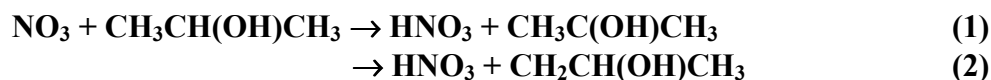


**IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet NO<sub>3</sub>\_VOC21**

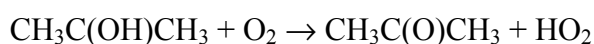
Website: <http://www.iupac-kinetic.ch.cam.ac.uk/>. See website for latest evaluated data. Datasheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission. This datasheet updated: 9<sup>th</sup> August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

**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>			
$\leq 2.3 \times 10^{-15}$	$298 \pm 2$	Wallington <i>et al.</i> , 1987 <sup>1</sup>	FP-A
$1.54 \times 10^{-12} \exp[-(1743 \pm 1009)/T]$	273-364	Langer and Ljungström, 1995 <sup>2</sup>	DF-A
$(3.13 \pm 0.64) \times 10^{-15}$	295		
<i>Relative Rate Coefficients</i>			
$\leq (1.8 \pm 0.2) \times 10^{-15}$	$298 \pm 2$	Chew, Atkinson and Aschmann, 1998 <sup>3</sup>	RR (a)
$k_1 = (1.4 \pm 0.3) \times 10^{-15}$	$298 \pm 2$	Chew, Atkinson and Aschmann, 1998 <sup>3</sup>	RR (a)

**Comments**

- (a) NO<sub>3</sub> radicals were generated by the thermal decomposition of N<sub>2</sub>O<sub>5</sub> 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 NO<sub>2</sub> 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 NO<sub>2</sub> was initially added). The rate coefficient ratios were independent of initial NO<sub>2</sub> concentration in the range  $(0\text{-}4.8) \times 10^{13} \text{ molecule cm}^{-3}$ , but increased for initial NO<sub>2</sub> 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 NO<sub>2</sub> concentrations of  $(0\text{-}4.8) \times 10^{13} \text{ molecule cm}^{-3}$ , decreasing at higher initial NO<sub>2</sub> 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 NO<sub>2</sub> concentration over the entire range studied [ $(0\text{-}2.4) \times 10^{14} \text{ molecule cm}^{-3}$ ], with an average value of  $0.40 \pm 0.06$  for experiments with initial NO<sub>2</sub> 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-propanol with the NO<sub>3</sub> radical and a reaction (gas-phase or heterogeneous) of N<sub>2</sub>O<sub>5</sub> with 2-propanol to form nitrates.<sup>2</sup> 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 NO<sub>2</sub> 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  $298 \pm 2 \text{ K}$ .<sup>3,4</sup> 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  $k(\text{NO}_3 + \text{methacrolein})$ .<sup>3,4</sup>

### Preferred Values

$$k = 1.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_1/k = 1.0 \text{ at } 298 \text{ K.}$$

#### Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(k_1/k) = \pm 0.3 \text{ at } 298 \text{ K.}$$

#### Comments on Preferred Values

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

### References

- <sup>1</sup> T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., *Int. J. Chem. Kinet.* **19**, 243 (1987).
- <sup>2</sup> S. Langer and E. Ljungström, *J. Chem. Soc. Faraday Trans.* **91**, 405 (1995).
- <sup>3</sup> A. A. Chew, R. Atkinson, and S. M. Aschmann, *J. Chem. Soc. Faraday Trans.* **94**, 1083 (1998).
- <sup>4</sup> 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).
- <sup>5</sup> R. Atkinson, *J. Phys. Chem. Ref. Data* **20**, 459 (1991).