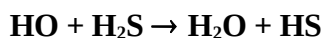


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx14

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



$$\Delta H^\circ = -115.4 \text{ kJ mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$2.3 \times 10^{-11} \exp(-443/T)$	298-885	Westenberg and deHaas, 1973	DF-EPR
$(5.48 \pm 0.33) \times 10^{-12}$	298		
$(3.1 \pm 0.5) \times 10^{-12}$	298	Stuhl, 1974	FP-RF
$(5.2 \pm 0.5) \times 10^{-12}$	298-423	Perry et al., 1976	FP-RF
$6.4 \times 10^{-12} \exp[-(55 \pm 58)/T]$	245-366	Wine et al., 1981	FP-RF
$(5.13 \pm 0.57) \times 10^{-12}$	297		
$2.27 \times 10^{-19} T^{2.5} \exp(725/T)$	228-518	Leu and Smith, 1982	DF-RF
$(3.9 \pm 0.7) \times 10^{-12}$	298		
$(5.01 \pm 0.55) \times 10^{-12}$	228-437	Michael et al., 1982	FP-RF
$7.8 \times 10^{-12} \exp[-(146 \pm 105)/T]$	239-425	Lin, 1982	FP-RF
$(4.42 \pm 0.48) \times 10^{-12}$	295		
$(4.3 \pm 0.6) \times 10^{-12}$	300	Wang and Lee, 1985	DF-RF
$3.81 \times 10^{-19} T^{2.43} \exp(732/T)$	245-450	Lin et al., 1985	DF-RF
$(4.4 \pm 0.7) \times 10^{-12}$	299		
$(4.9 \pm 0.9) \times 10^{-12}$	245	Lafage et al., 1987	DF-RF/LIF
$(3.8 \pm 0.6) \times 10^{-12}$	263		
$1.32 \times 10^{-11} \exp[-(394 \pm 190)/T]$	294-450		
$(3.3 \pm 0.5) \times 10^{-12}$	294		
<i>Relative Rate Coefficients</i>			
$(5.31 \pm 0.35) \times 10^{-12}$	297 ± 2	Cox and Sheppard, 1980	RR (a)
$(5.5 \pm 0.9) \times 10^{-12}$	300	Barnes et al., 1986	RR (b)

Comments

- HO radicals were generated by the photolysis of HONO-NO-air mixtures at atmospheric pressure. The decay of H₂S was measured relative to that of C₂H₄ by GC, and the relative rate coefficient placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{C}_2\text{H}_4) = 8.57 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K and atmospheric pressure of air (Atkinson, 1997).
- HO radicals were generated by the photolysis of CH₃ONO in N₂-O₂ mixtures at atmospheric pressure. The decay of H₂S was measured relative to that for ethene by GC, and the relative rate

coefficient placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{C}_2\text{H}_4) = 8.44 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K and atmospheric pressure of air (Atkinson, 1997).

Preferred Values

$k = 4.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 6.1 \times 10^{-12} \exp(-80/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220-520 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.

$\Delta(E/R) = \pm 80 \text{ K}$.

Comments on Preferred Values

The preferred values are obtained from a unit-weighted least-squares analysis of the absolute rate constants of Perry et al. (1976), Wine et al. (1981), Leu and Smith (1982), Michael et al. (1982), Lin (1982), Wang and Lee (1985), Lin et al. (1985) and Lafage et al. (1987), which are in good agreement. The earlier studies of Westenberg and deHaas (1973) and Stuhl (1974) reported a significantly higher temperature dependence of the rate coefficient and a lower room temperature rate coefficient, respectively, than later studies, and the data from these studies (Westenberg and deHaas, 1973; Stuhl, 1974) are not used in the evaluation of the preferred values. The studies of Leu and Smith (1982), Lin et al. (1985) and Lafage et al. (1987) show non-Arrhenius behavior of the rate coefficient, with a shallow minimum in the rate coefficient at ~ 270 -300 K. The rate coefficient is independent of pressure (Leu and Smith, 1982; Michael et al., 1982; Lin, 1982; Lin et al., 1985) and the nature of the diluent gas (Lin et al., 1985). These findings (Leu and Smith, 1982; Michael et al., 1982; Lin, 1982; Lin et al., 1985) cast some doubt upon the suggestion that the non-Arrhenius behavior is due to the occurrence of both addition and abstraction channels.

Despite the non-Arrhenius behavior of the rate coefficient k over an extended temperature range, the preferred expression is given in the Arrhenius form which is satisfactory for the temperature range covered by our recommendation.

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