Chemical Physics 109 (1986) 101–107
North-Holland, Amsterdam

KINETICS OF THE REACTION OF CH_3S WITH NO, NO_2 AND O_2

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Received 24 February 1986; in final form 1 May 1986

We have used the laser-induced fluorescence technique to study the reactions of the methyl thiyl radical (CH_3S) with NO, NO_2, and O_2 as a function of pressure (1–400 Torr N_2 or SF_6) and temperature (25–238°C). Rate constants for the reaction with NO are in the transition region between the low- and high-pressure limits and are fit using an expression developed by Troe. The resulting Arrhenius expression is $k_\infty(\pm 2\sigma) = (1.81 \pm 0.84) \times 10^{-12} \exp[(1800 \pm 320 \text{ cal/mol})/RT]$ cm^3/s. The rate constant for the reaction of CH_3S with NO_2 is essentially pressure independent and yields $k = (8.3 \pm 1.4) \times 10^{-11} \exp[(160 \pm 120 \text{ cal/mol})/RT]$ cm^3/s. The reaction with O_2 is too slow to measure in our system; we estimate that $k \leqslant 2 \times 10^{-17}$ cm^3/s at room temperature.

1. Introduction

Alkyl thiyl radicals (RS) are intermediates in combustion and atmospheric chemistry. Their precursor organosulfur compounds can be found in existing petrochemical energy production technologies as well as the newly emerging synthetic fuels [1,2]. These compounds although minor substituents [3,4] may play a role in the atmospheric sulfur cycle [5]. They have been shown to produce methanesulfonic acid under atmospheric conditions [6–8], which is relevant to the acid precipitation problem. It is therefore important to investigate the mechanisms by which these reactions proceed.

To date, most studies of organosulfur chemistry have obtained rate constant ratios by observing reaction product yields. The only reported absolute rate constant studies involve the HS radical [9–11]. Recently, the emission and laser-induced fluorescence spectra of CH_3S were published [12,13]. We report here direct measurements of the rate constants for the reaction of CH_3S with NO, NO_2, and O_2 as a function of temperature and pressure.

2. Experimental

Methyl thiyl radicals (CH_3S) are produced by pulsed laser photolysis of dimethyl disulfide $(CH_3S)_2$, at 266 nm. The methyl thiyl radical concentration is probed by monitoring the fluorescence resulting from laser excitation of the $\tilde{A}\,^2A_1 \leftarrow \tilde{X}\,^2E_{3/2}$ transition at 371.77 nm. The photolysis laser, a Quantel Nd:YAG (10 Hz, ≈ 10 ns pulse length), is frequency quadrupled to provide the photolysis radiation. The LIF excitation source is a Lambda Physik FL 2002 dye laser pumped by a Lambda Physik EMG 102 excimer laser. The dye QUI is used to obtain the excitation wavelength. The pulse energy of the YAG at 266 nm averaged 18 mJ while the dye laser output varied between 4 and 10 mJ.

The apparatus is described in previous publications [14,15]. Briefly, the pump and probe laser beams counterpropagate colinearly through the reaction cell which consists of a 5 cm diameter stainless-steel cross. The cell is contained in a forced-convection oven equipped with ports for the laser beams and light collection optics. Oven temperatures are constant to ±1 K. The fluorescence emission is collected at right angles to the laser beams. It is collimated, passes through a 1 cm path, liquid CS_2 filter and a 450 nm broad-

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band-pass dielectric filter, detected by an RCA 31000 photomultiplier, averaged by a boxcar integrator, and both digitized and processed by a laboratory microcomputer.

The delay time between the firing of the photolysis laser and the probe laser is controlled by the boxcar. In kinetic experiments, the delay time is scanned from 5 μs to 10 ms to obtain a time history for the decay. We wait 5–50 μs after the photolysis pulse to avoid effects due to vibrational relaxation, prompt emission of photolysis products, and NO_2 fluorescence.

Experiments are performed under pseudo-first-order conditions. In the absence of any reactant, methyl thiyl radicals decay via self reaction and diffusion. When reactants are present in sufficient concentrations, the CH_3S disappearance can be fit by a single exponential extending over 2–6 lifetimes.

