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Fast Peroxy Radical Isomerization and OH Recycling in the Reaction of OH Radicals with Dimethyl Sulfide

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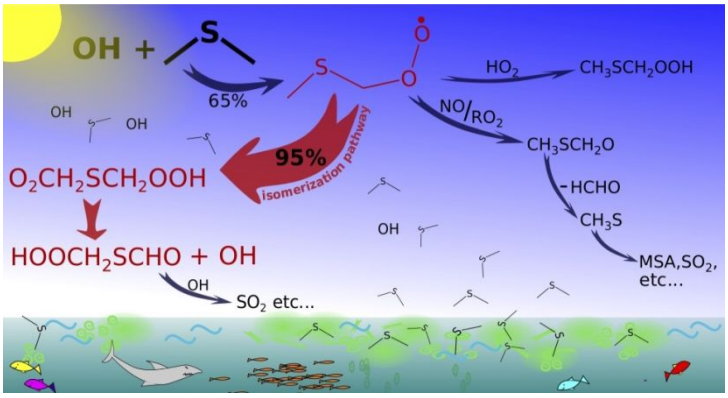
Abstract

Dimethyl sulfide (DMS), produced by marine organisms, represents the most abundant, biogenic sulfur emission into the Earth´s atmosphere. The gas-phase degradation of DMS is mainly initiated by the reaction with the OH radical forming first $CH_3SCH_2O_2$ radicals from the dominant H-abstraction channel. It is experimentally shown that these peroxy radicals undergo a two-step isomerization process finally forming a product consistent with the formula $HOOCH_2SCHO$. The isomerization process is accompanied by OH recycling. The rate-limiting first isomerization step, $CH_3SCH_2O_2 \rightarrow CH_2SCH_2OOH$, followed by O_2 addition, proceeds with $k = (0.23 \pm 0.12)\ s^{-1}$ at 295 ± 2 K. Competing bimolecular $CH_3SCH_2O_2$ reactions with NO, HO_2 or RO_2 radicals are less important for trace-gas conditions over the oceans. Results of atmospheric chemistry simulations demonstrate the predominance (≥95%) of $CH_3SCH_2O_2$ isomerization. The rapid peroxy radical isomerization, not yet considered in models, substantially changes the understanding of DMS´s degradation processes in the atmosphere.

TOC Graphic



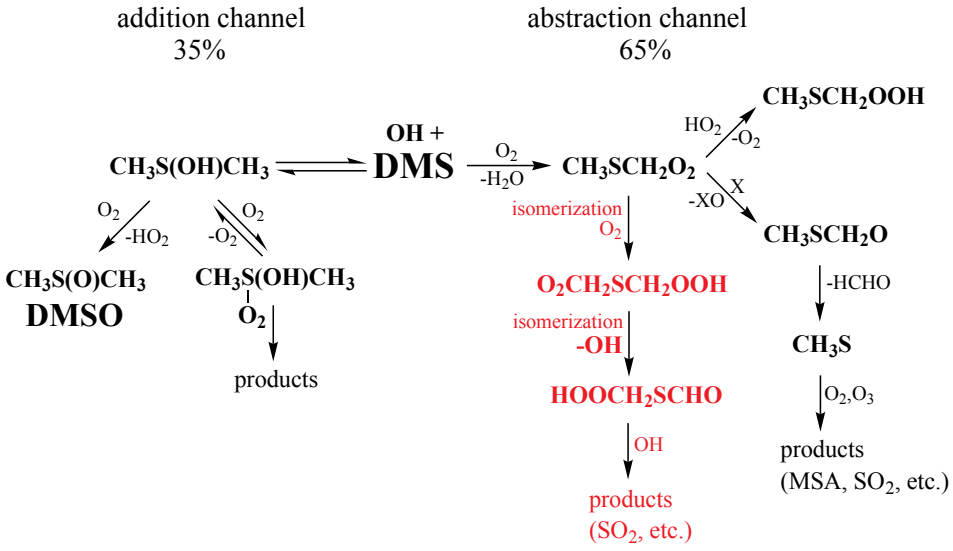
The emission of dimethyl sulfide (DMS: CH_3SCH_3) over the oceans is the largest natural sulfur source to the Earth´s atmosphere with an estimated rate of (10 - 35) × 10^6 metric tons of sulfur per year.[1-6] Gas-phase oxidation of DMS, mainly initiated by the reaction with OH radicals, leads to the formation of sulfuric acid (H_2SO_4) and methane sulfonic acid (MSA: CH_3SO_3H)[7] which are important for the formation of natural aerosols and clouds in the marine boundary layer.[8,9] Natural aerosols, including those from DMS oxidation, are assumed to account for the largest uncertainty of aerosol´s radiative forcing in climate models.[10]

A series of kinetic studies in absence and presence of molecular oxygen consistently describe the occurrence of two independent channels of the OH + DMS reaction, i.e. i) the reversible OH addition forming the adduct radical $CH_3S(OH)CH_3$ and ii) the H atom abstraction pathway forming the peroxy radical $CH_3SCH_2O_2$ after subsequent O_2 addition.[7, 11-13] The addition / abstraction branching ratio of about 35 / 65 can be derived from kinetic measurements between 295 to 299 K at atmospheric O_2 concentration. The experimentally observed molar formation yield of dimethyl sulfoxide (DMSO: $CH_3S(O)CH_3$) of 35 ± 8 % at 295 K[14] supports this branching ratio supposing DMSO as the predominate 1st generation product from the addition channel.[7]

The knowledge regarding the 1st generation product formation from the abstraction channel, however, is still sparse despite a large number of experimental and theoretical studies in the past.[7] It is assumed up to now and implemented in current models[15] that the primarily formed $CH_3SCH_2O_2$ radical reacts in the atmosphere with NO,[16-18] HO_2[19] and RO_2 radicals[16,18]. The main product of the $CH_3SCH_2O_2$ + NO reaction is the corresponding alkoxy radical, CH_3SCH_2O, which has been suggested to rapidly decompose forming HCHO and CH_3S.[18] CH_3S is believed to be the key intermediate forming MSA as well as SO_2, which leads to H_2SO_4 production from its OH radical reaction in the presence of water vapor.[7] CH_3SCH_2OOH formation is assumed from the $CH_3SCH_2O_2$ + HO_2 reaction analogous to the hydroperoxide channel known from a series of RO_2 + HO_2 reactions.[7,19] The $CH_3SCH_2O_2$ + RO_2 reaction proceeds either via the reduction channel forming CH_3SCH_2O, that rapidly results in HCHO and CH_3S, or via the dismutation channel forming CH_3SCH_2OH and CH_3SCHO.[7,19] A HCHO formation yield of unity has been reported from the $CH_3SCH_2O_2$ self-reaction emphasizing the predominance of the reduction channel in this case.[18]

