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

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 **C2H5O2 + NO  C2H5O + NO2 (1)**

 **C2H5O2 + NO + M  C2H5ONO2 + M (2)**

*H*°(1) = -45.2 kJ·mol-1

*H*°(2) = -217.0 kJ·mol-1

**Rate coefficient data (*k* = *k*1 + *k*2)**

|  |  |  |  |
| --- | --- | --- | --- |
| *k*/cm3 molecule-1 s-1  | Temp./K | Reference | Technique/ Comments |
| *Absolute Rate Coefficients* |  |  |  |
| (2.7 ± 0.2) × 10-12 | 298 | Adachi and Basco, 1979 | FP-AS |
| (8.9 ± 3.0) × 10-12 | 295 | Plumb et al., 1982 | DF-MS |
| (8.5 ± 1.2) × 10-12 | 298 | Sehested et al., 1993 | PR-AS |
| (8.2 ± 1.6) × 10-12 | 295 | Däele et al., 1995 | DF-MS (a) |
| 2.6 x 10-12 exp[(380 ± 70)/*T*] | 207-403  | Eberhard and Howard, 1996 | F-CIMS (b) |
| (9.3 ± 1.6) × 10-12 | 298 |  |  |
| 3.1 × 10-12 exp[(330 ± 110)/*T*] | 220-355  | Maricq and Szente, 1996 | PLP-AS (c) |
| (10.0 ± 1.5) × 10-12 | 295 |  |  |
| 3.8 x 10-12 exp[(290 ± 110)/*T*] | 213-299  | Ranschaert et al., 2000 | F-CIMS (d) |
| (10.1 ± 0.9) × 10-12 | 299 |  |  |
| (11 ± 0.8) × 10-12 | 298 | Xing et al., 2004 | LP-MS (e) |
| 1.75 × 10-12 exp[(462 ± 19)/*T*] | 203-298 | Bardwell et al., 2005 | F-CIMS (f) |
| (8.03 ± 0.35) × 10-12 | 298 |  |  |
| *Branching Ratio* |  |  |  |
| *k*2/*k*  0.014 (1 bar) | 299 | Atkinson et al., 1982 | (g) |
| *k*2/*k =* 1.2× 10-3 exp(610/*T*) | 213-298 | Ranschaert et al., 2000 | (h) |
| *k*2/*k* = 6 × 10-3 (100 Torr N2) | 298 |  |  |
| *k*2/*k* = 20 × 10-3 (100 Torr N2) | 213 |  |  |
| *k*1/*k* = 1.0 ± 0.05 (133-266 mbar N2) | 203-298 | Bardwell et al., 2005 | F-CIMS (f) |
| *k*2/*k*1 = (7.4 ± 1) × 10-3 (100 Torr N2) | 298 | Butkovskaya et al., 2010 | F-CIMS (i) |
| *k*2/*k*1 = (26.8 ± 3.4) × 10-3 (600 Torr N2) |  |  |  |
| *k*2/*k*1 = 72.2 × 10-3 (600 Torr N2) | 223 |  |  |
|  |  |  |  |

## Comments

(a) Conventional discharge flow system with LIF detection of C2H5O product. *k* determined by simulation of experimental C2H5O profiles.

(b) Ethylperoxy radicals formed by the thermal decomposition of *n*-propyl nitrate in the presence of O2, or by RF discharge through C2H5I (also in the presence of O2). Pseudo first order kinetics with excess NO and CIMS detection of C2H5O2 as the ethyl peroxy negative ion.

(c) Excimer laser photolysis of Cl2-C2H6-NO-O2-N2 mixtures. Time-resolved measurements of C2H5O2 decay and C2H5ONO formation using diode array UV absorption spectroscopy, and of NO loss and NO2 formation using diode laser absorption spectroscopy.

(d) Turbulent flow reactor at 100 Torr (133 mbar) N2 total pressure. C2H5O2 detected as C2H5OOH+(H2O)n and C2H5ONO2 detected as C2H5ONO2H+(H2O)n following proton transfer from H3O+.

(e) C2H5O2 generated by reaction of C2H5 with O2, whereby C2H5 radicals were generated in the 248 nm photolysis of C2H5I, the 193 nm photolysis of C2H5Br or the 193 nm photolysis of CCl4 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 CCl4 are reported to be less reliable as a result of secondary chemistry. C2H5O2 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 O2.

