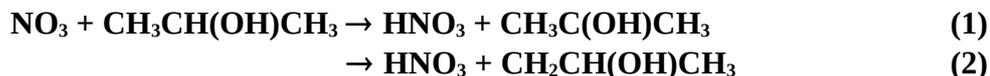


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO₃_VOC23

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet last evaluated 10th December 2007 (with no revision of the preferred values).

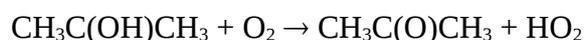


Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./ K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$\leq 2.3 \times 10^{-15}$	298 ± 2	Wallington et al., 1987	FP-A
$1.54 \times 10^{-12} \exp[-(1743 \pm 1009)/T]$ $(3.13 \pm 0.64) \times 10^{-15}$	273-364 295	Langer and Ljungström, 1995	DF-A
<i>Relative Rate Coefficients</i>			
$\leq (1.8 \pm 0.2) \times 10^{-15}$	298 ± 2	Chew et al., 1998	RR (a)
$k_1 = (1.4 \pm 0.3) \times 10^{-15}$	298 ± 2	Chew et al., 1998	RR (a)

Comments

- (a) NO₃ radicals were generated by the thermal decomposition of N₂O₅ 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 $k(\text{NO}_3 + 2\text{-propanol})/k(\text{NO}_3 + \text{methacrolein})$ were measured as a function of initially added NO₂ over the range $(0\text{-}2.4) \times 10^{14} \text{ molecule cm}^{-3}$ ($\sim 2 \times 10^{16} \text{ molecule cm}^{-3}$ of ethane were added when no NO₂ was initially added). The rate coefficient ratios were independent of initial NO₂ concentration in the range $(0\text{-}4.8) \times 10^{13} \text{ molecule cm}^{-3}$, but increased for initial NO₂ concentrations $\geq 9.6 \times 10^{13} \text{ molecule cm}^{-3}$. Acetone was observed as a reaction product, presumably from channel (1) followed by,



with a yield of $\sim 0.76 \pm 0.09$ at initial NO₂ concentrations of $(0\text{-}4.8) \times 10^{13} \text{ molecule cm}^{-3}$, decreasing at higher initial NO₂ concentrations. The values of $\{k(\text{NO}_3 + 2\text{-propanol}) (\text{yield of acetone})/k(\text{NO}_3 + \text{methacrolein})\}$ were independent of initial NO₂ concentration over the entire range studied [$(0\text{-}2.4) \times 10^{14} \text{ molecule cm}^{-3}$], with an average value of 0.40 ± 0.06 for experiments with initial NO₂ concentrations of $(0\text{-}4.8) \times 10^{13} \text{ molecule cm}^{-3}$. The observed behaviour is interpreted as involving a gas-phase reaction of 2-propanol with the NO₃ radical and a reaction (gas-phase or heterogeneous) of N₂O₅ with 2-propanol to form nitrates (Langer and Ljungström, 1995). The rate coefficient k is obtained from the rate coefficient ratio $k(\text{NO}_3 + 2\text{-propanol})/k(\text{NO}_3 + \text{methacrolein}) = 0.519 \pm 0.053$ at low added NO₂ concentrations, combined with a rate coefficient ratio of $k(\text{NO}_3 + \text{methacrolein}) = 3.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $298 \pm 2 \text{ K}$ (IUPAC, current recommendation). 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 $\{k(\text{NO}_3 + 2\text{-propanol})(\text{yield of 2-acetone})/k_2(\text{NO}_3 + \text{methacrolein}) = 0.40 \pm 0.06$ and the rate coefficient of $k(\text{NO}_3 + \text{methacrolein})$.

Preferred Values

$k = 1.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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. (1998) are consistent with the upper limit to the rate coefficient of Wallington et al. (1987), but are a factor of ~ 2 lower than the absolute rate coefficient of Langer and Ljungström (1995). It is expected (Atkinson, 1991) that the reaction of the NO_3 radical occurs almost entirely by H-atom abstraction from the tertiary C-H bond (and hence that $k_1/k \sim 1.0$). This expectation is consistent with the data of Chew et al. (1998). The 298 K preferred value is based on the value of k_1 obtained by Chew et al. (1998) with the expectation that $k_1/k = 1.0$ (Atkinson, 1991). No temperature dependence is recommended.

References

- Atkinson, R.: J. Phys. Chem. Ref. Data, 20, 459, 1991.
Chew, A. A., Atkinson, R. and Aschmann, S. M.: J. Chem. Soc. Faraday Trans., 94, 1083, 1998.
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Langer, S. and Ljungström, E.: J. Chem. Soc. Faraday Trans., 91, 405, 1995.
Wallington, T. J., Atkinson, R., Winer, A. M. and Pitts Jr., J. N.: Int. J. Chem. Kinet., 19, 243, 1987.