IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet RO_3

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$1\text{-}C_3H_7O + O_2 \rightarrow C_2H_5CHO + HO_2$

$\Delta H° = -131.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.4 \times 10^{-14} \exp[-(108 \pm 61)/T]$	223-303	Mund et al, 1998	PLP-LIF (a)
9.8×10^{-15}	298		
$2.5 \times 10^{-14} \exp[-(240 \pm 60)/T]$	289-381	Fittschen et al., 1999	PLP-LIF (b)
1.1×10^{-14}	298		
Relative Rate Coefficients			
$2.8 \times 10^{-13} \exp[-(879 \pm 117)/T]$	247-393	Zabarnick and Heicklen, 1985	RR (c)
1.5×10^{-14}	298		

Comments

(a) Pulsed laser photolysis of 1-propyl nitrite at 351 nm with laser-induced fluorescence detection of *n*-propoxy radical at a total pressure of 20 mbar He.

(b) Pulsed laser photolysis of $1\text{-}C_3H_7ONO$ at 351 nm in $1\text{-}C_3H_7ONO\text{-}O_2$-He mixtures in the range 40-133 mbar (30-100 Torr) with LIF detection of $1\text{-}C_3H_7O$ excited at 349 nm and fluorescence detection to the red of 375 nm. The upper temperature limit is set by the unimolecular decomposition rate of *n*-propoxy radical.

(c) Photolysis at 366 nm of $n\text{-}C_3H_7ONO$ in a static system in the presence of NO, O_2, and N_2 at total pressures of >200 mbar (>150 Torr). Rate data were based on the measured quantum yields of C_2H_5CHO product. The rate coefficient k was measured relative to $n\text{-}C_3H_7O + NO \rightarrow$ products with $k(n\text{-}C_3H_7O + O_2)/k(n\text{-}C_3H_7O + NO) = 6.8 \times 10^{-3} \exp(-879/T)$, and is placed on an absolute basis by use of $k(n\text{-}C_3H_7O + NO) = 4.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature.

Preferred Values

$k = 2.6 \times 10^{-14} \exp(-255/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220-380 K.
$k = 1.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred values are based on the absolute rate studies of Fittschen et al. (1999) and Mund et al. (1998), which are in excellent agreement in the overlapping temperature range. The temperature dependence is that of both data sets taking into account the A factor that differs by a factor of two. The rate coefficients derived from the relative rate study of Zabarnick and Heicklen (1985) are in significant disagreement with the absolute rate data of Mund et al. (1998) and Fittschen et al. (1999).

References

Fittschen, C., Frenzel, A., Imrik, K., and Devolder, P.: Int. J. Chem. Kin. 31, 860, 1999.

Mund, Ch., Fockenberg, Ch., and Zellner, R.: Ber. Bunsenges. Phys. Chem. 102, 709, 1998.

Zabarnick, S. and Heicklen, J.: Int. J. Chem. Kinet. 17, 455, 1985.