The dimethyl disulfide (97% minimum purity) is obtained from Kodak and used without further purification. Air Products industrial grade N_2 (99.998%) and O_2 (99.5%) and Matheson SF_6, chemically pure (99.8%) are also used without further purification. The NO_2 and NO are obtained from Matheson. The NO_2 is mixed with an excess of O_2, frozen at −196°C and allowed to warm to room temperature. This procedure is repeated until the blue color of N_2O_3 disappears and the mixture becomes pure white. The NO_2 is then distilled from −63 to −130°C and stored in O_2 until used. The NO is passed through silica gel maintained at dry-ice temperature and distilled from −186 to −196°C prior to each usage to maintain the highest possible purity.

Metered flows of $(CH_3S)_2$, reactants (O_2, NO or NO_2) and buffer gas (N_2 or SF_6) are combined and flowed through the cell at total flow rats ranging from 0.1 to 20 standard ℓ/min. All component gases in the experiment are combined at a distance from the cell which ensures uniform mixing (mixing time ≈ 0.25 s). The NO and NO_2 are prepared as mixtures in the buffer gas which range from 1 to 10% and are flowed from mixing tanks. Typical reactant pressures were 1–2 mTorr $(CH_3S)_2$, 0–400 mTorr NO, 0–35 mTorr NO_2, 0–300 Torr O_2, and 1–400 Torr total pressure using N_2 or SF_6.

3. Results

The LIF signal used for kinetic experiments was excited at 371.77 nm since this wavelength corresponds to the most intense peak of the excitation spectrum. Second-order rate constants were measured for the reactions of CH_3S with NO, NO_2, and O_2 over a range of temperatures (25–238°C) and total pressures (1–400 Torr). The total pressure was kept constant using N_2 or SF_6 as a buffer gas and the CH_3S decay was monitored over a range of reactant pressures. Pseudo-first-order decay constants are obtained from plots of LIF signal versus delay time between the photolysis and probe lasers. These rates are plotted against reactant pressure to obtain the second-order rate constants. Experiments performed at 211°C show that CH_3S decomposition is not observable up to 10 Torr total pressure of N_2.

Measured bimolecular rate constants for the reaction of CH_3S with NO are listed in table 1. The uncertainties listed ($\pm 2\sigma$) refer to the precision of the data as evidenced by the scatter in the second-order plots. Consideration of possible systematic errors leads us to estimate the accuracy of the bimolecular rate constants as ±20%. The rate constants measured at room temperature with N_2 as the buffer gas are plotted in fig. 1, along with the high-pressure limiting rate constant obtained from measurements using SF_6 as the buffer gas.

The pressure dependence of the bimolecular rate constant was fit to a semi-empirical expression developed by Troe [16]:

$$\log k_{\mathrm{bi}} = \log\left(\frac{k_0[\mathrm{M}]}{1 + k_0[\mathrm{M}]/k_\infty}\right) + \frac{\log F_\mathrm{c}}{1 + \left[\log(k_0[\mathrm{M}]/k_\infty)\right]^2},$$

where $k_0[\mathrm{M}]$ and k_∞ are the low- and high-pressure limiting bimolecular rate constants and F_c is the broadening factor derived by Troe. The results of the fit to the data at 295 K is shown as the solid line in fig. 1 and listed in table 2 along with the fits for the next three temperatures studied. At the highest temperature studied, 503 K, there was insufficient data to obtain a meaningful fit.

