

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO₃_VOC28

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This data sheet created March 2009.

NO₃ + 1-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> | | | |
| $2.5 \times 10^{-13} \exp[-(940 \pm 97)/T]$ | 299-473 | Canosa-Mas et al., 1992 | DF-A |
| $(1.1 \pm 0.2) \times 10^{-14}$ | 299 | | |
| $5.2 \times 10^{-13} \exp[-(1067 \pm 31)/T]$ | 232-401 | Rudich et al., 1996 | F-A (a) |
| $(1.4 \pm 0.10) \times 10^{-14}$ | 298 | | |
| $(1.04 \pm 0.11) \times 10^{-14}$ | 298 ± 2 | Berndt et al., 1998 | F-LIF (a) |
| <i>Relative Rate Coefficients</i> | | | |
| $(1.29 \pm 0.14) \times 10^{-14}$ | 300 | Japar and Niki, 1975 | RR (b) |
| $(1.24 \pm 0.02) \times 10^{-14}$ | 298 ± 1 | Atkinson et al., 1984 | RR (c) |
| $(1.24 \pm 0.05) \times 10^{-14}$ | 296 ± 2 | Atkinson et al., 1988 | RR (d) |
| $(1.21 \pm 0.06) \times 10^{-14}$ | 296 ± 1 | Andersson and Ljungström, 1989 | RR (b) |
| $(1.27 \pm 0.19) \times 10^{-14}$ | 298 ± 2 | Barnes et al., 1990 | RR (c) |
| $(1.19 \pm 0.09) \times 10^{-14}$ | 298 ± 2 | Chew et al., 1998 | RR (c) |
| $(1.24 \pm 0.08) \times 10^{-14}$ | 296 ± 2 | Aschmann et al., 2008 | RR (d) |

Comments

- (a) NO₃ radicals generated by the thermal decomposition of N₂O₅.
- (b) 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 $3.53 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ at 296 K (IUPAC, current recommendation).
- (c) NO₃ radicals were generated from the thermal decomposition of N₂O₅. The concentrations of 1-butene and propene (the reference compound) were measured by GC, and rate coefficient ratios of $k(\text{NO}_3 + \text{1-butene})/k(\text{NO}_3 + \text{propene}) = 1.304 \pm 0.012$ (Atkinson et al., 1984), 1.34 ± 0.20 (Barnes et al., 1990) and 1.25 ± 0.09 (Chew et al., 1998) obtained. These rate coefficient ratios are placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{propene}) = 9.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).
- (d) NO₃ radicals were generated by the thermal decomposition of N₂O₅. The concentrations of 1-butene and thiophene (the reference compound) were measured by GC, and rate coefficient ratios of $k(\text{NO}_3 + \text{1-butene})/k(\text{NO}_3 + \text{thiophene}) = 0.315 \pm 0.011$ (Atkinson et al., 1988) and 0.316 ± 0.020 (Aschmann et al., 2008) obtained. These rate coefficient ratios are placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{thiophene}) = 3.93 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (Atkinson, 1991).

Preferred Values

$$k = 1.3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 3.2 \times 10^{-13} \exp(-950/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 230\text{-}480 \text{ K.}$$

Reliability

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

$$\Delta(E/R) = \pm 200 \text{ K.}$$

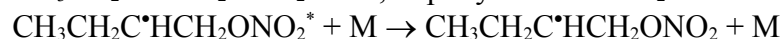
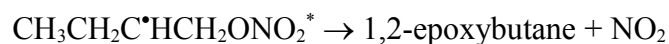
Comments on Preferred Values

The available absolute and relative room temperature rate coefficients are in good agreement. The temperature dependencies measured by Canosa-Mas et al. (1992) and Rudich et al. (1996) are also in good agreement. The preferred values are derived from an un-weighted least-squares analysis of the absolute and relative rate coefficients of Atkinson et al. (1984, 1988), Barnes et al. (1990), Canosa-Mas et al. (1992), Rudich et al. (1996), Berndt et al. (1998), Chew et al. (1998) and Aschmann et al. (2008). 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 Andersson and Ljungström (1989) are not used in the evaluation of the preferred values, although they are in agreement with the preferred value.

The NO_3 radical reaction with 1-butene proceeds by initial addition,



with the chemically-activated nitrooxyalkyl radicals decomposing to 1,2-epoxybutane + NO_2 in competition with collisional stabilization; for example



Under atmospheric conditions the thermalized nitrooxybutyl radicals react with O_2 to form the corresponding 1,2-nitrooxybutylperoxy radicals $\text{CH}_3\text{CH}_2\text{CH}(\text{OO}^*)\text{CH}_2\text{ONO}_2$ and $\text{CH}_3\text{CH}_2\text{CH}(\text{ONO}_2)\text{CH}_2\text{OO}^*$. At atmospheric pressure of air, Barnes et al. (1990) observed HCHO, propanal, and total nitrates with formation yields of 11%, 12% and ~60%, respectively, while Berndt and Böge (1995) observed formation of 1,2-epoxybutane, propanal and $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{ONO}_2$, with yields of 18%, 65% and ~17%, respectively, noting that the yields of Berndt and Böge (1995) are defined as $([\text{product}]/\Sigma[\text{product}])$.

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- Recommendation
- Canosa-Mas et al. (1992)
- ▼ Rudich et al. (1996)
- Berndt et al. (1998)
- ◆ Atkinson et al. (1984)
- ▲ Atkinson et al. (1988)
- Aschmann et al. (2008)
- ◆ Barnes et al. (1990)
- Chew et al. (1998)

