IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet RO_2

This data sheet updated: 12th June 2003.

$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$

$\Delta H° = -135.7$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	**Reference**	Technique/ Comments
Absolute Rate Coefficients			
8.0×10^{-15}	296	Gutman, Sanders and	PLP-LIF (a)
9.8×10^{-15}	353	Butler, 1982[1]	
$7.1 \times 10^{-14} \exp[-(552 \pm 64)/T]$	295-411	Hartmann *et al*., 1990[2]	PLP-LIF (b)
$(1.08 \pm 0.20) \times 10^{-14}$	295		
$(2.4)10^{-14}\exp[-(325 \pm 120)/T)]$	295-354	Fittschen *et al*., 1999[3]	PLP-LIF (c)
8.1×10^{-15}	298		

Comments

(a) Pulsed laser photolysis of C_2H_5ONO at 266 nm, with C_2H_5O radicals being monitored by LIF at a total pressure of 53 mbar (40 Torr).

(b) Pulsed laser photolysis of C_2H_5ONO at 266 nm in C_2H_5ONO-O_2-He mixtures, with LIF monitoring of C_2H_5O radicals in the wavelength range 310 nm to 330 nm. Studies were carried out at a total pressure of 35 mbar (26 Torr).

(c) Pulsed laser photolysis of C_2H_5ONO at 248 nm in C_2H_5ONO-O_2-He mixtures in the range 39.9-66.5 mbar (30-500 Torr) with LIF detection of C_2H_5O radicals excited at 323 nm and fluorescence detection to the red of 375 nm. The upper temperature limit is set by the unimolecular decomposition rate of ethoxy radical.

Preferred Values

$k = 8.1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.4 \times 10^{-14} \exp(-325/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 295 K to 354 K.

Reliability

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

Comments on Preferred Values

The preferred rate constant at 298 K is that of Gutman *et al*.[1] and Fittschen *et al*.[3] Their temperature dependence over the common range 296-353 K is in excellent agreement and is therefore recommended here. The relative rate measurements of Zabarnick and Heicklen[4] yield a value of k_{298} which is consistent with the preferred value within the recommended error limits.

It should be noted that the *A*-factor for the above reaction is very low, but in keeping with that for the analogous reaction $CH_3O + O_2 \rightarrow HCHO + HO_2$.

References

[1] D. Gutman, N. Sanders, and J. E. Butler, J. Phys. Chem. **86**, 66 (1982).

[2] D. Hartmann, J. Karthäuser, J. P. Sawerysyn, and R. Zellner, Ber. Bunsenges. Phys. Chem. **94**, 639 (1990).

[3] C. Fittschen, A. Frenzel, K. Imrik and P. Devolder, Int. J. Chem. Kin. **31**, 860 (1999).

[4] S. Zabarnick and J. Heicklen, Int. J. Chem. Kinet. **17**, 455 (1985).