# Production and trapping of $HOSO_2$ from the gaseous reaction $OH+SO_2$: the infrared absorption of $HOSO_2$ in solid argon

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Received 9 November 1990

$HOSO_2$ has been generated in a gaseous discharge–flow system at 300 K under 2–5 Torr of Ar by the reaction of OH with $SO_2$. A small portion of the gas mixture in the flow reactor was sampled and condensed onto a CsI window maintained at 12 K. In the infrared spectrum of the matrix, absorption lines at 3539.8, 1309.2, 1097.2, 759.3 and (with less certainty) 1296.2 $cm^{-1}$ have been assigned to $HOSO_2$ on the basis of $^{34}S$- and $^2H$-isotopic shifts. When $O_2$ was present in the flow reactor, $HOSO_2$ became undetectable, whereas $HO_2$ and $SO_3$ were identified.

## 1. Introduction

The homogeneous and heterogeneous oxidation of $SO_2$ to sulfuric acid is important in atmospheric chemistry [1–4]. It is now generally accepted that under atmospheric conditions, the reaction of $SO_2$ with OH is the rate-determining step of the oxidation of $SO_2$ in the gas phase

$$OH+SO_2+M \rightarrow HOSO_2+M\,. \qquad (1)$$

The rate of this reaction has been extensively studied in the laboratory by following the loss of OH in the presence of excess $SO_2$ using various techniques [5–7]. However, the direct spectroscopic identification of the sulfo radical ($HOSO_2$) as a product of reaction (1) has yet to be established.

Gleason et al. [8,9] studied the kinetics of the gaseous reaction between $HOSO_2$ and $O_2$,

$$HOSO_2+O_2 \rightarrow HO_2+SO_3\,, \qquad (2)$$

in a flowing afterglow system by means of the chemical ionization technique. For the determination of $[HOSO_2]$, they converted $HOSO_2$ to $SO_3^-$ by the reaction

$$Cl^-+HOSO_2 \rightarrow SO_3^-+HCl\,, \qquad (3)$$

and detected $SO_3^-$ by means of a quadrupole mass spectrometer. The concentration of the product ion $SO_3^-$ was taken to be directly proportional to $[HOSO_2]$ although ions corresponding to the intact $HOSO_2$ radical were not detected.

A possible atmospheric detection of $HOSO_2$ has been reported by Arnold et al. [10]; a series of negative ion clusters, $HSO_4^-(H_2SO_4)_nHSO_3$ with $n=1$–3, have been identified. However, they could not positively distinguish between $SO_3$ and $HOSO_2$ because of the limited resolution of their mass spectrometer. The $HOSO_2$ radical has also been generated and characterized by neutralization/reionization mass spectrometry [11]; it was produced from the decomposition of methanesulfonic acid ion ($CH_3$-$SO_2$-$OH^+$) instead of reaction (1).

In the condensed phase, $HOSO_2$ has been detected in the aqueous reaction between $H_2O_2$ and $SO_2$ by means of EPR spectroscopy [12]. Hashimoto and coworkers have recently photolyzed a matrix during codeposition of $H_2O_2$ (or $H_2O$) and $SO_2$ in Ar by means of a Hg lamp (or Xe lamp); the observed weak

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infrared absorption lines at 3539.9, 1309.2, 1097.3 and 759.5 $cm^{-1}$ were assigned to $HOSO_2$ based on the $^{18}O$-isotopic shifts [13,14]. They believed that $HOSO_2$ was produced from reactions in the argon matrix instead of reaction (1) in the gas phase because the pressure was too small for the slow termolecular reaction to take place. The reaction which occurs in the low-temperature matrix may differ from that in the gas phase.

We have employed the discharge–flow technique to carry out reaction (1) in the gas phase. A matrix isolation system was coupled to the flow tube in order to trap the reaction products. The IR spectra of these products indicated that $HOSO_2$ was indeed formed in reaction (1). By means of the isotopic shifts due to $^2H$ and $^{34}S$, we have confirmed the vibrational assignments of $HOSO_2$.

## 2. Experimental

The basic principles and the experimental setup have been previously described [15,16]. Briefly, the reaction was carried out in a discharge–flow tube from which a small portion of the gaseous mixture was sampled through a pinhole to deposit onto a low-temperature CsI window; the IR absorption spectra were recorded after 60–120 min of deposition.

