IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_4

This data sheet updated: 3rd July 2005.

$$n\text{-}C_3H_7O_2 + NO \rightarrow n\text{-}C_3H_7O + NO_2 \quad (1)$$

$$n\text{-}C_3H_7O_2 + NO + M \rightarrow n\text{-}C_3H_7ONO_2 + M \quad (2)$$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	*Reference*	Technique/ Comments
Absolute Rate Coefficients			
$2.9 \times 10^{-12} \exp[(350 \pm 60)/T]$	201-402	Eberhard and Howard, 1996	F-CIMS(a)
$(9.4 \pm 1.6) \times 10^{-12}$	298		
$4.3 \times 10^{-12} \exp[(268 \pm 56)/T]$	213-298	Chow et al., 2003	F-CIMS (b)
$(1.05 \pm 0.14) \times 10^{-11}$	298		
Branching Ratio			
$k_2/k = 0.020 \pm 0.009$ (1 bar)	299	Atkinson et al., 1982 Carter and Atkinson, 1989	(c)

Comments

(a) n-$C_3H_7O_2$ radicals were produced by pyrolysis of n-$C_3H_7ONO_2$ in the presence of O_2 and detected by CIMS. Pseudo-first order kinetics with excess NO.

(b) Turbulent flow reactor at 133 mbar N_2 total pressure. $C_3H_7O_2$ radicals were generated by the reaction of Cl atoms with C_3H_8 in the presence of O_2, thus both n-$C_3H_7O_2$ and i-$C_3H_7O_2$ were present and the rate coefficients measured are overall values for both isomers, which were detected as $C_3H_7OOH^+(H_2O)_3$ following reaction with $H^+(H_2O)_4$ ions.

(c) Based on yield of n-$C_3H_7ONO_2$ product from photo-oxidation of C_3H_8 in NO_x-air mixtures. Carter and Atkinson (1989) revised the analysis of original data to provide the values quoted.

Preferred Values

$k = 9.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.9 \times 10^{-12} \exp(350/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200 K to 410 K.

$k_2 / k = 0.020$ at 298 K and 1 bar pressure.

Reliability

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

$\Delta(E/R) = \pm 100$ K.

$\Delta \log(k_2/k) = \pm 0.3$ at 298 K and 1 bar pressure.

Comments on Preferred Values

The measurements of Eberhard and Howard (1996) provide the only experimental data on the isomer-specific rate coefficient. The data of Chow et al. (2003), who measured a

weighted average value for *n*-$C_3H_7O_2$ and *i*-$C_3H_7O_2$ are in good agreement, which confirms that *n*-$C_3H_7O_2$ and *i*-$C_3H_7O_2$ have similar rate coefficients for reaction with NO. The negative temperature coefficient is consistent with that observed for the rate coefficient for other RO_2 + NO reactions. The recommendation accepts the Arrhenius expression of Eberhard and Howard (1996).

The preferred branching ratio for *n*-propyl nitrate formation is that measured by Atkinson et al. (1982), as revised by Carter and Atkinson (1989).

References

Atkinson, R., Aschmann, S. M., Carter, W. P. L., Winer, A. M. and Pitts, Jr., J. N.: J. Phys. Chem. 86, 4563, 1982.

Carter, W. P. L. and Atkinson, R.: J. Atmos. Chem. 8, 165, 1989.

Chow, J. M., Miller, A. M. and Elrod, M. J.: J. Phys. Chem. A 107, 3040, 2003.

Eberhard, J and Howard, C. J.: Int. J. Chem. Kinet. 28, 731, 1996.