IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_5

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$$\boldsymbol{i\text{-}C_3H_7O_2 + NO \rightarrow i\text{-}C_3H_7O + NO_2} \qquad (1)$$

$$\boldsymbol{i\text{-}C_3H_7O_2 + NO + M \rightarrow i\text{-}C_3H_7ONO_2 + M} \qquad (2)$$

$\Delta H°(1) = -40.5\ kJ{\cdot}mol^{-1}$

$\Delta H°(2) = -212.2\ kJ{\cdot}mol^{-1}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(3.5 \pm 0.3) \times 10^{-12}$	298	Adachi and Basco, 1982	FP-AS
$(5.0 \pm 1.2) \times 10^{-12}$	290	Peeters et al., 1992	DF-MS (a)
$2.7 \times 10^{-12} \exp[(360 \pm 60)/T]$	201-401	Eberhard et al., 1996	F-CIMS (b)
$(9.0 \pm 1.5) \times 10^{-12}$	298		
$(9.1 \pm 1.5) \times 10^{-12}$	298	Eberhard and Howard, 1996	F-CIMS (c)
$4.3 \times 10^{-12} \exp[(268 \pm 56)/T]$	213-298	Chow et al., 2003	F-CIMS (d)
$(1.05 \pm 0.14) \times 10^{-11}$	298		
$(8.0 \pm 1.5) \times 10^{-12}$	298	Xing et al., 2005	LP-MS (e)
Branching Ratios			
$k_2/k = 0.042 \pm 0.003$ (1 bar air)	299	Atkinson et al., 1982; Carter and Atkinson, 1989	(f)
$k_2/k = 1.815\times10^{-4} \exp(1020/T)$ (133 mbar N_2)	213-298	Chow et al., 2003	F-CIMS (d)
$k_2/k = 0.005$ (133 mbar N_2)	298		

Comments

(a) Low pressure flow tube at 2.7 mbar He. Rate constant derived from analysis of NO_2 growth profiles.

(b) i-$C_3H_7O_2$ radicals produced by reaction of O_2 with i-C_3H_7 radicals produced by thermal decomposition of isobutyl nitrate. i-$C_3H_7O_2$ was detected as its parent negative ion formed by reaction with O_2^-. k determined by pseudo-first order loss of i-$C_3H_7O_2$ in the presence of NO.

(c) i-$C_3H_7O_2$ produced by reaction of O_2 with i-C_3H_7 produced in a low frequency RF discharge through i-propyl iodide.

(d) Turbulent flow reactor at 100 Torr (133 mbar) N_2 total pressure. $C_3H_7O_2$ radicals were generated by the reaction of Cl atoms with C_3H_8 in the presence of O_2, thus both n-$C_3H_7O_2$ and i-$C_3H_7O_2$ were present and the rate coefficients measured are overall values for both isomers, which were detected as $C_3H_7OOH^+(H_2O)_3$ following reaction with $H^+(H_2O)_4$ ions. For branching ratio measurements, i-$C_3H_7O_2$ was selectively generated from the reaction of

H atoms with C_3H_6 in the presence of O_2. *i*-$C_3H_7ONO_2$ was detected using $H^+(H_2O)_4$ ions; NO_2 was detected as NO_2- following electron transfer from SF_6^-.

(e) *i*-$C_3H_7O_2$ generated by reaction of *i*-C_3H_7 with O_2, whereby *i*-C_3H_7 radicals were generated in the 193 nm photolysis of *i*-C_3H_7Br, or the 248 nm photolysis of *i*-C_3H_7I. *i*-$C_3H_7O_2$ was detected as the negative parent ion following electron transfer from high Rydberg state Xe atoms. 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.

(e) Photolysis of CH_3ONO-NO-C_3H_8-air or Cl_2-NO-C_3H_8-air mixtures at a total pressure of 1 bar. The branching ratio was determined from the measured yields of *i*-$C_3H_7ONO_2$ and the consumption of C_3H_8. 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.

Preferred Values

$k = 9.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.7 \times 10^{-12} \exp(360/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200 K to 410 K.
$k_2/k = 0.042$ at 298 K and 1 bar pressure.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 100$ K.
$\Delta \log(k_2/k) = \pm 0.3$ at 298 K and 1 bar pressure.

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*-$C_3H_7O_2$ and *i*-$C_3H_7O_2$ are in good agreement, which confirms that *n*-$C_3H_7O_2$ and *i*-$C_3H_7O_2$ 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).

There are two studies of the branching ratio to *i*-$C_3H_7ONO_2$ formation. Chow et al. (2003) report values that vary from ≈ 0.005 at room temperature to 0.02 at 213 K, whereas Carter and Atkinson (1989) report 0.042 at 298 K. The differences in these results are a result of the pressure difference in the two experiments reported, implying that k_2 is in the third-order limit at 133 mbar N_2. For purpose of atmospheric modelling of the lower troposphere, the recommended branching ratio is that reported by Carter and Atkinson (1989). Chow et al. (2003) note that their temperature dependence is reproduced using a model based on $C_3 - C_8$ hydrocarbons (Arey et al., 2001).

References

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