



## Reactions of HS with NO and NO2 at 298 K

G. Black

Citation: The Journal of Chemical Physics **80**, 1103 (1984); doi: 10.1063/1.446838 View online: http://dx.doi.org/10.1063/1.446838 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/80/3?ver=pdfcov Published by the AIP Publishing

## Articles you may be interested in

Rate constant for the reaction of atomic oxygen with phosphine at 298 K J. Chem. Phys. **87**, 2112 (1987); 10.1063/1.453186

Kinetics of the isotope exchange reaction of 1 8O with NO and O2 at 298 K J. Chem. Phys. **83**, 1648 (1985); 10.1063/1.449402

Kinetics of the reactions of atomic bromine with HO2 and HCO at 298 K J. Chem. Phys. **80**, 1922 (1984); 10.1063/1.446953

Rate constant for the reaction of OH radicals with hydrogen peroxide at 298 K J. Chem. Phys. **70**, 2581 (1979); 10.1063/1.437725

Rate constants for the reaction of OH radicals with CHFCl2 and CH3Cl over the temperature range 298–423°K, and with CH2Cl2 at 298°K J. Chem. Phys. **64**, 1618 (1976); 10.1063/1.432335



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.216.129.208 On: Tue, 02 Dec 2014 21:26:44

# Reactions of HS with NO and NO<sub>2</sub> at 298 K

G. Black SRI International, Menlo Park, California 94025

(Received 22 August 1983; accepted 21 October 1983)

HS radicals have been generated by the photodissociation of H<sub>2</sub>S at 193 nm and their disappearance monitored by LIF. The reaction of HS with NO, like the analogous reaction of OH with NO, has been shown to involve a third body. The low pressure rate coefficients have been determined for He, Ar, and N<sub>2</sub>. The values are 2.1, 2.2, and  $2.4 \times 10^{-31}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>, respectively, with estimated uncertainties of  $\pm 10\%$ . The high pressure limit is  $(2.8 \pm 1.0) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The reaction with NO<sub>2</sub> (HS + NO<sub>2</sub> $\rightarrow$ HSO + NO) is second order with a rate coefficient of  $(3.5 \pm 0.4) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. An upper limit for the rate coefficient with O<sub>2</sub> has been estimated  $(4 \times 10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>).

#### INTRODUCTION

As our ability to measure trace atmospheric constituents continues to improve, it has become evident that the chemistry of sulfur plays important roles in the terrestrial and planetary atmospheres. Unfortunately, very little kinetic information exists on reactions of the odd-sulfur radicals SO, CS, and HS which are involved as intermediates in atmospheric reactions of sulfur-containing molecules like OCS, CS<sub>2</sub>, and H<sub>2</sub>S. We have recently<sup>1,2</sup> reported studies of SO reactions with O<sub>2</sub> and O<sub>3</sub>. This paper is concerned with reactions of HS with NO, NO<sub>2</sub>, and O<sub>2</sub>.

Very recently,<sup>3</sup> in a study of HS reactions important in coal combustion chemistry, an upper limit for the rate coefficient of

$$HS + O_2 \rightarrow products$$
 (1)

of  $3.2 \times 10^{-15}$  cm<sup>3</sup> molecule  $^{-1}$  s<sup>-1</sup> was determined as well as a value of  $5.6 \times 10^{-13}$  cm<sup>3</sup> molecule  $^{-1}$  s<sup>-1</sup> for the reaction with NO:

$$HS + NO \rightarrow products.$$
(2)

Earlier work<sup>4</sup> has been reinterpreted<sup>5</sup> to give a value of  $6.3 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>1</sup> s<sup>-1</sup> for reaction (2). In contrast to these findings, we find no evidence for a two-body process of this magnitude for reaction (2) but find the interaction to involve a third body

$$HS + NO + M \rightarrow HSNO + M$$
(3)

analogous to the well characterized process with OH:

$$HO + NO + M \rightarrow HONO + M.$$
 (4)

This paper reports the three-body rate coefficients for M = He, Ar, and N<sub>2</sub> and an estimate of the limiting high pressure rate coefficient. We also report the first measurement of the rate coefficient for the reaction with NO<sub>2</sub> and an even lower limit for the rate of the reaction with O<sub>2</sub>.

