^{-1}$)[16a] and

---

[*] B. F. Zhu, Prof. Dr. X. Q. Zeng
The Key Lab of Health Chemistry and Molecular Diagnosis of Suzhou, College of Chemistry
Chemical Engineering and Materials Science
Soochow University, Suzhou 215123 (China)
E-mail: xqzeng@suda.edu.cn

Dr. H. Beckers
Freie Universität Berlin, Institut für Chemie und Biochemie
14195 Berlin (Germany)
E-mail: h.beckers@fu-berlin.de

Prof. Dr. J. S. Francisco
Department of Chemistry, Purdue University
West Lafayette, IN 47907 (USA)
E-mail: francisc@purdue.edu

Prof. Dr. H. Willner
FB C—Anorganische Chemie, Bergische Universität Wuppertal
42119 Wuppertal (Germany)

[**] This research was supported in part by the National Natural Science Foundation of China (21372173, 21422304), the Beijing National Laboratory for Molecular Sciences (20140128), and the Deutsche Forschungsgemeinschaft (WI 663/26-1).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201503776.

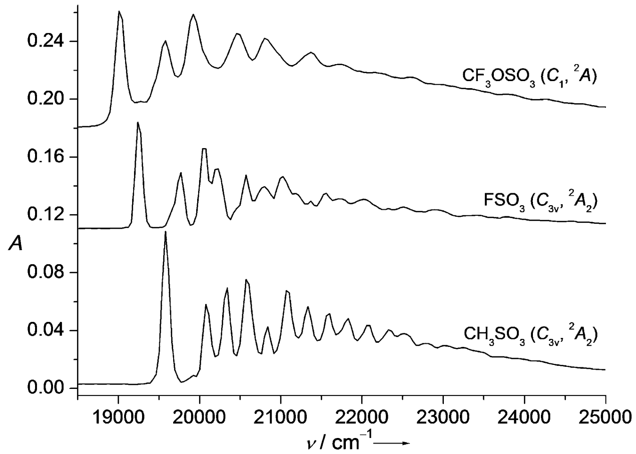


Figure 1. UV/Vis spectra of matrix-isolated sulfonyloxyl radicals in solid neon at 5 K. The spectra of FSO$_3$[16a] and CF$_3$OSO$_3$[17] were taken from the literature.

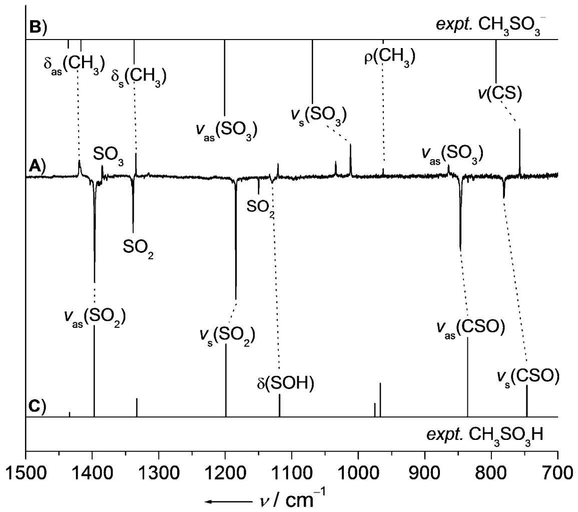


Figure 2. A) IR difference spectrum of the pyrolysis products of CH$_3$S(O)$_2$OOS(O)$_2$CH$_3$ showing the spectral changes after photolysis ($\lambda \geq 360$ nm) in an Ar matrix at 16 K. Bands of the depleted and formed species point upward and downward, respectively. B, C) Simulated IR spectra of CH$_3$SO$_3^-$[18] and CH$_3$SO$_3$H,[19] respectively, according to their experimentally observed IR data.

