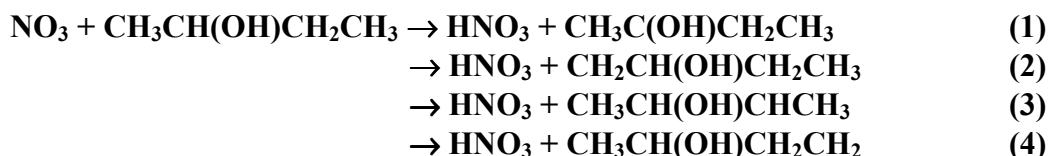


IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet NO₃_VOC22

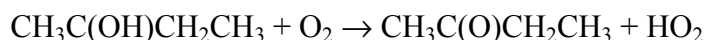
Website: <http://www.iupac-kinetic.ch.cam.ac.uk/>. See website for latest evaluated data. Datasheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission. This datasheet updated: 9th August 2002.

**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, 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) 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 $k(\text{NO}_3 + 2\text{-butanol})/k(\text{NO}_3 + \text{methacrolein})$ 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 $\geq 9.6 \times 10^{13} \text{ molecule cm}^{-3}$. 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 $(0\text{-}4.8) \times 10^{13} \text{ molecule cm}^{-3}$, and decreasing at higher initial NO₂ concentrations. The values of $\{k(\text{NO}_3 + 2\text{-butanol}) \text{ (yield of 2-butanone)} / k(\text{NO}_3 + \text{methacrolein})\}$ 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 0.60 ± 0.07 for experiments with initial NO₂ concentrations of $(0\text{-}4.8) \times 10^{13} \text{ molecule cm}^{-3}$. The observed behavior 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.² The rate coefficient k is obtained from the rate coefficient ratio $k(\text{NO}_3 + 2\text{-butanol})/k(\text{NO}_3 + \text{methacrolein}) = 0.754 \pm 0.065$ at low added NO_2 concentrations, combined with a rate coefficient ratio of $k(\text{NO}_3 + \text{methacrolein}) = 3.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $298 \pm 2 \text{ K}$.^{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 $\{k(\text{NO}_3 + 2\text{-butanol})(\text{yield of 2-butanone})/k_2(\text{NO}_3 + \text{methacrolein})\} = 0.60 \pm 0.07$ and the rate coefficient $k(\text{NO}_3 + \text{methacrolein})$.^{1,3}

Preferred Values

$k = 2.1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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.*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).