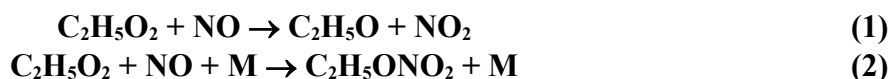


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO\_2

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: 3<sup>rd</sup> July 2005.



$$\Delta H^\circ(1) = -45.2 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -217.0 \text{ kJ}\cdot\text{mol}^{-1}$$

## 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>			
$(2.7 \pm 0.2) \times 10^{-12}$	298	Adachi and Basco, 1979	FP-AS
$(8.9 \pm 3.0) \times 10^{-12}$	295	Plumb et al., 1982	DF-MS
$(8.5 \pm 1.2) \times 10^{-12}$	298	Sehested et al., 1993	PR-AS
$(8.2 \pm 1.6) \times 10^{-12}$	295	Däele et al., 1995	DF-MS (a)
$2.6 \times 10^{-12} \exp[(380 \pm 70)/T]$	207-403	Eberhard and Howard, 1996	F-CIMS (b)
$(9.3 \pm 1.6) \times 10^{-12}$	298		
$3.1 \times 10^{-12} \exp[(330 \pm 110)/T]$	220-355	Maricq and Szente, 1996	PLP-AS (c)
$(10.0 \pm 1.5) \times 10^{-12}$	295		
$3.8 \times 10^{-12} \exp[(290 \pm 110)/T]$	213-299	Ranschaert et al., 2000	F-CIMS (d)
$(10.1 \pm 0.9) \times 10^{-12}$	299		
$(11 \pm 0.8) \times 10^{-12}$	298	Xing et al., 2004	LP-MS (e)
$1.75 \times 10^{-12} \exp[(462 \pm 19)/T]$	203-298	Bardwell et al., 2005	F-CIMS (f)
$(8.03 \pm 0.35) \times 10^{-12}$	298		
<i>Branching Ratio</i>			
$k_2/k \leq 0.014$ (1 bar)	299	Atkinson et al., 1982	(g)
$k_2/k = 1.2 \times 10^{-3} \exp(610/T)$	213-298	Ranschaert et al., 2000	(h)
$k_2/k = 0.006$ (100 Torr N <sub>2</sub> )	298		
$k_2/k = 0.02$ (100 Torr N <sub>2</sub> )	213		
$k_2/k = 1.0 \pm 0.05$ (133-266 mbar N <sub>2</sub> )	203-298	Bardwell et al., 2005	F-CIMS (f)

## Comments

- Conventional discharge flow system with LIF detection of C<sub>2</sub>H<sub>5</sub>O product.  $k$  determined by simulation of experimental C<sub>2</sub>H<sub>5</sub>O profiles.
- Ethylperoxy radicals formed by the thermal decomposition of *n*-propyl nitrate in the presence of O<sub>2</sub>, or by RF discharge through C<sub>2</sub>H<sub>5</sub>I (also in the presence of O<sub>2</sub>). Pseudo first order kinetics with excess NO and CIMS detection of C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> as the ethyl peroxy negative ion.
- Excimer laser photolysis of Cl<sub>2</sub>-C<sub>2</sub>H<sub>6</sub>-NO-O<sub>2</sub>-N<sub>2</sub> mixtures. Time-resolved measurements of C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> decay and C<sub>2</sub>H<sub>5</sub>ONO formation using diode array UV absorption spectroscopy, and of NO loss and NO<sub>2</sub> formation using diode laser absorption spectroscopy.

- (d) Turbulent flow reactor at 100 Torr (133 mbar) N<sub>2</sub> total pressure. C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> detected as C<sub>2</sub>H<sub>5</sub>OOH<sup>+</sup>(H<sub>2</sub>O)<sub>n</sub> and C<sub>2</sub>H<sub>5</sub>ONO<sub>2</sub> detected as C<sub>2</sub>H<sub>5</sub>ONO<sub>2</sub>H<sup>+</sup>(H<sub>2</sub>O)<sub>n</sub> following proton transfer from H<sub>3</sub>O<sup>+</sup>.
- (e) C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> generated by reaction of C<sub>2</sub>H<sub>5</sub> with O<sub>2</sub>, whereby C<sub>2</sub>H<sub>5</sub> radicals were generated in the 248 nm photolysis of C<sub>2</sub>H<sub>5</sub>I, the 193 nm photolysis of C<sub>2</sub>H<sub>5</sub>Br or the 193 nm photolysis of CCl<sub>4</sub> in the presence of ethane. Owing to poor sensitivity, the experiments could not be performed under pseudo first-order conditions, and the data obtained using CCl<sub>4</sub> are reported to be less reliable as a result of secondary chemistry. C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> was detected as the negative parent ion following electron transfer from high Rydberg state rare gas atoms. The bath gas was 5.3 mbar He and 0.8 mbar O<sub>2</sub>.
- (f) Turbulent flow reactor at 133 or 266 mbar N<sub>2</sub> total pressure. C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> was generated in the reaction Cl + C<sub>2</sub>H<sub>6</sub> (+O<sub>2</sub>) and detected as C<sub>2</sub>H<sub>5</sub>O<sub>2</sub><sup>-</sup> following electron transfer from SF<sub>6</sub><sup>-</sup>. Yield of NO<sub>2</sub> (detected as NO<sub>2</sub><sup>-</sup>) was found to be 1.0 ± 0.05.
- (g) GC analysis of C<sub>2</sub>H<sub>5</sub>ONO<sub>2</sub> product from photo-oxidation of C<sub>2</sub>H<sub>6</sub> in Cl<sub>2</sub>-C<sub>2</sub>H<sub>6</sub>-NO-air mixtures.
- (h) Temperature dependent values of the rate coefficient  $k_2 = 1.6 \times 10^{-15} \exp(1160/T)$  for the temperature range 213 to 299 K and 100 Torr (133 mbar) N<sub>2</sub> pressure also presented. The authors state that the branching ratios are associated with large errors as the measurements were conducted near the detection limit for CH<sub>3</sub>ONO<sub>2</sub> and were complicated by secondary chemistry.

### Preferred Values

$k = 9.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 2.55 \times 10^{-12} \exp(380/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200-410 K.

$k_2/k \leq 0.014$  at 298 K and 1 bar pressure.

#### Reliability

$\Delta \log k = \pm 0.1$  at 298 K.

$\Delta(E/R) = \pm 50 \text{ K}$ .

#### Comments on Preferred Values

With the exception of the measurement of Adachi and Basco (1979), all measurements at room temperature are in reasonable agreement. The preferred value of the rate coefficient at room temperature is an average of the data from the direct studies of Plumb et al. (1982), Eberhard and Howard (1996), Ranschaert et al. (2000) and Bardwell et al. (2005). The temperature coefficients ( $E/R$ ) from the temperature dependent studies also show good agreement. The preferred value was obtained from a weighted fit to the data of Eberhard and Howard (1996), Ranschaert et al. (2000) and Bardwell et al. (2005). The data of Maricq and Szente (1996) are consistent with these datasets, but significantly more scattered.

The two sets of data for the branching ratio for C<sub>2</sub>H<sub>5</sub>ONO<sub>2</sub> formation (Ranschaert et al., 2000 and Atkinson et al., 1982) are self consistent at the common temperature of 298 K, and show that this channel is minor under atmospheric conditions. The observation of a temperature independent, 100 % yield of NO<sub>2</sub> confirms this (Bardwell et al., 2005).

### References

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