IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx20

This data sheet last evaluated: 28th June 2007; no revision of preferred values.

$HOCS_2 + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.4 \times 10^{-14} \exp[(217 \pm 301)/T]$	251-348	Hynes et al., 1988	PLP-LIF (a)
$(3.26 \pm 0.70) \times 10^{-14}$	295 ± 1		
$(2.6 \pm 1.0) \times 10^{-14}$	249-299	Murrells et al., 1990	PLP-LIF
$(2.4 \pm 0.4) \times 10^{-14}$	273	Lovejoy et al., 1990a	PLP-LIF (b)
$(3.1 \pm 0.6) \times 10^{-14}$	298	Diau and Lee, 1991	PLP-LIF (c)

Comments

(a) The effects of He, N_2, air and O_2 were studied, and the total pressure was varied over the range 87-920 mbar (65-690 Torr). If the rate coefficient k is assumed to be temperature independent, the average of the measured values is $(2.9 \pm 1.1) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} over the range 251-348 K.

(b) A rate coefficient for the reaction of the $DOCS_2$ radical with O_2 of $(2.3 \pm 0.4) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 273 K was also measured (Lovejoy et al., 1990a), showing no significant deuterium isotope effect and hence no evidence for a direct H-atom abstraction process.

(c) Values of $k(HOCS_2 + NO) = (7.3 \pm 1.8) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and $k(HOCS_2 + NO_2) = (4.2 \pm 1.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K were also obtained in this work. The latter is the first measurement of the rate coefficient for the reaction with NO_2. The rate coefficient for the reaction with NO is consistent with the values of $k(HOCS_2 + NO) = (1.3 \pm 0.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 249 K and $k(HOCS_2 + NO) = (9.1 \pm 3.5) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 299 K measured by Lovejoy et al. (1990b).

Preferred Values

$k = 2.8 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 240-350 K.

Reliability

$\Delta\log k = \pm 0.15$ over the temperature range 240-350 K.

Comments on Preferred Values

The reaction of $HOCS_2$ with O_2 is an intermediate step in the overall reaction of the HO radical with CS_2 under atmospheric conditions. The $HOCS_2$ is formed by the addition of HO to CS_2; once formed it may undergo dissociation back to HO and CS_2 or react with O_2.

The four studies (Hynes et al., 1988; Murrells et al., 1990; Lovejoy et al., 1990a; Diau and Lee, 1991) of the kinetics of this reaction, all using the same general experimental technique, are in good agreement. The rate coefficients measured by Hynes et al. (1988) over the temperature range 251-348 K could equally well be represented by either the Arrhenius expression cited in the table, with a small negative temperature dependence, or by a temperature-independent rate coefficient. The results of Murrells et al. (1990) favor the latter. For the preferred values we assume the rate coefficient to be temperature independent over the temperature range studied and take a mean of the values of Hynes et al. (1988), Murrells et al. (1990), Lovejoy et al. (1990a) and Diau and Lee (1991).

Lovejoy et al. (1990b; 1994) used PLP-LIF to measure an HO_2 radical formation yield of 0.95 ± 0.15 (249-300 K) from the reaction of the HO radical with CS_2 in the presence of O_2 (by converting HO_2 radicals to HO radicals by reaction with NO) (Lovejoy et al., 1990b), and used DF-CIMS to measure an SO_2 yield from the HO radical reaction with CS_2 in the presence of O_2 of 0.90 ± 0.20 at 340 K (Lovejoy et al., 1994).

The main steps in the atmospheric oxidation of CS_2 initiated by HO are then

$$HO + CS_2 \leftrightarrow HOCS_2$$
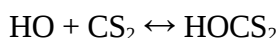
followed by the overall reaction

