IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_21

This data sheet last evaluated: May 2008.

$CH_3C(O)O_2 + NO_3 \rightarrow CH_3CO_2 + NO_2 + O_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(4 \pm 1) \times 10^{-12}$	403-443	Canosa-Mas et al., 1996	DF (a)

Comments

(a) Flow tube at ≈ 3 mbar. NO_3 (0.1-4 x10^{13} molecule cm^{-3}) was formed in the reaction of F atoms with HNO_3 and detected by multi-pass absorption spectroscopy at 662 nm. $CH_3C(O)O_2$ was formed by thermal decomposition of $CH_3C(O)O_2NO_2$ and detected as NO_2 (by LIF) following reaction with NO. Derivation of the rate constant required numerical modelling of a complex reaction mixture, including $CH_3C(O)O_2NO_2$ decomposition.

Preferred Values

$k = 4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.4$ at 298 K.

Comments on Preferred Values

The single study of this reaction was indirect and required a complex analysis (numerical modelling of assumed reaction schemes) to extract kinetic data. The rate constant derived is consistent with other reactions of NO_3 with small, organic peroxy radicals. The preferred value is taken from Canosa-Mas et al (1996) with extended uncertainty to reflect the facts that there is only one study, the method was indirect and the temperature range did not cover 298 K. By analogy to other reactions of $RO_2 + NO_3$ the most likely product channel is that listed in the title, though there is no experimental confirmation of this. Note that CH_3CO_2 decomposes rapidly (at a rate of approximately 5 x 10^8 s^{-1} at 298 K, Braun et al., 1962) to $CH_3 + CO_2$.

References

Braun, W., Rajbenbach, L., Eirich, F. R.: J. Phys. Chem. 66, 1591, 1962.
Canosa-Mas, C. E., King, M. D., Lopez, R., Percival, C. J., Wayne, R. P., Shallcross, D. E., Pyle, J. A., Daële, V.: J. Chem. Soc. Faraday Trans. 92, 2211, 1996.