IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet NO3_VOC21
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$$NO_3 + CH_3CH(OH)CH_3 \rightarrow HNO_3 + CH_3C(OH)CH_3 \quad (1)$$
$$\rightarrow HNO_3 + CH_2CH(OH)CH_3 \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$\leq 2.3 \times 10^{-15}$	298 ± 2	Wallington *et al*., 1987[1]	FP-A
$1.54 \times 10^{-12} \exp[-(1743 \pm 1009)/T]$	273-364	Langer and Ljungström, 1995[2]	DF-A
$(3.13 \pm 0.64) \times 10^{-15}$	295		
Relative Rate Coefficients			
$\leq (1.8 \pm 0.2) \times 10^{-15}$	298 ± 2	Chew, Atkinson and Aschmann, 1998[3]	RR (a)
$k_1 = (1.4 \pm 0.3) \times 10^{-15}$	298 ± 2	Chew, Atkinson and Aschmann, 1998[3]	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-propanol and methacrolein (the reference organic) were measured by GC. Rate coefficient ratios $k(NO_3$ + 2-propanol$)/k(NO_3$ + 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}. Acetone was observed as a reaction product, presumably from channel (1) followed by,

$$CH_3C(OH)CH_3 + O_2 \rightarrow CH_3C(O)CH_3 + HO_2$$

with a yield of ~0.76 ± 0.09 at initial NO_2 concentrations of (0-4.8) x 10^{13} molecule cm^{-3}, decreasing at higher initial NO_2 concentrations. The values of $\{k(NO_3$ + 2-propanol) (yield of acetone)$/k(NO_3$ + 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 0.40 ± 0.06 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-propanol with the NO_3 radical and a reaction (gas-phase or heterogeneous) of N_2O_5 with 2-propanol to form nitrates.[2] The rate coefficient k is obtained from the rate coefficient ratio $k(NO_3 + \text{2-propanol})/k(NO_3 + \text{methacrolein}) = 0.519 \pm 0.053$ 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.[3,4] 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 $\{k(NO_3 + \text{2-propanol})(\text{yield of 2-acetone})/k_2(NO_3 + \text{methacrolein}) = 0.40 \pm 0.06$ and the rate coefficient of $k(NO_3 + \text{methacrolein})$.[3,4]

Preferred Values

$k = 1.4 \times 10^{-15}$ 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 room temperature values for the overall reaction rate coefficient k and for k_1 obtained by Chew *et al*.[3] are consistent with the upper limit to the rate coefficient of Wallington *et al*.,[1] but are a factor of ~2 lower than the absolute rate coefficient of Langer and Ljungström.[2] It is expected that the reaction of the NO_3 radical occurs almost entirely by H-atom abstraction from the tertiary C-H bond (and hence that $k_1/k \sim 1.0$).[5] This expectation is consistent with the data of Chew *et al*.[3] The 298 K preferred value is based on the value of k_1 obtained by Chew *et al*.[3] with the expectation that $k_1/k = 1.0$.[5] No temperature dependence is recommended.

References

1 T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **19**, 243 (1987).
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5 R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).