Table 1
Bimolecular rate constants for the reaction of CH_3S with NO

T (K)	M	Total pressure (Torr)	$10^{12}\,k_{bi} \pm 2\sigma$ (cm^3/s)
295	N_2	1.5	1.44 ±0.18
		1.5	1.70 ±0.32
		2.0	1.64 ±0.22
		2.0	1.56 ±0.14
		2.5	2.27 ±0.16
		3.0	2.67 ±0.34
		4.0	2.95 ±0.14
		5.0	3.48 ±0.30
		7.0	4.58 ±0.30
		7.0	4.20 ±0.06
		10	4.68 ±0.74
		10	5.65 ±1.28
		15	6.45 ±0.48
		15	7.99 ±0.70
		20	8.25 ±0.36
		30	9.96 ±0.74
		30	11.0 ±2.2
		50	16.5 ±2.2
		50	15.2 ±1.4
		50	15.6 ±2.4
		80	16.9 ±1.0
		100	15.0 ±2.0
		100	18.3 ±1.8
		200	26.4 ±3.6
		202	23.4 ±4.2
		300	15.4 ±5.6
		300	20.3 ±6.4
	SF_6	200	38.4 ±4.2
		300	39.7 ±4.4
351	N_2	2.0	1.03 ±0.12
		4.0	1.64 ±0.12
		7.0	2.28 ±0.10
		10	3.12 ±0.22
		20	4.76 ±0.22
		40	7.60 ±0.28
		70	10.7 ±0.6
		100	14.7 ±1.6
		200	19.0 ±0.8
		300	20.7 ±1.8
	SF_6	200	22.9 ±1.4
		300	24.0 ±2.0
397	N_2	2.0	0.745±0.148
		2.0	0.811±0.110
		3.0	0.864±0.148
		4.0	0.926±0.040
		7.0	1.36 ±0.12
		10	2.97 ±0.58
		20	3.51 ±0.42
		40	5.06 ±0.24
		70	7.16 ±0.50
		100	9.69 ±1.00
		200	12.0 ±1.6
		300	14.0 ±1.6
	SF_6	200	18.3 ±1.0
		300	18.7 ±3.6
453	N_2	5.0	0.648±0.038
		7.0	0.756±0.066
		10	0.977±0.066
		20	1.57 ±0.16
		40	2.99 ±0.26
		70	5.07 ±0.46
		100	6.86 ±0.38
		200	9.79 ±0.84
		300	10.2 ±1.2
	SF_6	200	10.8 ±0.7
		400	13.4 ±2.4
503	N_2	4.0	0.384±0.076
		7.0	0.471±0.058
		10	0.570±0.062
		20	1.20 ±0.22
		40	1.93 ±0.18
		70	2.75 ±0.22
		100	4.55 ±0.40
		200	7.14 ±0.52
		300	7.09 ±0.62
	SF_6	400	8.53 ±1.84

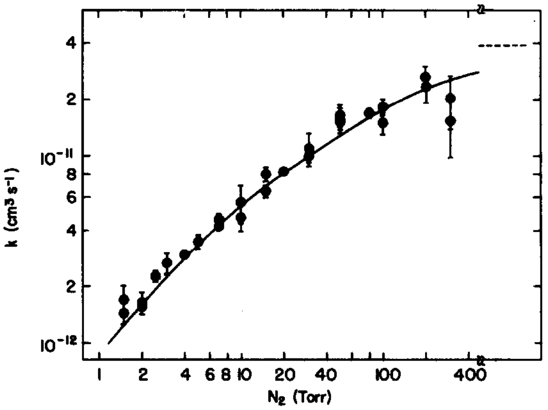


Fig. 1. Pressure dependence of the bimolecular rate constants for the reaction of CH_3S with NO at 295 K. The circles represent measurements in N_2 and the dotted line is the high-pressure limit determined from measurements in SF_6 at 200 and 300 Torr total pressure. The line shown is the result of a semi-empirical fit described in the text.

Table 2
Measured and fitted coefficients for the pressure dependence of the reaction $CH_3S + NO$ as a function of temperature

T(K)	$10^{29}\, k_0$ [a)] (cm^6/s)	$10^{11}\, k_\infty$ [a)] (cm^3/s)	F_c [a)]
295	3.24 ± 0.36	3.90 ± 0.60 [b)]	0.57 ± 0.06
	3.26 ± 0.48	3.60 ± 1.60 [c)]	0.60 ± 0.20
351	1.43 ± 0.36	2.35 ± 0.24 [b)]	0.86 ± 0.16
397	1.13 ± 0.20	1.85 ± 0.38 [b)]	0.77 ± 0.12
453	0.584 ± 0.066	1.34 ± 0.30 [b)]	0.94 ± 0.11

[a)] All uncertainties are $\pm 2\sigma$.

[b)] Derived from measurements in SF_6.

[c)] Derived from a fit to the data obtained using N_2 as the buffer gas.

