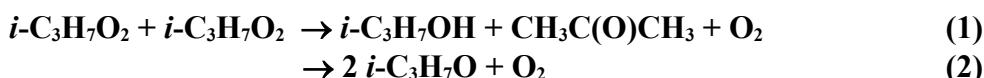


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO33

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This data sheet updated: 12<sup>th</sup> 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 <sup>1</sup>	MM-UVAS (a,b)
$8.10 \times 10^{-16}$	300		
$(1.3 \pm 0.4) \times 10^{-15}$	298	Adachi and Basco, 1989 <sup>2</sup>	FP-UVAS (a,c)
$(5.3 \pm 0.5) \times 10^{-14}$	298	Munk <i>et al.</i> , 1986 <sup>3</sup>	PR-UVAS (a,d)
<i>Branching Ratios</i>			
$k_1/k_2 = 1.39 \pm 0.04$	302	Kirsch <i>et al.</i> , 1979 <sup>4</sup>	P-GC (e)
$k_2/k_1 = 56.3 \exp(-1130/T)$	302-372	Cowley, Waddington, and Woolley, 1982 <sup>5</sup>	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 ( $k_{\text{obs}}$ ) 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  $\text{O}_2$  and  $\text{N}_2$  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.<sup>4</sup>
- (c) Flash photolysis of 2,2'-azopropane in the presence of  $\text{O}_2$  and added  $\text{N}_2$  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  $\text{H}_2$  at 1 bar in the presence of  $\text{C}_3\text{H}_6$ ;  $i\text{-C}_3\text{H}_7$  radicals were generated from the reaction of  $\text{H}$  atoms with  $\text{C}_3\text{H}_6$ . The absorption spectrum of the  $i\text{-C}_3\text{H}_7\text{O}_2$  radical was observed on the addition of  $\text{O}_2$  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  $k_{\text{obs}}$  or  $k$ .

- (e) Steady-state photolysis of 2,2'-azopropane in the presence of O<sub>2</sub> and added N<sub>2</sub> at total pressures up to 670 mbar (500 Torr). Ratio of rate coefficients based on analyses of CH<sub>3</sub>COCH<sub>3</sub> and (CH<sub>3</sub>)<sub>2</sub>CHOH by GC.
- (f) Extension of the experiments by Kirsch *et al.*<sup>4</sup> 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.*<sup>4</sup>

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

The measurements of the branching ratio and its temperature dependence<sup>4,5</sup> 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*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> radical, which is in keeping with the trend observed in studies of the interactions of alkylperoxy radicals in solution,<sup>6</sup> i.e.,  $k(\text{primary RO}_2) > k(\text{secondary RO}_2) > k(\text{tertiary RO}_2)$ .

### References

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