### EXPERIMENTAL

A schematic of the apparatus is shown in Fig. 1. The HS is produced by photodissociation of H<sub>2</sub>S with an ArF laser  $(\sigma \approx 7 \times 10^{-18} \text{ cm}^2)$ .<sup>6</sup> This is a particularly convenient source of HS(v'' = 0) for kinetic studies since few radicals are produced<sup>7,8</sup> with v'' > 0 and the excess translational energy is easily removed by a buffer gas. No evidence was found for

any effect of vibrationally excited HS on the present results. Only  $\leq 1$  mJ of 193 nm radiation traversed the photolysis cell. The Quanta-Ray Nd: Yag-dye laser system provided approximately 2 mJ in the region of the (0,0) band of the HS  $(A^2\Sigma^+ \leftarrow X^2\Pi)$  system in a pulse of  $\approx 5$  ns duration with a linewidth of  $\approx 0.5$  cm<sup>-1</sup>. For these measurements, the lasers were operated at 10 Hz and were adjusted to overlap spatially along the length of the reaction cell. A variable delay could be introduced between the two laser pulses. Baffles with 1 cm diam holes were situated in the side arms of the cell to reduce scattered light. The cell was also equipped with MKS Baratron pressure gauges and was evacuated with a small rotary pump which gave  $\approx 20$  s for the residence time of the gas in the cell.

The detection system, situated perpendicular to the laser beams, consisted of a 1/4 m monochromator equipped with an RCA C31034A photomultiplier. Its output passed to a boxcar averager and then to a chart recorder. For most of the kinetic studies, in order to avoid scattered light, the dye laser was tuned to the  $(0,0) R_1 + {}^RQ_{21}$  band head of the  $A {}^2\Sigma \leftarrow X {}^2\Pi_{3/2}$  system at 323.7 nm and the fluorescence was monitored on the (0,1) band at 354.5 nm.

The gases used were supplied by Matheson Gas Products and were used without further purification. The  $H_2S$ was used as a 5% mixture in helium and 5% mixtures of NO in helium and argon were also available. For the NO<sub>2</sub> experiments, a 0.7% mixture of NO<sub>2</sub> in helium was used. The gases



FIG. 1. Schematic of the experimental apparatus for HS production by 193 nm photodissociation of  $H_2S$  and for monitoring its decay by LIF.

J. Chem. Phys. 80 (3), 1 Feb. 1984

0021-9606/84/031103-05\$02.10

© 1984 American Institute of Physics 1103



FIG. 2. Laser excitation spectrum of HS. Fluorescence monitored on the (0,1) band of the  $A^{2}\Sigma - X^{2}\Pi_{3/2}$  system of HS at 354.5 nm (bandpass = 2.7 nm). Dye laser bandwidth  $\approx 0.5$  cm<sup>-1</sup>, 2  $\mu$ s between laser pulses, H<sub>2</sub>S = 40 mTorr and He = 100 Torr.

were passed through flowmeters and mixed before entering the reaction cell.

## **RESULTS AND DISCUSSION**

Figure 2 shows a laser excitation spectrum recorded for a mixture of 40 mTorr of  $H_2$ S in 100 Torr of helium with  $\approx 2$  $\mu$ s between the laser pulses when the probing dye laser was scanned from 322 to 326.8 nm. The monochromator was set at 354.5 nm with a bandpass of 2.7 nm to record emission in the (0,1) band of the  $A^{2}\Sigma^{+}-X^{2}\Pi_{3/2}$  system. No effort has been made to correct this spectrum for variations in the laser energies. Identification of the rotational transitions of the (0,0) band of the  $A^{2}\Sigma^{+}-X^{2}\Pi_{3/2}$  of HS are shown. At  $\lambda > 326.8$  nm a similar laser excitation spectrum revealed rotational lines of the (0,0) band of the  $A^{2}\Sigma^{+}-X^{2}\Pi_{1/2}$  transition. The spectrum shown is very similar to those in recent publications<sup>3,7</sup> except for the much higher resolution of the present spectrum. This strong fluorescence spectrum is obtained despite the fact that predissociation of the upper state reduces the fluorescence efficiency to  $\sim 1\%$ .<sup>9</sup>