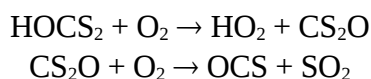$$HOCS_2 + 2O_2 \rightarrow HO_2 + SO_2 + OCS$$
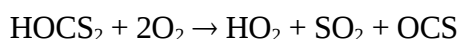
In the atmosphere, reaction of the $HOCS_2$ with O_2 predominates over reaction with NO or NO_2. The study by Stickel et al. (1993) has provided some further insight into the mechanism of this complex reaction. Two types of experiment were performed. In one, the reaction was initiated by pulsed laser photolysis and product concentrations monitored in real time by tunable diode laser absorption spectroscopy. In the other, continuous photolysis was used with FTIR product detection. Products observed were OCS, SO_2, CO, and CO_2. Both experiments gave concordant values for the yields of OCS and CO of 0.83 ± 0.08 and 0.16 ± 0.03, respectively. The yield of CO_2 was small (<0.01). The overall yield of SO_2 (1.15 ± 0.10) was made up of two components, a "prompt" value of 0.84 ± 0.20 resulting from SO_2 produced in a primary channel of the reaction and a longer-time component assumed due to production of SO_2 from reaction of O_2 with S or SO produced in another primary channel. The data of Stickel et al. (1993) thus suggest two primary channels, the major one leading to OCS and SO_2 and a minor channel leading to CO and SO. There are a number of possible reaction channels leading directly to these species or to their precursors which subsequently produce them on a very short time scale.

Lovejoy et al. (1994) used DF-CIMS to investigate the products of the reaction of the $H^{18}O$ radical with CS_2 in $^{16}O_2$ at ~340 K, and observed the formation of $^{16}OS^{18}O$ with a yield of 0.90 ± 0.20. $S^{16}O_2$ formation was observed (Lovejoy et al., 1994), and this may be consistent with the formation of S atoms or SO radicals (Stickel et al., 1993).
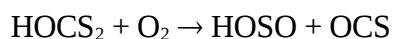
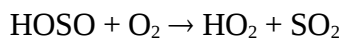These studies suggest that the reaction pathway

$$HOCS_2 + O_2 \rightarrow HCO + SO_2 + S$$
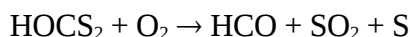
followed by reactions of HCO and S to form HO_2 + CO and SO_2 accounts for ~15% of the overall reaction (Stickel et al., 1993), with the remainder (~85%) proceeding by (Lovejoy et al., 1994)
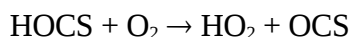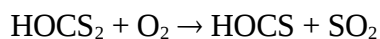
$$HOCS_2 + O_2 \rightarrow HO_2 + CS_2O$$
$$CS_2O + O_2 \rightarrow OCS + SO_2$$

or

$$HOCS_2 + O_2 \rightarrow HOSO + OCS$$

$$HOSO + O_2 \rightarrow HO_2 + SO_2$$

or

$$HOCS_2 + O_2 \rightarrow HOCS + SO_2$$
$$HOCS + O_2 \rightarrow HO_2 + OCS$$

Theoretical studies of the $HOCS_2$-O_2 intermediate by Zhang and Qin (2000) and McKee and Wine (2001) suggest that HOSO and OCS are the main dissociation products, which would then be followed by the reaction $HOSO + O_2 \rightarrow HO_2 + SO_2$.

References

Diau, E. W.-G. and Lee, Y.-P.: J. Phys. Chem. 95, 7726, 1991.

Hynes, A. J., Wine, P. H. and Nicovich, J. M.: J. Phys. Chem. 92, 3846, 1988.

Lovejoy, E. R., Kroeger, K. S. and Ravishankara, A. R.: Chem. Phys. Lett. 167, 183, 1990a.

Lovejoy, E. R., Murrells, T. P., Ravishankara, A. R. and Howard, C. J.: J. Phys. Chem. 94, 2386, 1990b.

Lovejoy, E. R., Ravishankara , A. R. and Howard, C. J.: Int. J. Chem. Kinet. 26, 551, 1994.

McKee, M. L. and Wine, P. H.: J. Am. Chem. Soc. 123, 2344, 2001.

Murrells, T. P., Lovejoy, E. R. and Ravishankara, A. R.: J. Phys. Chem. 94, 2381, 1990.

Stickel, R. E., Chin, M., Daykin, E. P., Hynes, A. J., Wine, P. H. and Wallington, T. J.: J. Phys. Chem. 97, 13653, 1993.

Zhang, L. and Qin, Q.: J. Mole. Struct. 531, 375, 2000.