The jacketed flow tube is fitted inside with 15 mm inner diameter teflon tubing to reduce possible surface reaction. A movable injector of 10 mm outer diameter permitted adjustment of the reaction duration. Hydroxyl radicals were generated in the sidearm of the flow tube by reacting excess $NO_2$ with H atoms which were produced from a microwave-discharged mixture of $H_2$ and He. A mixture of $SO_2$ and Ar was admitted through the movable injector. A stream of Ar carrier gas was also added upstream from the inlet of the OH radicals. An OH detection system using resonance fluorescence and photon-counting techniques was installed downstream from the sampling port to determine the concentration of OH. The reaction was carried out under conditions similar to those described in our kinetic studies of reaction (1) except that the concentration of $SO_2$ was reduced to minimize its interference in IR absorption [6]. Typical experimental conditions were as follows: total pressure $P=2$–5 Torr; total flow rate $F_T=4$–10 STP $cm^3\ s^{-1}$; average flow velocity $\bar{v}=1500$–2300 cm $s^{-1}$; reaction distance 10–25 cm; $[OH]_0 \approx (1\text{–}8)\times10^{11}$ molecule $cm^{-3}$; and $[SO_2] \approx (2\text{–}8)\times10^{14}$ molecule $cm^{-3}$.

A teflon cap having a small pinhole (≈0.3 mm inner diameter) was fitted to the end of the flow tube to allow sampling of the gas mixture into the chamber of the matrix isolation system. Most gas in the flow tube was pumped away by a Roots pump (speed 1900 $m^3\ h^{-1}$), leaving only about 1% to pass the pinhole so as to deposit onto the CsI window located ≈1.5 cm from the pinhole. The rotatable CsI window was cooled to ≈11 K by a closed-cycle cryogenic system (Air Products, DE208L).

The IR absorption spectra were recorded with a FTIR spectrometer (Bomem DA3.002), using a KBr beam splitter and a wide-range Hg/Cd/Te detector cooled by liquid $N_2$. Typically 400 scans were taken to produce a spectrum at resolution 0.5 $cm^{-1}$ in the spectral range 500–4000 $cm^{-1}$.

To condition the surface of the flow reactor, a large concentration of OH was flowed for 30 min before the matrix was cooled down in each experiment. To prepare the $NO_2$, NO (99%) was reacted with excess $O_2$, and stored under about 2 atm of $O_2$ before use. The He (99.999%), Ar (99.999%), $H_2$ (0.3% in He), $SO_2$ (99.98%) were used without further purification. The stated isotopic purities of $^{34}SO_2$ and $D_2$ are 93.15 and 99%, respectively.

## 3. Results and discussion

Two blank experiments as described were carried out: one with identical flow conditions except that the microwave discharge on the OH source was turned off, and one with the OH source operating but without $SO_2$ in the system. The IR spectrum of the matrix produced in the former blank experiment showed absorption due to only $SO_2$ (1350, 1150 and 519 $cm^{-1}$, all being multiplets due to the high concentration) [17,18], and $NO_2$ (2902.3 and 1610.9 $cm^{-1}$) [19]; the spectrum from the latter blank experiment exhibited absorption lines of $HNO_3$ (3522.6, 1699.3, 1321.4 and 896.8 $cm^{-1}$) [20,21] and NO (1874.6 $cm^{-1}$) [22]. Portions of the IR absorption spectrum of the matrix which was deposited for 2 h with reaction (1) taking place in the flow

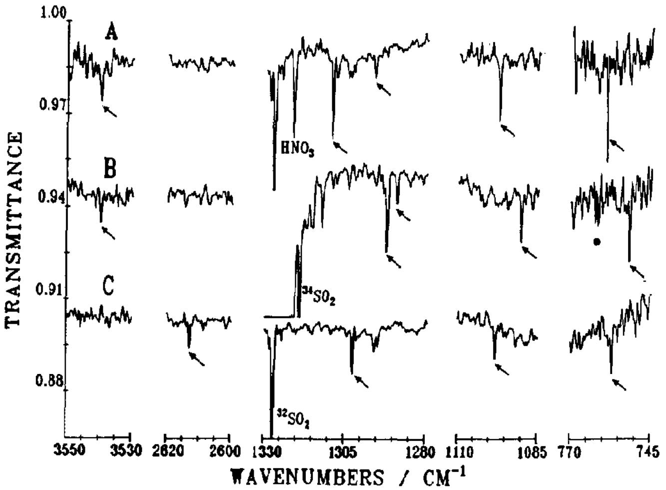

Fig. 1. Portions of the infrared spectra of the products of the gaseous reaction of $OH+SO_2$ trapped in Ar matrices. (A) $OH+SO_2$; (B) $OH+{}^{34}SO_2$; (C) $OD+SO_2$. Traces B and C are shifted downward by 0.04 and 0.07, respectively. The lines due to various isotopic $HOSO_2$ species are indicated by arrows.

