IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_49

This data sheet last evaluated: June 2010; last change in preferred values: June 2010.

$$CH_3CH(OH)CH(O_2)CH_3 + NO \rightarrow CH_3CH(OH)CH(O)CH_3 + NO_2 \quad (1)$$
$$CH_3CH(OH)CH(O_2)CH_3 + NO + M \rightarrow CH_3CH(OH)CH(ONO_2)CH_3 + M \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(9.3 \pm 1.4) \times 10^{-12}$	298	Miller et al., 2004	DF-CIMS (a)
Branching ratios			
$k_2/k = 0.037 \pm 0.009$ (1013 mbar*)	298*	Muthuramu et al., 1993	UVP-GC-ECD (b)
$k_2/k = 0.034 \pm 0.005$ (1013 mbar*)	296	O'Brien et al., 1998	UVP-GC-CL (c)
$k_2/k = 0.068 \pm 0.023$ (133 mbar)	298	Patchen et al., 2007	DF-CIMS (d)

Comments

(a) HO radicals generated from the reaction of F atoms with H_2O, following production of F from microwave discharge of CF_4-He mixtures. $CH_3CH(OH)CH(O_2)CH_3$ radicals generated in HO-but-2-ene-O_2-N_2 mixtures in a high pressure turbulent flow system at 133 mbar (100 Torr), and monitored via proton transfer following reaction with $H^+(H_2O)_n$. Kinetics determined under pseudo-first order conditions by sequential addition of an HO scavenger (an unspecified alkene) followed by the reagent NO. The HO scavenger was added at a sufficient excess concentration to preclude significant regeneration of $CH_3CH(OH)CH(O_2)CH_3$ under the experimental conditions, which was confirmed though simulations of the system.

(b) Blacklight photolysis of CH_3ONO-but-2-ene-NO-air mixtures in a 220 dm^3 chamber, with mixtures sampled onto charcoal traps. $CH_3CH(OH)CH(ONO_2)CH_3$ formation analysed by GC-ECD. Identification and calibration achieved through synthesis of reference. Reported value of k_2/k based on the yield of the nitrate relative to but-2-ene consumed, as quantified by GC-FID.

(c) Blacklight photolysis of $(CH_3)_2CHONO$-but-2-ene-NO-air mixtures in a 9.6 m^3 chamber. Formation of $CH_3CH(OH)CH(ONO_2)CH_3$ was detected through separation in a capillary chromatographic column and quantification by pyrolytic conversion to NO_2, followed by chemiluminescent reaction of NO_2 with luminol. Reported value of k_2/k based on the total yield of the nitrate relative to but-2-ene consumed, as quantified by GC-FID.

(d) HO radicals generated from the reaction of F atoms with H_2O, following production of F from microwave discharge of CF_4-He mixtures. HO added to but-2-ene-NO-air mixtures in a high pressure turbulent flow system at 133 mbar (100 Torr). Products monitored via proton

transfer following reaction with $H^+(H_2O)_n$. Relative flux through channels (1) and (2) determined from the measured formation of the nitrate and NO_2. The latter was corrected for secondary formation, which was typically calculated to account for about 30% of the observed total NO_2 on the basis of simulations of the system.

Preferred Values

Parameter	Value	T/K
k/cm^3 molecule^{-1} s^{-1}	9.3 x 10^{-12}	298
Reliability		
$\Delta \log k$	± 0.2	298

Comments on Preferred Values

The preferred value of k is based on the results of Miller et al. (2004), in which the time dependence of the $CH_3CH(OH)CH(O_2)CH_3$ concentration was monitored directly under pseudo-first order conditions. Although this is the only reported kinetics study, the value of k is generally consistent with the wider kinetics database of reactions of NO with hydrocarbon-derived RO_2 radicals, which generally show little sensitivity to the size or structure of the organic group (e.g., see discussion in Miller et al., 2004).

The reported determinations of k_2/k confirm the existence of a minor nitrate-forming channel, but show some variability. Further studies are required before a recommendation can be made. Systematic studies and a function of temperature and pressure would also be valuable.

References

Miller, A. M., Yeung, L. Y., Kiep, A. C. and Elrod, M. J.: Phys. Chem. Chem. Phys., 6 , 3402 – 3407, 2004.

Muthuramu, K., Shepson, P. B. and O'Brien, J. M. : Environ. Sci. Technol., 27, 1117–1124, 1993.

O'Brien, J. M., Czuba, E., Hastie, D. R., Francisco, J. S. and Shepson, P. B.: J. Phys. Chem. A, 102, 8903–8908, 1998.

Patchen, A. K., Pennino, M. J., Kiep, A. C. and Elrod, M. J.: Int. J. Chem. Kinet., 39, 353–361, 2007.