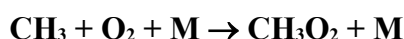


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet II.A4.86 R_Oxygen1

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This data sheet last evaluated: June 2012; last change in preferred values: June 2012.



$$\Delta H^\circ = -136.0 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$2.6 \times 10^{-31} [\text{N}_2]$	298	Basco et al., 1972	FP-AS (a)
$3.1 \times 10^{-31} [\text{N}_2]$	298	Parkes, 1977	MM-AS (b)
$4.5 \times 10^{-31} [\text{N}_2]$	296	Selzer and Bayes, 1983	PLP-MS (c)
$(7.0 \pm 1.0) \times 10^{-31} [\text{Ar}]$	298	Cobos et al., 1985	PLP-AS (d)
$(8.0 \pm 1.0) \times 10^{-31} [\text{N}_2]$	298		
$(4.8 \pm 0.6) \times 10^{-31} [\text{Ar}]$	298	Pilling and Smith, 1985	PLP-AS (e)
$(1.0 \pm 0.3) \times 10^{-30} (T/300)^{-3.3} [\text{Ar}]$	334-582	Keiffer et al., 1987	PLP-AS (f)
$7 \times 10^{-31} (T/300)^{-3.0} [\text{N}_2]$	300-700	Fernandes et al., 2006	PLP-UVA (g)
<i>Relative Rate Coefficients</i>			
$6.1 \times 10^{-33} \exp(1000/T) [\text{N}_2]$	259-339	Washida and Bayes, 1976	DF-MS (h)
$1.8 \times 10^{-31} [\text{N}_2]$	298		
$8.0 \times 10^{-32} \exp(243/T) [\text{Ar}]$	230-568	Pratt and Wood, 1984	(i)
$1.8 \times 10^{-31} [\text{Ar}]$	298		
$(7.56 \pm 1.1) \times 10^{-31} (T/300)^{-3.64} [\text{N}_2]$	264-370	Kaiser, 1993	(j)

Comments

- Pressure range 40-500 mbar. A Lindemann-Hinshelwood plot (i.e. $F_c = 1$) was used for falloff extrapolation which leads to too small values of k_0 and k_∞ .
- Molecular modulation spectroscopy. Pressure range 25-1000 mbar. Lindemann-Hinshelwood extrapolation to k_0 and k_∞ , see comment (a).
- Pressure varied between 0.6 and 8 mbar.
- Pressure of the bath gases N_2 , Ar and O_2 varied between 0.2 and 150 bar. Falloff curves were constructed with $F_c = 0.27$ and $k_\infty = 2.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The low value of the theoretically modeled F_c leads to a high limiting value of k_0 extracted from the measurements.
- Pressures of bath gas Ar varied between 4.2 and 645 mbar. Falloff curves constructed using $F_c = 0.57$ (including strong and weak collision contributions).

- (f) Measurements in the pressure range 25-790 mbar. Falloff curves constructed with $F_c = 0.6$. Various fitting procedures were applied and discussed.
- (g) Experiments between 2 and 1000 bar in Ar and N₂. CH₃ generated by laser flash photolysis of azomethane or acetone. CH₃O₂ detected by UV absorption at 240 nm. Evaluation of the falloff curves with $F_c = 0.33$ and $k_\infty = 2.2 \times 10^{-12}(T/300)^{0.9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (h) The rate coefficients $k(\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M})$ plus $k(\text{CH}_3 + \text{O}_2 \rightarrow \text{HCHO} + \text{HO})$ were measured relative to $k(\text{O} + \text{CH}_3 \rightarrow \text{products})$. Evaluation with $k(\text{O} + \text{CH}_3) = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Extrapolation to k_0 .
- (i) Discharge-flow system at pressures of 2.6-13 mbar. CH₃ radicals were produced from the H + C₂H₄ reaction. Reaction rates were determined from the effect of added O₂ on the radical combination products. Falloff curves were constructed assuming that k_∞ and F_c are independent of temperature.
- (j) Mixtures of Cl₂, CH₄, diluent (N₂, Ar, He, or SF₆) were irradiated with a fluorescent lamp. CH₄ loss and CH₃Cl formation were measured by GC. Data were obtained (for N₂ or O₂) between 3 mbar and 13 bar at 297 K, 25 mbar and 2 bar at 370 K and 50 mbar and 15 bar at 264 K. The data were fitted using $F_c = 0.48$ at 264 K, 0.46 at 297 K and 0.42 at 370 K.