tube are shown in trace (A) of fig. 1. In addition to the lines readily assigned to $SO_2$, $HNO_3$, $NO_2$ and NO, four new features (3539.8, 1309.2, 1097.2 and 759.3 $cm^{-1}$, indicated by arrows in fig. 1A) appeared to belong to one species based on the correlation of intensities in various experiments under different experimental conditions. These lines are identical to those reported previously for $HOSO_2$ produced from matrix reaction of OH with $SO_2$ by Hashimoto et al. [13], except that the quality of the spectrum has been much improved and the unidentified lines at 1286.5 and 1285.4 $cm^{-1}$ reported previously were not observed in the present work.

When ${}^{32}SO_2$ was replaced by ${}^{34}SO_2$, the IR spectrum of the matrix deposited for 2 h is shown in trace (B) of fig. 1. The wavenumbers of the observed lines of various isotopic species are listed in table 1. The line at 3539.8 $cm^{-1}$ did not shift, whereas those at 1309.2, 1097.2 and 759.3 $cm^{-1}$ shifted −16.6, −7.1 and −7.4 $cm^{-1}$, respectively. When OH was replaced by OD in the flow reactor, the IR spectrum of the matrix deposited for 2 h is shown in trace (C) of fig. 1. As listed in table 1, the lines at 1309.2, 1097.2 and 759.3 $cm^{-1}$ shifted slightly (−6.4, 0.7 and −2.1 $cm^{-1}$, respectively), whereas that at 3539.8 $cm^{-1}$ shifted −926.9 $cm^{-1}$. Because the product is expected to contain only H, S and O atoms, we consider first the vibrational modes containing these atoms. The line at 3539.8 $cm^{-1}$ corresponds to an OH stretching mode, based on the observed isotopic shift and its characteristic wavenumber. The lines at 1309.2 and 1097.2 $cm^{-1}$ are approximately 40–50 $cm^{-1}$ below those of the two stretching modes of $SO_2$. The ${}^{34}S$-isotopic shifts of −16.6 and −7.1 $cm^{-1}$ are

Table 1
Wavenumbers of various isotopic $HOSO_2$ species in solid Ar

| Assignments | $HOSO_2$ | $HO^{34}SO_2$ | $DOSO_2$ | $H^{18}OSO_2$ [a] |
|---|---|---|---|---|
| OH str. | 3539.8 | 3539.8 | 2612.9 | 3528.6 |
| $SO_2$ asym. str. | 1309.2 | 1292.6 | 1302.8 | 1308.7 |
| HOS bend | 1296.2 | 1289.4 | 916? | - |
| $SO_2$ sym. str. | 1097.2 | 1090.1 | 1097.9 | 1096.0 |
| SO str | 759.3 | 751.9 | 757.2 | 735.1 |

[a] From ref. [13].

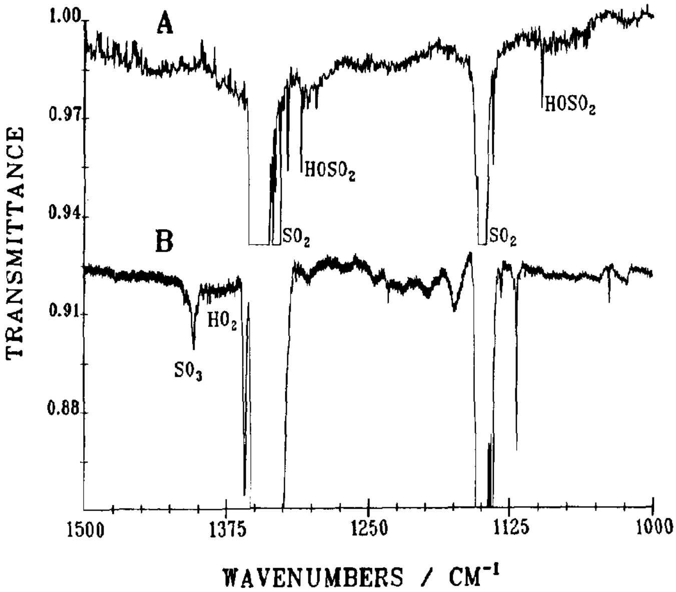

Fig. 2. Portions of the infrared spectra of the products of the gaseous reaction of $OH+SO_2(+O_2)$ trapped in Ar matrices. (A) $OH+SO_2$; (B) $OH+SO_2+O_2$.

