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Rate Constants for Reaction Between Hydroxyl Radical and Dimethyl Sulfide Under Real Atmospheric Condition

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The rate constants of the reaction between hydroxyl radical (OH·) and dimethyl sulfide (DMS) were investigated by using the relative methods in air, N₂, and O₂. Strong influences of ground state oxygen O(³P) on DMS consumption were found by the photolysis of HONO and CH₃ONO as OH· sources, and the rate constants obtained in these systems varied significantly. The rate constants of the reaction between DMS and OH· (generated by photolysis of H₂O₂) at room temperature were 8.56×10⁻¹², 11.31×10⁻¹², and 4.50×10⁻¹² cm³/(molecule·s), in air, O₂, and N₂, respectively. The temperature dependence of the rate constants for OH· with DMS over the temperature range of 287-338 K was also investigated in nitrogen and air, and the Arrhenius expression was obtained as follows: $k_{\text{air}}=(7.24\pm 0.28)\times 10^{-13}\exp[(770.7\pm 97.2)/T]$, $k_{\text{N}_2}=(3.40\pm 0.15)\times 10^{-11}\exp[-(590.3\pm 165.9)/T]$.

Key words: Dimethyl sulfide, Hydroxyl radical, Ground state oxygen, Kinetics

I. INTRODUCTION

Dimethyl sulfide (DMS) is the most predominant reduced sulfur compound emitted from biological activities [1], and presents at parts per trillion levels in the Earth's troposphere [2]. It has been postulated that emission of DMS from the oceans may have a significant influence on the Earth's radiation budget and possibly in climate regulation [3]. DMS may also influence sulfate aerosol formation in the upper troposphere and lower stratosphere over convective regions [4,5]. Because of its high reactivity, DMS can be removed by many photochemical oxidation pathways, such as OH· radicals during the daytime, NO₃ radicals [6,7] during nighttime, and Cl atoms [8-10] and BrO radicals [11-13] in the marine boundary layer. In addition, the interaction between DMS and ozone chemistry has been discussed in recent work, where DMS has been found to react with O₃ [14-17], indicating that the heterogeneous aqueous-phase reaction of O₃ with DMS could be another important sink for DMS in the marine atmosphere, forming readily soluble dimethyl sulphoxide (DMSO). Even so, studies on oxidation of DMS in the troposphere [18] suggested that the combination of the reactions OH·+DMS and NO₃+DMS can be predominating channels for the consumption of DMS in the atmosphere. Therefore, the gas-phase reaction between DMS and OH·, which is the main loss mechanism for DMS in the atmosphere, has been intensively studied by using a wide variety of absolute and relative techniques in the past decades [19-36]. However, it has been known since the 1980s that sec-

ondary chemistry problems resulted in erroneous rate constants for OH· reactions with DMS when RONO species were used in the OH· generation process. In these measured rate constants, there are significant discrepancies ranging from 3.2×10⁻¹² cm³/(molecule·s) to 4.7×10⁻¹¹ cm³/(molecule·s). The possible reasons for the large discrepancies have been identified and summarized by Abbatt *et al.* [31]. Although product chemistry is thought to enhance the overall loss rate of DMS within the reaction chamber with the presence of NO_x [37], the secondary reactions in these systems are not yet clearly identified. In addition, there are only three measurements for the temperature dependence of the rate coefficient under atmospheric conditions [26,34,35]. Although the same trend was observed by these studies, the rate constants measured by Albu *et al.* [35] and Williams *et al.* [34] are significantly higher than the value reported by Hynes *et al.* [26] at temperature below 260 K.

The present work reinvestigates the rate constants of the reaction between OH· and DMS in air and O₂ by HONO and CH₃ONO as OH· precursors. The objective of these experiments is to examine why the rate constants obtained by the relative methods in presence of NO_x are much higher than those by using other techniques. Temperature dependence rate coefficients were also determined by employing H₂O₂ as the OH· source in both N₂ and air over the temperature range of 287-338 K. The aim of these experiments is to extend the database of the kinetics for the reaction between DMS and OH· to higher temperature in the air.

