# **IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO\_5**

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 ***i*-C3H7O2 + NO  *i*-C3H7O + NO2 (1)**

 ***i*-C3H7O2 + NO + M  *i*-C3H7ONO2 + M (2)**

*H*°(1) = -40.5 kJ·mol-1

*H*°(2) = -212.2 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* |  |  |  |
| (3.5  0.3) × 10-12 | 298 | Adachi and Basco, 1982 | FP-AS |  |
| (5.0  1.2) × 10-12 | 290 | Peeters et al., 1992 | DF-MS (a) |  |
| 2.7 × 10-12 exp[(360 ± 60)/*T*] | 201-401 | Eberhard et al., 1996 | F-CIMS (b) |  |
| (9.0 ± 1.5) × 10-12 | 298 |  |  |  |
| (9.1 ± 1.5) × 10-12 | 298 | Eberhard and Howard, 1996 | F-CIMS (c) |  |
| 4.3 × 10-12 exp[(268 ± 56)/*T*] | 213-298 | Chow et al., 2003 | F-CIMS (d) |  |
| (1.05 ± 0.14) × 10-11 | 298 |  |  |  |
| (8.0 ± 1.5) × 10-12 | 298 | Xing et al., 2005 | LP-MS (e) |  |
| *Branching Ratios* |  |  |  |  |
| *k*2/*k* = 0.042 ± 0.003 (1 bar air) | 299 | Atkinson et al., 1982;Carter and Atkinson, 1989 | (f) |  |
| *k*2/*k* = 1.815 × 10-4 exp(1020/*T*)(133 mbar N2) | 213-298 | Chow et al., 2003 | F-CIMS (d) |  |
| *k*2/*k* = 0.005 (133 mbar N2) | 298 |  |  |  |
| *k*2/*k*1 = (6.0 ± 1.1) × 10-3 (55 Torr N2) | 298 | Butkovskaya et al., 2010 | F-CIMS (g) |  |
| *k*2/*k*1 = (27.4 ± 6.6) × 10-3 (500 Torr N2) |  |  |  |  |

## Comments

(a) Low pressure flow tube at 2.7 mbar He. Rate constant derived from analysis of NO2 growth profiles.

(b) *i*-C3H7O2 radicals produced by reaction of O2 with *i*-C3H7 radicals produced by thermal decomposition of isobutyl nitrate. *i*-C3H7O2 was detected as its parent negative ion formed by reaction with O2-. *k* determined by pseudo-first order loss of *i*-C3H7O2 in the presence of NO.

1. *i*-C3H7O2 produced by reaction of O2 with *i*-C3H7 produced in a low frequency RF discharge through *i*-propyl iodide.
2. Turbulent flow reactor at 100 Torr (133 mbar) N2 total pressure. C3H7O2 radicals were generated by the reaction of Cl atoms with C3H8 in the presence of O2, thus both *n*-C3H7O2 and *i*-C3H7O2 were present and the rate coefficients measured are overall values for both isomers, which were detected as C3H7OOH+(H2O)3 following reaction with H+(H2O)4 ions. For branching ratio measurements, *i*-C3H7O2 was selectively generated from the reaction of H atoms with C3H6 in the presence of O2. *i*-C3H7ONO2 was detected using H+(H2O)4 ions; NO2 was detected as NO2- following electron transfer from SF6-.
3. *i*-C3H7O2 generated by reaction of *i*-C3H7 with O2, whereby *i*-C3H7 radicals were generated in the 193 nm photolysis of *i*-C3H7Br, or the 248 nm photolysis of *i*-C3H7I. *i*-C3H7O2 was detected as the negative parent ion. The bath gas was was 4 – 5.3 mbar (He). Owing to poor sensitivity, and resultant side/secondary reactions the rate coefficient was extracted by numerical modelling of a complex reaction scheme.
4. Photolysis of CH3ONO-NO-C3H8-air or Cl2-NO-C3H8-air mixtures at a total pressure of 1 bar. The branching ratio was determined from the measured yields of *i*-C3H7ONO2 and the consumption of C3H8. Carter and Atkinson (1989) have re-evaluated the branching ratio, cited above, from the original data (Atkinson et al., 1982) on the basis of revised data for the rate coefficients of the HO radical reactions with alkanes.
5. Turbulent flow reactor with CIMS detection of products using F- primary ions. Branching ratios (*k*2 / *k*1) were derived by monitoring the formation of C2H5ONO2 (detected as NO3-) relative to CH3C(O)CH3, the latter formed (at a yield of 0.16 ± 0.025) in the reaction of *i*-C3H7O2 (from reaction 1) with NO.

