IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet I.A4.86 SOx15

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$HO + SO_2 + M \rightarrow HOSO_2 + M$

ΔH° = -125 kJ·mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	**Reference**	Technique/ Comments
Absolute Rate Coefficients			
(2.54 ± 0.33) x 10^{-31} [N_2]	298	Leu, 1982	DF-RF (a)
1.6 x 10^{-31} [N_2]	297	Paraskevopoulos et al., 1983	FP-RA (b)
5.8 x 10^{-31} (T/300)$^{-2.6}$ [N_2]	260-420	Wine et al., 1984	FP-RF (c)
(2.4 ± 0.7) x 10^{-31} [N_2]	298	Lee et al., 1990	DF-RF (d)

Comments

(a) Pressure range 0.9-4.0 Torr. Temperature dependence measured for M = He over the range 261-414 K and the pressure range 0.9-10 Torr, leading to k_0 = (7.91±0.4) x 10^{-32} (T/298)$^{-2.85}$ [He] cm^3 molecule^{-1} s^{-1}. Experiments with M = He, Ar, N_2, O_2, CO_2, and SO_2.

(b) Pressure range 55-760 Torr. Falloff representation with F_c = 1 responsible for too low values of k_0 and k_∞.

(c) Pressure range 13-696 Torr, bath gases He, Ar, N_2, and SF_6. Falloff representation with F_c = exp(-T/388), corresponding to F_c = 0.46 at 300 K.

(d) Pressure range 0.6-45 Torr, bath gases He, N_2, and SO_2.

Preferred Values

k_0 = 2.5 x 10^{-31} (T/300)$^{-2.6}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200-400 K.

Comments on Preferred Values

Work published before 1980 has been discussed in Fulle et al. (1999) and is not shown here. The preferred value at 300 K is based on the low pressure results from Leu (1982) and Lee et al.

(1990); the temperature coefficient is from Wine et al. (1984). Falloff curves with F_c = 0.53 and k_∞ = 2. x 10^{-12} cm^3 $molecule^{-1}$ s^{-1} from Fulle et al. (1999) give k(1bar) in good agreement with data from Pavaskevopoulos et al. (1983), Wine et al. (1984), Harris et al. (1980), Izumi et al. (1984), Barnes et al. (1986), and Martin et al. (19869.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	**Reference**	Technique/ Comments
Absolute Rate Coefficients			
1.2 x 10^{-12}	297	Pavaskevopoulos et al., 1983	FP-RA (a)
1.26 x 10^{-12} (T/300)$^{-0.7}$	260-420	Wine et al.,1984	FP-RF (b)
1.2 x 10^{-11} exp(-360/T)	220-400	Fulle et al., 1999	LP-LIF(c)
3.6 x 10^{-11}	300		
(2.04±0.10) x 10^{-12} (T/300)$^{-0.27}$	295-673	Blitz et al., 2003	LP-LIF (d)

Comments

(a) See comment (b) for k_0.
(b) See comment (c) for k_0.
(c) Measurements in the pressure range 1-96 bar of He. Detailed analysis of earlier work and of full falloff curves.
(d) Studies of vibrational relaxation OH(v=1) + SO_2 as well as OH + SO_2 + M in the pressure range 100-200 Torr of He at 295, 373, and 473 K.

Preferred Values

k_∞ = 2.0 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1} over the temperature range 200-400 K.

Comments on Preferred Values

The direct derivation of k_∞ from the high pressure falloff curves by Fulle et al. (1999) gives somewhat larger values than the vibrational relaxation results from Blitz et al. (2005). Inspecting the data from Fulle et al. (1999) and taking into account that asymmetric broadening of the falloff curves like for OH + NO_2 + M may have been present, one may conclude that the difference to the values from Blitz et al. (2003) is not large. Theoretical studies of the reaction and its potential by Somnitz (2004) and Glowacki et al. (2009) so far appear inconclusive with respect to the temperature dependence of k_∞.

Preferred Values

Parameter	Value	T/K
k_0/cm^3 molecule^{-1} s^{-1}	2.5 x 10^{-31} [N_2]	298
k_0/cm^3 molecule^{-1} s^{-1}	2.5 x 10^{-31} (T/300)$^{-2.6}$ [N_2]	250-300
k_∞/cm^3 molecule^{-1} s^{-1}	2.0 x 10^{-12}	298
k_∞/cm^3 molecule^{-1} s^{-1}	2.0 x 10^{-12}	250-300
k(1 bar N_2)/cm^3 molecule^{-1} s^{-1}	8.9 x 10^{-13}	298
F_c	0.53	250-300
Reliability		
Δlog k_0	± 0.3	298
Δn_0	± 1	250-300
Δlog k_∞	± 0.3	298
Δn_∞	± 0.3	250-300

The following text-line combines the preferred values for the high and low pressure limiting rate coefficients to generate a single, cut-and-paste expression for calculation of k:

=((2.5e-31*(T/300)^-2.6)*M*(2.0e-12))/((2.5e-31*(T/300)^-2.6)*M+(2.0e-12))*10^(log10(0.53)/(1+(log10((2.5e-31*(T/300)^-2.6)*M/(2.0e-12))/(0.75-1.27*log10(0.53)))^2))

The molecular density, M = 7.243×10^{21}P(bar)/T(K)

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