IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_20

This data sheet last evaluated May 2008 (with no change to the preferred values).

$$C_2H_5O_2 + NO_3 \rightarrow C_2H_5O + NO_2 + O_2 \quad (1)$$
$$\rightarrow \text{other products} \quad (2)$$

$\Delta H°(1) = -28.7$ kJ·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			
(2.5 ± 1.5) x 10^{-12}	298 K	Biggs et al., 1995	DF-LIF/AS (a)
(2.3 ± 0.5) x 10^{-12}	298 K	Ray et al., 1996	DF-LIF/MS (b)
(2.3 ± 0.7) x 10^{-12}	295 ± 4	Vaughan et al., 2006	DF (c)

Comments

(a) LIF detection of C_2H_5O; NO_3 detection by absorption spectroscopy at 662 nm. k was derived by modelling the kinetics of $C_2H_5O_2 + NO_3$ in systems using $C_2H_5 + O_2$ and $C_2H_5O + NO_3$ to generate $C_2H_5O_2$. Pressure = 2.9 mbar of He.

(b) LIF detection of C_2H_5O, MS detection of NO_3. k was derived from a model simulation of system using $C_2H_5O_2$ as initial reactant, with NO_3 in excess.

(c) Flow tube at ≈ 6.7 mbar. NO_3 (0.3-8 x10^{11} molecule cm^{-3}) was formed in the reaction of F atoms with HNO_3 and detected by cavity enhanced absorption spectroscopy (CEAS) at 663 nm. $C_2H_3O_2$ (excess reactant with 0.9-50 x10^{11} molecule cm^{-3}) was formed in the reaction of F atoms with CH_4 / O_2 and detected as NO_2 (by CEAS at 404 nm) following titration with NO. Derivation of the $C_2H_5O_2$ concentration required numerical modelling. Time dependent decays of NO_3 were not observed, but the analysis was based on NO_3 changes for a fixed reaction time when the $C_2H_5O_2$ was modulated on and off.

Preferred Values

$k_1 = 2.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

All studies of this reaction used similar methods and, despite the complex analyses (numerical modelling of assumed reaction schemes) necessary to extract kinetic data, the rate constants obtained are in good agreement. Channel (1) is most important, and Biggs et al. (1995) suggest that $k_1 / k \approx 0.8$.

References

Biggs, P., Canosa-Mas, C. E., Fracheboud, J.-M., Shallcross, D. E., and Wayne, R. P.: J. Chem. Soc. Faraday Trans. 91, 817, 1995.
Ray, A., Daële, V., Vassalli, I., Poulet, G., and LeBras, G-.: J. Phys. Chem. 100, 5737, 1996.
Vaughan, S., Canosa-Mas, C. E., Pfrang, C., Shallcross, D. E., Watson, L., and Wayne, R. P.: Phys. Chem. Chem. Phys. 8, 3749, 2006.