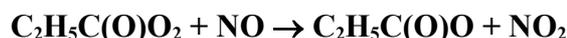


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_8

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This data sheet updated: 12th November 2002.



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6.7 \pm 1.7) \times 10^{-12} \exp[(340 \pm 80)/T]$	226-406	Froyd and Lovejoy, 1999 ¹	F-CIMS(a)
$(2.1 \pm 0.2) \times 10^{-11}$	298		
<i>Relative Rate Coefficients</i>			
$1.25 \times 10^{-11} \exp(240/T)$	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 N₂. C₂H₅C(O)O₂ was formed by thermal decomposition of C₂H₅C(O)ONO₂ and detected as C₂H₅C(O)O₂⁻ or C₂H₅C(O)O⁻ ion following reaction with SF₆⁻ or I⁻. Results at 15 Torr N₂ analysed to set an upper limit to the association reaction of $k_0(298 \text{ K}) < 1.9 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$.
- (b) Ratio $k / k(\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2 + \text{NO}_2) = 2.33 \pm 0.38$, independent of temperature over the range 249-302 K. C₂H₅C(O)O₂ produced by photolysis of C₂H₅C(O)Cl in a flow system at 1 atm pressure with analysis of C₂H₅C(O)O₂NO₂ by GC, as a function of the [NO/NO₂] ratio. k calculated with $k(\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2 + \text{NO}_2) = k_{\square}(\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2)$ from the present evaluation (in Arrhenius form, $k_{\infty}(\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2) = 5.4 \times 10^{-12} \exp(240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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 CH₃C(O)O₂, which is consistent with a higher rate coefficient for the RO₂ + NO₂ (+M) reaction for the C₃ acylperoxy radical.
- (c) Ratio $k / k(\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2 + \text{NO}_2) = 1.89 \pm 0.21$. k calculated with $k(\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2 + \text{NO}_2) = k_{\infty}(\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2)$ from the present evaluation (in Arrhenius form, $k_{\infty}(\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2) = 5.4 \times 10^{-12} \exp(240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the range 250 K to 300 K.⁴

Preferred Values

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

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

Reliability

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

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

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 $k(\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2 + \text{NO}_2)$, 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>