CF$_3$OSO$_3$ (526.8 nm, 19027 cm^{-1})[17] in Ne matrices. From the fine-structure of the visible band, three vibrational progressions at 1004 ± 10, 747 ± 10, and 505 ± 10 cm^{-1} are assigned to the excited-state vibrational modes ν_s(SO$_3$), ν(CS), and δ_s(SO$_3$), respectively. To confirm the assignment, calculations of the electronic spectrum of CH$_3$SO$_3$ by the EOM-CCSD method (using the CCSD(T)/6-311++G(2df,2pd) optimized geometries) predicted a strong absorption at 483 nm ($f = 0.0262$) for the transition $^2E(2) \leftarrow X^2A_2$ (see Table S1), which is primarily confined to the three oxygen atoms. Two weaker absorptions at 220 ($f = 0.0223$) and 162 nm ($f = 0.0028$) were also calculated for CH$_3$SO$_3$, and indeed a rather broad and structureless band at $\lambda_{max} = 230$ nm was observed in the UV spectrum of the pyrolysis products (see Figure S2). However, other species such as the peroxide precursor and SO$_3$ may also partially contribute to this band.

In accordance with the UV/Vis spectrum, irradiation of the matrix-isolated pyrolysis products with light of $\lambda \geq 360$ nm selectively destroyed the carrier (CH$_3$SO$_3$) of the visible band, and the aforementioned new weak IR bands of the pyrolysis products were depleted with simultaneous appearance of another set of bands in the region 1500–700 cm^{-1}. The IR difference spectrum showing the spectral changes after irradiation is shown in Figure 2 A. To assign the IR bands of CH$_3$SO$_3$ and its photolysis product, ab initio calculations of the IR frequencies of CH$_3$SO$_3$ and its isomers CH$_3$OSO$_2$ and CH$_2$SO$_3$H were performed at the CCSD(T)/6-311++G-(2df,2pd) level of theory (see Table S2).

The degenerate ground-state e-SO$_3$ vibrations are involved in vibronic pseudo-Jahn–Teller interactions, a common feature of C_{3v}-symmetric sulfonyloxyl radicals RSO$_3$ ($^2A_2$).[16] Thus, these vibrations are not well reproduced by calculations of the harmonic vibrational frequencies. This vibronic coupling becomes most instructive on comparing the spectrum of the CH$_3$SO$_3$ radical (Figure 2 A) with that of the CH$_3$SO$_3^-$ ion (Figure 2 B).[18] The observed frequencies for the bending (ν_8/e: 1419.4 cm^{-1}, ν_2/a_1: 1334.6 cm^{-1}) and rocking (ν_9/e: 962.9 cm^{-1}) modes of the CH$_3$ moiety in CH$_3$SO$_3$ are very similar to those of the anion (Figure 2 B) and to the calculated ones (see Figure S3). The CS stretch (ν_4/a_1) appeared at 757.6 cm^{-1}, which is in reasonable agreement with a predicted frequency of 767 cm^{-1} (see Table S3). The most striking differences between the IR spectra of CH$_3$SO$_3$ and its anion CH$_3$SO$_3^-$ are related to the SO$_3$ stretches, particular for the e-type asymmetric one, which appeared at 864.3 cm^{-1} (ν_{10}/e) as a rather weak band for the radical in Ar matrices, while a strong band is observed for the anion at 1201 cm^{-1}. The large frequency shift and the low intensity of this band is consistent with the expected vibronic perturbation.[16] The corresponding ν_{as}(SO$_3$) for the related FSO$_3$ radical was recently assigned to a weak band at 931.5 cm^{-1}.[16b] The red-shift of ν_s(SO$_3$) (ν_3/a_1: 1011.9 cm^{-1}) relative to that of the anion is much smaller and solely due to the longer SO bonds in the radical. In addition, a weak band at 524.0 cm^{-1} is attributed to the SO$_3$ bending mode of CH$_3$SO$_3$ (ν_5/a_1), which is close to the vibrational spacing of 505 ± 10 cm^{-1} observed in the UV/Vis spectrum (Figure 1). Another two weak bands at 1120.8 and 1033.9 cm^{-1} were found to have the same photochemical behavior as the fundamental bands of CH$_3$SO$_3$. These are tentatively assigned to the combination bands $\nu_9 + \nu_{12}$ and $\nu_{10} + \nu_{12}$, respectively. However, the lowest IR fundamental, predicted to be at 199 cm^{-1} (ν_{12}/e, Table S3), is out of our spectral range and could not be observed experimentally.

