IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet II.A4.88 R_Oxygen3

 The citation for this data sheet is: Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys. 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, (http://iupac.pole-ether.fr).
This data sheet last evaluated: June 2012; last change in preferred values: June 2012.

$$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$$

$\Delta H° = -54.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$<10^{-13}$	1000	Wagner et al., 1990	PLP-MS (a)
$1.61 \times 10^{-12}(T/298)^{-1.87}\exp(-707/T)$	296-700	DeSain et al., 2003	(b)
Relative Rate Coefficients			
1.9×10^{-14} (130 mbar, air)	298	Kaiser et al., 1990	(c)
3.8×10^{-15} (1 bar, air)	298		
9.8×10^{-16} (8 bar, air)	298		
$3.4 \times 10^{-13}\exp(-855/T)$	298-680	Kaiser, 2002	(d)

Comments

(a) Experimental and theoretical study of the $C_2H_5 + O_2$ reaction. Experiments were carried out in tubular flame reactor. C_2H_5 radicals were formed by laser photolysis of C_2H_5Br or CCl_4-C_2H_6 mixtures. Concentrations of C_2H_5 and C_2H_4 were monitored by photoionization MS.

(b) Pulsed photolytic Cl-initiated oxidation of ethane with time-resolved observation of OH by LIF. Detailed master equation modelling of the complex-forming bimolecular reaction. Partial suppression of the reaction with increasing pressure by collisional stabilization of $C_2H_5O_2$. The given rate coefficient corresponds to zero pressure.

(c) Study of the yields of C_2H_4 produced relative to C_2H_6 consumed (GC analysis) in a system in which C_2H_5 radicals were generated by UV irradiation of Cl_2-C_2H_6-O_2-N_2 (or air) mixtures. Up to 8 bar the percentage of C_2H_4 produced, relative to the C_2H_6 consumed, decreased from 12% to 0.02%, following a $P^{(-0.8 \pm 0.1)}$ pressure dependence in air. The listed pressure-dependent k values are relative to values of $k(C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M)$ calculated from Baldwin et al. (1980).

(d) Steady-state photolysis of Cl_2-C_2H_6-O_2 mixtures at constant density of 6.8×10^{18} molecule cm^{-3}. GC/MS analysis after irradiation.

Preferred Values

$k_0 = 1.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K
$k_0 = 1.61 \times 10^{-12} (T/298)^{-1.87} \exp(-707/T)$ cm^3 molecule^{-1} s^{-1} over the range 298-700 K

Comments on Preferred Values

This is a chemical activation system for which HO_2 formation competes with collisional stabilization of $C_2H_5O_2$ (see data sheet for $C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$). HO_2 yields decrease with increasing pressure and increase with increasing temperature. The preferred pressure-dependent values of k at 298 K are from the product study of Kaiser et al. (1990). The zero-pressure limiting rate coefficient is from DeSain et al. (2003). For a full discussion of the $C_2H_5 + O_2$ reaction, see Wagner et al. (1990), DeSain et al. (2003), Carstensen et al. (2005), and Taatjes (2006). For atmospheric conditions the interaction of C_2H_5 with O_2 predominantly leads to $C_2H_5O_2$.

Preferred Values

Parameter	Value	T/K
k_0/cm^3 molecule^{-1} s^{-1}	1.5×10^{-13}	298
k_0/cm^3 molecule^{-1} s^{-1}	$1.6 \times 10^{-12} (T/300)^{-1.87} \exp(-707/T)$	298-700
k(1 bar N_2)/cm^3 molecule^{-1} s^{-1}	3.8×10^{-15}	298
Reliability		
$\Delta \log k_0$	± 0.5	298
$\Delta E_0/R$	± 300 K	298-700

References

Baldwin, R. R., Pickering, I. A., and Walker, R. W.: J. Chem. Soc. Faraday Trans. 1, 76, 2374, 1980.
Carstensen, H.-H., Naik, C. V., and Dean, A. M.: J. Phys. Chem. A 109, 2264, 2005.
DeSain, J. D., Klippenstein, S. J., Miller, J. A., and Taatjes, C. A.: J. Phys. Chem. A 107, 4415, 2003.
Kaiser, E. W., Lorkovic, I. M., and Wallington, T. J.: J. Phys. Chem. 94, 3352, 1990.
Kaiser, E. W.: J. Phys. Chem. A 106, 1256, 2002.
Taatjes, C. A.: J. Phys. Chem. A 110, 4299, 2006.
Wagner, A. F., Slagle, I. R., Sarzynski, D., and Gutman, D.: J. Phys. Chem. 94, 1853, 1990.