IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet I.A4.77 SOx6

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$O + SO_2 + M \rightarrow SO_3 + M$

$\Delta H° = -348.1$ 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			
3.1 x 10^{-32} exp(-1009/T) [Ar]	299-400	Atkinson and Pitts, 1978	FP-CL (a)
1.05 x 10^{-33} [Ar]	298		
1.37 x 10^{-33} [N_2]	298		
9.5 x 10^{-23} T^{-3} exp(-2400/T) [Ar]	290-840	Naidoo et al., 2005	PLP-RF (b)
1.14 x 10^{-33} [Ar]	298		
{8.0x$10^{-13}$$T^{-6}$ exp(-4780/T) + 1.7x$10^{-23}$$T^{-3}$ exp(-1980/T)} [Ar]	300 - 2500	Hwang et al., 2010	(c)

Comments

(a) Flash photolysis with detection of O(^{3}P) atoms by NO_2 chemiluminescence. Relative efficiencies of k(M=N_2): k(M=Ar): k(M=SO_2) = 1.0:0.77:6.9 were determined.

(b) Measurements in Ar over the range 100-880 mbar, evaluated with F_c = 0.65 and 0.58, and k_∞ = 0.33 x 10^{-13} and 0.70 x 10^{-13} cm^3 molecule^{-1} s^{-1} at T = 289 and 399 K, respectively.

(c) Shock wave measurements in Ar at 970 – 1150 K combined with the data from Atkinson and Pitts (1978) and from Naidoo et al. (2005), confirming a rate constant maximum near 800 K.

Preferred Values

k_0 = 1.4 x 10^{-33} [N_2] cm^3 molecule^{-1} s^{-1} at 298 K.
k_0 = 4.7 x 10^{-30} (T/298)$^{-3}$ exp(-2400/T) [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200-400 K.

Comments on Preferred Values

The preferred values are based on the study by Naidoo et al. (2005) which, after accounting for falloff effects, agrees reasonably well with the data from Atkinson and Pitts (1978).The relative efficiencies from Atkinson and Pitts (1978) are used to convert data for M = Ar to N_2. $F_c \approx 0.6$ is recommended over the range 200-400 K. Data for the reverse dissociation of SO_3 from Astholz et al. (1979) and Yilmaz et al. (2006) and their analysis by Troe (1978) and Naidoo et al. (2005) are shown to be consistent with the preferred values. Shock wave measurements at 970-1150 K by Hwang et al. (2010), combined with the results from Atkinson and Pitts (1978) and Naidoo et al. (2005), confirmed the rate constant maximum near 800 K found in the analysis by Troe (1978). A representation by $k_0 = [Ar] \{8.0 \times 10^{-13} T^{6.0} \exp(-4780/T) + 1.7 \times 10^{-23} T^{3.0} \exp(-1980/T)\}$ accounts for this behaviour.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	**Reference**	Technique/ Comments
Absolute Rate Coefficients			
$6.1 \times 10^{-13} \exp(-850/T)$	290-840	Naidoo et al., 2005	PLP-RF (a)
3.5×10^{-14}	298		

Comments

(a) See comment (b) for k_0.

Preferred Values

$k_\infty = 3.5 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_\infty = 6.1 \times 10^{-13} \exp(-850/T)$ cm^3 molecule^{-1} s^{-1} over the range 200-400 K.

Comments on Preferred Values

The preferred values are based on the study by Naidoo et al. (2005) which included a theoretical analysis of the full falloff curve with $F_c = 0.6$. Measurements by Mueller et al. (2000) and Yilmaz et al. (2006) at temperatures above 1000 K were shown to be consistent with the preferred values.

Preferred Values

Parameter	Value	T/K
k_0/cm^3 molecule^{-1} s^{-1}	1.4×10^{-33} [N_2]	298
k_0/cm^3 molecule^{-1} s^{-1}	$4.7 \times 10^{-30} (T/300)^{-3.0} \exp(-2400/T)$ [N_2]	200-400
k_∞/cm^3 molecule^{-1} s^{-1}	3.5×10^{-14}	298
k_∞/cm^3 molecule^{-1} s^{-1}	$6.1 \times 10^{-13} \exp(-850/T)$	200-400
k(1 bar N_2)/cm^3 molecule^{-1} s^{-1}	1.1×10^{-14}	298
F_c	0.6	200-400
Reliability		
$\Delta \log k_0$	± 0.2	298
$\Delta E_0/R$	± 200 K	200-400
$\Delta \log k_\infty$	± 0.3	298

$\Delta E_\infty/R$	± 200 K	200-400

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*:

=((4.7e-30*(*T*/298)^-3*exp(-2400/*T*))*M*(6.1e-13*exp(-850/*T*)))/((4.7e-30*(*T*/298)^-3*exp(-2400/*T*))*M+(6.1e-13*exp(-850/*T*)))*10^(log10(0.6)/(1+(log10((4.7e-30*(*T*/298)^-3*exp(-2400/*T*))*M/(6.1e-13*exp(-850/*T*)))/(0.75-1.27*log10(0.6)))^2))

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

References

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