The assignment of the IR bands for the photolysis ($\lambda \geq 360$ nm) product of CH$_3$SO$_3$ was accomplished by comparison with calculated IR spectra of various isomers of CH$_3$SO$_3$ (see Table S2). The calculated IR spectrum of the radical CH$_2$SO$_3$H (^2A) shows the best agreement to the observation (see Figure S3). This assignment is corroborated by the similarity of its spectrum to that of matrix-isolated CH$_3$SO$_3$H (Figure 2 C).[19]

In addition to the two sulfuryl SO$_2$ stretches at 1396.4 (ν_{as}) and 1184.1 cm^{-1} (ν_s) and two C-S-O single bond stretches at

846.4 (ν_{as}) and 781.1 cm^{-1} (ν_s), a strong band appeared at 3568.9 cm^{-1}, which is assigned to the OH stretching mode. The SOH bending mode was found at 1129.6 cm^{-1} as a rather weak band. Thus, a hydrogen shift from the methyl group of CH_3SO_3 to the oxygen atom occurs upon irradiation ($\lambda \geq$ 360 nm) and forms the carbon-centered radical CH_2SO_3H. EOM-CCSD calculations on CH_2SO_3H (see Table S1) reveal that the first vertical transition occurs at 262 nm ($f = 0.0043$), which also explains the photostability of CH_2SO_3H upon irradiation at $\lambda \geq 360$ nm. In contrast, another candidate radical, CH_3OSO_2 (379 nm, $f = 0.0004$), was predicted to have absorptions in this region (see Table S1). A broad near-UV absorption band ($\lambda_{max} = 347$ nm) has previously been reported for CH_3OSO_2 in isooctane,[20] although further spectroscopic information on this elusive radical has not been reported.

Interestingly, traces of SO_2 were formed upon irradiation ($\lambda \geq 360$ nm) of CH_3SO_3. Its IR band positions at 1338.4 and 1149.9 cm^{-1} are slightly shifted relative to the reported band positions at 1351.3 and 1152.3 cm^{-1} of SO_2 isolated in an Ar matrix.[15] These matrix shifts might be caused by weak interactions with other species trapped in the same matrix cages. The mass balance for the elimination of SO_2 from CH_3SO_3 requires the simultaneous formation of the CH_3O radical or its derivatives; however, no IR bands of CH_3O or its isomer CH_2OH[21] were observed, probably because of low IR intensities and low abundances in the matrices.

The potential-energy surface (PES) for the isomerization of CH_3SO_3 to CH_2SO_3H and CH_3OSO_2 and its dissociation into CH_3 and SO_3 was explored theoretically by using CCSD(T)/6-311++G(2df,2pd) and CBS-QB3 methods. The structures and relative energies of the minima and transition states (TS) on the PES are shown in Figure 3.

In general, the results are consistent with those previously determined with different calculation methods.[11] The three stable isomers on the PES are close in energy, and the most stable one is CH_3OSO_2, which is 48.5 and 28.0 kJ mol^{-1} lower in energy than CH_3SO_3 and CH_2SO_3H, respectively, at the CCSD(T)/6-311++G(2df,2pd) level of theory. The calculated relative stability of the latter two isomers depends on the theoretical methods applied (see Table S4). The activation barrier for the CH_3 shift (TS2) from CH_3SO_3 to the global minimum CH_3OSO_2 is 154.4 kJ mol^{-1}, which is slightly higher than that for the hydrogen shift (TS1) to yield CH_2SO_3H (128.4 kJ mol^{-1}). Nonetheless, the similar energies of the three isomers and their comparable moderate energy barriers to interconversion suggest that the other two isomers might be formed by irradiation of matrix-isolated CH_3SO_3. The absence of CH_3OSO_2 in these experiments is probably due to its facile photofragmentation into CH_3O and SO_2. In fact, the S–O bond in CH_3OSO_2 was found to be rather weak, with an estimated dissociation energy of 59.0 kJ mol^{-1} at the CCSD(T)/6-311++G(2df,2pd) level of theory. This barrier is significantly lower than that for the CH_3OSO_2 to CH_3SO_3 rearrangement (Figure 3), but comparable to that of $CF_3OSO_2 \rightarrow SO_2 + CF_3O$, for which a dissociation energy of 63.4 kJ mol^{-1} was computed for the S–O single bond at the B3LYP/6-311++G(3df,3pd) level of theory. Photodissociation of CF_3OSO_2 was indeed observed in cryogenic matrices under UV irradiation at $\lambda \geq 280$ nm.[21]