Results of a recent theoretical study, however, propose rapid isomerization of the $CH_3SCH_2O_2$ radical that could be able to outrun the rate of the bimolecular $CH_3SCH_2O_2$ reactions for typical NO, HO_2 and RO_2 radical concentrations present over the oceans.[20]

Findings of the calculations indicate the occurrence of a new peroxy radical $O_2CH_2SCH_2OOH$ that is formed from $CH_3SCH_2O_2$ isomerization with subsequent O_2 addition. A next isomerization step can occur resulting in $HOOCH_2SCHO$ and an OH radical. It is to be noted, that an analog sequence of RO_2 radical isomerization steps has been reported from the low-temperature combustion of dimethyl ether forming the analog $HOOCH_2OCHO$ as a closed-shell product.[21] Experimental evidence for these processes from the OH + DMS reaction and kinetic measurements of the $CH_3SCH_2O_2$ isomerization do not exist up to now. Previous DMS product studies in the laboratory were affected by insufficient product detection sensitivity and by too high NO, HO_2 or RO_2 radical levels in the experiments, suppressing possible isomerization steps of peroxy radicals by excessive bimolecular reaction rates.[14, 22-24] Scheme 1 summarizes the current knowledge on the first steps of the OH + DMS reaction in the literature[7] along with the proposed reaction scheme based on theoretical calculations.[20] The formation of SO_2 has been proposed from the subsequent OH + $HOOCH_2SCHO$ reaction.[20]



Scheme 1. First reaction steps of the OH + DMS reaction, the established scheme from the review by Barnes *et al.*[7] in black and proposed pathways from theoretical calculations[20] in red. Detected products from the present study are given in bold red. "X" stands for the reactants NO and RO_2 that can reduce the peroxy radical to the corresponding alkoxy radical.

Here we report on results of a mechanistic study of the OH + DMS reaction with focus on the 1st generation products from the abstraction channel. Experiments have been conducted at 295 ± 2 K and 1 bar of purified air in a free-jet flow system, that allows for investigations in the absence of wall interactions for a reaction time of 7.9 s.[25,26] The chosen reaction

conditions ensured monitoring of the possible $CH_3SCH_2O_2$ isomerization products without interference from bimolecular $CH_3SCH_2O_2$ reactions. Product formation was followed either by a chemical ionization - atmospheric pressure interface - time-of-flight mass spectrometer (CI-APi-TOF) using iodide (I^-)[27,28], acetate (CH_3COO^-)[29,30], protonated n-propylamine (n-$C_3H_7NH_3^+$)[31] or protonated acetone ($(CH_3)_2CO\text{-}H^+$)[32] as the reagent ion or by a chemical ionization - time-of-flight mass spectrometer (CI3-TOF) applying ammonium (NH_4^+)[33,34] for product ionization at reduced pressure. Quantum chemical calculations support the assessment of used ionization schemes for product detection (see Supporting Information). OH radicals were formed from ozonolysis of tetramethylethylene (TME)[35] or, alternatively, via isopropyl nitrite photolysis.[36]

Sensitive detection of the sulfur containing products has been achieved using I^--CI-APi-TOF analysis for a DMS conversion down to 4×10^6 molecules cm^{-3}. Observed signals in the mass spectra are consistent with the formation of the peroxy radical $O_2CH_2SCH_2OOH$ from $CH_3SCH_2O_2$ isomerization, pathway (1), as well as the closed-shell product $HOOCH_2SCHO$ from a subsequent isomerization step followed by rapid decomposition of the unstable $HOOCH_2SCHOOH$[20] via pathway (2) (see the black spectrum in Figure 1 and Figure S1 for conditions of isopropyl nitrite photolysis).

$$CH_3SCH_2O_2\ (+\ O_2) \rightarrow O_2CH_2SCH_2OOH \quad (1)$$

$$O_2CH_2SCH_2OOH \rightarrow \{HOOCH_2SCHOOH\} \rightarrow HOOCH_2SCHO + OH \quad (2)$$

These products are in accordance with predictions from theoretical calculations.[20] An additional weak signal attributed to $C_2H_6O_4S$, possibly $HOOCH_2SCH_2OOH$ formed via $RO_2 + HO_2 \rightarrow ROOH + O_2$, became detectable for higher DMS conversions with higher HO_2 radical levels (see Figure S1). (HO_2 radicals are formed along with DMSO via the addition channel and from other pathways mainly related to the OH radical generation.) On the other hand, signals of $CH_3SCH_2O_2$ have not been detected with any of the ionization schemes applied. The $CH_3SCH_2O_2$ adducts with the used reagent ions are not stable enough for the successful detection as shown by quantum chemical calculations (see details in Supporting Information). DMSO, formed from the addition channel, was detectable by all ionization techniques, but will be not further discussed here.

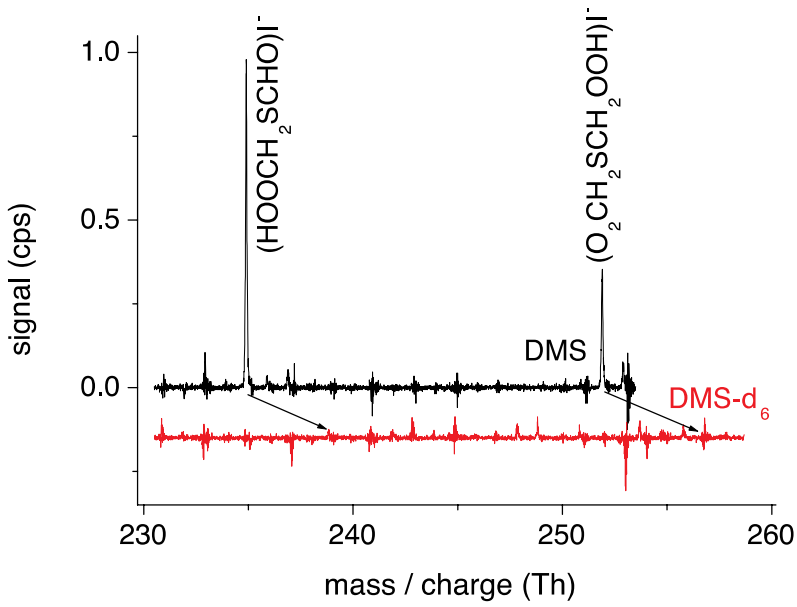


Figure 1. Background corrected spectra from OH + DMS (black spectrum) and OH + DMS-d_6 (red spectrum) using I^--CI-APi-TOF analysis and TME ozonolysis for OH formation. The calculated DMS conversion is 4.5×10^7 molecules cm^{-3} and that of DMS-d_6[37] about 2.8×10^7 molecules cm^{-3}. Reactant concentrations are $[O_3] = 1.6\times10^{11}$, $[TME] = 3\times10^{10}$, [DMS] or [DMS-d_6] = 5×10^{12} molecules cm^{-3}.

