IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet RO_1

This datasheet updated: 12th June 2003.

$CH_3O + O_2 \rightarrow HCHO + HO_2$

$\Delta H° = -111.2$ kJ·mol^{-1}

k/cm^3 molecule^{-1} s^{-1}	Temp./K	**Reference**	Technique/ Comments
Absolute Rate Coefficients			
$1.05 \times 10^{-13} \exp(-1310/T)$	413-628	Gutman, Sanders and	PLP-LIF (a)
1.3×10^{-15}	298	Butler, 1982[1]	
$5.5 \times 10^{-14} \exp(-1000/T)$	298-450	Lorenz *et al*., 1985[2]	PLP-LIF (b)
1.9×10^{-15}	298		
$2.3 \times 10^{-14}(1000/T)^{-9.5} \exp(2768/T)$	298-973	Wantuck *et al*., 1987[3]	PLP-LIF (c)
2.1×10^{-15}	298		

Comments

(a) CH_3O generated from pulsed laser photolysis of CH_3ONO at 266 nm. [CH_3O] was monitored by LIF at a total pressure of 53 mbar (40 Torr).

(b) Pulsed laser photolysis of CH_3ONO with monitoring of CH_3O by LIF, at pressures of 100 mbar (75 Torr) of He. At 298 K the rate coefficient was shown to be independent of pressure over the range 10 mbar to 200 mbar (7.5 Torr to 150 Torr) of He.

(c) Pulsed laser photolysis of CH_3OH or CH_3ONO at 193 nm in the presence of O_2 plus 33 mbar (25 Torr) of Ar. CH_3O radicals were monitored by LIF. Non-Arrhenius behavior was observed over entire temperature range and fitted by the cited empirical equation. Rate coefficients combined with the data of Gutman *et al*.[1] and Lorenz *et al*.[2] were found to obey a double exponential expression, with $k = \{1.5 \times 10^{-10} \exp(-6028/T) + 3.6 \times 10^{-14} \exp(-880/T)\}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k = 1.9 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.2 \times 10^{-14} \exp(-1080/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290 K to 610 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The direct measurements of the rate coefficients by Lorenz *et al*.[2] (298 K to 450 K) and Wantuck *et al*.[3] (298 K to 973 K) are in good agreement with the similar measurements of Gutman *et al*.[1] (413 K to 608 K), where the temperature ranges overlap. The preferred values

are derived from a least mean-squares analysis of these three sets of data[1-3] over the temperature range 298 K to 608 K The higher temperature measurements of Wantuck *et al*.[3] give a clear indication of non-Arrhenius behavior over the extended temperature range. The anomalously low *A*-factor for a simple H-atom transfer reaction and the possibility of a more complicated mechanism have both been noted.[4]

References

1 D. Gutman, N. Sanders, and J. E. Butler, J. Phys. Chem. **86**, 66 (1982).

2 K. Lorenz, D. Rhäsa, R. Zellner, and B. Fritz, Ber. Bunsenges. Phys. Chem. **89**, 341 (1985).

3 P. J. Wantuck, R. C. Oldenborg, S. L. Baughcum, and K. R. Winn, J. Phys. Chem. **91**, 4653 (1987).

4 NASA Evaluation No. 12, 1997 (see references in Introduction).