

# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO<sub>3</sub>\_VOC27

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 created March 2009.

## NO<sub>3</sub> + 2-Methylpropene → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(3.38 \pm 0.43) \times 10^{-13}$	298	Ravishankara and Mauldin, 1985	F-A (a)
$(3.4 \pm 0.7) \times 10^{-13}$	295 ± 2	Canosa-Mas et al., 1988	DF-A (b)
$(3.3 \pm 0.5) \times 10^{-13}$	298	Rahman et al., 1988	DF-MS
$(3.87 \pm 0.42) \times 10^{-13}$	298	Benter et al., 1992	DF-MS
$(3.6 \pm 0.4) \times 10^{-13}$	298	Wille et al., 1992	DF-MS
<i>Relative Rate Coefficients</i>			
$(1.81 \pm 0.17) \times 10^{-13}$	300	Japar and Niki, 1975	RR (c)
$(3.13 \pm 0.02) \times 10^{-13}$	298 ± 1	Atkinson et al., 1984	RR (d)
$(3.33 \pm 0.51) \times 10^{-13}$	298 ± 2	Barnes et al., 1990	RR (d)

### Comments

- NO<sub>3</sub> radicals generated by the thermal decomposition of N<sub>2</sub>O<sub>5</sub>, and monitored by diode laser absorption at 662 nm.
- Rate coefficients derived from a second-order kinetic treatment of the experimental data.
- NO<sub>3</sub> radicals were generated from the thermal decomposition of N<sub>2</sub>O<sub>5</sub>. The experimental data were relative to the equilibrium coefficient  $K$  for the NO<sub>3</sub> + NO<sub>2</sub> ↔ N<sub>2</sub>O<sub>5</sub> reactions, and are placed on an absolute basis by use of  $K = 2.15 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$  at 300 K (IUPAC, current recommendation).
- NO<sub>3</sub> radicals were generated from the thermal decomposition of N<sub>2</sub>O<sub>5</sub>. The concentrations of 2-methylpropene and *trans*-2-butene (the reference compound) were measured by GC, and rate coefficient ratios of  $k(\text{NO}_3 + 2\text{-methylpropene})/k(\text{NO}_3 + \textit{trans}\text{-2-butene}) = 0.808 \pm 0.005$  (Atkinson et al., 1984) and  $0.86 \pm 0.13$  (Barnes et al., 1990) obtained. These rate coefficient ratios are placed on an absolute basis by use of a rate coefficient of  $k(\text{NO}_3 + \textit{trans}\text{-2-butene}) = 3.87 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (IUPAC, current recommendation).

### Preferred Values

$$k = 3.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

#### Reliability

$$\Delta \log k = \pm 0.10 \text{ at } 298 \text{ K.}$$

#### Comments on Preferred Values

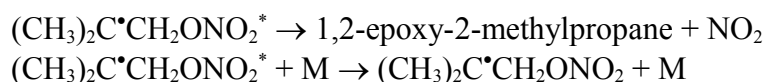
Rate coefficients are only available at room temperature, and the absolute and relative rate coefficients of Atkinson et al. (1984), Ravishankara and Mauldin (1985), Canosa-Mas et al.

(1988), Rahmann et al., (1988), Barnes et al. (1990), Benter et al. (1992) and Wille et al. (1992) are in excellent agreement. The rate coefficient of Japar and Niki (1975) relative to the equilibrium constant for the  $\text{N}_2\text{O}_5 \leftrightarrow \text{NO}_3 + \text{NO}_2$  reactions, which is subject to significant uncertainties, is a factor of  $\sim 2$  lower than the other rate coefficients and is not used in the evaluation of the rate coefficient  $k$ . The preferred value is obtained from an average of the rate coefficients of Atkinson et al. (1984), Ravishankara and Mauldin (1985), Canosa-Mas et al. (1988), Rahmann et al., (1988), Barnes et al. (1990), Benter et al. (1992) and Wille et al. (1992).

The  $\text{NO}_3$  radical reaction with 2-methylpropene proceeds by initial addition,



with the chemically-activated nitrooxyalkyl radicals decomposing to oxirane +  $\text{NO}_2$  in competition with collisional stabilization; for example



Under atmospheric conditions the thermalized nitrooxybutyl radicals react with  $\text{O}_2$  to form the corresponding peroxy radicals  $(\text{CH}_3)_2\text{C}(\text{OO}^*)\text{CH}_2\text{ONO}_2$  and  $(\text{CH}_3)_2\text{C}(\text{ONO}_2)\text{CH}_2\text{OO}^*$ . At atmospheric pressure of air, the observed products and their formation yields are: HCHO, 80% (Barnes et al., 1990) and  $24 \pm 8\%$  (Hjorth et al., 1990); acetone, 85% (Barnes et al., 1990),  $24 \pm 8\%$  (Hjorth et al., 1990), and 88% (Berndt and Böge, 1995);  $(\text{CH}_3)_2\text{CHCHO}$ ,  $\sim 5\%$  (Berndt and Böge, 1995); 1,2-epoxy-2-methylpropane, 7% (Berndt and Böge, 1995); and total nitrates,  $\sim 25\%$  (Barnes et al., 1990). Some of the differences in reported yields are likely due to the experimental conditions and procedures used, with Barnes et al. (1990) and Berndt and Böge (1995) adding NO after the reaction to promote thermal decomposition of peroxy nitrates and concurrently convert peroxy radicals to alkoxy radicals.

## References

- Atkinson, R., Plum, C. N., Carter, W. P. L., Winer, A. M. and Pitts Jr., J. N.: *J. Phys. Chem.*, 88, 1210, 1984.
- Barnes, I., Bastian, V., Becker, K. H. and Tong, Z.: *J. Phys. Chem.*, 94, 2413, 1990.
- Benter, Th., Becker, E., Wille, U., Rahman, M. M. and Schindler, R. N.: *Ber. Bunsenges. Phys. Chem.*, 96, 769, 1992.
- Berndt, T. and Böge, O.: *J. Atmos. Chem.*, 21, 275, 1995.
- Canosa-Mas, C., Smith, S. J., Toby, S. and Wayne, R. P.: *J. Chem. Soc. Faraday Trans. 2*, 84, 247, 1988.
- Hjorth, J., Lohse, C., Nielsen, C. J., Skov, H. and Restelli, G.: *J. Phys. Chem.*, 94, 7494, 1990.
- IUPAC: <http://iupac.pole-ether.fr>, 2013.
- Japar, S. M. and Niki, H.: *J. Phys. Chem.*, 79, 1629, 1975.
- Rahman, M. M., Becker, E., Benter, Th. and Schindler, R. N.: *Ber. Bunsenges. Phys. Chem.*, 92, 91, 1988.
- Ravishankara, A. R. and Mauldin III, R. L.: *J. Phys. Chem.*, 89, 3144, 1985.
- Wille, U., Rahman, M. M. and Schindler, R. N.: *Ber. Bunsenges. Phys. Chem.*, 96, 833, 1992.