II. EXPERIMENTS

Kinetic experiments were carried out in a previously described system [38,39], which was modified

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by replacing the cubic ligneous chamber with a thermostatic chamber (1.3 m×1.3 m×1.2 m). Three OH-sources were used in this study: (i) photolysis of HONO (365 nm) in air and oxygen; (ii) photolysis of methyl CH₃ONO (365 nm) in the presence of NO in air and oxygen; (iii) photolysis of H₂O₂ in N₂/O₂/air at 101 kPa total pressure. Irradiation was carried out in a ~300 L Teflon bag surrounded by 8 germicidal lamps (Philips, TUV 30 W with maximum output at 254 nm) for photolysis H₂O₂ and 16 fluorescent lamps (30 W, Academy of Electric Lamp-House in Beijing) for photolysis CH₃ONO and HONO. The Teflon bag was hung inside the cubic thermostatic chamber. HONO was introduced to the Teflon bag by purging a freshly prepared solution containing 20 mL 1%NaNO₂ in 45 mL 30%H₂SO₄. CH₃ONO was prepared by adding 100 mL 50%H₂SO₄ to 90 mL 50%NaNO₂ methanol and water mixture ($V_{\text{methanol}}:V_{\text{water}}=5:4$), and further purified by repeated freeze, pump, and thaw cycles and fractional distillation before use.

Typical reaction mixtures consisting of samples CH₃SCH₃ ~20 μmol/L, references (propene, ethene, *c*-hexane and isoprene) ~20 μmol/L, H₂O₂ 30%, 0.2 mL, CH₃ONO ~10 μmol/L, NO ~5 μmol/L, were used in the experiments.

Because these three relative rate techniques require that DMS and the reference organics are consumed only by reactions with OH· radicals



Then the following expression holds

$$\ln \frac{[\text{DMS}]_{t_0}}{[\text{DMS}]_t} = \frac{k_1}{k_2} \ln \frac{[\text{R}]_{t_0}}{[\text{R}]_t} \quad (3)$$

where $[\text{DMS}]_{t_0}$ and $[\text{R}]_{t_0}$ are the concentrations of DMS and reference organics, respectively, at time t_0 , $[\text{DMS}]_t$ and $[\text{R}]_t$ are the corresponding concentrations at time t , and k_1 and k_2 are the rate constants for reactions (1) and (2), respectively. Thus a plot of $\ln([\text{DMS}]_{t_0}/[\text{DMS}]_t)$ against $\ln([\text{R}]_{t_0}/[\text{R}]_t)$ should yield a straight line of slope k_1/k_2 and zero intercept.

A gas chromatograph (GC-6AM, Shimadzu, Japan) equipped with a flame photometer detector (FPD) was used for the CH₃SCH₃ quantitative analysis. CH₃SCH₃ in the reaction mixtures were separated on a 3 m×4 mm glass column packed with 20%SE30 on Chromosorb P (0-80 mesh). A gas chromatograph (GC-FID, HP5890, Agilent Technologies) equipped with flame ionization detector was used for other organic quantitative analysis. The references (propene, ethene, *c*-hexane and isoprene) in the reaction mixtures were separated on a 2 m×3 mm Teflon column packed with GDX 103 (60-80 mesh). GC-PID (GC4400, East&West Analytical

Instruments, Inc.) was also used for analyzing the reactants by using different columns to prevent the interference of the reaction products with the reactants.

The chemicals were as follows: propene, standard gas with mixing ratio of 1.97% in nitrogen; NO₂, standard gas with mixing ratio of 0.25% in nitrogen; Ethene, >99%. All these chemicals were products of National Research Center for Certified Reference Materials of China. DMS (Fluka, 98%), isoprene (Fluka, 98%) and cyclohexane (Concord, ≥99%) were further purified by repeated freeze, pump, and thaw cycles and fractional distillation before use; H₂O₂ (30%, Tianjin Oriental Chemical Plant); NaNO₂ (99%, Beijing chemical reagent company); H₂SO₄ (98%, Beijing chemical reagent company); N₂ (>99.999%) and O₂ (>99.999%) were products of Beijing Haipu Gas Industry Company; Compressed air (Beijing Huayuan Gas Industry Company) was purified by passing it through silica gel, 5A molecular sieves and active carbon before use.

III. RESULTS AND DISCUSSION

A. Rate constant of DMS measurement in HONO system

The rate constant was first studied by irradiation on DMS/cyclohexane/HONO/air mixture at 101 kPa total pressure and 298±1.5 K. DMS was consumed completely after 15 min irradiation when the first data point was collected. The rate constant could roughly be estimated based on the one point decays of cyclohexane and DMS as $\sim 9 \times 10^{-10}$ cm³/(molecule·s), was about two magnitudes higher than the value reported by Cox and Sheppard [21], who used the same method as ours in air. As byproducts of producing HONO, NO_x would also be introduced in the reaction bag and extremely high concentrations of NO_x were indeed observed in the reaction mixture (Fig.1). There seems to be a general agreement that relative techniques using systems containing NO_x give erroneous rate constant data for the reaction of OH· with DMS due to unknown sec-