### Preferred Values

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | **T/K** |
|  |  |  |
| *k* /cm3 molecule-1 s-1 | 9.0 × 10-12 | 298 |
| *k* /cm3 molecule-1 s-1 | 2.7 × 10-12 exp(360/*T*) | 200-410 |
| *α*  | 1.95 × 10-22 |  |
| *β*  |  |  |
| $$Y\_{0}^{300}$$ |  |  |
| $$m\_{0}$$ |  |  |
| $$m\_{\infty }$$ |  |  |
| *F* |  |  |
| *k*2/*k* (1 bar) |  | 298  |

*Reliability*

|  |  |  |
| --- | --- | --- |
|  log *k* | ± 0.1 | 298 |
| Δ*E*/*R*  | ± 100 | 200-410 |
| Δ log*k*2/*k*) | ± 0.3 | 213-320 |

*Comments on Preferred Values*

The data from Eberhard et al. (1986) give a rate coefficient at 298 K which is significantly larger that the values obtained by Adachi and Basco (1982) or Peeters et al. (1992) and is close to the value obtained for a range of alkyl peroxy radicals at 298 K. In addition, the data of Chow et al. (2003), who measured a weighted average value for *n*-C3H7O2 and *i*-C3H7O2 are in good agreement, which confirms that *n*-C3H7O2 and *i*-C3H7O2 have similar rate coefficients for reaction with NO. The rather indirect measurement of Xing et al. (2005) is also in broad agreement. The preferred value for *k*298 and the temperature dependence is that reported by Eberhard et al. (1996).

The three studies of the branching ratio to *i*-C3H7ONO2 formation indicate that *k*2/*k* increases with increasing pressure, with a value of circa 0.04 at one bar pressure and 298 K. Although the data of Chow et al. (2003) are not precise enough to accurately define the trend, the formation of *i*-C3H7ONO2 is also favoured by low temperatures (Chow et al., 2003) as expected. The datasets of Carter and Atkinson (1989), Chow et al. (2003) and Butkovykaya et al (2010) are reasonably consistent with the temperature dependent fall-off parameterisation of Carter et al (1985) (see below) when multiplied by a factor 1.5. Note that later parametzerisations from the same group used a much weaker temperarure dependence and do not reproduce the increase in branching ratio at low temperatures (at 100 Torr total pressure) obseved by Chow et al. (2003).

$$\frac{k\_{2}}{k}= 1.5\left[\frac{Y\_{0}^{300}[M](T/300)^{-m\_{0}}}{1+\frac{Y\_{0}^{300}[M](T/300)^{-m\_{0}}}{Y\_{\infty }^{300}(T/300)^{-m\_{\infty }}}}\right]F^{Z}$$

Where $Z= \left\{1+\left[log\left\{\frac{Y\_{0}^{300}[M](T/300)^{-m\_{0}}}{Y\_{\infty }^{300}(T/300)^{-m\_{\infty }}}\right\}\right]^{2}\right\}^{-1}$ and

$$Y\_{0}^{300}= αe^{βn}$$

The uncertainty in the branching ratio has been increased to reflect the data quality in the only study of the temperature dependence.

### References

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Rate constants for *i*-C3H7O2  + NO. The solid line represents the prefered values. The data of Chow et al are for a mixture of *i*-C3H7O2 and *n*-C3H7O2.



Branching ratio, *k*2 / (*k*1+*k*2), for formation of C3H7ONO2  in the reaction between *i*‑C3H7O2 and NO. The solid lines are derived from the parameterisation given by Carter and Atkinson et al. (1985) multipled by a factor of 1.5.