The corresponding product formation starting from OH + DMS-d_6 was also tested for otherwise identical reaction conditions (see red spectrum in Figure 1). While the $CD_3SCD_2O_2$ formation rate is already slowed down by a factor of 2.4 compared to the rate of the non-deuterated compound[37], intramolecular D-shifts in the course of peroxy radical isomerization are assumed to be much slower than the corresponding H-shifts in non-deuterated compounds. For instance, a deceleration factor of about 15 has been found for D-shifts in the isoprene system.[38] Hence, absence of the expected $O_2CD_2SCD_2OOD$ and $DOOCD_2SCDO$ signals clearly above background level is consistent with an isomerization mechanism (intramolecular H-shifts) leading to the observed products from the abstraction channel.

Addition of propane, acting as OH radical scavenger, led to total product suppression. This behavior demonstrates that the observed products exclusively arose from OH + DMS, not affected by any reactions of ozonolysis products with DMS under ozonolysis conditions (see Figure S2). The product concentrations increased linearly with rising DMS conversion in line with the first-order kinetics of product formation from radical isomerization via pathways (1) and (2) (see Figure 2). Based on results of reaction modeling in the flow system, bimolecular $CH_3SCH_2O_2$ reactions consumed less than 0.2% of the formed $CH_3SCH_2O_2$ radicals for DMS

conversions < 5×10^7 molecules cm^{-3} ensuring fully undisturbed reaction conditions for radical isomerization steps.

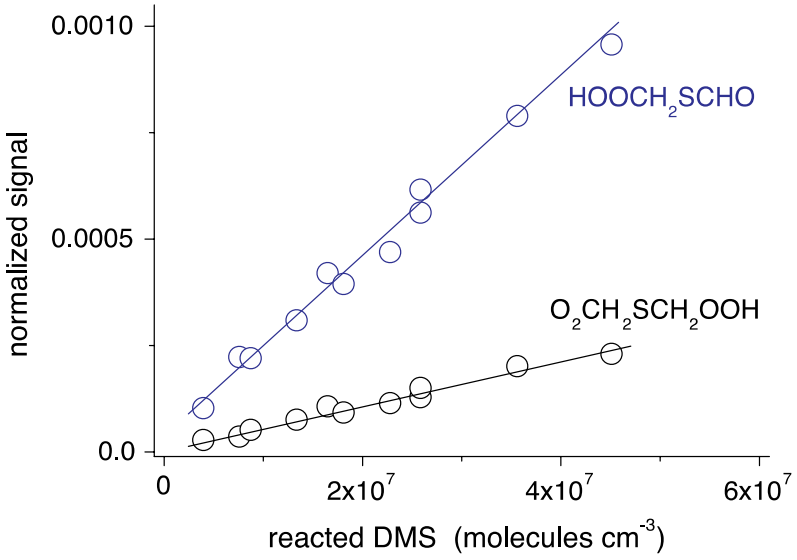


Figure 2. Product formation from OH + DMS as a function of calculated DMS conversion. Analysis was carried out by I^--CI-APi-TOF and TME ozonolysis served as the OH radical source. Reactant concentrations are $[O_3] = (2.7 - 16)\times10^{10}$, [TME] = 1.5 or 3.0×10^{10} and [DMS] = 2.5 or 5.0×10^{12} molecules cm^{-3}.

Product analysis for elevated DMS conversion applying other ionization techniques confirmed the findings as observed by I^- ionization. Both isomerization products, as well as $C_2H_6O_4S$, have been measured by means of NH_4^+-CI3-TOF (see Figure S3). There was no indication for the occurrence of further products from the abstraction channel. Generally, the lack of justified calibration factors prevents the determination of absolute product concentrations. However, results obtained by NH_4^+-CI3-TOF and I^--CI-APi-TOF consistently point to $HOOCH_2SCHO$ as the predominant reaction product based on its signal strength compared with that of $O_2CH_2SCH_2OOH$. The formation of $HOOCH_2SCHO$ was also detected by CH_3COO^-- and $(CH_3)_2CO$-H^+-CI-APi-TOF (see Figures S4 and S5).

The kinetics of the $CH_3SCH_2O_2$ isomerization relative to the $CH_3SCH_2O_2$ + NO reaction, i.e. the ratio of the rate coefficients k_1 / k_3, has been obtained by monitoring the $CH_3SCH_2O_2$ isomerization products for rising NO concentrations. (The individual rate coefficients belong to the reaction pathways with the same numbering.)

$$CH_3SCH_2O_2 + NO \rightarrow \text{products} \quad (3)$$

At the same time, addition of NO to the reaction gas led to increasing OH radical formation via the $NO + HO_2 \rightarrow OH + NO_2$ reaction, and consequently enhanced product formation from OH + DMS (see Figure 3A). Lowering of the HO_2 radical concentration with rising NO became clearly visible following the $(HO_2)I^-$ signal[39] (see Figure 3A). Increasing OH levels were indirectly monitored by the SO_3 formation via the reaction sequence $OH + SO_2 \rightarrow HOSO_2$ and $HOSO_2 + O_2 \rightarrow SO_3 + HO_2$.[40] SO_2 additives were chosen in such a way that $OH + SO_2$ did not disturb the OH + DMS reaction, i.e. a reaction rate ratio $r(OH+SO_2) / r(OH+DMS) = 0.05$. The measured SO_3 signal, standing for the integral OH radical concentration, enables the normalization of the isomerization product formation for changing OH radical conditions (see Figure 3B). The normalized signals of $O_2CH_2SCH_2OOH$ and $HOOCH_2SCHO$ declined parallel to each other with rising NO consistent with the behavior of isomerization products from the consecutive reaction pathways (1) and (2). The second isomerization step is supposed to be much faster than the first one based on theoretical calculations stating $k_1 = 2.1\ s^{-1}$ and $k_2 = 73\ s^{-1}$ at 293 K.[20] That means that pathway (1) is rate limiting for the $CH_3SCH_2O_2$ isomerization process. The rapid $O_2CH_2SCH_2OOH$ isomerization via pathway (2) represses the importance of its bimolecular reaction with NO. Hence, the $O_2CH_2SCH_2OOH + NO$ reaction has been neglected in the data analysis. The normalized signals of the $CH_3SCH_2O_2$ isomerization products as a function of NO at a fixed reaction time t, $[\text{iso-prod}]_t^{\text{norm}} = f([NO])$, allow the determination of $B = k_1 / k_3$ from Eq.(I) (see Supporting Information).

$$[\text{iso-prod}]_t^{\text{norm}} = A /(1 + [NO]/B) \quad (I)$$

The analysis yielded $k_1 / k_3 = (2.1 \pm 0.4)\times10^{10}$ and $(1.5 \pm 0.3)\times10^{10}$ molecule cm^{-3} for the decline of $HOOCH_2SCHO$ and $O_2CH_2SCH_2OOH$ (Figure 3B), respectively, leading to the mean value $k_1 = 0.23 \pm 0.12\ s^{-1}$ based on $k_3 = (1.3 \pm 0.6)\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} taken from the literature data[16-18].