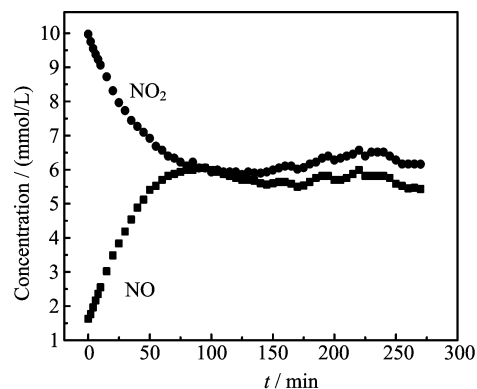


FIG. 1 Concentrations of NO_x vs. irradiation time for the HONO-air system at 298 K and atmospheric pressure.

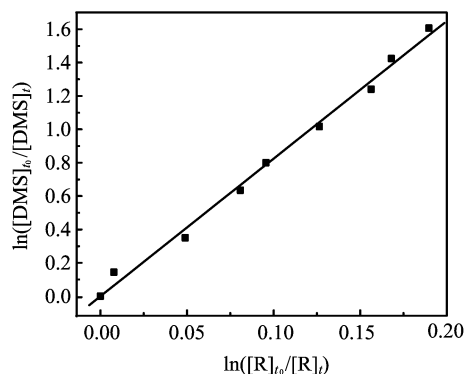


FIG. 2 Plot of relative rate constant data for the reaction of OH· with DMS in HONO-O₂ system at 298 K and atmospheric pressure using C₂H₄ as a reference compound.

ondary reactions in these systems. To explore the reason, the rate constant was also studied by irradiation on DMS/ethene/HONO/O₂ mixture at 101 kPa total pressure and 298±1.5 K. The decay rate of DMS was much slower than that in the air, and enough data points were obtained under this system. The typical plot according to Eq.(3) obtained from this mixture is shown in Fig.2. The observed rate constant for reaction (1) obtained relative to C₂H₄ ($8.0 \times 10^{-12} \text{ cm}^3/(\text{molecule}\cdot\text{s})$) [40] is $(6.60 \pm 0.21) \times 10^{-11} \text{ cm}^3/(\text{molecule}\cdot\text{s})$ (the specified error indicates two standard deviations). Because the conditions are identical for the two studied mixtures, the different rate constants obtained by the two studied mixtures could only be explained by the reaction of DMS with oxygen atoms O(³P) which were produced by photolysis of NO₂ in the systems. The rate constant of the reaction between DMS and O(³P) is about one magnitude higher than that of DMS with OH·. The concentration of O(³P) in the O₂ mixture would be greatly suppressed due to the fast reaction of O(³P)+O₂+M→O₃+M. Compared with the reported values [41], the rate constant obtained in the O₂ mixture is very high, indicating there is still enough O(³P) in the reaction bag under our experimental conditions. To provide further evidence for the influence of O(³P) on the measured rate constants in our systems, we studied the decay rates of DMS by irradiation on DMS/NO₂(~5 mmol/L)/N₂, air, and O₂ mixtures, respectively, as shown in Fig.3. It is evident that O(³P) must have important impact on consuming DMS in the mixtures of DMS/ethene/HONO/O₂ and DMS/cyclohexane/HONO/air under our experimental conditions, because extremely high initial concentration of NO₂ existed in mixtures.

B. Rate constant of DMS measurement in CH₃ONO-NO system

A second set of measurements of the rate constant for reaction (1) were carried out by irradiation on the mixtures of DMS/references/CH₃ONO/air and O₂, re-

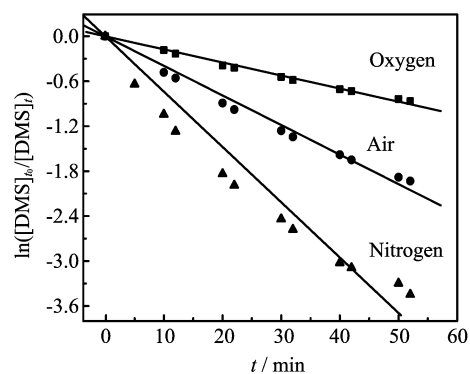


FIG. 3 Plots of DMS consumed vs. irradiation time in 5 mmol/L NO₂ at 298 K and atmospheric pressure.