The disappearance of the HS radical after the excimer pulse was followed by measuring the decay of the LIF signal as a function of time delay between the two lasers. In the absence of any added reactant (that is, with only H<sub>2</sub>S and helium) the HS lifetime was found to be long (1 - 6 ms) and increased with increasing helium pressure. Such lifetimes are consistent with those expected for diffusion from the  $\approx 1$ cm diam cylindrical overlap region of the two laser beams. This indicates that the diffusive loss of HS is important and losses by the fast reactions

$$HS + HS \rightarrow H_2S + S , \qquad (5)$$

$$k = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 (Ref. 5) and  
H + HS $\rightarrow$ H<sub>2</sub> + S ,

 $k = 2.5 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Ref. 5) are only playing a minor role. This is not surprising in view of the fact that with ArF laser energies of  $\leq 1$  mJ/pulse and H<sub>2</sub>S pressures of  $\approx 35$  mTorr, we are only generating atom and radical densities of  $\leq 10^{13}$  cm<sup>-3</sup>. With ArF laser pulse energies of > 1 mJ and with high helium pressures to retard diffusion, the HS decays did exhibit curvature on semilog plots of LIF signal vs time indicating the occurrence of these processes and perhaps others of a radical-radical or radical-atom nature. Some curvature in the HS decay plots under these conditions may also result from the generation of more HS by the reaction

$$\mathbf{H} + \mathbf{H}_2 \mathbf{S} \rightarrow \mathbf{H}_2 + \mathbf{H} \mathbf{S} , \qquad (7)$$

 $k = 7.4 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Ref. 5). No attempt was made to derive rate coefficients to fit the HS decays under such conditions. All these processes played a very minor role in the presence of added NO or NO<sub>2</sub> when the HS decay time was typically 100  $\mu$ s or less. These measurements will now be described.

## **REACTION WITH NO**

For these and most of the subsequent kinetic experiments the  $H_2S$  pressure was 35 mTorr. As found previously,<sup>3</sup> addition of NO to the  $H_2S/He$  mixture gave linear semilog plots of LIF signal vs delay time between the laser pulses. The slope of these plots was found to be a linear function of the added NO concentration as shown in Fig. 3 for a helium pressure of 160 Torr. The slope of the line gives a rate coefficient of

$$8.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
.

The dependence of this rate coefficient k (He) on helium pressure is shown in Fig. 4. Similar plots for argon and nitrogen are shown in Figs. 5 and 6.

(6)



FIG. 3. Decay rate of the HS radical vs NO addition.  $H_2S = 35$  mTorr, He = 160 Torr.

The lines fitting the experimental points in Figs. 4–6 are calculated from a nonlinear least squares fit of the experimental data to the expression suggested by Troe<sup>10</sup> to describe the pressure dependence of a recombination reaction in its "fall-off" region:

$$k(\mathbf{M}) = \frac{k_{\infty} k_{0}[\mathbf{M}]}{k_{\infty} + k_{0}[\mathbf{M}]} F^{\left[1 + (\log[k_{0}[\mathbf{M}]/k_{\infty}])^{2}\right]^{-1}}$$
(8)

in which F was fixed at 0.6 following the suggestion of Golden<sup>11</sup> and  $k_0$  and  $k_{\infty}$  are the low and high pressure limiting rate coefficients, respectively. Their values for the three sets of experiments are shown in Table I. Fitting with a Lindemann mechanism (F = 1) gave values of  $k_0$  about 15% lower but values of  $k_{\infty}$  a factor of 2.5-3.0 lower. The error in the three-body rate coefficients is estimated at  $\pm 10\%$ . The uncertainty in the high pressure limit is much larger, which is not surprising since the data are very far removed from this limit (they extend <15% of the way to the high pressure



FIG. 4. Dependence of the rate coefficient for HS removal by NO on helium pressure.  $H_2S = 35$  mTorr.



