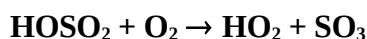


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx16

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

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



$$\Delta H^\circ = 4 \text{ kJ mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(4 \pm 2) \times 10^{-13}$	250	Margitan, 1984	FP-RF (a)
$(4 \pm 2) \times 10^{-13}$	298		
$(3.5 \pm 1) \times 10^{-13}$	298	Martin et al., 1986	DF-EPR (b)
$(4.37 \pm 0.66) \times 10^{-13}$	$297 \pm 1$	Gleason et al., 1987	DF-CIMS (c)
$1.34 \times 10^{-12} \exp[-(330 \pm 70)/T]$	297-423	Gleason and Howard, 1988	DF-CIMS (c)
$(4.37 \pm 0.66) \times 10^{-13}$	297		

### Comments

- The reaction was studied at 53 and 133 mbar (40 and 100 Torr) of Ar diluent at 250 and 298 K. HO radicals were removed by the  $\text{HO} + \text{SO}_2 + \text{M} \rightarrow \text{HOSO}_2 + \text{M}$  reaction, but the addition of  $\text{O}_2$  and NO regenerated HO radicals by the reactions  $\text{HOSO}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{SO}_3$  and  $\text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2$ . The effects of varying the amounts of  $\text{O}_2$  were studied. The same rate coefficient was measured at 250 K and 298 K, but it was suggested (Margitan, 1984) that this was due to a lack of precision in the technique rather than indicating that  $k$  is temperature independent.
- The effects of addition of NO and  $\text{O}_2$  on the HO radical decays were studied. A system of 12 reactions was used to model the reaction system to obtain the rate coefficient  $k$ .
- HO radicals were produced by the  $\text{H} + \text{NO}_2$  reaction, and  $\text{SO}_2$  and  $\text{O}_2$  were added down-stream.  $\text{HOSO}_2$  was monitored by sampling into a flowing afterglow containing  $\text{Cl}^-$  ions.  $\text{SO}_3^-$  ions, formed by the reaction  $\text{Cl}^- + \text{HOSO}_2 \rightarrow \text{SO}_3^- + \text{HCl}$ , were detected by quadrupole MS. The  $\text{SO}_3$  product of the reaction was also detected by  $\text{Cl}^- + \text{SO}_3 + \text{M} \rightarrow (\text{ClSO}_3)^- + \text{M}$  with MS measurement of  $(\text{ClSO}_3)^-$ . The total pressure was varied over the range 2.7-10.7 mbar (2-8 Torr), and no change in  $k$  was observed, allowing an upper limit of  $3.4 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  ( $\text{M} = \text{N}_2$ ) for the rate coefficient for the reaction  $\text{HOSO}_2 + \text{O}_2 + \text{M} \rightarrow \text{HOSO}_2\text{O}_2 + \text{M}$  to be set.

### Preferred Values

$$k = 4.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.3 \times 10^{-12} \exp(-330/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 290\text{-}420 \text{ K.}$$

Reliability

$\Delta \log k = \pm 0.10$  at 298 K.

$\Delta(E/R) = \pm 200$  K.

#### *Comments on Preferred Values*

In the earlier studies of Margitan (1984) and Martin et al. (1986), HO radical decays due to the reaction  $\text{HO} + \text{SO}_2 + \text{M} \rightarrow \text{HOSO}_2 + \text{M}$  were monitored in the presence of NO and O<sub>2</sub>. The reaction sequence  $\text{HOSO}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{SO}_3$  and  $\text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2$  then regenerates HO radicals. Modeling of the NO decay led to the rate coefficient  $k$ . This method of determining  $k$  is less direct than the more recent measurements of Gleason et al. (1987) and Gleason and Howard (1988), where HOSO<sub>2</sub> radicals were monitored by MS. We therefore accept the temperature-dependent expression obtained by Gleason and Howard (1988). The earlier results of Margitan (1984) and Martin et al. (1986), though less precise, are in good agreement with the preferred values.

#### **References**

- Gleason, J. F. and Howard, C. J.: J. Phys. Chem. 92, 3414, 1988.  
Gleason, J. F., Sinha, A. and Howard, C. J.: J. Phys. Chem. 91, 719, 1987.  
Margitan, J. J.: J. Phys. Chem. 88, 3314, 1984.  
Martin, D., Jourdain, J. L. and Le Bras, G.: J. Phys. Chem. 90, 4143, 1986.