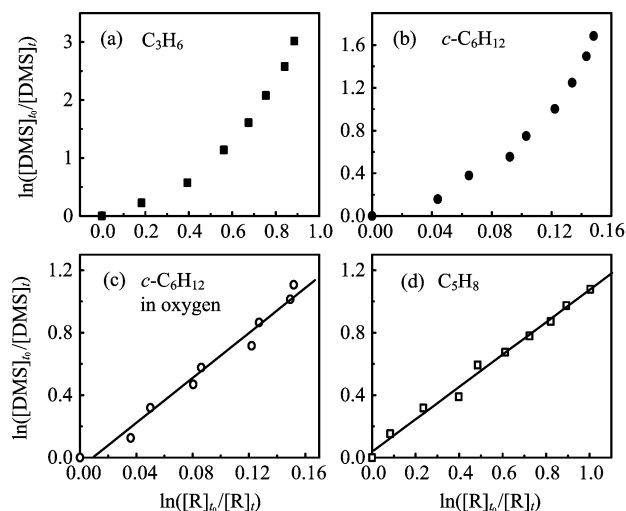
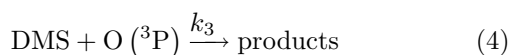


FIG. 4 Relative rate constant data for OH· reaction with DMS in CH₃ONO-NO system at 298 K and atmospheric pressure, using cyclohexane, propene, and isoprene as reference compounds.

spectively. Propene, isoprene, and cyclohexane were selected as the reference compounds. The concentration-time data from the relative experiments plotted according to Eq.(3) are shown in Fig.4. As can be seen, Figure 4 (a) and (c) did not give the expected straight lines (in air). The curvature of the plots in Fig.4 (a) and (c) from the relative measurements has previously been reported by Atkinson *et al.* [23] and Nielsen *et al.* [30], who also used CH₃ONO as OH· precursor. Atkinson *et al.* suggested that the main reason for this curvature was the formation of NO₃ under conditions where O₃ generation was significant [23]. Nielsen *et al.* thought that CH₃SNO and CH₃SO formed in the gas mixtures were responsible for the additional loss of DMS [30]. However, straight lines were obtained in the O₂ system (Fig.4(b)) and in the air with isoprene as reference compound (Fig.4(d)). As mentioned in the above section, O₂ can greatly suppress the concentration of O(³P), Thus it is clear that O(³P) must

be the additional loss of DMS and responsible for the curvature of the plots in the air systems by photolysis of CH_3ONO as the $\text{OH}\cdot$ source. Because at least one NO_2 molecule will be produced when one $\text{OH}\cdot$ radical is formed for using CH_3ONO as the $\text{OH}\cdot$ source, NO_2 will accumulate in the reaction mixture as the photochemistry proceeds and more $\text{O}(^3\text{P})$ will be produced. NO_3 , CH_3SNO , and CH_3SO should be at the same level in both the air and O_2 systems, and could not account for the different concentration-time data observed between the air and O_2 systems. The rate constant for reaction (1) derived from Fig.4(b) was $(4.79 \pm 0.32) \times 10^{-11} \text{ cm}^3/(\text{molecule}\cdot\text{s})$, which was in good agreement with the previously measured value (in air) by Barnes *et al.* [29], but much larger than those measured in other laboratories at all O_2 levels by using other $\text{OH}\cdot$ sources without NO_x presence. The slope of Fig.4(d) was 1.09 ± 0.02 , which is far from the ratio of the rate constant of DMS with $\text{OH}\cdot$ to that of isoprene with $\text{OH}\cdot$, but close to the ratio of the rate constant of DMS with $\text{O}(^3\text{P})$ ($k_{\text{O}+\text{DMS}} = 5.08 \times 10^{-11} \text{ cm}^3/(\text{molecule}\cdot\text{s})$) [42] to that of isoprene with $\text{O}(^3\text{P})$ ($k_{\text{O}+\text{isoprene}} = (3.5 \pm 0.6) \times 10^{-11} \text{ cm}^3/(\text{molecule}\cdot\text{s})$) [43], indicating that $\text{O}(^3\text{P})$ must be the dominant loss path in the systems under our experimental conditions.

In order to explain the increase in the overall reaction rate of $\text{OH}\cdot$ with DMS in the presence of $\text{O}(^3\text{P})$, a mechanism involving the following reaction is proposed.