The measured high-pressure limiting rate constants for the reaction of CH_3S with NO using SF_6 as the buffer gas are shown plotted in Arrhenius form in the lower panel of fig. 2. The rate constant expression derived from a fit to these data is:

$$k_\infty(T) = (1.81 \pm 0.84) \times 10^{-12} \times \exp[(1800 \pm 320 \text{ cal/mol})/RT] \text{ cm}^3/\text{s},$$

where the uncertainties are $\pm 2\sigma$ and are statistical only.

Table 3
Bimolecular rate constants for the reaction of CH_3S with NO_2

T(K)	Pressure (Torr)	$10^{10}\, k_{bi} \pm 2\sigma$ (cm^3/s)	Residence time (s)
295	1	0.804 ± 0.074	4.0
	5	0.899 ± 0.056	5.4
	10	0.813 ± 0.074	7.3
	50	0.984 ± 0.086	11.0
	100	0.988 ± 0.092	7.3
295	50	1.04 ± 0.02	1.8
	100	1.08 ± 0.06	2.0
	200	1.06 ± 0.06	2.2
351	200	1.08 ± 0.10	2.3
387	200	1.06 ± 0.06	2.3
443	200	0.952 ± 0.166	2.6
511	200	0.932 ± 0.068	2.7

For the reaction $CH_3S + NO_2$, the measured bimolecular rate constants are listed in table 3. We assume that the data at 200 Torr total pressure of N_2 are in the high-pressure limit and these data are plotted in the upper panel of fig. 2. The rate constant derived is

$$k_\infty(T) = (8.3 \pm 1.4) \times 10^{-11} \times \exp[(160 \pm 120 \text{ cal/mol})/RT] \text{ cm}^3/\text{s}.$$

The rate constant for the reaction of CH_3S with O_2 is too slow to measure in our system. We estimate an upper limit of 2×10^{-17} cm^3/s.

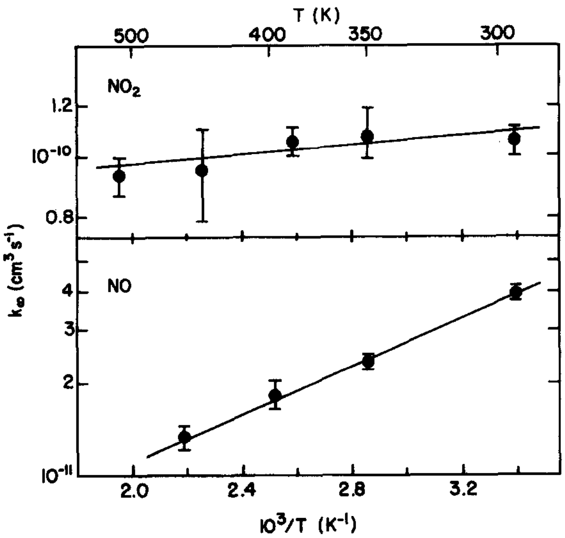


Fig. 2. Arrhenius plots for the high-pressure limiting rate constants for the reaction of CH_3S with NO_2 (upper panel) and NO (lower panel).

4. Discussion

Dimethyl disulfide, $(CH_3S)_2$, was chosen as the photolytic precursor because it is a clean source of CH_3S with no other observable decomposition channels [17]. Other possible precursors, such as CH_3SH or CH_3SCH_3, produce H atoms or alkyl radicals which could complicate the kinetic system. In the absence of added reactant, the CH_3S radicals decay due to self reaction and diffusion. We keep the precursor concentration low to minimize the contribution of self reaction.

In the presence of added NO, CH_3S has two possible additional reaction paths:

$$CH_3S + NO \xrightarrow{M} CH_3SNO, \quad \Delta H^0_{298} = -55 \pm 5 \text{ kcal/mol}; \tag{1}$$

$$CH_3S + NO \rightarrow CH_2S + HNO, \quad \Delta H^0_{298} = -7.7 \text{ kcal/mol}. \tag{2}$$

Reaction (1) is well known [17–19]. There is no conclusive evidence in our work or from the literature for reaction (2). It is known that the quantum yield for the production of CH_3SNO is approximately 2 when dimethyl disulfide is photolyzed in the presence of excess NO [17]. This implies that, at most, a few percent of the CH_3S is consumed via reaction (2).

