The impact of HS radicals on the measured rate constant of H₂S with OH radicals

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The rate constant for the reaction of OH radicals and hydrogen sulfide (H₂S) was studied in different bath gases (including N₂, air, O₂ and He) by using relative technique at 298 K. The small difference of the measured rate constants between N₂ and those with the presence of O₂ suggested possible influence of HS self reaction. Further experiments with NO_x presence for scavenging HS demonstrated this assumption. The rate constant of $(5.48 \pm 0.12) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained with $4.09 \times 10^{-4} \text{ mol m}^{-3}$ NO presence may be accurate for estimating the atmospheric lifetime of H₂S. The results provided circumstantial evidence that the rapid reaction of HS with N₂O is suspected.

OH radicals, hydrogen sulfide, rate constants, HS, relative technique

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A large amount of H₂S is emitted from natural and anthropogenic sources to the atmosphere, with the global sources of H₂S currently estimated to be about 7.72 Tg a⁻¹ [1]. The influences of H₂S on the environment have been widely studied, such as the acid rain, human health effect and visibility reduction [2–4]. Hydroxyl radicals (OH) have been recognized as the major sink for atmospheric H₂S. Therefore, for reliably evaluating the influences of H₂S on the environment, the accurate value is required for the rate constant of the reaction between H₂S and OH radicals.

The rate constant for reaction (1) has been extensively studied, especially

during the 1980s. However, the room temperature rate constant for the reaction (k_1) previously reported varied from $3.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to $5.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [5–15]. It is problematic to arbitrate which value is more accurate to be used for evaluating the influences of H₂S.

Lin et al. [13] pointed out that HS formed in reaction (1)

and HSO formed via other secondary reaction in their system could make a significant contribution to the OH removal. Lafage et al. [15] measured the rate constant by using discharge flow-laser-induced fluorescence (DF-LIF) technique with excess of NO₂ to scavenge the HS radicals, and obtained a minimal value of $(3.3 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ around 294 K. However, the upper value of $5.25 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (room temperature) was reported by Perry et al. [7] who regarded that the secondary reaction of OH radicals with HS was negligible in their system. Therefore, it is of interest to investigate the possible influence of secondary reactions on the measured rate constant of k_1 by using different methods.

In this study, H₂O₂ was used to initiate OH radicals and a relative method was adopted to measure the room temperature rate constant for k_1 . Significant influence of HS formed in reaction (1) on the measured rate constant was found due to the rapid secondary reaction (2) ($>1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [16–18].

Based on our experimental data, we regarded that the

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upper values obtained from previous reports could be adopted for evaluating the influences of H₂S. The rapid reaction of HS with N₂O is suspected.

1 Experimental

The kinetic experiments were carried out in a previously described system [19,20], which was modified by replacing the cubic ligneous chamber to a thermostatic chamber (1.3 m × 1.3 m × 1.2 m). The experiments were carried out in a ~300 L Teflon bag surrounded by 6 germicidal lamps (Philips, TUV 30W with the maximum output at 254 nm) for photolysis of H₂O₂ as OH radicals. The Teflon bag was hung inside the cubic thermostatic chamber. Typical reaction mixtures consisted of samples H₂S (~8.18×10⁻⁴ mol m⁻³), the references (propane and ethanol ~8.18×10⁻⁴ mol m⁻³), and H₂O₂ (30%, 0.2 mL).

The relative rate technique indicated that H₂S and the reference compounds were consumed exclusively by reactions with OH radicals.

Then we obtained the following expression,

$$\ln \left\{ \frac{[\text{H}_2\text{S}]_{t_0}}{[\text{H}_2\text{S}]_t} \right\} = \frac{k_1}{k_3} \ln \left\{ \frac{[\text{R}]_{t_0}}{[\text{R}]_t} \right\}, \quad (4)$$

where [H₂S]_{t₀} and [R]_{t₀} are the concentrations of H₂S and the reference compounds, respectively, at time t₀, [H₂S]_t and [R]_t are the corresponding concentrations at time t, and k₁ and k₃ are the rate constants for reactions (1) and (3), respectively. Thus a plot of ln([H₂S]_{t₀}/[H₂S]_t) against ln([R]_{t₀}/[R]_t) yields a straight line with a slope of k₁/k₃ and zero intercept.