In this scheme the overall consumption of DMS should not only depend on the concentration of $\text{OH}\cdot$ radicals, but also depend on the concentration of O atoms. For the rate constant for the reaction of $\text{O}(^3\text{P})$ with DMS is shown to be more than 1 order magnitude faster than the reaction of $\text{OH}\cdot$ with DMS. To compete with the consumption of $\text{OH}\cdot$ radicals, the concentration of O atoms does not need to be large enough. A simple co-operation between reaction (1) and reaction (4) gives

$$\frac{d[\text{DMS}]}{dt} = -k_1 \left\{ 1 + \frac{k_3 [\text{O}(^3\text{P})]}{k_1 [\text{OH}\cdot]} \right\} [\text{OH}\cdot] [\text{DMS}] \quad (5)$$

where k_1 and k_3 are the rate constants of $\text{OH}\cdot + \text{DMS}$ and $\text{O}(^3\text{P}) + \text{DMS}$. Since the fraction of $[\text{O}(^3\text{P})]$ *vs.* $[\text{OH}\cdot]$ is not known in RONO system, accurate values of the correction factor to account for reactive loss processes of the $\text{O}(^3\text{P}) + \text{DMS}$ cannot be calculated. However, a lower limit to this factor can be obtained by assuming that the concentration of $\text{O}(^3\text{P})$ is equal to the zero, then the correction factor would be 1 for the reaction of $\text{OH}\cdot + \text{DMS}$ in the RONO system.

C. Rate constant of DMS measurement in H_2O_2 system

In order to eliminate the influence of NO_x present in the reaction system, photolysis of H_2O_2 was used as the $\text{OH}\cdot$ source, which was potentially a much cleaner system to study the reaction. The experiments were carried out with nitrogen, air, and oxygen as bath gases, respectively. The experimental data when plotted according to Eq.(3) gave reasonable straight lines. Typical plots of the results derived from these mixtures are shown in Fig.5. The rate constants at room temperature ($298 \pm 1.5 \text{ K}$) derived from the plots for the reaction of $\text{OH}\cdot$ with propene ($k_1 = 2.6 \times 10^{-11}$) [44] were 8.56×10^{-12} , 11.31×10^{-12} , and 4.50×10^{-12} in air, O_2 , and N_2 , respectively. It can be seen that the rate constant determined for the reaction of $\text{OH}\cdot$ with DMS increases with the increasing partial pressure of O_2 in the system.

The rate coefficients k_1 were also measured over the temperature range 287-348 K both in air and in nitrogen, and summarized in Table I. k_1 was measured relative to that of propene ($k = 4.85 \times 10^{-12} \exp[(504 \pm 46)/T]$) recommended by Wallington [27], and the data are also plotted in Arrhenius form

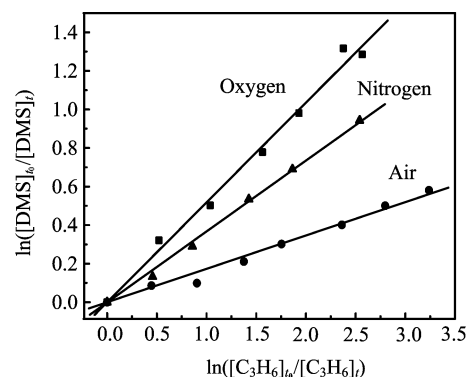


FIG. 5 Plots of the results according to Eq.(3) for DMS and propene as obtained for experiments performed at 101 kPa by using H_2O_2 as $\text{OH}\cdot$ radicals source in N_2 , O_2 , and air at 298 K.

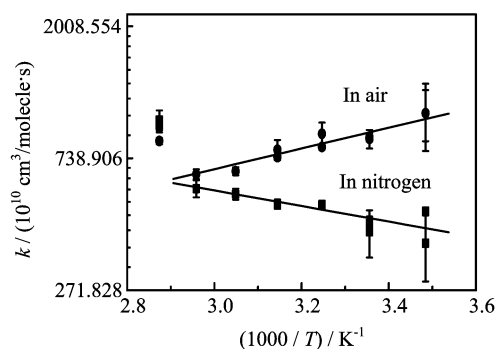


FIG. 6 Arrhenius plots of the rate coefficients determined for $\text{DMS} + \text{OH}\cdot$ in the temperature range from 287 K to 348 K in air and N_2 by using H_2O_2 as $\text{OH}\cdot$ radicals source.

TABLE I The rate constant of OH·+DMS by photolysis of H₂O₂ as OH· source.