similar to those for $SO_2$, $-17.0$ and $-6.6$ $cm^{-1}$ [17,18]. The small $^2H$-shifts also suggest that H atom is not directly involved in these modes. Likely assignments for these lines are, hence, the $SO_2$ asymmetric stretching (1309.2 $cm^{-1}$) and symmetric stretching (1097.2 $cm^{-1}$) modes. The small ($-2.1$ $cm^{-1}$) $^2H$-isotopic shift and the $-7.4$ $cm^{-1}$ $^{34}S$-isotopic shift for the 759.3 $cm^{-1}$ line indicate that this mode involves S but not H. The isotopic ratio 759.3/751.9 = 1.0098 is practically equal to the square root of the ratio of the reduced masses of $^{34}SO$ to $^{32}SO$, 1.0099; accordingly, a likely assignment for this line is to a S–O stretching mode. The new features observed in our experiments are thus assigned to $HOSO_2$. Our vibrational assignments derived on the basis of the $^{34}S$- and $^2H$-isotopic shifts are identical to those proposed by Hashimoto et al. [13] on the basis of $^{18}O$-isotopic shifts.

A weak line at 1296.2 $cm^{-1}$ also showed good correlation of intensities with the four new lines although its small intensity prevents us from drawing a definitive conclusion. This line may be assigned to the HOS bending of $HOSO_2$. The corresponding line for $HO^{34}SO_2$ lies at 1289.4 $cm^{-1}$, the isotopic shift $-6.8$ $cm^{-1}$ being reasonable for the HOS bending mode. However, the corresponding line for $DOSO_2$ was too weak to be confidently assigned. A very weak feature about 916 $cm^{-1}$ has an acceptable isotopic shift, although it is less intense than expected. The 1296.2 $cm^{-1}$ value is also consistent with the theoretical calculation (at HF/3-21G level) which yielded the predicted values 1181 $cm^{-1}$ for the HOS bending mode of $HOSO_2$ and 1319 and 1125 $cm^{-1}$ for the $SO_2$ asymmetric and symmetric stretching modes, respectively [14].

When the concentration of $SO_2$ was increased in the flow reactor, the yield of $HOSO_2$ increased; however, the lines at 3539.8 and 1309.2 $cm^{-1}$ became multiplets, and the line at 759.3 $cm^{-1}$ shifted to 770.2 and 772.1 $cm^{-1}$. This change is presumably due to the interaction between $HOSO_2$ radicals and nearby $SO_2$ molecules.

When $O_2$ was added into the flow reactor to replace a small portion of the Ar carrier gas, the lines assigned to $HOSO_2$ disappeared (as shown in fig. 2B), indicating a rapid reaction of $HOSO_2$ with $O_2$. The spectrum was compared with that recorded with similar flow conditions but without the addition of $O_2$, as shown in fig. 2A. In addition to the slightly shifted lines near the $SO_2$ region which resulted from the matrix effect due to $O_2$, new features at 1403.9, 1391.6, 1389.2, 1232.8, 1118.5, 1037.8 $cm^{-1}$ were observed. The line at 1389.2 $cm^{-1}$ has been assigned to $HO_2$ [23–25]. The lines at 1391.6 and 1403.9 $cm^{-1}$ are assigned to $SO_3$ and its complex with $H_2O$, respectively [26]. The observation of both $HO_2$ and $SO_3$ as products of reaction (2) is in agreement with the previous product analysis by means of the chemical ionization technique [8]. The weak intensity of the $HO_2$ line is probably partly due to the reaction of $HO_2$ with NO in the flow system. The line at 1037.8 $cm^{-1}$ may be due to $O_3$ [27]. The lines at 1232.8 and 1118.5 $cm^{-1}$ cannot, at present, be identified; they were also observed in the experiments when no $NO_2$ was added to the flow reaction (presumably the primary reaction was $H+SO_2$), and the positions are in the regions for $SO_x$ [28].

In conclusion, our experiments have provided a direct identification of $HOSO_2$ as the product of the gaseous reaction of OH with $SO_2$. The vibrational assignments based on the isotopic shifts of species containing $^{34}S$ or $^2H$ are consistent with those proposed based on the $^{18}O$-isotopic shifts [13]. When $O_2$ was present in the flow reactor, $HOSO_2$ reacted rapidly with $O_2$; $HO_2$ and $SO_3$ were identified to be the reaction products.

## Acknowledgement

We thank the National Science Council of the Republic of China and the Chemical Manufacturers Association (USA) for support of this research.

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