FIG. 5. Dependence of the rate coefficient for HS removal by NO on argon pressure.  $H_2S = 35$  mTorr.

limit). Until measurements are made at higher pressures, the mean value of  $k_{\infty}$  is recommended with an estimated uncertainty of 35%, that is,  $k_{\infty} = (2.8 \pm 1.0) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Experiments are under way to determine the variation of  $k_0$  and  $k_{\infty}$  over the temperature range 230–420 K and will be the subject of a future paper.



FIG. 6. Dependence of the rate coefficient for HS removal by NO on  $N_2$  pressure.  $H_2S = 35$  mTorr.

#### J. Chem. Phys., Vol. 80, No. 3, 1 February 1984

TABLE I. Rate coefficients for the reaction HS + NO + M $\rightarrow$ HSNO + M at 298 K.

	M = He	$\mathbf{M} = \mathbf{A}\mathbf{r}$	$M = N_2$
$\overline{k_0(\times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1})}$	2.1	2.2	2.4
$k_{\infty}^{-1}$ (×10 <sup>-11</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	1.8	2.4	4.1

The discrepancy between these findings and the results of earlier work must now be addressed. These earlier experiments<sup>3,4,5</sup> were carried out at low pressure ( $\leq 10$  Torr) and the reaction was found to be two-body

$$HS + NO \rightarrow products$$
 (2)

and have a rate coefficient of  $\approx 6 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. It is suggested that the occurrence of reaction (2) as a homogeneous reaction is unlikely and that this rate coefficient may refer to the second-order heterogeneous removal of HS at the walls. Such a process has been characterized in an earlier study<sup>12</sup> of the reaction with OH with NO in which the experiments were restricted to low pressure ( $\leq 10$  Torr). In fact, the results at the lowest pressures shown in Fig. 4 suggest the possibility of such a heterogeneous process—the experimental points lie above the predictions of Eq. (8) with the discrepancy largest at the lowest pressure. This effect is not apparent in the Ar (or N<sub>2</sub>) data. Since binary diffusion coefficients are about four times larger in helium than argon,<sup>13</sup> this observation suggests the occurrence of a heterogeneous process.

#### **REACTION WITH NO<sub>2</sub>**

In contrast to the findings with NO, the reaction of HS with  $NO_2$  was independent of He pressure at least over the 28.5–300 Torr range. The results are shown in Fig. 7 and



FIG. 7. Decay rate of the HS radical vs  $NO_2$  addition at various helium pressures.  $H_2S = 35$  mTorr.

give a rate coefficient of  $(3.5 \pm 0.4) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K for the reaction

$$HS + NO_2 \rightarrow HSO + NO.$$
(9)

From thermochemical information,<sup>14</sup> it can be shown that this reaction is strongly exothermic ( $\Delta H \approx -26$  kcal). It is interesting to note that this behavior is in marked contrast to the reaction of OH with NO<sub>2</sub> which is dominated by the three-body reaction

$$HO + NO_2 + M \rightarrow HONO_2 + M.$$
(10)

The minor role of a reaction analogous to reaction (9), that is,

$$HO + NO_2 \rightarrow HO_2 + NO(\Delta H = 7 \text{ kcal})$$
(11)

can be understood in light of the large exothermicity of reaction (9) and the endothermicity of reaction (11). This results in reaction (11) having a rate coefficient  $\approx 10^5$  smaller<sup>15</sup> than that of reaction (9) at 298 K.

The lack of a detectable three-body reaction over the pressure range studied sets an upper limit of  $\approx 7 \times 10^{-31}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> for the reaction

$$HS + NO_2 + He \rightarrow HSNO_2 + He.$$
(12)

It may be that the rate coefficient for reaction (12) can be measured (or, at least, a lower upper limit established) by extending the measurements to helium pressures > 300 Torr. Such experiments are planned.

Although no previous measurement of the rate coefficient for reaction (9) could be found, the effect of NO<sub>2</sub> on the chemiluminescence and ozone consumption in an  $H_2S/O_3$  mixture has been attributed<sup>16</sup> to a rapid reaction of NO<sub>2</sub> with HS. The present experiments confirm this.

It was also observed that a small LIF signal was present even without the excimer. It was reduced by minimizing the contact time of the  $NO_2$  and  $H_2S$  prior to their entry into the cell. The variability of the HS generated by the reaction of these two gases suggested that a heterogeneous reaction was involved.

