IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet NO3_VOC22
Website: http://www.iupac-kinetic.ch.cam.ac.uk/. See website for latest evaluated data.
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$$NO_3 + CH_3CH(OH)CH_2CH_3 \rightarrow HNO_3 + CH_3C(OH)CH_2CH_3 \quad (1)$$
$$\rightarrow HNO_3 + CH_2CH(OH)CH_2CH_3 \quad (2)$$
$$\rightarrow HNO_3 + CH_3CH(OH)CHCH_3 \quad (3)$$
$$\rightarrow HNO_3 + CH_3CH(OH)CH_2CH_2 \quad (4)$$

Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$\leq(2.6 \pm 0.3) \times 10^{-15}$	298 ± 2	Chew, Atkinson and Aschmann, 1998[1]	RR (a)
$k_1 = (2.1 \pm 0.3) \times 10^{-15}$	298 ± 2	Chew, Atkinson and Aschmann, 1998[1]	RR (a)

Comments

(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in air at atmospheric pressure. Experiments were carried out in a ~7000 liter Teflon chamber, and the concentrations of 2-butanol and methacrolein (the reference organic) were measured by GC. Rate coefficient ratios $k(NO_3$ + 2-butanol$)/k(NO_3$ + methacrolein) were measured as a function of initially added NO_2 over the range (0-2.4) x 10^{14} molecule cm^{-3} (~2 x 10^{16} molecule cm^{-3} of ethane were added when no NO_2 was initially added). The rate coefficient ratios were independent of initial NO_2 concentration in the range (0-4.8) x 10^{13} molecule cm^{-3}, but increased for initial NO_2 concentrations ≥9.6 x 10^{13} molecule cm^{-3}. 2-Butanone was observed as a reaction product, presumably from channel (1) followed by,

$$CH_3C(OH)CH_2CH_3 + O_2 \rightarrow CH_3C(O)CH_2CH_3 + HO_2$$

with a yield of ~0.79 ± 0.09 at initial NO_2 concentrations of (0-4.8) x 10^{13} molecule cm^{-3}, and decreasing at higher initial NO_2 concentrations. The values of {$k(NO_3$ + 2-butanol) (yield of 2-butanone)$/k(NO_3$ + methacrolein)} were independent of initial NO_2 concentration over the entire range studied [(0-2.4) x 10^{14} molecule cm^{-3}], with an average value of 0.60 ± 0.07 for experiments with initial NO_2 concentrations of (0-4.8) x 10^{13} molecule cm^{-3}. The observed behavior is interpreted as involving a gas-phase reaction of 2-butanol with the NO_3 radical and a reaction (gas-phase or heterogeneous) of N_2O_5 with 2-butanol

to form nitrates.[2] The rate coefficient k is obtained from the rate coefficient ratio $k(NO_3 + 2\text{-butanol})/k(NO_3 + \text{methacrolein}) = 0.754 \pm 0.065$ at low added NO_2 concentrations, combined with a rate coefficient ratio of $k(NO_3 + \text{methacrolein}) = 3.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 ± 2 K.[1,3] This overall rate coefficient could still be an upper limit, and the true-rate coefficient may be the value obtained for k_1 obtained from the ratio $\{k(NO_3 + 2\text{-butanol})(\text{yield of 2-butanone})/k_2(NO_3 + \text{methacrolein}) = 0.60 \pm 0.07$ and the rate coefficient $k(NO_3 + \text{methacrolein})$.[1,3]

Preferred Values

$k = 2.1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 1.0$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(k_1/k) = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred values are based on the sole study of Chew *et al*.[1] In view of the magnitude of the rate coefficient compared to that for reaction of the NO_3 radical with *n*-butane,[4] reaction is expected to occur almost totally at the tertiary C-H bond (i.e., $k_1/k = 1.0$). The preferred value therefore uses the measured rate coefficient k_1 combined with the expectation that $k_1/k = 1.0$.

References

1 A. A. Chew, R. Atkinson, and S. M. Aschmann, J. Chem. Soc. Faraday Trans. **94**, 1083 (1998).
2 S. Langer and E. Ljungström, J. Chem. Soc. Faraday Trans. **91**, 405 (1995).
3 C. E. Canosa-Mas, S. Carr, M. D. King, D. E. Shallcross, K. C. Thompson, and R. P. Wayne, Phys. Chem. Chem. Phys. **1**, 4195 (1999).
4 IUPAC, http://www.iupac-kinetic.ch.cam.ac.uk/ (2002).