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

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

$\Delta H° = -125$ 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			
$(2.54 \pm 0.33) \times 10^{-31}$ [N_2]	298	Leu, 1982	DF-RF (a)
1.6×10^{-31} [N_2]	297	Paraskevopoulos et al., 1983	FP-RA (b)
$5.8 \times 10^{-31} (T/300)^{-2.6}$ [N_2]	260-420	Wine et al., 1984	FP-RF (c)
$(2.4 \pm 0.7) \times 10^{-31}$ [N_2]	298	Lee et al., 1990	DF-RF (d)
$1.1 \times 10^{-30} (T/298)^{-3.62}$ [N_2]	200-600	Blitz et al., 2017b	LP-LIF (e)

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 $k_0 = (7.91 \pm 0.4) \times 10^{-32} (T/298)^{-2.85}$ [He] cm^3 molecule^{-1} s^{-1}. Experiments with M = He, Ar, N_2, O_2, CO_2, and SO_2. Falloff representation with $F_c = 1$ responsible for low values of k_0 and k_∞.

(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. Falloff representation with $F_c = 1$ responsible for too low values of k_0 and k_∞.

(e) HO produced by two-photon photolysis of SO_2 at 248 nm, generating $O(^1D)$ which reacts with H_2. Pressure range 25-300 Torr He. Falloff curve at 298 K fitted with $F_c = 0.13$. The value of k(1 bar) = 5.8×10^{-31} cm^3 molecule s^{-1} at 298 K is lower than the preferred value by about a factor of 0.7. The discrepancy is suggested to be due to the neglect of two-photon photolysis of

SO_2 in earlier studies from other laboratories. The derived large value of k_0 is a consequence of the use of a markedly smaller F_c than employed in earlier falloff representations. The parameters listed in the table were obtained via fitting to simulated data using $k_\infty(T) = (7.8 \pm 2.2) \times 10^{-13}(T/298)^{0.1}$ cm^3 molecule^{-1} s^{-1} and $\langle \Delta E_{down} \rangle (N_2)/cm^{-1} = 600 \times (T/298)^{0.3}$.

Preferred Values

$k_0 = 2.8 \times 10^{-31} (T/300)^{-2.6}$ [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 $k_\infty = 2 \times 10^{-12}$ 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. (1986). The data from Blitz et al. (2017b) at 100 Torr of He within the error limits are consistent with earlier results.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	**Reference**	Technique/ Comments
Absolute Rate Coefficients			
1.2×10^{-12}	297	Pavaskevopoulos et al., 1983	FP-RA (a)
$1.26 \times 10^{-12} (T/300)^{-0.7}$	260-420	Wine et al.,1984	FP-RF (b)
$1.2 \times 10^{-11} \exp(-360/T)$	220-400	Fulle et al., 1999	LP-LIF(c)
3.6×10^{-12}	300		
$(2.04 \pm 0.10) \times 10^{-12} (T/300)^{-0.27}$	295-673	Blitz et al., 2003	LP-LIF (d)
$(7.2 \pm 3.3) \times 10^{-13}$	295-810	Blitz et al., 2017a	LP-LIF (e)

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.
(e) Studies of vibrational relaxation HO(v=1, 2, 3) + SO_2 in He. Presence of a weakly bound complex OH-OSO* prior to adduct formation suggested. Evaluation of the composite mechanism leads to 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 larger values than the vibrational relaxation results from Blitz et al. (2003, 2017a). This may be explained by the formation of an OH-OSO* pre-reaction complex with different redissociation to OH + SO_2 in recombination and vibrational relaxation experiments. 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, 2017a) 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_∞, but a very weak temperature dependence has been fitted by Blitz et al. (2017b). The preferred value is a compromise between the direct data from Fulle et al. (1999), extending to high pressures, and the less direct data from Blitz et al. (2017a) using vibrational relaxation of HO by SO_2 as a proxy. Falloff curves here are represented with F_c = exp(-T/472), corresponding to F_c = 0.53 at 300 K from Fulle et al. (1999).

Preferred Values

Parameter	Value	T/K
k_0/cm^3 $molecule^{-1}$ s^{-1}	2.8 x 10^{-31} [N_2]	298
k_0/cm^3 $molecule^{-1}$ s^{-1}	2.8 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}	9.3 x 10^{-13}	298
F_c	exp(-T/472)	250-400
	0.53	298
Reliability		
$\Delta \log k_0$	± 0.3	298
Δn_0	± 1	250-300
$\Delta \log k_\infty$	± 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:

=((2.8e-31*(T/300)^-2.6)*M*(2.0e-12))/((2.8e-31*(T/300)^-2.6)*M+(2.0e-12))*10^(log10(EXP(-T/472))/(1+(log10((2.8e-31*(T/300)^-2.6)*M/(2.0e-12))/(0.75-1.27*log10(EXP(-T/472))))^2))

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

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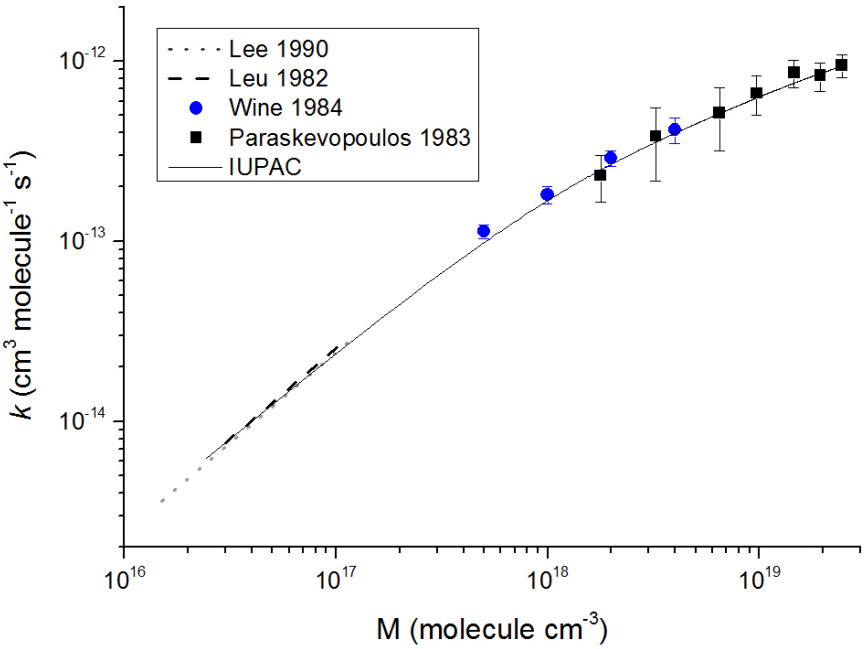

Rate coefficients for OH + SO_2 in N_2 at 298 K and the IUPAC preferred values (solid line)