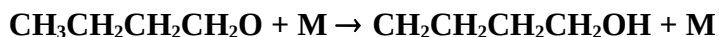


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet RO_6

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This data sheet updated: 16th November 2006.



$$\Delta H^\circ = -14.7 \text{ kJ.mol}^{-1}$$

Rate coefficient data

k/ s^{-1}	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(3.5 \pm 2) \times 10^4$	293	Hein et al., 1999	PLP-AS/LIF (a)
<i>Relative Rate Coefficients</i>			
2.2×10^5	303	Carter et al., 1979	S-GC (b)
$(2.1 \pm 0.5) \times 10^5$	296	Cox et al., 1981	S-GC (c)
$(2.7 \pm 0.2) \times 10^5$	298	Niki et al., 1981	S-FTIR (d)
$9.5 \times 10^{10} \exp(-3864/T)$	265-393	Morabito and Heicklen, 1987	S-GC (e)
$(2.7 \pm 0.9) \times 10^5$	298	Geiger et al., 2002	S-FTIR (f)
$1.8 \times 10^{10} \exp(-3270/T)$	250-318	Cassanelli et al., 2005	FR-GC (g), (h)
$4.9 \times 10^{10} \exp(-3570/T)$	253-295	Cassanelli et al., 2006	S-FTIR (i), (h)

Comments

- Pulsed laser photolysis at 248 nm of a mixture of 1-bromobutane, O₂ and NO in N₂ at 50 mbar total pressure in a slow-flow system. OH and NO₂ were monitored in real-time using laser long-path absorption at 308.417 nm and cw laser-excited fluorescence after excitation at 488 nm, respectively. The rate coefficient was derived from a computer simulation of the OH and NO₂ temporal concentration profiles and is believed to be in the fall-off range.
- Smog chamber photolysis of *n*-C₄H₁₀-NO_x-air mixtures at 1 bar pressure. End-product analysis of C₃H₇CHO by GC. $k/k(1\text{-C}_4\text{H}_9\text{O} + \text{O}_2) = 1.6 \times 10^{19} \text{ molecule cm}^{-3}$ obtained from yields of C₃H₇CHO and the rate of disappearance of *n*-C₄H₁₀. The above value of k is calculated by using a rate coefficient of $k = 1.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reference reaction $1\text{-C}_4\text{H}_9\text{O} + \text{O}_2 \rightarrow \text{C}_3\text{H}_7\text{CHO} + \text{HO}_2$ at 298 K (this evaluation).
- Smog chamber photolysis of *n*-C₄H₁₀-HONO-air mixtures at 1 bar (760 Torr) pressure. End product analysis of C₃H₇CHO by GC. $k/k(1\text{-C}_4\text{H}_9\text{O} + \text{O}_2) = (1.5 \pm 0.5) \times 10^{19} \text{ molecule cm}^{-3}$ was derived from the yields of C₃H₇CHO and the rate of disappearance of *n*-C₄H₁₀ as a function of [O₂]. Above value of k was calculated by using a rate coefficient of $k = 1.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reference reaction, $1\text{-C}_4\text{H}_9\text{O} + \text{O}_2 \rightarrow \text{C}_3\text{H}_7\text{CHO} + \text{HO}_2$ at 298 K (this evaluation).
- Photolysis of 1-C₄H₉ONO-NO-O₂-N₂ mixtures at 930 mbar (700 Torr) pressure in an FTIR cell. $k/k(1\text{-C}_4\text{H}_9\text{O} + \text{O}_2) = (1.9 \pm 0.2) \times 10^{19} \text{ molecule cm}^{-3}$ was derived from yields of C₃H₇CHO and the rate of disappearance of 1-C₄H₉ONO measured by calibrated FTIR spectroscopy. Above value of k calculated using a rate coefficient of $k = 1.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reference reaction, $1\text{-C}_4\text{H}_9\text{O} + \text{O}_2 \rightarrow \text{C}_3\text{H}_7\text{CHO} + \text{HO}_2$ at 298 K (this evaluation).