The data in fig. 1 and table 1 demonstrate that this reaction is in the fall-off region between 1 and 300 Torr total pressure with N_2 as the buffer gas. Accordingly, we have fit the pressure dependence of the measured rate constant using the expression derived by Troe [16]. A non-linear least-squares procedure was used to obtain values for k_0 and F_c using k_∞, the high-pressure limiting value of the bimolecular rate constant, derived from measurements in SF_6. The results of these fits are listed in table 2. At room temperature, our measurements cover a major portion of the fall-off region between the low- and high-pressure limits. This is confirmed by a fit to all three parameters in the Troe expression for the rate constants measured in N_2 at 295 K which results in a value of k_∞ within 9% of that measured in SF_6. At the higher temperatures, we do not cover as much of the fall-off region within our experimentally accessible pressures of N_2 and the measured k_∞ in SF_6 is required for a reasonable fit. At the highest temperature studied, 503 K, 400 Torr of SF_6 is not sufficient to reach the high-pressure limit, therefore no fit was attempted.

At the lowest total pressures at each temperature there appears to be some leveling out of the measured rate constant. There are two possible explanations for this observation. First, a small NO_2 impurity in the NO used. For example, at 295 K and 5 Torr total pressure, a 1% NO_2 impurity would contribute 30% of the observed rate constant while at 1 Torr total pressure it would contribute 67%. Alternately, reaction (2), the abstraction channel, may be contributing to the observed rate constant. We are unable to provide a definitive explanation for the observed leveling out of the rate constant at lower total pressure, but our experience with NO mixture impurities leads us to suspect that an NO_2 impurity is responsible. These data imply that $< 5\%$ of the CH_3S is removed by reaction (2) under our experimental conditions.

In the presence of NO_2, the CH_3S radical should, by analogy with known reactions of CH_3O, undergo the following reactions:

$$CH_3S + NO_2 \overset{M}{\rightarrow} CH_3SNO_2, \tag{3}$$

$$CH_3S + NO_2 \rightarrow CH_2S + HONO. \tag{4}$$

Reaction (4) is exothermic by 36.2 kcal/mol. We are unable to find an estimate for $D(CH_3S\text{–}NO_2)$ or $\Delta H^0_{298}(CH_3SNO_2)$. Unlike the reaction with NO, we are unable to exclude the abstraction channel, reaction (4).

Our measured rate constants for the reaction $CH_3S + NO_2$ as a function of temperature and pressure are listed in table 3. There appears to be some fall-off in the rate constant at lower pressures. We believe however, that the data also contain a contribution from the thermal reaction between NO_2 and the photolysis precursor [20]:

$$(CH_3S)_2 + 4NO_2 \rightarrow (CH_3SO_2)_2 + 4NO. \tag{5}$$

The rate constant for reaction (5) is unknown, but it does remove four molecules of NO_2 for every molecule of $(CH_3S)_2$ consumed. Even at our highest NO_2 concentration, up to 15% of the NO_2 could be removed by this thermal reaction, decreasing the observed rate constant. As is shown in table 3, a six-fold decrease in the cell residence time at 50 Torr total pressure and room temperature increases the apparent rate constant by ≈ 10%. We therefore use the rate constants obtained at 200 Torr total pressure and a 2 s cell residence time as true measures of this reaction in the high-pressure limit. These values were used to obtain the Arrhenius expression.

Our data indicate that the reaction of CH_3S with NO_2 and NO proceed differently. One possibility is that $O(^3P)$, produced by the photolysis of NO_2, rapidly removes CH_3S. A photolysis laser energy of 18 mJ results in 0.4% photolysis of NO_2. The measured removal rate of CH_3S would imply a rate contant for $O(^3P) + CH_3S$ of $\approx 3 \times 10^{-8}$ cm^3/s for this fraction $O(^3P)$ production. This leads us to conclude that NO_2 photolysis followed by reaction of $O(^3P)$ is at most a minor contribution.