(f) Turbulent flow reactor at 133 or 266 mbar N2 total pressure. C2H5O2 was generated in the reaction Cl + C2H6 (+O2) and detected as C2H5O2- following electron transfer from SF6-. Yield of NO2 (detected as NO2-) was found to be 1.0  0.05.

(g) GC analysis of C2H5ONO2 product from photo-oxidation of C2H6 in Cl2-C2H6-NO-air mixtures.

(h) Temperature dependent values of the rate coefficient *k*2 = 1.6  10-15 exp (1160/*T*) for the temperature range 213 to 299 K and 100 Torr (133 mbar) N2 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 C2H5ONO2 and were complicated by secondary chemistry.

(i) Turbulent flow reactor with CIMS detection of products. Branching ratios (*k*2 / *k*1) were derived from monitoring the formation of C2H5ONO2 relative to either NO2, C2H5ONO or CH3CHO, the latter two both arising from reactions of alkoxy radical co-product of NO2 in reaction (1). The in-situ calibration of C2H5ONO2 and C2H5ONO was via formation of C2H5O at known yield (0.55) in the reaction of F atoms with C2H5OH and its further reactions with NO2 or NO, respectively. Consistent results were reported when using NO2, C2H5ONO or CH3CHO as a measure of the flux through reaction (1).

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | **T/K** |
|  |  |  |
| *k* /cm3 molecule-1 s-1 | 9.1 × 10-12 | 298 |
| *k* /cm3 molecule-1 s-1 | 2.55 × 10-12 exp(380/*T*) | 200-410 |
| *k*2/*k \** | (1/(0.01 × (1.18e-19 ×[M]+0.365) × (1+900 × (1/*T*-1/298)))+1)-1 |  |
| *k*2/*k* (1 bar) |  | 298 K |

*Reliability*

|  |  |  |
| --- | --- | --- |
|  log *k* | ± 0.1 | 298 |
| Δ*E*/*R*  | ± 50 | 200-410 |
| Δ log*k*2/*k*) | ± 0.2 | 220-320 |

\*The expression was adapted from the parameterization for *k*2/*k*1 given by Butkovskaya et al. (2010) using *k*2/*k*= (*k*1/*k*2 +1)-1.

## Preferred Values

# 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*) also show good agreement and 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 observation of a temperature independent, (100 ± 5)% yield of NO2 confirms that the reaction proceeds predominantly via formation of an alkoxy radical + NO2 under atmospheric conditions (Bardwell et al., 2005), with low yields of C2H5ONO2 at room temperature (Atkinson et al., 1982). However, the work of Ranschaert et al. (2000) and Butkovskaya et al, (2010) indicate that the yield of C2H5ONO2 increases with increasing pressure and decreasing temperature. The extensive experiments of Butkovskaya et al. (2010), covering temperatures between 222 and 323 K and pressures between 100 and 600 Torr, enabled the authors to derive a pressure and temperature dependent expression for *k*2/*k*1, which reproduces their own data and is roughly consistent with the observations of Raenschaert et al (2000). The data of Butkovykaya et al (2010) are reasonably consistent with predictions of temperature dependent nitrate formation in C2H5O2 + NO extrapolated from larger RO2 (Carter and Atkinson, 1985) but not with latter recommendations from the same group (Carter and Atkinson, 1989, Arey et al., 2001).

We have adopted the parameterisation of Butkovykaya et al (2010) as our preferred branching ratio for ethyl-nitrate formation, but have expanded the uncertainty to account for the difference between their results at one bar and room temperature compared to Atkinson et al. (1982).

### References

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Rate coefficients (*k*) for C2H5O2  + NO. The solid line is the IUPAC preferred value.



Branching ratio, *k*2 / (*k*1+*k*2), for formation of C2H5ONO2  in the reaction between C2H5O2 and NO. The solid lines are adapted from the parameterisation given by Butkovykaya et al. (2010). To preserve clarify of presentation, only selections of the datasets of Butkovskaya et al. (2010) and Ranschaert et al. (2000) are shown. The down-arrow on the data point of Atkinson (1982) indicates an upper-limit.