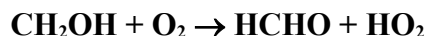


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet R_Oxygen_12

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: June 2008; last change in preferred values June 2008.



$$\Delta H^\circ = -76.2 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(9.5 \pm 2.5) \times 10^{-12}$	298	Grotheer et al., 1985	DF-MS (a)
$(10.6 \pm 2.5) \times 10^{-12}$	296	Dobé et al., 1985	DF-LMR (b)
$(10.5 \pm 4.7) \times 10^{-12}$	296		
$(8.6 \pm 2.0) \times 10^{-12}$	298	Payne et al., 1988	DF-MS (c)
$\{2.5 \times 10^{-9} T^{-1.0} + 4.0 \times 10^{-10} \exp(-2525/T)\}$	370-684	Grotheer et al., 1988	DF-MS (d)
$5.6 \times 10^{-9} \exp(-1700/T)$	215-250	Nesbitt, Payne and Stief, 1988	DF-MS (e)
$(8.61 \pm 1.14) \times 10^{-12}$	300		
$(8.8 \pm 0.2) \times 10^{-12}$	298	Pagsberg et al., 1989	PR-AS (f)
$(1.17 \pm 0.12) \times 10^{-11}$	296	Miyoshi et al., 1990	PLP-MS (g)
$(1.00 \pm 0.14) \times 10^{-11}$	294	Hanoune et al., 2001	PLP-AS (h)
$4.8 \times 10^{-12} \exp(202/T)$	236-600	Schocker et al., 2007	PLP-AS (i)
$(9.9 \pm 0.5) \times 10^{-12}$	298		

Comments

- CH₂OH was generated from Cl + CH₃OH at total pressures of 0.4 mbar to 1.2 mbar (0.3 Torr to 0.9 Torr). k was derived from the rate of disappearance of CH₂OH in excess O₂ by MS.
- CH₂OH was generated from F + CH₃OH at total pressures of 0.69 mbar to 6.5 mbar (0.52 Torr to 4.9 Torr). Two values of k were derived from the rate of disappearance of CH₂OH and of the appearance of HO₂, both monitored by LMR spectroscopy.
- CH₂OH was generated from Cl + CH₃OH at total pressures of ~1.3 mbar (~1 Torr). k was derived from the rate of disappearance of CH₂OH in excess O₂ by MS.
- As for comment (a) at pressures of ~1.1 mbar (~0.8 Torr).
- As for comment (c) at pressures of ~1.3 mbar (~1 Torr).
- CH₂OH was generated from F + CH₃OH at total pressures of 1 bar (760 Torr). k was derived from the rate of disappearance of CH₂OH in excess of O₂ by absorption at 285.5 nm.
- Pulsed laser photolysis of CH₃COCH₂OH, with the decay of CH₂OH being monitored by photoionization MS, at total pressures of 1.7 mbar to 7.3 mbar (1.3 Torr to 5.5 Torr).
- Pulsed laser photolysis of a mixture of CH₃OH and Cl₂ at 355 nm with monitoring of CH₂O at 1707.9 cm⁻¹ by tunable diode laser absorption in the range 7.71-20.22 mbar (5.8-15.2 Torr). Only data with [O₂] > 2 × 10¹⁵ molecule cm⁻³ have been used in the analysis.
- Pulsed laser photolysis of a mixture of Cl₂-CH₃OH-O₂ in 66.5 mbar N₂ at 355 nm using a multipass optical cell and two-tone frequency modulation absorption spectroscopy for the

sensitive detection of HO₂. The initial CH₂OH radical concentration was in the range (1.6 – 5) x 10¹³ molecule cm⁻³. The temperature dependence of *k* was slightly negative over the given range. No pressure dependence was detected at 66.5 mbar of N₂ within the stated temperature range.

Preferred Values

$k = 9.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 5.5 \times 10^{-12} \exp(155/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–500 K.

Reliability

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

$\Delta (E/R) = \pm 170 \text{ K}$

Comments on Preferred Values

The rate coefficient at 298 K is now well established for this reaction, and our recommendation is the average of the results of Grotheer et al. (1985), Dóbé et al. (1988), Payne et al. (1988), Nesbitt et al. (1988), Pagsberg et al. (1989), Miyoshi et al. (1990), Hanoune et al. (2001) and Schocker et al. (2007) comprising eight values. The earlier data of Wang et al. (1984) and Radford (1980) are rejected on the basis that they involved high concentrations of radicals, leading to mechanistic complications (Radford, 1980). The three studies of the temperature dependence of this reaction (Nesbitt et al., 1988; Grotheer et al., 1989; Schocker et al., 2007) indicate that the rate coefficient follows a complicated non-Arrhenius behavior over the range 200 to 700 K. The data agree well over the restricted temperature range of 250 to 500K. The Schocker et al. (2007) data are given as preferred values in this temperature range together with two values of Grotheer et al. (1989) for $T < 500\text{K}$ for a total of 19 data points (see appended Arrhenius plot). Beyond 500 K the data of Grotheer et al. (1989) show a positive, those of Nesbitt et al. (1988) show a negative deviation for $T \leq 250\text{K}$ relative to the data of Schocker et al. (2007). Relevant temperature-dependent data are displayed in the appended Arrhenius plot with the “Best Fit Line” corresponding to the preferred value expression. Variational transition state calculations based on an *ab initio* PES on the G3 level of theory agree with the experimental data of Schocker et al. (2007) including the absence of a pressure dependence of *k* up to 600 K.

Grotheer et al. (1989) have carried out experiments replacing CH₃OH by CH₃OD and have observed no kinetic effect for the CH₂OH/CH₂OD + O₂ reactions.

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