IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx40

This data sheet updated: 19th November 2001.

$$\mathbf{HSO + O_3 \rightarrow HS + 2O_2} \quad \mathbf{(1)}$$
$$\mathbf{\rightarrow HO + SO + O_2} \quad \mathbf{(2)}$$
$$\mathbf{\rightarrow HSO_2 + O_2} \quad \mathbf{(3)}$$

$\Delta H^\circ(1) = 4$ kJ·mol^{-1}
$\Delta H^\circ(2) = -95$ kJ·mol^{-1}
$\Delta H^\circ(3) = -361$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$k_3 = 1 \times 10^{-12} \exp(-1000/T)$		Wang and Howard, 1990[1]	(a,b)
$k_3 = (3.5 \pm 1.5) \times 10^{-14}$	297		
$k_3 = 2.1 \times 10^{-12} \exp[(-1120 \pm 320)/T]$	273-423	Lee, Lee and Wang, 1994[2]	DF-LIF/A
$k_3 = (4.7 \pm 1.0) \times 10^{-14}$	298		
Relative Rate Coefficients			
$k_1 = 7 \times 10^{-14}$	297	Wang and Howard, 1990[1]	DF-LMR (c)
$k_1 = 2.7 \times 10^{-13} \exp(-400/T)$	377-405		(b)
1.1×10^{-13}	298	Friedl, Brune and Anderson, 1985[3]	(d)

Comments

(a) DF-LMR. Monitoring HSO decay gives the sum of all reaction channels apart from (1). However, OH is not detected (see below) and in the absence of further information on other reaction channels we equate this to reaction 3.

(b) No error limits given as only a very limited data set obtained.

(c) Value obtained by numerical fitting to HS profile in excess of O_3. Value of rate coefficient for HS + O_3 used in simulation (4.4×10^{-12} cm^3 molecule^{-1} s^{-1}) was taken from the same study. Use of the recommended value for k (HS + O_3) will reduce the value obtained for k_1.

(d) Discharge flow system. The HS + O_3 reaction was studied with HS radicals being monitored by LIF. Addition of O_3 gave an initial decrease in [HS], which finally attained a steady state indicating

regeneration of HS, postulated to be by the HSO + O_3 reaction. A rate coefficient ratio of k/k(HS + O_3) = 0.031 was obtained and placed on an absolute basis by use of k(HS + O_3) = 3.7 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}.

Preferred Values

k = 1.1 x 10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 298 K.
k_1 = 6 x 10^{-14} cm^3 $molecule^{-1}$ s^{-1} at 298 K.
k_3 = 5 x 10^{-14} cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta \log k_1 = \pm 0.3$ at 298 K.
$\Delta \log k_3 = \pm 0.3$ at 298 K.

Comments on Preferred Values

In the recent study by Lee *et al*.,[2] the rate coefficient measured is that for HSO removal by all channels other than channel 1 giving HS as a product, which subsequently regenerates HSO by reaction with the O_3 present. However, in our recommendations the rate coefficients measured by Lee *et al*.[2] are assigned to channel 3 on the grounds that Friedl *et al*.[3] could not detect HO production (channel 2); some further support for channel 3 comes from the work of Lovejoy *et al*.[4] who found that HSO_2 is readily formed by the HSO + NO_2 reaction.

Both Wang and Howard[1] and Lee *et al*.[2] measured a similar temperature coefficient for k_3, the preferred values are only given at 298 K until further studies are made on the effects of temperature on all of the rate coefficients.

References

1 N. S. Wang and C. J. Howard, J. Phys. Chem. **94**, 8787 (1990).
2 Y.-Y. Lee, Y.-P. Lee, and N. S. Wang, J. Chem. Phys. **100**, 387 (1994).
3 R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **89**, 5505 (1985).
4 E. R. Lovejoy, N. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).