At present, there is little evidence for the existence of the addition channel, reaction (3). It was proposed because the analogous radical CH_3O is known to react with NO_2 to produce CH_3ONO_2 [21,22]. Also, the CH_3SNO_2 molecule has been proposed as an end product in several systems [8,19,20,23–25]. Attempts to detect CH_3SNO_2 with a mass spectrometer by photolyzing $(CH_3S)_2$ with 254 nm radiation in an excess of NO_2 failed [26]. Niki et al. [19] have tentatively assigned bands seen in an FTIR study of the photolysis of CH_3SNO under atmospheric conditions to CH_3SNO_2. Therefore, either CH_3SNO_2 exists as an intermediate in low concentrations [20,25] or it is not formed as the product of this reaction.

Our data indicate that reaction of CH_3S with NO_2 is essentially pressure independent from 1 to 200 Torr of N_2 and exhibits a small negative temperature dependence. The room temperature rate constant is only about half the collision frequency. If the reaction proceeds by an addition mechanism, the fall-off region would not be expected to be shifted by two orders of magnitude as compared to the $CH_3S + NO$ reaction. Perhaps the following reactions should be considered.

$$CH_3S + NO_2 \rightarrow CH_3S\text{-}ONO^*, \tag{6}$$

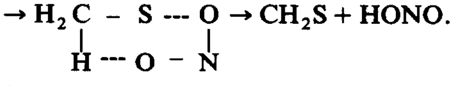
$$CH_3S\text{-}ONO^* \rightarrow CH_3S{=}O + NO. \tag{7}$$

Since $D(O\text{-}NO) = 73.2$ kcal/mol and assuming $D(CH_3S{=}O) > 100$ kcal/mol by analogy with other $-S{=}O$ bond strengths [27], the sum of reactions (6) and (7) would be expected to be more than 26.8 kcal/mol exothermic. A similar reaction has been seen by other researchers for the reaction of HS with NO_2 [9–11]

$$HS + NO_2 \rightarrow HSO + NO. \tag{8}$$

Another possible reaction to be considered involves addition followed by the formation of a six-membered ring and decomposition

$CH_3S + ONO$



$$\rightarrow \begin{array}{ccccc} H_2C & - & S & \cdots & O \\ | & & & & | \\ H & \cdots & O & - & N \end{array} \rightarrow CH_2S + HONO. \tag{9}$$

This seems unlikely in view of the large measured *A* factor. Notice that reaction (9) is essentially an alternate channel for reaction (4).

Finally, the reaction may proceed by the abstraction channel, reaction (4). This is an exothermic channel and should exhibit the observed pressure independence. It should not, however, be characterized by a negative temperature dependence. Therefore, with the information currently available, we are unable to unambiguously determine the reaction path in the $CH_3S + NO_2$ system.

Attempts to measure a rate constant for the reaction of CH_3S with O_2 failed. Total pressures were varied from 1 to 300 Torr N_2 and oxygen pressures ranged from 1 to 300 Torr. The reaction rate coefficient is $< 2 \times 10^{-17}$ cm^3/s. This is in contrast to the reaction $CH_3O + O_2$ which has a room temperature rate constant of $\approx 1.5 \times 10^{-15}$ cm^3/s. The methoxy $+O_2$ reaction is assumed to proceed through a five-membered ring intermediate with subsequent elimination of HOO. The analogous CH_3S reaction is substantially less exothermic, almost thermoneutral, and may not proceed at a measurable rate.

Rate constant ratios for the reactions of CH_3S with NO and O_2 as well as NO_2 and O_2 are $k(NO/O_2) > 2 \times 10^6$ and $k(NO_2/O_2) > 5 \times 10^6$ at 298 K. These values agree with data taken by Grosjean [23] where $k(NO_2/O_2) \approx 2 \times 10^6$ but disagree with the ratio obtained by Hatakeyama and Akimoto [7] where $k(NO/O_2) \approx 2 \times 10^3$. Since the atmospheric concentration ratio of O_2 to both NO and NO_2 is $\approx 1 \times 10^8$, reaction with O_2 may not be the sole atmospheric fate of the CH_3S radical.

Acknowledgement

We would like to express our thanks to Mr. Scott McGuire for technical assistance.

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