- (e) Photolysis of 1-C₄H₉ONO-air mixtures at 1013 mbar (760 Torr) pressure. Analysis by GC. $k/k(1\text{-C}_4\text{H}_9\text{O} + \text{NO}) = (2.5 \pm 0.2) \times 10^{23} \text{ molecule cm}^{-3}$ was derived from [O₂]-dependence of yields of C₃H₇CHO and the rate of disappearance of 1-C₄H₉ONO. Above value of k calculated using a rate coefficient of $k = 2.3 \times 10^{-11} \exp(150/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reference reaction, 1-C₄H₉O + NO → C₄H₉NO, recommended by Atkinson (1997).
- (f) Photolysis of 1-C₄H₉I-NO-O₂-N₂ mixtures at 1013 mbar (760 Torr) pressure. $k/k(1\text{-C}_4\text{H}_9\text{O} + \text{O}_2) = (1.8 \pm 0.6) \times 10^{19} \text{ molecule cm}^{-3}$ was derived from yields of C₃H₇CHO and the rate of disappearance of 1-C₄H₉ONO measured by calibrated FTIR spectroscopy. The observed [O₂] dependence of this ratio was attributed to influence of 10-20% production of 'hot' 1-butoxy produced in the RO₂ + NO reaction. Cited value of the ratio k refers to the thermally relaxed 1-butoxy and k is calculated using a rate coefficient of $k(1\text{-C}_4\text{H}_9\text{O} + \text{O}_2) = 1.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reference reaction, 1-C₄H₉O + O₂ → C₃H₇CHO + HO₂ at 298 K (this evaluation).
- (g) Photolysis of 1-C₄H₉NO-NO-O₂-N₂ mixtures or n-C₄H₁₀-HONO(or CH₃ONO)-NO-O₂-N₂ mixtures at 1013 mbar (760 Torr) pressure. Analysis by GC. $k/k(1\text{-C}_4\text{H}_9\text{O} + \text{O}_2) = (1.98 \pm 0.50) \times 10^{23} \exp\{-(2720 \pm 470)/T\} \text{ molecule cm}^{-3}$ was derived from [O₂]-dependence of yields of C₃H₇CHO and the rate of disappearance of 1-C₄H₉ONO. Evidence for the influence of 10% production of 'hot' 1-butoxy produced in the photolysis of 1-C₄H₉NO. Cited value of the ratio k refers to the thermally relaxed 1-butoxy.
- (h) Above value of k calculated using a rate coefficient of $k = 8.9 \times 10^{-14} \exp(-550/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reference reaction, 1-C₄H₉O + O₂ → C₃H₇CHO + HO₂, based on $k(298 \text{ K}) = 1.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ from this evaluation, and the temperature dependence recommended by Atkinson (1997, 2000): $E/R = 550 \text{ K}$.
- (i) Photolysis of 1-C₄H₉ONO-air mixtures at 930 mbar (700 Torr) pressure. Analysis by FTIR. $k/k(1\text{-C}_4\text{H}_9\text{O} + \text{O}_2) = 5.5 \times 10^{23} \exp\{-(3020 \pm 110)/T\} \text{ molecule cm}^{-3}$ was derived from [O₂]-dependence of relative yields of C₃H₇CHO and HOC₃H₇CHO (the main product formed following isomerization), adjusted to take account of secondary reactions.

Preferred Values

$k = 4.6 \times 10^{10} \exp(-3570/T) \text{ s}^{-1}$ over the temperature range 250 to 350 K and 1 bar pressure.
 $k = 2.9 \times 10^5 \text{ s}^{-1}$ at 298 K and 1 bar pressure.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The preferred rate coefficient at room temperature is the mean from the relative rate studies of Cassanelli et al. (2005, 2006) and Geiger et al.(2002) which both take into account the influence of 'hot' 1-butoxy radicals. The studies of Carter et al. (1979), Cox et al. (1981), Niki et al. (1981), Morabito and Heicklen, (1987) all give similar results. The values of k are all calculated using a rate coefficient of $k(1\text{-C}_4\text{H}_9\text{O} + \text{O}_2) = 8.9 \times 10^{-14} \exp(-550/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reference reaction (this evaluation). The direct measurement of Hein et al.(1999) at 50 mbar total pressure of N₂ shows that the reaction is in the fall-off region below 1 bar. The preferred value of E/R is a mean of the results from the 2 studies of Cassanelli et al. (2005, 2006) and that of Morabito and Heicklen (1987), and the A -factor fitted to give the recommended k_{298} . The pre-exponential factor obtained is lower than estimated by Atkinson (1997), but is consistent with the theoretical calculations of Vereecken and Peters (2003) using a rigorous multirotamer TST treatment.

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