#### **REACTION WITH O2 AND O3**

No evidence could be found for any reaction with  $O_2$ 

$$HS + O_2 \rightarrow SO + HO. \tag{13}$$

In fact, replacing 500 Torr of helium with 500 Torr of oxygen reduced the rate of loss of HS—this could arise both from a reduced rate of diffusion in  $O_2$  and  $O_2$  removal of atom/radical species which were reacting with the HS radical. This and our other measurements with  $O_2$  suggest an upper limit of  $4 \times 10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for reaction (14). This is almost two orders of magnitude smaller than the previous upper limit estimates of  $3.2 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Ref. 3) and  $5 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Refs. 5 and 17).

The reaction of HS with  $O_3$  could not be studied because of an extremely large HS signal from the reaction of H<sub>2</sub>S with O<sub>3</sub>. This was accompanied by destruction of some of the O<sub>3</sub> (monitored by 253.7 nm absorption in a 10 cm cell through which the mixed gases flowed prior to entering the reaction cell). O<sub>3</sub> concentrations of > 0.1 Torr completely removed the H<sub>2</sub>S prior to the reaction cell. This does not involve a simple bimolecular reaction of O<sub>3</sub> with H<sub>2</sub>S since this has an upper limit on the rate coefficient of  $2 \times 10^{-20}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Ref. 16). It must involve either chain reaction(s) or heterogeneous processes.

### ACKNOWLEDGMENTS

The experimental work was carried out with the able assistance of Len Jusinski. The help of Roger Patrick in fitting Eq. (8) to the experimental results is gratefully acknowledged as well as helpful discussions on the thermochemistry of reaction (9). This work was supported by Grant No. ATM-8011283 from the National Science Foundation.

- <sup>1</sup>G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **90**, 55 (1982).
- <sup>2</sup>G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Let. **93**, 598 (1982).
- <sup>3</sup>J. J. Tiee, F. B. Wampler, R. C. Oldenborg, and W. W. Rice, Chem. Phys. Lett. **82**, 80 (1981).
- <sup>4</sup>J. N. Bradley, S. P. Trueman, D. A. Whytock, and T. A. Zaleski, J. Chem.

- Soc. Faraday Trans. 1, 69, 416 (1973).
- <sup>5</sup>D. L. Baulch, D. D. Drysdale, J. Duxbury, and S. Grant, Evaluated Kinetic Data for High Temperature Reactions (Butterworths, London, 1976), Vol. 3.
- <sup>6</sup>C. F. Goodeve and N. O. Stein, Trans. Faraday Soc. 27, 393 (1931).
- <sup>7</sup>W. G. Hawkins and P. L. Houston, J. Chem. Phys. 73, 297 (1980).
- <sup>8</sup>G. N. A. Van Veen, K. A. Mohamed, T. Baller, and A. E. De Vries, Chem. Phys. 74, 261 (1983).
- <sup>9</sup>R. R. Friedl, Wm. H. Brune, and J. G. Anderson, The 15th Informal Conference on Photochemistry, Stanford, CA, June 1982.
- <sup>10</sup>J. Troe, J. Phys. Chem. 83, 114 (1979).
- <sup>11</sup>W. B. DeMore, R. T. Watson, D. M. Golden, R. F. Hampson, M. Kurylo, C. J. Howard, M. J. Molina, and A. R. Ravishankara, Evaluation No. 5, JPL Publication 82–57, July 1982.
- <sup>12</sup>J. G. Anderson, J. J. Margitan, and F. Kaufman, J. Chem. Phys. 60, 3310 (1974).
- <sup>13</sup>J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 508.
- <sup>14</sup>S. W. Benson, Chem. Rev. 78, 23 (1978).
- <sup>15</sup>C. J. Howard, J. Am. Chem. Soc. 102, 6937 (1980).
- <sup>16</sup>K. H. Becker, M. A. Inocêncio, and V. Schurath, Proceedings of the Symposium on Chemical Kinetics Data for the Lower and Upper Atmosphere, September 1974.
- <sup>17</sup>L. T. Cupitt and G. P. Glass, Proceedings of the Symposium on Chemical Kinetics Data for the Lower and Upper Atmosphere, September 1974.