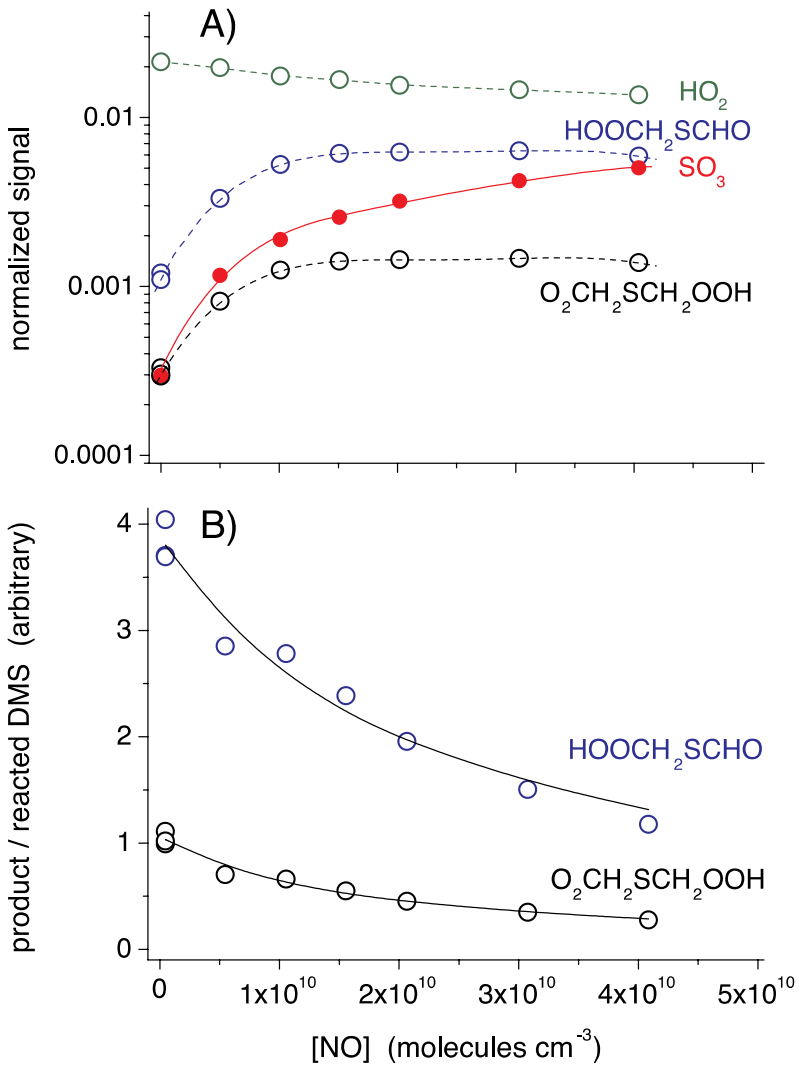


Figure 3. Product formation from OH + DMS as a function of NO using OH radical formation via isopropyl nitrite photolysis. **A** Concentrations of isomerization products and HO_2 radicals measured by I^--CI-APi-TOF and SO_3 formation by n-$C_3H_7NH_3^+$-CI-APi-TOF. **B** Normalized isomerization product signals considering changing DMS conversion with rising NO due to enhanced OH radical production. The lines show the best fit results from kinetic analysis of k_1 / k_3. Reactant concentrations are [isopropyl nitrite] = 5.0×10^{10}, [SO_2] = 1.5×10^{12}, [DMS] = 5.0×10^{12} and [NO] = $(5.0\text{-}40.4)\times10^9$ molecules cm^{-3}. The final NO concentration from isopropyl nitrite photolysis has been calculated to be 9.3×10^8 molecules cm^{-3}.

Furthermore, the OH recycling has been probed, which is expected as an associated product channel of the $HOOCH_2SCHO$ formation via pathway (2). SO_3 formation from OH + SO_2, as a measure of the integral OH radical concentration, has been followed for conditions of a fixed OH formation rate via isopropyl nitrite photolysis and a constant OH consumption rate via OH + hydrocarbon (HC) or OH + DMS, i.e. k(OH+HC)×[HC] = k(OH+DMS)×[DMS] = constant. The selected HCs were TME, α-pinene and decalin. The needed rate coefficients k(OH+HC) at room temperature are available with good precision in

the literature, i.e. k(OH+TME) = 1.1×10^{-10} [41], k(OH+α-pinene) = 5.33×10^{-11} [41] and k(OH+cis/trans-decalin) = 2.03×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. The latter represents the mean value of the individual rate coefficients of both isomers.[42] The SO_2 additive also consumed a constant, minor fraction of OH, again with the reaction rate ratio r(OH+SO_2) / r(OH+HC(or DMS)) = 0.05 in order to keep the OH + HC(or DMS) reaction less influenced. If no OH recycling occurs, constant OH formation and loss terms result in a constant integral OH radical concentration (constant SO_3 signal) independent of the HC(or DMS) used. This behavior was visible in the case of TME, α-pinene and decalin where OH recycling has not been reported so far in the literature (see Figure 4). For OH + DMS, however, the SO_3 signal increased by about 55% relative to the other reaction systems indicating efficient OH recycling. Model calculations show an increase of the integral OH radical concentration by 43% due to $CH_3SCH_2O_2$ isomerization with $k_1 = 0.23$ s^{-1} for the reaction time of 7.9 s in the experiment. This measurement supports the rapid $CH_3SCH_2O_2$ isomerization including OH recycling being at least as fast as determined from the competition kinetics as shown before.

