IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_7

This data sheet updated: 12th November 2002.

$CH_3C(O)O_2 + NO \rightarrow CH_3C(O)O + NO_2$

$\Delta H° = -93$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$2.1 \times 10^{-12} \exp[(570 \pm 140)/T]$	228-354	Maricq and Szente, 1996[1]	PLP-AS (a)
$(1.4 \pm 0.2) \times 10^{-11}$	298		
$8.1 \times 10^{-12} \exp[(270 \pm 60)/T]$	200-402	Villalta and Howard, 1996[2]	F-CIMS (b)
$(2.0 \pm 0.3) \times 10^{-11}$	298		
$(2.0 \pm 0.3) \times 10^{-11}$	295	Sehested *et al*., 1998[3]	PR-A (c)
$6.0 \times 10^{-12} \exp[(320 \pm 40)/T]$	218-370	Moise, Denzer and Rudich 1999[4]	F-CIMS (d)
$(2.0 \pm 0.3) \times 10^{-11}$	296		
Relative Rate Coefficients			
$8.9 \times 10^{-12} \exp[(312 \pm 46)/T]$ (1 bar air)	247-298	Seefeld, Kinnison and Kerr, 1997[5]	(e)
$(2.5 \pm 0.4) \times 10^{-11}$ (1 bar air)	298		
$(2.17 \pm 0.23) \times 10^{-11}$ (0.93 bar)	295	Sehested *et al*., 1998[3]	(f)

Comments

(a) Pulsed laser photolysis of Cl_2-CH_3CHO-O_2-NO mixtures at 351 nm. Time-resolved absorption spectroscopy using a gated diode array for $CH_3C(O)O_2$ in the UV and using a diode laser for NO and NO_2 in the IR. Correction to k required for competing reactions of $CH_3C(O)O_2$.

(b) $CH_3C(O)O_2$ produced by thermal decomposition of peroxyacetyl nitrate and detected by CIMS through its reaction with SF_6^-. NO_2, CH_3 and CO_2 were positively identified as products implying rapid decomposition of $CH_3C(O)O$ to CH_3 and CO_2. Experiments conducted at pressures of 1.2 – 6 Torr (1.6 – 8 mbar) He.

(c) Pulse radiolysis of CH_3CHO-O_2-CO_2-NO and CH_3CHO-O_2-SF_6-NO mixtures at 1 bar pressure. The rate coefficient was obtained from the formation of NO_2, measured by absorption at 400.5 nm.

(d) $CH_3C(O)O_2$ produced by thermal decomposition of peroxyacetyl nitrate and detected by CIMS through its reaction with SF_6^-. Experiments conducted at 2-5 Torr (2.7 – 6.7 mbar) He.

(e) $CH_3C(O)O_2$ produced by steady state photolysis of biacetyl in the presence of O_2. Yields of peroxyacetyl nitrate were measured as a function of the [NO]/[NO_2] ratio. Data gave $k/k(CH_3C(O)O_2 + NO_2) = 2.44 \pm 0.18$ at 1 bar, independent of temperature over the range 247 K to 298 K. The expression in the table is calculated using the recommended value for $k(CH_3C(O)O_2 + NO_2)$ at 1 bar pressure.[6]

(f) $CH_3C(O)O_2$ radicals were produced by photolysis of Cl_2-CH_3CHO-O_2 mixtures, and reactants and products monitored by FTIR spectroscopy. The measured rate coefficient ratio $k(CH_3C(O)O_2 + NO) / k(CH_3C(O)O_2 + NO_2) = 2.07 \pm 0.21$ at 932 mbar N_2 is placed on an absolute basis using the recommended value of $k(CH_3C(O)O_2 + NO_2)$.[6]

Preferred Values

$k = 2.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.5 \times 10^{-12} \exp(290/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200 K to 350 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

The direct measurements at 298 K of Villalta and Howard[2], Moise, Denzer and Rudich[4] and Sehested *et al*.[3] are in excellent agreement, all returning values of 2×10^{-11} cm^3 molecule^{-1}s^{-1} and provide the basis of the 298 K recommendation. Those of Maricq and Szente[1] give a value of $k(298)$ approximately 30% lower. Of the three temperature dependent data sets, those of Villalta and Howard[2] and Moise, Denzer and Rudich[4] agree within error limits and present a significantly weaker dependence than the more highly scattered data of Maricq and Szente.[1] The recommended temperature dependence was obtained by weighted least squares fitting to the data of Villalta and Howard[2] and Moise, Denzer and Rudich.[4]

The earlier data for k, obtained relative to $k(CH_3C(O)O_2 + NO_2)$,[7-11] are generally consistent with this recommendation.

References

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