Preferred Values

$k_0 = 7.0 \times 10^{-31} (T/300)^{-3.0} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200-700 K.

Comments on Preferred Values

Because of the large range of conditions applied, the preferred values are from Fernandes et al. (2006) in good agreement with the data from Keiffer et al. (1987) and Kaiser (1993), although different values of F_c were employed. The preferred values have been obtained with $F_c = 0.33$ and $k_\infty = 2.2 \times 10^{-12}(T/300)^{0.9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

High-pressure rate coefficients Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
1.8×10^{-12}	298	Van den Bergh and Callear, 1971	FP-AS (a)
5×10^{-13}	298	Basco et al., 1972	FP-AS (b)
1.2×10^{-12}	298	Parkes, 1977	FP-AS (c)
2.2×10^{-12}	295	Hochanadel et al., 1977	FP-AS (d)
$(2.2 \pm 0.3) \times 10^{-12} (T/300)^{0.94}$	200-400	Cobos et al., 1985	PLP-AS (e)
$(1.05 \pm 0.12) \times 10^{-12}$	298	Pilling and Smith, 1985	PLP-AS (f)
$(1.2 \pm 0.2) \times 10^{-12} (T/300)^{1.2}$	334-582	Keiffer et al., 1987	PLF-AS (g)
$2.2 \times 10^{-12}(T/300)^{0.9}$	300-700	Fernandes et al., 2006	PLP-UVA (h)
2.0×10^{-12}	300	Fernandes et al., 2010	PLP-UVA (i)
<i>Relative Rate Coefficients</i>			
1.7×10^{-12}	298	Laufer and Bass, 1975	FP-GC (j)
$(1.31 \pm 0.1) \times 10^{-12} (T/300)^{1.2}$	264-370	Kaiser, 1993	(k)

Comments

- (a) Pressure range 40-400 mbar of C₃H₈. RRKM extrapolation to k_∞ .
- (b) See comment (a) for k_0 .

- (c) See comment (b) for k_0 .
- (d) 12 percent falloff correction applied using the results of Basco et al. (1972).
- (e) See comment (d) for k_0 .
- (f) See comment (e) for k_0 .
- (g) See comment (f) for k_0 .
- (h) See comment (g) for k_0 .
- (i) See comment (g) for k_0 . Experiments over the pressure range 2-450 bar at 298-315 K in M = CO₂. k_∞ from measurements below 100 bar; above 100 bar, an increase of k is observed which is attributed to the radical-complex mechanism.
- (j) Pressure range 66-920 mbar, RRKM extrapolation to k_∞ . Rate measured relative to CH₃ + CH₃ → C₂H₆ and evaluated with $k(\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6) = 9.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ from the same work.
- (k) See comment (j) for k_0 .

Preferred Values

$k_\infty = 1.8 \times 10^{-12} (T/300)^{1.1} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200 K to 300 K.

Comments on Preferred Values

The preferred values are from Fernandes et al. (2006) in good agreement with the results from Cobos et al. (1985), Keiffer et al. (1987) and Kaiser (1993) (see comments on preferred values for k_0). At pressures above 100 bar a contribution from the radical-complex mechanism becomes noticeable.

Preferred Values

Parameter	Value	T/K
$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$7.0 \times 10^{-31} [\text{N}_2]$	298
$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$7.0 \times 10^{-31} (T/300)^{-3.0} [\text{N}_2]$	200-700
$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.8×10^{-12}	298
$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.8 \times 10^{-12} (T/300)^{1.1}$	200-300
$k(1 \text{ bar N}_2)/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	7.8×10^{-13}	298
F_c	0.33	200-700
<i>Reliability</i>		
$\Delta \log k_0$	± 0.2	298
Δn_0	± 1.0	200-700
$\Delta \log k_\infty$	± 0.2	298
Δn_∞	± 1.0	200-300

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 :

$$= ((7.0 \times 10^{-31} (T/300)^{-3.0} M + (1.8 \times 10^{-12} (T/300)^{1.1})) / ((7.0 \times 10^{-31} (T/300)^{-3.0} M + (1.8 \times 10^{-12} (T/300)^{1.1})) * 10^{(\log_{10}(0.33) / (1 + \log_{10}((7.0 \times 10^{-31} (T/300)^{-3.0} M / (1.8 \times 10^{-12} (T/300)^{1.1})) / (0.75 - 1.27 * \log_{10}(0.33))))^2}))$$

The molecular density, $M = 7.243 \times 10^{21} P(\text{bar}) / T(\text{K})$

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