A gas chromatograph (GC-6AM, Shimadzu, Japan) equipped with a flame photometer detector (FPD) was used for quantitative analysis of H₂S. H₂S in the reaction mixtures was separated on a 3 m × 4 mm glass column packed with 20% SE 30 on Chromosorb P (60–80 mesh). A gas chromatograph (GC-FID, HP5890, Agilent Technologies) equipped with a flame ionization detector was used for quantitative analysis of the references. The references (propane, ethanol) in the reaction mixtures were separated on a 2 m × 3 mm Teflon column packed with GDX 103 (60–80 mesh). N₂O was separated on two 2 m × 3 mm stain steel columns (one is used for back flush) packed with Porapak Q (80–100 mesh), and analyzed by GC-ECD (SP-3400).

The chemicals were as follows: H₂S, standard gas with the concentration of 9.46×10⁻² mol m⁻³ in nitrogen, propane, standard gas with the mixing ratio of 1.97% (v/v) in nitrogen; NO₂, standard gas with the mixing ratio of 0.25% (v/v)

in nitrogen; NO, standard gas with the mixing ratio of 2.0 % (v/v) in helium; N₂O, standard gas with the mixing ratio of 2.0% (v/v) in argon. All the above chemicals were products of the National Research Center for Certified Reference Materials of China. Ethanol (>99%, Beijing Chemical Agent Company) was further purified by repeated freezing, pumping, and thawing cycles and fractional distillation before use. H₂O₂ (≥30%, Tianjin Oriental Chemical Plant), N₂ (>99.999%), O₂ (>99.999%) and He (>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.

2 Results and discussion

A series of tests indicated that the studied H₂S and the references were photochemically stable, and the mixtures of H₂S and the references with H₂O₂ were also stable in the dark for several hours in the Teflon bag.

The linear regressions of the natural logarithm of the concentration ratios of H₂S and propane in N₂, air and O₂ are shown in Figure 1. The rate constants for the reaction of OH radicals with H₂S were calculated using the value of k_(OH+propane)=1.08×10⁻¹² cm³ molecule⁻¹ s⁻¹ at 298 K [21] and the value of k_(OH+ethanol)=3.3×10⁻¹² cm³ molecule⁻¹ s⁻¹ at 298 K [19] according to eq. (4), and the results are listed in Table 1. The errors quoted are twice the standard deviation arising from the least-squares fit of the straight lines and do not include an estimate of the error in the reference rate constant. Although the measured values for the rate constant in these experiments are within the range of reported values, secondary reactions were suspected based on the small difference of the rate constant between N₂ and the other two bath gases with the presence of O₂. HS formed in reaction (1) was first assumed to influence the measured rate constant in our system due to reaction (2) and reaction (5).

Figure 1 Relative rate data for the OH reaction with H₂S using C₃H₈ and C₂H₅OH as reference compounds at 298 K and 1 atm O₂, air, and N₂.

Table 1 Reactant concentrations, slopes k_1/k_3 and rate constants obtained for the reaction of H_2S with OH radicals at (298 ± 2) K