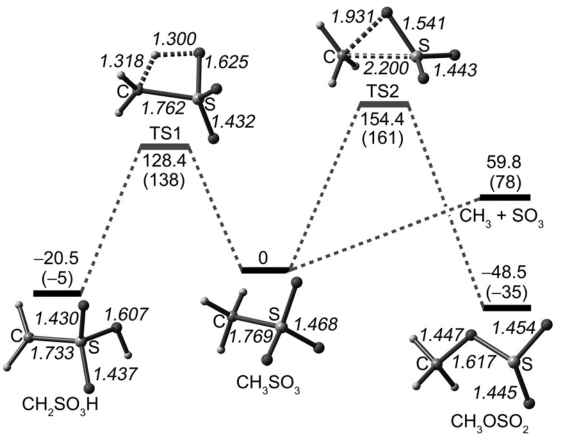


Figure 3. Calculated potential-energy surface for the isomerization of CH_3SO_3 at the CCSD(T)/6-311++G(2df,2pd) and CBS-QB3 (in parentheses) levels of theory. Calculated relative energies are given in kJ mol^{-1} and selected bond lengths (*italics*) in [Å].

The S–O bond lengths in CH_3SO_3 (1.468 Å) are between the double bonds (1.430 Å and 1.437 Å) and the single bond (1.606 Å) in CH_2SO_3H. This structural feature is consistent with the presence of one equally delocalized unpaired electron on three equal oxygen atoms in CH_3SO_3. The optimized C_{3v} molecular structure of CH_3SO_3 is in contrast to the formerly predicted C_s molecular symmetry.[7]

The photochemical behavior of CH_3SO_3 may shed light on its role in the atmosphere. In addition to the formation of acid rain in the form of CH_3SO_3H (MSA) through direct hydrogen abstraction from volatile organic compounds,[5] its photorearrangement to the reactive isomeric radicals CH_2SO_3H and CH_3OSO_2 may initiate more complex radical reactions in the atmosphere; in particular, the sulfur-centered radical CH_3OSO_2 can readily dissociate into SO_2 and the atmospherically important CH_3O radical.[22]

Keywords: atmosphere chemistry · IR spectroscopy · photochemistry · radicals · UV/Vis spectroscopy

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 11404–11408
Angew. Chem. **2015**, *127*, 11404–11570

---

[1] See, for example: a) B. P. Lomans, C. van der Drift, A. Pol, H. J. M. Op den Camp, *Cell. Mol. Life Sci.* **2002**, *59*, 575–588; b) R. J. Charlson, J. E. Lovelock, M. O. Andreae, S. G. Warren, *Nature* **1987**, *326*, 655–661.

[2] See, for example: a) J. E. Lovelock, R. J. Maggs, R. A. Rasmussen, *Nature* **1972**, *237*, 452–453; b) B. Alexander, R. J. Park, D. J. Jacob, Q. B. Li, R. M. Yantosca, J. Savarino, C. C. W. Lee, M. H. Thiemens, *J. Geophys. Res.* **2005**, *110*, D10307; c) S. M. Vallina, R. Simó, M. Manizza, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 16004–16009.

[3] See, for example: a) H. Castebrunet, P. Martinerie, C. Genthon, E. Cosme, *Atmos. Chem. Phys.* **2009**, *9*, 9449–9469; b) K. A. Read, A. C. Lewis, S. Bauguitte, A. M. Rankin, R. A. Salmon, E. W. Wolff, A. Saiz-Lopez, W. J. Bloss, D. E. Heard, J. D. Lee, J. M. C. Plane, *Atmos. Chem. Phys.* **2008**, *8*, 2985–2997; c) R. von Glasow, P. J. Crutzen, *Atmos. Chem. Phys.* **2004**, *4*, 589–608; d) D. Davis, G. Chen, P. Kasibhatla, A. Jefferson, D. Tanner, F. Eisele, D. Lenschow, W. Neff, H. Berresheim, *J. Geophys. Res.*

1998, *103*, 1657 – 1678; e) A. Ray, I. Vassalli, G. Laverdet, G. L. Bras, *J. Phys. Chem.* **1996**, *100*, 8895 – 8900; f) A. Saltelli, J. Hjorth, *J. Atmos. Chem.* **1995**, *21*, 187 – 221.