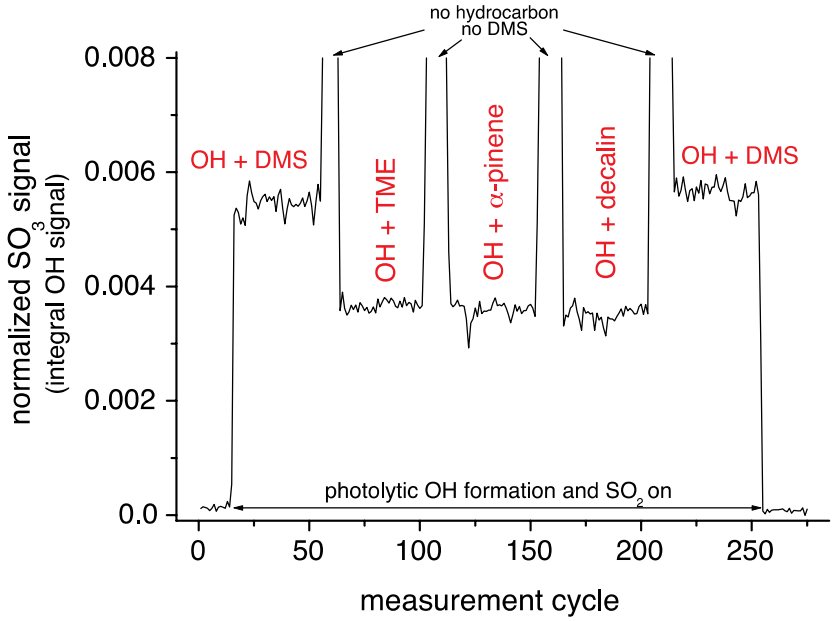


Figure 4. SO_3 signal, standing for the integral OH radical concentration, measured for constant OH production via isopropyl nitrite photolysis and constant OH consumption via OH + hydrocarbon (HC) or OH + DMS, HCs: TME, α-pinene and decalin. No SO_3 signal has been measured in the absence of the SO_2 additive. One measurement cycle comprises 60 s data accumulation. Reactant concentrations are [isopropyl nitrite] = 4.5×10^{11}, [SO_2] = 5.01×10^{11}, [DMS] = 1.67×10^{12}, [TME] = 1.18×10^{11}, [α-pinene] = 2.44×10^{11} and [cis/trans-decalin] = 6.40×10^{11} molecules cm^{-3}.

Multiphase chemistry investigations with an air parcel model were carried out to validate the impact of the $CH_3SCH_2O_2$ isomerization process for pristine ocean conditions at 295 K (see Figure S6).[43,44] The model results clearly demonstrate that isomerization dominates the chemical fate of $CH_3SCH_2O_2$. The mean contribution ranges from 95 to 98.5% considering $k_1 = 0.23 \pm 0.12$ s^{-1} within its range of uncertainty (see Figure S7). Average concentrations of NO, HO_2 and total RO_2 radicals in the model were 6×10^6, 1×10^8 and 4×10^8 molecules cm^{-3} resulting in pseudo first-order rate coefficients of the corresponding bimolecular $CH_3SCH_2O_2$ reactions of 7.0×10^{-5}, 1.0×10^{-3} and 1.5×10^{-3} s^{-1} at 295 K, respectively. The dominance of the isomerization process entails consequences for the OH budget and the subsequent product formation. The simulations reveal that the isomerization process increases the total OH radical formation rate by 2% on average and by 17% during nighttime when $CH_3SCH_2O_2$ formation via NO_3 + DMS[7,45] is active (see Figure S8). Furthermore, MSA formation from consecutive reactions of $HOOCH_2SCHO$ is impossible because no methyl group is left in this molecule. Hence, MSA formation from the abstraction channel, as thought up to now via the CH_3S intermediate[7,15], is inhibited leading to reduction of the modeled gas-phase MSA concentration by 30% (see Figure S9). $HOOCH_2S$ formation from the subsequent OH + $HOOCH_2SCHO$ reaction via H abstraction and CO elimination has been proposed, that finally leads to SO_2 and HCHO including OH recycling.[20] This scenario, however, is speculative at the moment and needs experimental verification. Moreover, $HOOCH_2SCHO$ could be also subject to the particle-phase chemistry because of its high oxidation state and the expected partitioning into the particle phase.

In conclusion, 1st generation product formation from the abstraction channel of the OH + DMS reaction has been investigated at 295 ± 2 K and atmospheric pressure of air. The experimental findings reveal a two-step isomerization process of $CH_3SCH_2O_2$ radicals finally forming $HOOCH_2SCHO$ accompanied by OH recycling. This process is in accordance with predictions based on theoretical calculations.[20] The rate-limiting first isomerization step, $CH_3SCH_2O_2 \rightarrow CH_2SCH_2OOH$, proceeds with $k = (0.23 \pm 0.12)$ s^{-1} at 295 ± 2 K. This rate coefficient is about one order of magnitude smaller than the result of the theoretical calculations[20]. The $CH_3SCH_2O_2$ isomerization process is clearly faster than the traditional bimolecular $CH_3SCH_2O_2$ reactions with NO, HO_2 and RO_2 radicals for trace gas conditions over the oceans accounting for ≥95% of the $CH_3SCH_2O_2$ removal as shown by a modeling study at 295 K. Continuing experimental work is needed in order to discover the 2nd generation product formation with special attention to SO_2 and MSA.

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Note

The authors declare no competing financial interests.

Supporting Information

Experimental.
Reaction mechanism.
Kinetic analysis k_1 / k_3.
Computational methods and (product)reagent-ion cluster stability.
Atmospheric modeling approach.
Figures S1 to S9.