$[\text{H}_2\text{S}]$ ($\times 10^{-3}$ mol m^{-3})	Reference	[Reference] ($\times 10^{-3}$ mol m^{-3})	Bath gases	k_1/k_3	k_1 ($\times 10^{-12}$ cm ³ molecule ⁻¹ s ⁻¹)
1.30	C_3H_8	1.30	air	3.74 ± 0.04	4.04 ± 0.04
1.65	C_3H_8	1.30	O_2	3.70 ± 0.04	4.00 ± 0.04
		average			4.02 ± 0.04
1.39	C_3H_8	1.30	N_2	3.40 ± 0.04	3.67 ± 0.04
0.51	C_3H_8	0.72	He	3.57 ± 0.24	3.86 ± 0.26
0.51	$\text{C}_2\text{H}_5\text{OH}$	1.21	He	1.13 ± 0.24	3.71 ± 0.26
		average			3.75 ± 0.19
1.20	C_3H_8	1.31	N_2+NO_2 (4.09×10^{-4} mol m^{-3})	4.20 ± 0.29	4.52 ± 0.31
1.20	$\text{C}_2\text{H}_5\text{OH}$	1.97	N_2+NO_2 (4.09×10^{-4} mol m^{-3})	1.35 ± 0.05	4.46 ± 0.17
		average			4.49 ± 0.24
0.88	C_3H_8	1.93	$\text{N}_2+\text{N}_2\text{O}$ (4.09×10^{-4} mol m^{-3})	3.57 ± 0.12	3.86 ± 0.13
0.96	$\text{C}_2\text{H}_5\text{OH}$	2.59	$\text{N}_2+\text{N}_2\text{O}$ (4.09×10^{-4} mol m^{-3})	1.12 ± 0.05	3.70 ± 0.17
		average			3.78 ± 0.15
1.55	C_3H_8	0.67	N_2+NO (4.09×10^{-5} mol m^{-3})	3.51 ± 0.17	3.79 ± 0.18
1.55	$\text{C}_2\text{H}_5\text{OH}$	2.82	N_2+NO (4.09×10^{-5} mol m^{-3})	1.12 ± 0.11	3.70 ± 0.36
1.50	C_3H_8	0.78	N_2+NO (1.23×10^{-5} mol m^{-3})	4.37 ± 0.13	4.71 ± 0.14
1.50	$\text{C}_2\text{H}_5\text{OH}$	2.50	N_2+NO (1.23×10^{-5} mol m^{-3})	1.31 ± 0.09	4.32 ± 0.30
1.30	C_3H_8	1.30	N_2+NO (4.09×10^{-4} mol m^{-3})	4.92 ± 0.11	5.31 ± 0.12
1.65	$\text{C}_2\text{H}_5\text{OH}$	1.73	N_2+NO (4.09×10^{-4} mol m^{-3})	1.71 ± 0.05	5.64 ± 0.17
1.18	C_3H_8	0.99	N_2+NO (2.05×10^{-3} mol m^{-3})	4.66 ± 0.09	5.03 ± 0.10
1.18	$\text{C}_2\text{H}_5\text{OH}$	2.78	N_2+NO (2.05×10^{-3} mol m^{-3})	1.56 ± 0.07	5.13 ± 0.23

Although reaction (5) is very slow (4×10^{-19} cm³ molecule⁻¹ s⁻¹) [22,23], the large amount of O_2 might suppress HS accumulation in our system, and reduce H_2S reformation through reaction (2), and hence resulted in slightly higher values in the presence of O_2 .

To demonstrate the above assumption, NO, NO_2 and N_2O were added into the reaction mixture of H_2S /references/ $\text{N}_2/\text{H}_2\text{O}_2$, respectively, to be used as the HS scavenger. The linear regressions of the natural logarithm of the concentration ratios of H_2S and references with and without NO presence (4.09×10^{-4} mol m^{-3}) are shown in Figure 2. The values of the rate constant for reaction (1) measured with different HS scavengers are listed in Table 1. Significant increase of the measured rate constant for reaction (1) with the presence of NO is shown in Figure 2 and Table 1. To further demonstrate the influence of NO on the measured rate constant, different concentrations of NO were introduced into the chamber, and the measured rate constants are listed in Table 1. As shown in Table 1, the measured rate constant increased with increasing concentration of NO and reached a nearly stable value when NO concentration was above 4.09×10^{-4} mol m^{-3} . This relationship between the measured rate constant and NO concentration indicated that secondary reactions have significant impact on the measured rate constant. The reaction of HS with NO has been shown to involve a third body, and the second rate constant for the reaction under 1 atm N_2 condition is about 3×10^{-12} cm³ molecule⁻¹ s⁻¹ [24]. The lifetime of HS in the mixture was less than 1.3 ms when NO was above 4.09×10^{-4} mol m^{-3} , and hence HS might not accumulate to reach a concentration enough to affect the rate constant measurement through

Figure 2 Relative rate data for the OH reaction with H_2S using C_3H_8 and $\text{C}_2\text{H}_5\text{OH}$ as reference compounds at 298 K and 1 atmospheric pressure of inert bath gases (N_2 and He) with or without NO presence ($\sim 4.09\times 10^{-4}$ mol m^{-3}).

reaction (2).