<i>T</i> /K	Bath gas	$k_2 \times 10^{12}$ cm ³ /(molecule·s)	k_1/k_2	$(k_1 \pm 2\sigma)/10^{-12}$ (cm ³ /(molecule·s))
273	Air	30.72	0.31±0.01	11.3±6.1
287	Air	28.08	0.37±0.01	10.4±2.0
	Nitrogen		0.14±0.02	3.88±0.98
298	Air	26.02	0.33±0.01	8.56±2.80
	Nitrogen		0.17±0.01	4.50±0.25
308	Air	24.91	0.32±0.01	8.05±0.17
	Nitrogen		0.21±0.01	5.19±0.17
318	Air	23.66	0.32±0.01	7.45±0.11
	Nitrogen		0.22±0.01	5.22±0.18
328	Air	22.54	0.30±0.01	6.70±0.21
	Nitrogen		0.25±0.01	5.63±0.24
338	Air	21.54	0.30±0.01	6.55±0.24
	Nitrogen		0.27±0.01	5.87±0.38
348	Air	20.64	0.41±0.01	8.42±0.20
	Nitrogen		0.46±0.01	9.66±0.74

in Fig.6. The observed rate coefficients were fitted to give the Arrhenius expressions: $k_{\text{DMS+Air}} = (7.24 \pm 0.28) \times 10^{-13} \exp[(770.7 \pm 97.2)/T]$, $k_{\text{DMS+N}_2} = (3.40 \pm 0.15) \times 10^{-11} \exp[-(590.3 \pm 165.9)/T]$, $k_{\text{DMS+Air}}$ represents the rate coefficient of DMS+OH· in air and $k_{\text{DMS+N}_2}$ represents the rate coefficient in nitrogen, and the indicated errors are two least-squares standard deviations.

It should be mentioned that the rate coefficients obtained in both N₂ and air at 348 K departed from the lines of the plots in the Arrhenius forms. The Teflon bag was cleaned by a textile towel before every experiment, because a wall loss of DMS was indeed measured after several experiments. There was no change in the DMS wall loss rate ever observed between the pre- and post-irradiation periods under this treatment at temperature below 338 K; significant DMS wall loss was only observed at 348 K after irradiation. Therefore, the departure from the lines of the plots in Arrhenius form at 348 K should be ascribed to DMS wall loss under our experimental conditions. The rate coefficient obtained at 338 K in N₂ was very close to that in air, indicating the adduct CH₃S(OH·)CH₃ formation for reaction (1) has no contribution under the temperature around 338 K.

The rate constant obtained in this study for the reaction between DMS and OH· at room temperature in N₂ is in very good agreement with most of the other results obtained using absolute and relative methods (Table II). The substantially lower values obtained by three absolute studies were ascribed to the influence of O(³P) under extremely high OH· concentrations employed in their systems [35].

Table III shows a comparison between the overall rate constant obtained in this work for the reaction of DMS with OH· in the purified air at 298 K, 101 kPa, and

TABLE II The rate constant for reaction of OH·+DMS k_1 (in cm³/(molecule·s)) in absence of O₂ at room temperature.

$k_1 \times 10^{-12}$	<i>T</i> /K	Technique
4.26±0.56	298	FP-RF ^a [22]
3.22±0.16	293	DF-EPR ^a [25]
4.44±0.23	298	FP-RF ^a [26]
4.80±0.11	298	PLP-PLIF ^a [26]
3.60±0.20	297	FP-RF ^a [27]
5.30±0.50	296	DS-FTIR ^b [27]
5.50±1.00	298	DF-RF ^a [28]
4.40±0.40	298	CP-GC ^b [29]
3.50±0.20	295	PR-KS ^a [30]
4.98±0.46	297	HPF-LIF ^a [31]
4.94±0.35	298	PLP-PLIF ^a [32]
5.00±1.00	299	CP-FTIR ^b [35]
4.50±0.25	298	CP-GC ^b

^a Absolute technique: FP=flash photolysis, RF=resonance fluorescence, DF=discharge flow, EPR=electron paramagnetic resonance, PLP=pulsed laser photolysis, PLIF=pulsed laser induced fluorescence, PR=pulse radiolysis, KS=kinetic spectroscopy, HPF=high pressure flow, LIF=laser induced fluorescence.

^b Relative technique: DS=dark source of OH· (O₃+N₂H₄), FTIR=Fourier transform infrared spectroscopy, CP=continuous photolysis, GC=gas chromatography.

those reported in other studies under similar conditions which are considered free of potential artifacts.

The value obtained in this work for atmospheric conditions at room temperature is in reasonable agreement with other values measured using relative kinetics techniques, but is approximately 27% higher than the value reported by Hynes *et al.* [26], who used an absolute

TABLE III The rate constant k_1 (in $\text{cm}^3/(\text{molecule}\cdot\text{s})$) for reaction of $\text{OH}\cdot + \text{DMS}$ in air (or the O_2 partial pressure equal to the air).