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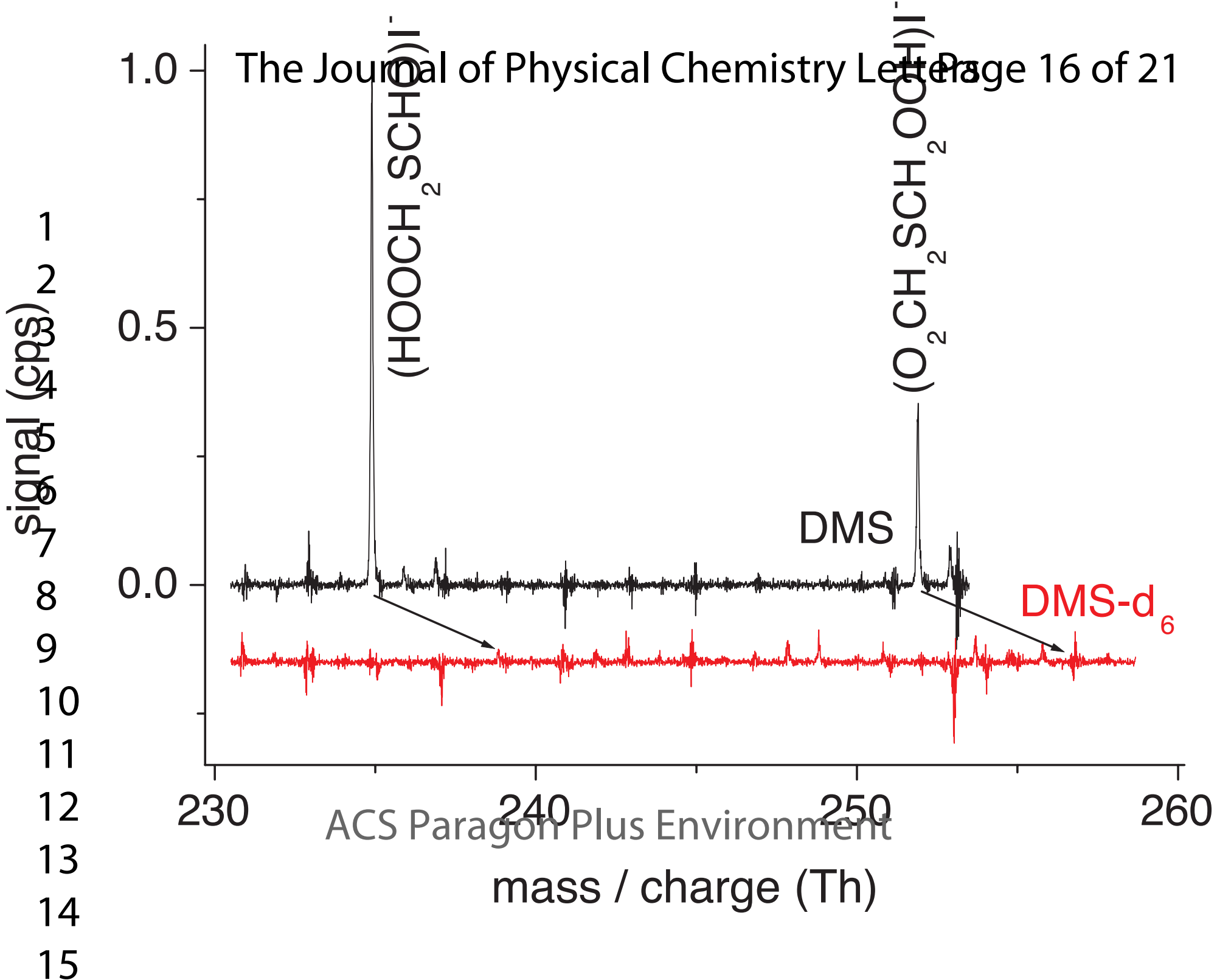
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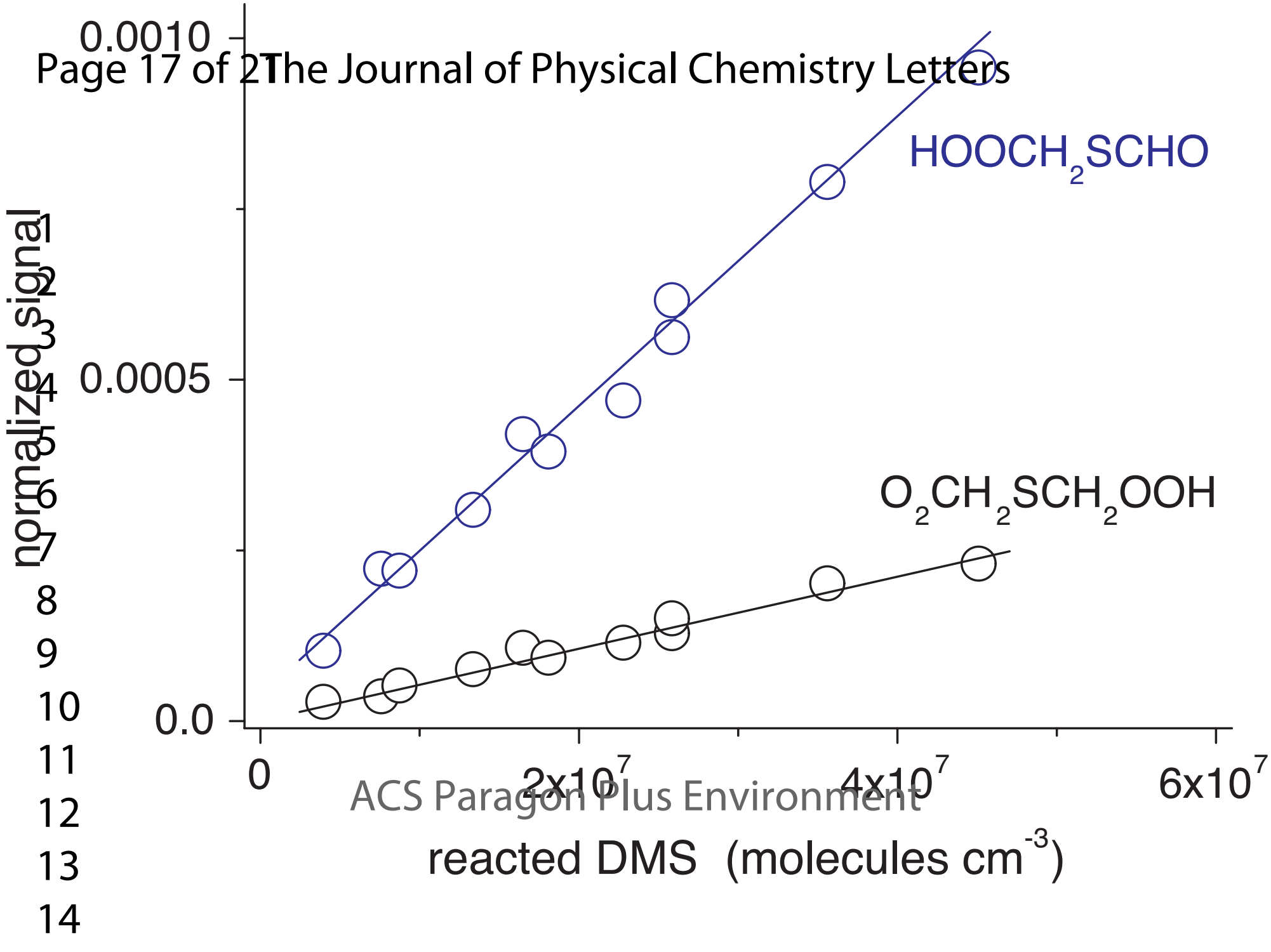
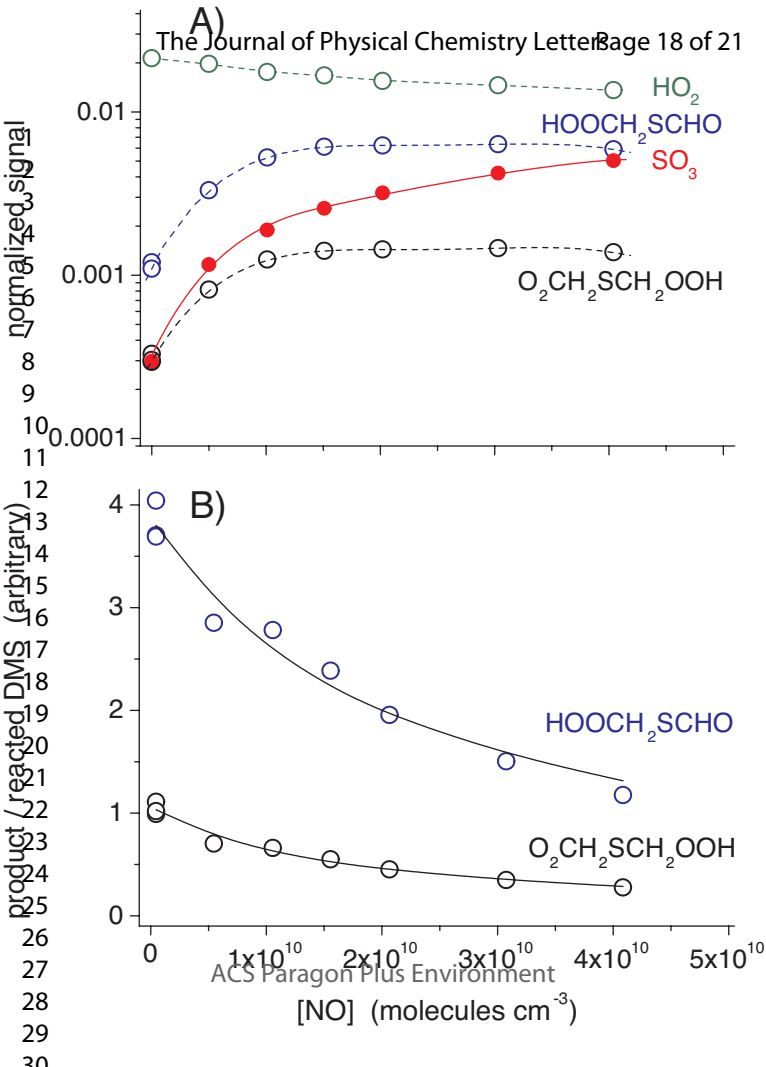
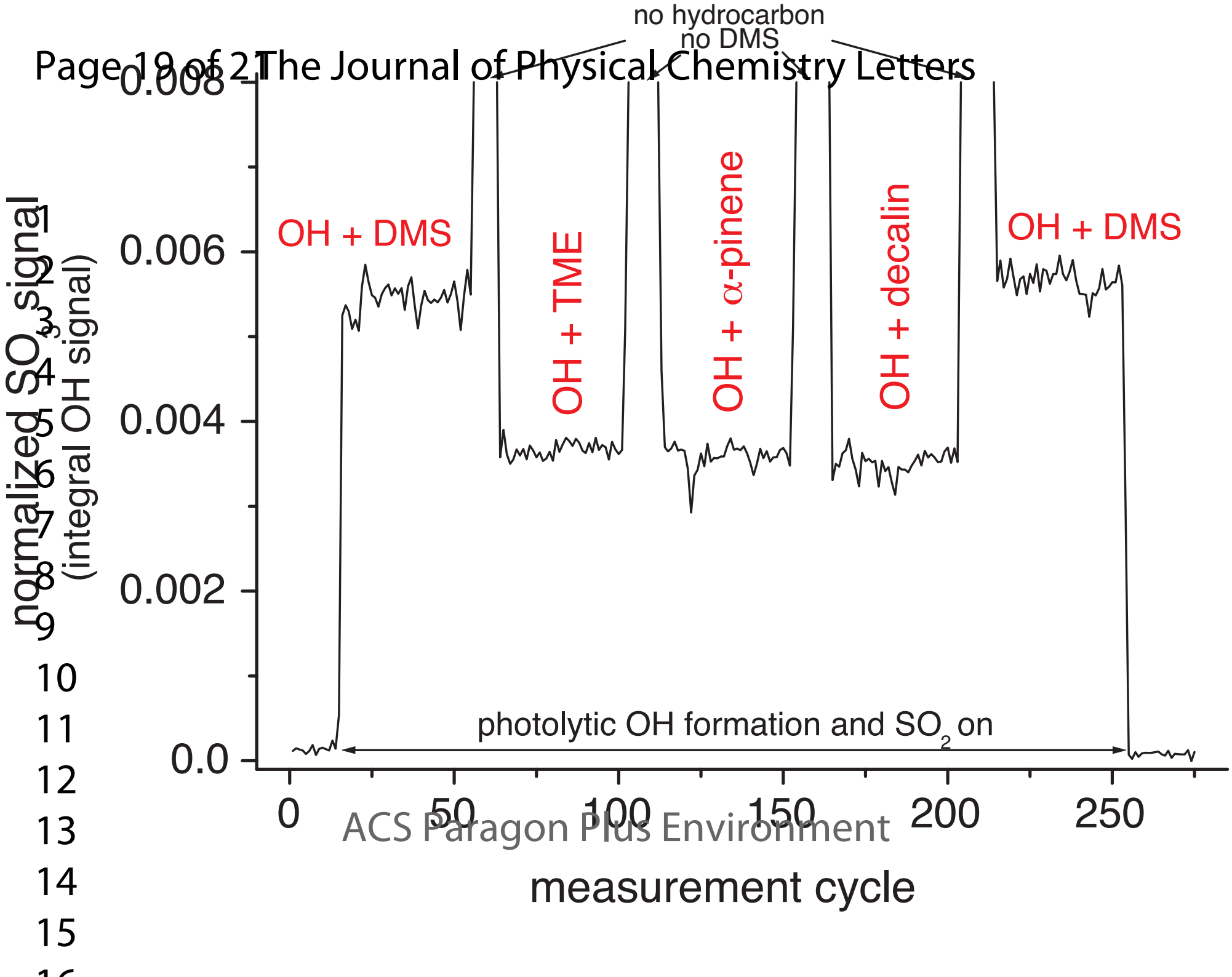
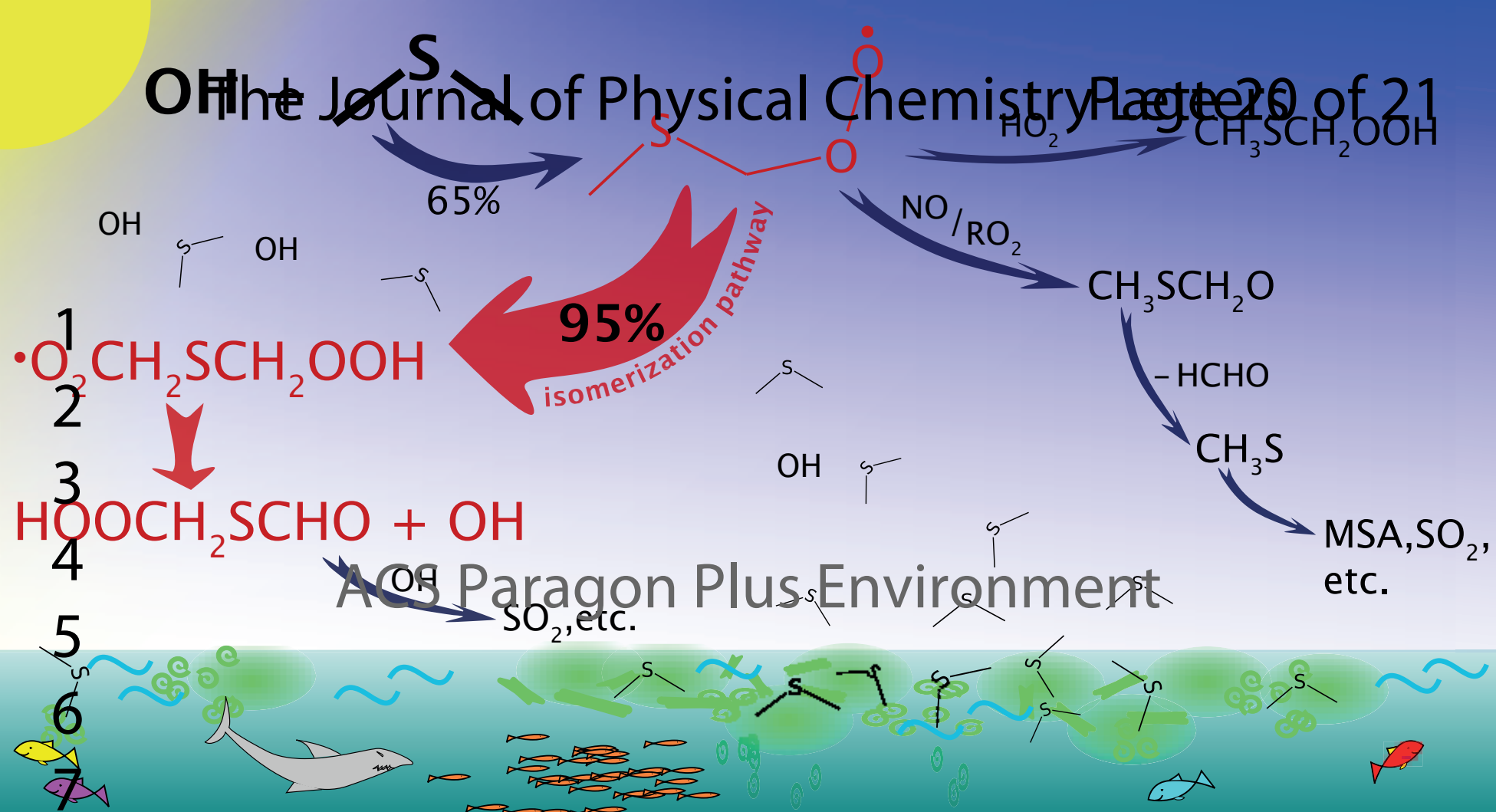
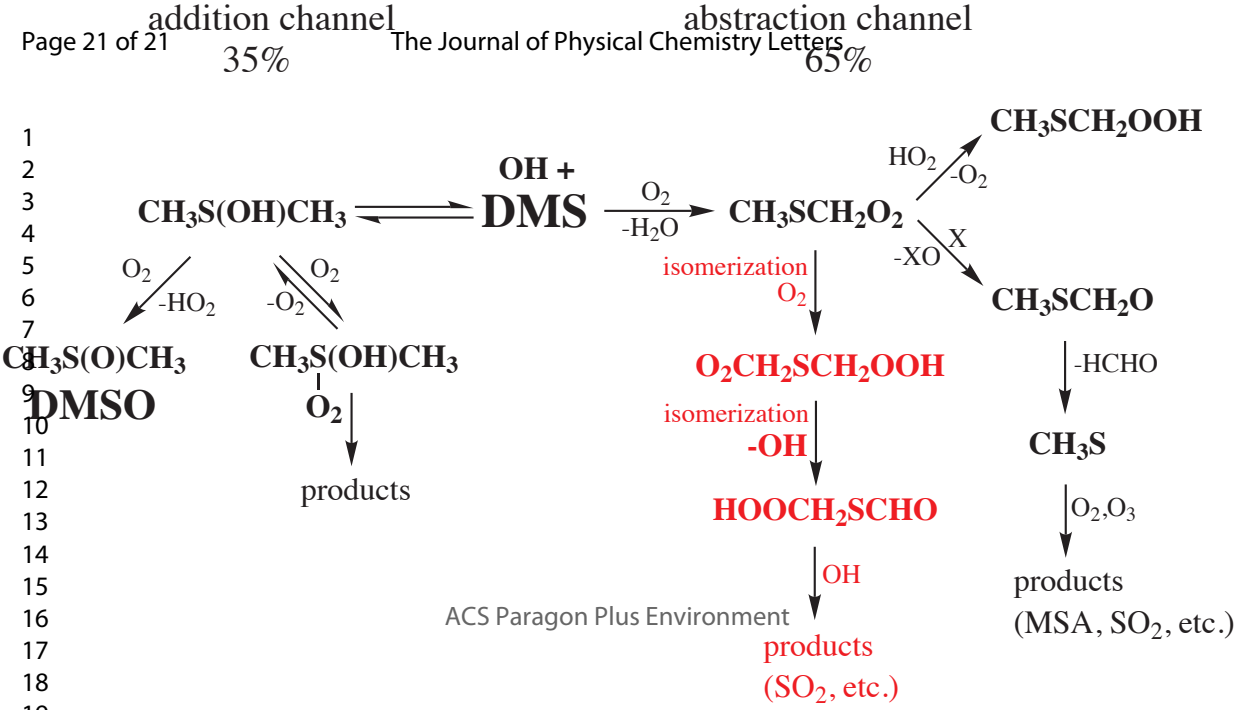







OH + DMS
65%
95%
isomerization pathway
•O2CH2SCH2OOH
HOOCH2SCHO + OH
HO2
CH3SCH2OOH
NO/RO2
CH3SCH2O
– HCHO
CH3S
MSA,SO2, etc.
OH
SO2,etc.
ACS Paragon Plus Environment


addition channel
35%
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OH +
DMS
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O2
-H2O
CH3SCH2O2
HO2
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CH3SCH2OOH
-XO
X
CH3SCH2O
O2
-HO2
CH3S(O)CH3
DMSO
O2
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CH3S(OH)CH3
O2
products
isomerization
O2
O2CH2SCH2OOH
isomerization
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products
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