IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_8

This data sheet updated: 12th November 2002.

$C_2H_5C(O)O_2 + NO \rightarrow C_2H_5C(O)O + NO_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.7 \pm 1.7) \times 10^{-12} \exp[(340 \pm 80)/T]$	226-406	Froyd and Lovejoy, 1999[1]	F-CIMS(a)
$(2.1 \pm 0.2) \times 10^{-11}$	298		
Relative Rate Coefficients			
$1.25 \times 10^{-11} \exp(240/T)$	249-302	Seefeld and Kerr, 1997[2]	RR(b)
$(2.8 \pm 0.4) \times 10^{-11}$	298		
$(2.3 \pm 0.2) \times 10^{-11}$	302	Kerr and Stocker, 1985[3]	RR(c)

Comments

(a) Low pressure flow tube at 1.5 to 15 Torr (2-20 mbar) He or N_2. $C_2H_5C(O)O_2$ was formed by thermal decomposition of $C_2H_5C(O)ONO_2$ and detected as $C_2H_5C(O)O_2^-$ or $C_2H_5C(O)O^-$ ion following reaction with SF_6^- or I^-. Results at 15 Torr N_2 analysed to set an upper limit to the association reaction of $k_0(298\ K) < 1.9 \times 10^{-30}$ cm^6 molecule^{-2} s^{-1}.

(b) Ratio k / $k(C_2H_5C(O)O_2 + NO_2) = 2.33 \pm 0.38$, independent of temperature over the range 249-302 K. $C_2H_5C(O)O_2$ produced by photolysis of $C_2H_5C(O)Cl$ in a flow system at 1 atm pressure with analysis of $C_2H_5C(O)O_2NO_2$ by GC, as a function of the $[NO/NO_2]$ ratio. k calculated with $k(C_2H_5C(O)O_2 + NO_2) = k_□(CH_3C(O)O_2 + NO_2)$ from the present evaluation (in Arrhenius form, $k_\infty(CH_3C(O)O_2 + NO_2) = 5.4 \times 10^{-12} \exp(240/T)$ cm^3 molecule^{-1} s^{-1} over the range 250 K to 300 K.[4] Also showed that the above rate constant ratio was 11% lower than the corresponding ratio for $CH_3C(O)O_2$, which is consistent with a higher rate coefficient for the $RO_2 + NO_2$ (+M) reaction for the C_3 acylperoxy radical.

(c) Ratio k / $k(C_2H_5C(O)O_2 + NO_2) = 1.89 \pm 0.21$. k calculated with $k(C_2H_5C(O)O_2 + NO_2) = k_\infty(CH_3C(O)O_2 + NO_2)$ from the present evaluation (in Arrhenius form, $k_\infty(CH_3C(O)O_2 + NO_2) = 5.4 \times 10^{-12} \exp(240/T)$ cm^3 molecule^{-1} s^{-1} over the range 250 K to 300 K.[4]

Preferred Values

$k = 2.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.7 \times 10^{-12} \exp(340/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220 K to 410 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred values are based on the absolute determination of Froyd and Lovejoy.[1] The relative rate measurements[2,3] are in agreement with this number, but suffer from the lack of an absolute measurement for $k(C_2H_5C(O)O_2 + NO_2)$, the reference reaction rate coefficient (see comments above).

References

1 K.D. Froyd and E.R. Lovejoy, Int. J. Chem. Kin. **31**, 221 (1999).
2 S. Seefeld and J. A. Kerr, Environ. Sci. Technol. **31**, 2949 (1997).
3 J. A. Kerr and D. W. Stocker, J. Photochem. **28**, 475 (1985).
4 IUPAC (2013), http://iupac.pole-ether.fr