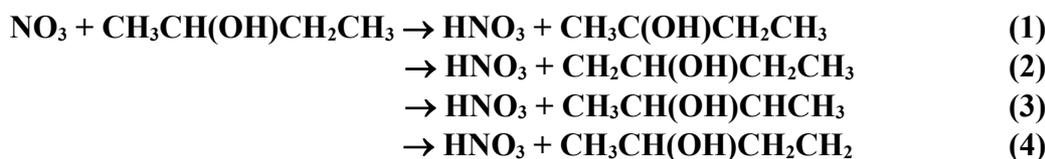


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO₃_VOC24

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 updated: 10th December 2007 (with revision of the preferred values).

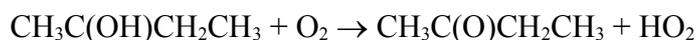


Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Relative Rate Coefficients</i>			
$\leq (2.6 \pm 0.3) \times 10^{-15}$	298 ± 2	Chew et al., 1998	RR (a)
$k_1 = (2.0 \pm 0.3) \times 10^{-15}$	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-butanol and methacrolein (the reference organic) were measured by GC. Rate coefficient ratios $k(\text{NO}_3 + \text{2-butanol})/k(\text{NO}_3 + \text{methacrolein})$ were measured as a function of initially added NO₂ over the range $(0-2.4) \times 10^{14} \text{ molecule cm}^{-3}$ (~2 x 10¹⁶ 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 $(0-4.8) \times 10^{13} \text{ molecule cm}^{-3}$, but increased for initial NO₂ concentrations $\geq 9.6 \times 10^{13} \text{ molecule cm}^{-3}$. 2-Butanone was observed as a reaction product, presumably from channel (1) followed by,



with a yield of $\sim 0.79 \pm 0.09$ at initial NO₂ concentrations of $(0-4.8) \times 10^{13} \text{ molecule cm}^{-3}$, and decreasing at higher initial NO₂ concentrations. The values of $\{k(\text{NO}_3 + \text{2-butanol}) (\text{yield of 2-butanone})/k(\text{NO}_3 + \text{methacrolein})\}$ were independent of initial NO₂ concentration over the entire range studied [$(0-2.4) \times 10^{14} \text{ molecule cm}^{-3}$], with an average value of 0.60 ± 0.07 for experiments with initial NO₂ concentrations of $(0-4.8) \times 10^{13} \text{ molecule cm}^{-3}$. The observed behaviour is interpreted as involving a gas-phase reaction of 2-butanol with the NO₃ radical and a reaction (gas-phase or heterogeneous) of N₂O₅ with 2-butanol to form nitrates (Langer and Ljungström, 1995). The rate coefficient k is obtained from the rate coefficient ratio $k(\text{NO}_3 + \text{2-butanol})/k(\text{NO}_3 + \text{methacrolein}) = 0.754 \pm 0.065$ 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 $\{k(\text{NO}_3 + \text{2-butanol})(\text{yield of 2-butanone})/k_2(\text{NO}_3 + \text{methacrolein})\} = 0.60 \pm 0.07$ and the rate coefficient $k(\text{NO}_3 + \text{methacrolein})$.

Preferred Values

$k = 2.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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 preferred values are based on the sole study of Chew et al. (1998). In view of the magnitude of the rate coefficient compared to that for reaction of the NO₃ radical with *n*-butane (IUPAC, 2007), 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

Chew, A. A., Atkinson, R. and Aschmann, S. M.: J. Chem. Soc. Faraday Trans., 94, 1083, 1998.

IUPAC, : <http://iupac.pole-ether.fr>, 2013.

Langer, S. and Ljungström, E.: J. Chem. Soc. Faraday Trans., 91, 405, 1995.