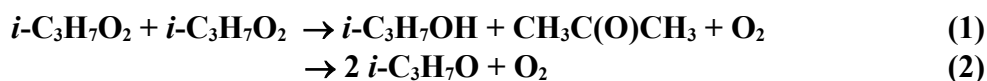


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO33

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet updated: 12th November 2002.



$$\Delta H^\circ(1) = -352.1 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = 33.0 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.43 \times 10^{-12} \exp[-(2243 \pm 69)/T]$	300-373	Kirsch <i>et al.</i> , 1978 ¹	MM-UVAS (a,b)
8.10×10^{-16}	300		
$(1.3 \pm 0.4) \times 10^{-15}$	298	Adachi and Basco, 1989 ²	FP-UVAS (a,c)
$(5.3 \pm 0.5) \times 10^{-14}$	298	Munk <i>et al.</i> , 1986 ³	PR-UVAS (a,d)
<i>Branching Ratios</i>			
$k_1/k_2 = 1.39 \pm 0.04$	302	Kirsch <i>et al.</i> , 1979 ⁴	P-GC (e)
$k_2/k_1 = 56.3 \exp(-1130/T)$	302-372	Cowley, Waddington, and Woolley, 1982 ⁵	P-GC (f)

Comments

- (a) k is defined by $-d[i\text{-C}_3\text{H}_7\text{O}_2]/dt = 2k[i\text{-C}_3\text{H}_7\text{O}_2]^2$ and has been derived from the observed overall second-order decay of $i\text{-C}_3\text{H}_7\text{O}_2$ radicals (k_{obs}) by correcting for secondary removal of the $i\text{-C}_3\text{H}_7\text{O}_2$ radicals.
- (b) Molecular modulation study of the photolysis of 2,2'-azopropane in the presence of O_2 and N_2 at total pressures up to 950 mbar (710 Torr). $i\text{-C}_3\text{H}_7\text{O}_2$ radicals were monitored by absorption at 265 nm. The rate coefficient, k , has been calculated from the experimental value of $k_{\text{obs}} = (2.37 \pm 0.17) \times 10^{-12} \exp[-(2243 \pm 60)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and the branching ratio $k_2/k_1 = 1.39$ at 302 K determined in the subsequent study.⁴
- (c) Flash photolysis of 2,2'-azopropane in the presence of O_2 and added N_2 at total pressures up to 960 mbar (720 Torr). $i\text{-C}_3\text{H}_7\text{O}_2$ radicals were monitored by absorption at 240 nm, for which $\sigma(240 \text{ nm}) = 4.86 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The rate coefficient, k , has been calculated from the experimental value of $k_{\text{obs}} = (2.03 \pm 0.58) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, on the basis of a proposed mechanism of 12 elementary reactions including secondary consumption of $i\text{-C}_3\text{H}_7\text{O}_2$ radicals.
- (d) Pulsed radiolysis of H_2 at 1 bar in the presence of C_3H_6 ; $i\text{-C}_3\text{H}_7$ radicals were generated from the reaction of H atoms with C_3H_6 . The absorption spectrum of the $i\text{-C}_3\text{H}_7\text{O}_2$ radical was observed on the addition of O_2 and the decay of $i\text{-C}_3\text{H}_7\text{O}_2$ radicals monitored by UV absorption at 253 nm, and found to obey second-order kinetics. It is not clear if the reported value of the rate coefficient is k_{obs} or k .

- (e) Steady-state photolysis of 2,2'-azopropane in the presence of O₂ and added N₂ at total pressures up to 670 mbar (500 Torr). Ratio of rate coefficients based on analyses of CH₃COCH₃ and (CH₃)₂CHOH by GC.
- (f) Extension of the experiments by Kirsch *et al.*,⁴ to obtain k_2/k_1 at 333 K and 372 K. The Arrhenius equation calculated from these data and a value of k_2/k_1 at 302 K was reported by Kirsch *et al.*⁴

Preferred Values

$k = 1.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.6 \times 10^{-12} \exp(-2200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 300 K to 400 K.

$k_1/k = 0.44$ at 298 K.

$k_1/k = 3.7 \times 10^{-2} \exp(740/T)$ over the temperature range 300 K to 400 K.

$k_2/k = 0.56$ at 298 K.

$k_2/k = 2.0 \exp(-380/T)$ over the temperature range 300 K to 400 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.15$ at 298 K.

Comments on Preferred Values

The recommended rate coefficient, k , at 298 K is the average of the rate coefficients from the data of Kirsch *et al.*¹ and Adachi and Basco,² which are in reasonable agreement. We have not taken into account the rate coefficient reported by Munk *et al.*,³ for which experimental details are lacking. The recommended temperature dependence of k is based on the results of Kirsch *et al.*,¹ which have been rounded-off and adjusted to the recommended value of k_{298} .

The measurements of the branching ratio and its temperature dependence^{4,5} appear to be reliable and have been adopted here, but require further confirmation.

The value of k_{298} is considerably lower than that for the analogous reaction of the *n*-C₃H₇O₂ radical, which is in keeping with the trend observed in studies of the interactions of alkylperoxy radicals in solution,⁶ i.e., $k(\text{primary RO}_2) > k(\text{secondary RO}_2) > k(\text{tertiary RO}_2)$.

References

- ¹ L. J. Kirsch, D. A. Parkes, D. J. Waddington, and A. Woolley, *J. Chem. Soc. Faraday. Trans. 1*, **74**, 2293 (1978).
- ² H. Adachi and N. Basco, *Int. J. Chem. Kinet.* **14**, 1125 (1982).
- ³ J. Munk, P. Pagsberg, E. Ratajczak, and A. Sillesen, *Chem. Phys. Lett.* **132**, 417 (1986).
- ⁴ L. J. Kirsch, D. A. Parkes, D. J. Waddington, and A. Woolley, *J. Chem. Soc. Faraday Trans. 1*, **75**, 2678 (1979).
- ⁵ L. T. Cowley, D. J. Waddington, and A. Woolley, *J. Chem. Soc. Faraday Trans. 1*, **78**, 2535 (1982).
- ⁶ J. E. Bennett, D. M. Brown, and B. Mile, *Trans. Faraday Soc.* **66**, 386 (1970).