

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC30

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NO₃ + *trans*-2-Butene → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(3.78 \pm 0.41) \times 10^{-13}$	298	Raviskankara and Mauldin, 1985	F-A/LIF (a)
$(1.78 \times 10^{-12} \exp[-(530 \pm 100)/T] + (1.28 \times 10^{-14} \exp[(570 \pm 110)/T])$	204-378	Dlugokencky and Howard, 1989	F-LIF (b)
$(3.96 \pm 0.48) \times 10^{-13}$	298		
$(3.88 \pm 0.30) \times 10^{-13}$	298	Benter et al., 1992	DF-MS
$(3.55 \pm 0.33) \times 10^{-13}$	267	Rudich et al., 1996	F-A (b)
$(4.06 \pm 0.36) \times 10^{-13}$	298		
$(3.74 \pm 0.45) \times 10^{-13}$	298 ± 2	Berndt et al., 1998	F-LIF (b)
$(3.78 \pm 0.17) \times 10^{-13}$	298 ± 2	Kasyutich et al., 2002	DF-A (c)
<i>Relative Rate Coefficients</i>			
$(2.31 \pm 0.17) \times 10^{-13}$	300	Japar and Niki, 1975	RR (d)
$(3.09 \pm 0.27) \times 10^{-13}$	298 ± 1	Atkinson et al., 1984	RR (d)

Comments

- (a) NO₃ radicals generated by the thermal decomposition of N₂O₅ and were monitored by LIF at 662 nm, or were generated by the reaction F + HNO₃ and were monitored by long-path absorption at 662 nm.
- (b) NO₃ radicals generated by the thermal decomposition of N₂O₅.
- (c) NO₃ radicals were generated by the reaction F + HNO₃ and were monitored by off-axis cavity-enhanced laser absorption spectroscopy at 662 nm.
- (d) NO₃ radicals were generated from the thermal decomposition of N₂O₅. The experimental data were relative to the equilibrium coefficient K for the NO₃ + NO₂ ↔ N₂O₅ 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 and $2.75 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ at 298 K (IUPAC, current recommendation).

Preferred Values

$k = 3.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = \{1.78 \times 10^{-12} \exp(-530/T) + 1.28 \times 10^{-14} \exp(570/T)\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200-380 K.

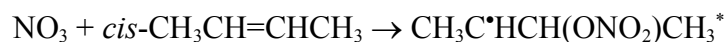
Reliability

$\Delta \log k = \pm 0.08$ over the temperature range 200-380 K.

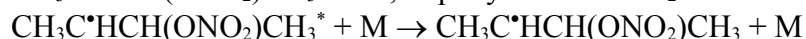
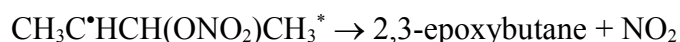
Comments on Preferred Values

The available absolute 298 K rate coefficients are in excellent agreement, as are those of Dlugokencky and Howard (1989) and Rudich et al. (1996) at 267 K. Because of uncertainties in the equilibrium constant for the $\text{N}_2\text{O}_5 \leftrightarrow \text{NO}_3 + \text{NO}_2$ reactions, the data of Japar and Niki (1975) and Atkinson et al. (1984) are not used in the evaluation of the preferred values. The temperature-dependent rate expression of Dlugokencky and Howard (1989) is accepted as the preferred value.

The NO_3 radical reaction with *trans*-2-butene proceeds by initial addition,



with the chemically-activated nitrooxyalkyl radicals decomposing to *cis*- or *trans*-2,3-epoxybutane + NO_2 in competition with collisional stabilization.



Under atmospheric conditions the thermalized nitrooxybutyl radical reacts with O_2 to form the peroxy radical $\text{CH}_3\text{CH}(\text{OO}^*)\text{CH}(\text{ONO}_2)\text{CH}_3$. At atmospheric pressure of air, the observed products and their molar formation yields are: CH_3CHO , 70% (Barnes et al., 1990), $34 \pm 12\%$ (Hjorth et al., 1990) and $\sim 100\%$ (Berndt and Böge, 1995); $\text{CH}_3\text{C}(\text{O})\text{CH}(\text{ONO}_2)\text{CH}_3$, 55% (Barnes et al., 1990), $41 \pm 13\%$ (Hjorth et al., 1990) and 38% (Berndt and Böge, 1995); $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}_3$, $15 \pm 5\%$ (Hjorth et al., 1990); $\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}(\text{ONO}_2)\text{CH}_3$, 4% (Barnes et al., 1990); and 2,3-epoxybutane, $\leq 1\%$ (Skov et al., 1994) and 12% (Berndt and Böge, 1995). Some of these 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

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- Recommendation
- Ravishankara and Mauldin (1985)
- ▼ Dlugokencky and Howard (1989)
- Benter et al. (1992)
- ◆ Rudich et al. (1996)
- ▲ Berndt et al. (1998)
- ◆ Kasyutich et al. (2002)