The measured rate constant with NO_2 (4.09×10^{-4} mol m^{-3}) presence significantly increased compared with that in pure inert bath gases, N_2 and He (Table 1). However, the increment is much less than that with the same amount of NO presence. The rate constant for the reaction of HS with NO_2 (7×10^{-11} cm³ molecule⁻¹ s⁻¹) [22–25] is one magnitude higher than the second rate constant of HS with NO at 1 atm N_2 , i.e., NO_2 would be more efficient to scavenge HS than NO. The possible reasons for the larger rate constant measured in the presence of NO than that in the presence of NO_2 might be as follows.

(1) The products from the reaction of HS with NO_2 might reproduce H_2S more efficiently through self reaction or reaction with HS than that from the reaction of HS with NO.

Table 2 Summary of the present results and other measurements near 298 K of OH+H₂S^{a)}

<i>T</i> (K)	<i>k</i> (10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹)	Buffer gas and pressure	Technique	Reference
298	5.5±0.3	He (1.5–2.2 torr)	FF-ESR	[5]
298	3.1±0.5	He (20 torr)	PP-RF	[6]
297.5	5.25±0.53	Ar (30–50 torr)	FP-RF	[7]
297	5.0±0.3	1 atm air	CP-GC	[8]
297	5.13±0.57	Ar (40 torr)	FP-RF	[9]
298	3.9±0.7	He	DF-RF	[10]
298	4.42±0.36	Ar (20–120 torr)	FP-RF	[11]
295	4.42±0.48	Ar (50–90 torr)	FP-RF	[12]
299	4.38±0.08	He (0.8–3.5 torr)	DF-RF	[13]
300	4.38±0.03	N ₂ (1.1–3.5 torr)		
300	4.34±0.08	O ₂ (1.1–3.0 torr)		
300	5.2±0.8	1 atm air	CP-GC	[14]
294	3.3±0.5	He (0–10 torr)	DF-RF&DF-LIF	[15]
298	2.62		TS	[28]
298	5.48±0.15*	1 atm N ₂ (10 ppm NO)	CP-GC	This work

a) FF=fast flow, PP=pulsed photolysis, FP = flash photolysis, DF = discharge flow, CP = continuous photolysis; ESR= electron spin resonance, RF = resonance fluorescence, LIF = laser induced fluorescence, GC = gas chromatography, TS=theoretical study. *average value. 1 torr=1.33×10² Pa.

(2) The complex radicals (such as O(³P) and O(¹D)) formed through photolysis of NO₂ might be more reactive towards the references than H₂S. However, the latter case could be excluded, because the changes of the concentrations for propane, ethanol and H₂S were almost at the same level (less than 5%) during photolysis of the mixture of C₃H₆/C₂H₅OH/H₂S/NO₂ (10 ppm)/N₂ for 2 h.

The measured rate constants with 10 ppmv N₂O presence are in agreement with those in pure inert gases, N₂ and He (Table 1), indicating N₂O might not be reactive towards HS. There are two controversial reports about the rate constant for the reaction of N₂O with HS [26,27]. One reported the reaction at room temperature is very rapid, with a rate constant of 1.3×10⁻¹¹ cm³ molecule⁻¹ s⁻¹ [26], and the other implied the reaction is slow, with a rate constant of <5×10⁻¹⁶ cm³ molecule⁻¹ s⁻¹ [27]. Compared with NO_x presence, the same value for the rate constant measured with N₂O presence as that in pure inert bath gases as well as the stable concentration of N₂O during two hours irradiation indicated that the rapid reaction of HS with N₂O previously reported is suspected.

The values of the rate constant for reaction (1) measured in different laboratories are summarized in Table 2. The value measured in this study with 4.09×10⁻⁴ mol m⁻³ NO presence agrees with the upper values previously reported. The upper values measured by the two relative methods in the literature might also be due to a large amount of NO_x presence in the systems because of HONO and CH₃ONO, respectively, used as OH precursors [8,14].

3 Conclusions

We have found the significant influence of HS in the mixture of H₂S-H₂O₂ on the measured rate constant for reaction of H₂S with OH. The value of the rate constant of (5.48±0.12)×10⁻¹² cm³ molecule⁻¹ s⁻¹ measured under a high con-

centration of NO may be more accurate for estimating the atmospheric lifetime of H₂S. Our results provided circumstantial evidence that the rapid reaction of HS with N₂O is suspected.

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