[4] T. Chen, M. Jang, *Atmos. Chem. Phys.* **2012**, *12*, 10257 – 10269, and references therein.

[5] I. Barnes, J. Hjorth, N. Mihalopoulos, *Chem. Rev.* **2006**, *106*, 940 – 975, and references therein.

[6] See, for example: a) S. Mukhopadhyay, A. T. Bell, *Angew. Chem. Int. Ed.* **2003**, *42*, 1019 – 1021; *Angew. Chem.* **2003**, *115*, 1049 – 1051; b) S. Mukhopadhyay, A. T. Bell, *Org. Process Res. Dev.* **2003**, *7*, 754 – 757; c) N. Basickes, T. E. Hogan, A. Sen, *J. Am. Chem. Soc.* **1996**, *118*, 13111 – 13112.

[7] H. G. Korth, A. G. Neville, J. Lusztyk, *J. Phys. Chem.* **1990**, *94*, 8835 – 8839.

[8] P. A. Arnold, L. E. Fratesi, E. Bejan, J. Cameron, G. Pohlers, H. Liu, J. C. Scaiano, *Photochem. Photobiol. Sci.* **2004**, *3*, 864 – 869.

[9] I. A. Shkrob, T. W. Martin, S. D. Chemerisov, J. F. Wishart, *J. Phys. Chem. B* **2011**, *115*, 3872 – 3888.

[10] H. P. Reisenauer, J. Romanowski, G. Mloston, P. R. Schreiner, *Chem. Commun.* **2015**, *51*, 10022 – 10025.

[11] a) J. Cao, W. L. Wang, L. J. Gao, F. Fu, *Acta Phys.-Chim. Sin.* **2013**, *29*, 1161 – 1167; b) S. Jørgensen, C. Jensen, H. G. Kjaergaard, J. M. Anglada, *Phys. Chem. Chem. Phys.* **2013**, *15*, 5140 – 5150; c) Z. Salta, A. M. Kosmas, A. Lesar, *Comput. Theor. Chem.* **2012**, *1001*, 67 – 76.

[12] X. Q. Zeng, H. Beckers, H. Willner, *J. Am. Chem. Soc.* **2013**, *135*, 2096 – 2099.

[13] X. Q. Zeng, H. Beckers, H. Willner, *Angew. Chem. Int. Ed.* **2013**, *52*, 7981 – 7984; *Angew. Chem.* **2013**, *125*, 8139 – 8142.

[14] X. Q. Zeng, H. Beckers, H. Willner, C. W. Lehmann, *Z. Anorg. Allg. Chem.* **2010**, *636*, 2447 – 2453.

[15] H. Chaabouni, L. Schriver-Mazzuoli, A. Schriver, *J. Phys. Chem. A* **2000**, *104*, 3498 – 3507.

[16] a) H. Beckers, P. Garcia, H. Willner, G. A. Argüello, C. J. Cobos, J. S. Francisco, *Angew. Chem. Int. Ed.* **2007**, *46*, 3754 – 3757; *Angew. Chem.* **2007**, *119*, 3828 – 3831; b) H. Beckers, H. Willner, D. Grote, W. Sander, *J. Chem. Phys.* **2008**, *128*, 084501.

[17] M. Kronberg, S. von Ahsen, H. Willner, J. S. Francisco, *Angew. Chem. Int. Ed.* **2005**, *44*, 253 – 257; *Angew. Chem.* **2005**, *117*, 258 – 261.

[18] E. D. Risberg, L. Eriksson, J. Mink, L. G. M. Pettersson, M. Y. Skripkin, M. Sandström, *Inorg. Chem.* **2007**, *46*, 8332 – 8348.

[19] A. Givan, A. Loewenschuss, C. J. Nielsen, *J. Mol. Struct.* **2005**, *748*, 77 – 90.

[20] C. Chatgilialoglu, D. Griller, M. Guerra, *J. Phys. Chem.* **1987**, *91*, 3747 – 3750.

[21] M. E. Jacox, D. E. Milligan, *J. Mol. Spectrosc.* **1973**, *47*, 148 – 1973.

[22] R. J. Buszek, A. Sinha, J. S. Francisco, *J. Am. Chem. Soc.* **2011**, *133*, 2013 – 2015, and references therein.

Received: April 24, 2015