$k_1 \times 10^{-12}$	T/K	Method
6.28 ± 0.10	298	PLP-PLIF ^a [26]
8.5 ± 0.2	296	DS-FTIR ^b [27]
8.0 ± 0.5	298	CP-GC ^b [29]
7.80	298	CP-FTIR ^b [35]
8.56 ± 0.06	298	CP-GC ^b

^a Absolute technique: PLP=pulsed laser photolysis, PLIF=pulsed laser induced fluorescence.

^b Relative technique: CP=continuous photolysis, GC=gas chromatography, DS=dark source of $\text{OH}\cdot$, FTIR=Fourier transform infrared spectroscopy.

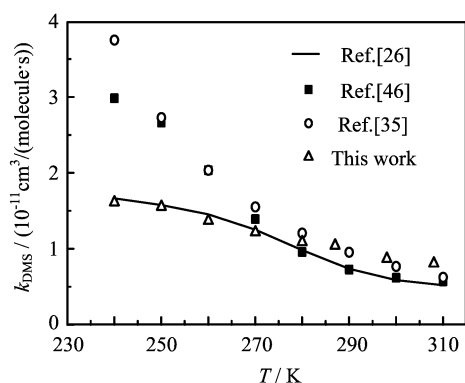


FIG. 7 Variation in the overall rate coefficient k_1 for $\text{DMS} + \text{OH}\cdot$ in air as a function of temperature.

technique (see Fig.7). One possibility which could explain the discrepancy between the values from relative kinetics techniques and those from the absolute technique employed by Hynes *et al.* [26] would be the regeneration of $\text{OH}\cdot$ in their absolute technique.

The Arrhenius expressions derived in this work from the measurement in N_2 and air for the reaction of DMS with $\text{OH}\cdot$ in the temperature range of 287-338 K is compared with other measurements in the absence of O_2 and in air (Table IV).

The activation energy for H-abstraction of reaction (1) is still not well characterized. A positive Arrhenius activation energy was reported by most of the investigators who used absolute techniques, and is also recommended by the latest IUPAC data evaluation [45]. However, a negative Arrhenius activation energy was also observed by Willington *et al.*, who used an absolute technique [27] and by Albu *et al.*, who used a relative method [35]. The observation of a positive Arrhenius activation energy has been taken as indicating the dominance of the hydrogen abstraction for reaction (1) in the systems used to study the reaction, while measurement of a negative Arrhenius activation energy has been taken as an indication that the adduct $\text{CH}_3\text{S}(\text{OH}\cdot)\text{CH}_3$

TABLE IV Arrhenius expressions for $\text{DMS} + \text{OH}\cdot$ reaction in different ranges of temperature in the absence of O_2 .

$k_{\text{air}}/10^{-12}$ ($\text{cm}^3/(\text{molecule}\cdot\text{s})$)	T/K	Method
$(6.8 \pm 1.1)\exp[(-138 \pm 46)/T]$	248-363	FP-RF ^a [22]
$(1.4 \pm 0.4)\exp[(-332 \pm 96)/T]$	276-397	FP-RF ^a [26]
$(0.25 \pm 0.09)\exp[(130 \pm 102)/T]$	297-400	FP-RF ^a [27]
$(11.8 \pm 2.2)\exp[(-236 \pm 150)/T]$	260-393	DF-RF ^a [28]
$(1.35 \pm 0.62)\exp[(-285 \pm 135)/T]$	297-368	HPF-LIF ^a [31]
$11.3\exp(-253/T)$	240-400	Review [45]
$(1.56 \pm 0.20)\exp[(369 \pm 27)/T]$	250-400	CP-FTIR ^b [35]
$(34.0 \pm 1.5)\exp[(-590.3 \pm 165.9)/T]$	287-338	CP-GC ^b

^a Absolute technique: FP=flash photolysis, RF=resonance fluorescence, DF=discharge flow, HPF=high pressure flow, LIF=laser induced fluorescence.

^b Relative technique: CP=continuous photolysis, FTIR=Fourier transform infrared spectroscopy, CP=continuous photolysis, GC=gas chromatography.

formation for reaction (1) is also probably contributing to the rate constant measurement under the conditions employed. The most recent work [34] of Williams *et al.* includes low temperature (~ 240 K) studies of the equilibration of $\text{OH}\cdot$ with DMS and DMS-d_6 as a function of pressure and the variation of the effective rate coefficients for $\text{OH}\cdot + \text{DMS}$ and $\text{OH}\cdot + \text{DMS-d}_6$ as a function of O_2 partial pressure at 27 and 80 kPa total pressure [36]. Although this reaction proceeds via a complex two channel, mechanisms cannot be described by a simple Arrhenius expression. The negative Arrhenius activation energy observed by Albu *et al.* was forced to ascribed to the presence of small quantities of O_2 due to the leakage, the impurity of N_2 , and chemical formation [35]. In this work, further evidence was provided for the hydrogen abstraction as the dominant loss path for reaction (1) in the absence of O_2 as a positive Arrhenius activation energy was also observed. The pre-exponential factor and the Arrhenius activation energy obtained in this work are slightly higher than those of a positive Arrhenius activation energy obtained by using absolute techniques, but the Arrhenius activation energy is close to those of Hynes *et al.* [26], Hsu *et al.* [28], and Abbatt *et al.* [31], when the uncertainties are considered. At the high temperature end of our experimental temperature regime, the adduct is unstable so only the H-transfer pathway should be observed. Hence, at $T=335$ K, the activation energy in air should be the same as the activation energy in N_2 . As the temperature is reduced, the reversible addition pathway contributes to the rate constant and the temperature dependence become non-Arrhenius. Further evidence from Stickel *et al.* showed via direct detection of the HDO product in a flash photolysis experiment, in the absence of O_2 , the $\text{OD} + \text{DMS}$ reaction produces HDO with a yield near unity [46].

However, the measured rate constant of Hynes *et al.*

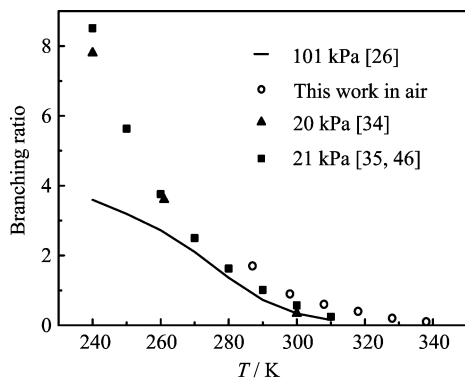


FIG. 8 Temperature dependence of the branching ratio between the addition and abstraction channels for DMS+OH· as measured.

at 250 K [26] was still about 29% lower than the calculated value at 260 K from the new recommended fit given in Atkinson *et al.* [45], which incorporates the new data of Williams *et al.* [34]. It is evident that a relatively small error in the temperature measurements cannot explain the large difference between the data of Hynes *et al.* [26] and Williams *et al.* [34]. Therefore, it is still difficult to draw a clear conclusion for the temperature dependence of the rate coefficients for the reaction between DMS and OH· under the atmospheric condition because of large differences among the above measurements.

Figure 8 compares the temperature dependence of the branching ratio between the addition and abstraction channel for DMS+OH· obtained from different laboratories. The branching ratio is defined as $(k_{\text{DMS+air}} - k_{\text{DMS+N}_2})/k_{\text{DMS+N}_2}$. It should be mentioned that the data points of Albu *et al.* [35] is derived from their measured values of the overall reaction ($k_{\text{DMS+air}}$) at $p_{\text{O}_2}=20$ kPa and the value for the abstraction channel taken from Atkinson *et al.* [45]. If the abstraction channel of Albu *et al.* [35] was adopted, the data points would be far from others. The branch ratios measured or calculated by this work above 270 K are in good agreement with others, while somewhat less than those of Williams *et al.* [34], Atkinson *et al.* [45] and Albu *et al.* [35] when the temperature is below 270 K.

IV. CONCLUSION

Oxygen atoms ($\text{O}(^3\text{P})$) produced by photolysis of NO_2 were found to be a dominant additional loss pathway for the reaction of OH· with DMS, by using the relative techniques with CH_3ONO and HONO as OH· precursors. The rate constant for the reaction of OH· with DMS obtained in these systems should be suspected.

A positive Arrhenius activation energy was observed in this work using H_2O_2 as the OH· source. This further confirms the dominance of the hydrogen abstraction re-

action in inert bath gases. The rate constants calculated from the fit expression obtained in air by this work agree very well with those of Hynes *et al.* [26]. Williams *et al.* [34] and Albu *et al.* [35] found a sharp increase in the rate constant for the reaction of OH· with DMS in air at temperature below 260 K compared with the calculated data from the fit expressions of Hynes *et al.* [26]. However, to accurately evaluate the influence of DMS on the upper troposphere/lower stratosphere, further measurements with higher precision are required to determine more accurately the Arrhenius parameters for the overall rate coefficients (abstraction and addition channels) for DMS with OH· in the air.

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