

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO₃_VOC18

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This data sheet updated: 10th December 2007 (with no revision of the preferred values).

NO₃ + Pinonaldehyde → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Relative Rate Coefficients</i>			
$(2.40 \pm 0.38) \times 10^{-14}$	299 ± 2	Hallquist et al., 1997	RR (a)
$(6.0 \pm 2.0) \times 10^{-14}$	300 ± 5	Gladius et al., 1997	RR (b)
$(1.99 \pm 0.52) \times 10^{-14}$	296 ± 2	Alvarado et al., 1998	RR (c,d)
$(2.16 \pm 0.53) \times 10^{-14}$	296 ± 2	Alvarado et al., 1998	RR (c,e)
$(1.93 \pm 0.44) \times 10^{-14}$	296 ± 2	Alvarado et al., 1998	RR (c,f)

Comments

- (a) NO₃ radicals were generated by the thermal decomposition of N₂O₅ in N₂O₅-pinonaldehyde-propene (the reference compound)-air mixtures at 1013 ± 5 mbar pressure. The concentrations of pinonaldehyde and propene were measured by FTIR spectroscopy. Dark decays of pinonaldehyde in the 153 L chamber used were observed, and taken into account in the data analysis. The measured rate coefficient ratio $k(\text{NO}_3 + \text{pinonaldehyde})/k(\text{NO}_3 + \text{propene})$ is 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).
- (b) NO₃ radicals were generated by the thermal decomposition of N₂O₅ in N₂O₅-pinonaldehyde-1-butene (the reference compound)-air mixtures at 987 ± 7 mbar pressure. The concentrations of pinonaldehyde and 1-butene were measured by FTIR spectroscopy. Dark decays of pinonaldehyde in the 480 L chamber used were observed, and taken into account in the data analysis. The measured rate coefficient ratio $k(\text{NO}_3 + \text{pinonaldehyde})/k(\text{NO}_3 + 1\text{-butene})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + 1\text{-butene}) = 1.38 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K (Atkinson and Arey, 2003).
- (c) NO₃ radicals were generated by the thermal decomposition of N₂O₅ in N₂O₅-pinonaldehyde-reference compound (propene, 1-butene or thiophene)-air mixtures at 987 mbar pressure. The concentrations of pinonaldehyde, propene, 1-butene and thiophene were measured by GC. No dark decays of pinonaldehyde (<5%) were observed in the 7000 L Teflon chamber used. The measured rate coefficient ratios $k(\text{NO}_3 + \text{pinonaldehyde})/k(\text{NO}_3 + \text{propene}) = 2.09 \pm 0.54$, $k(\text{NO}_3 + \text{pinonaldehyde})/k(\text{NO}_3 + 1\text{-butene}) = 1.64 \pm 0.40$ and $k(\text{NO}_3 + \text{pinonaldehyde})/k(\text{NO}_3 + \text{thiophene}) = 0.49 \pm 0.11$ are placed on an absolute basis by use of rate coefficients at 296 K of $k(\text{NO}_3 + \text{propene}) = 9.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation), $k(\text{NO}_3 + 1\text{-butene}) = 1.32 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003) and $k(\text{NO}_3 + \text{thiophene}) = 3.93 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1991).
- (d) Relative to $k(\text{NO}_3 + \text{propene})$.
- (e) Relative to $k(\text{NO}_3 + 1\text{-butene})$.
- (f) Relative to $k(\text{NO}_3 + \text{thiophene})$.

Preferred Values

$$k = 2.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.25 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

Pinonaldehyde is a low volatility product of the atmospheric reactions of α -pinene which is prone to wall losses, making measurement of its reaction rate coefficients difficult. The available rate coefficients are all from relative rate studies carried out at room temperature, and range over a factor of ~ 3 (Hallquist et al., 1997; Glasius et al., 1997; Alvarado et al., 1998). The rate coefficient measured by Glasius et al. (1997) is a factor of ~ 2.5 -3 higher than those of Hallquist et al. (1997) and Alvarado et al. (1998), possibly because of unresolved wall adsorption problems. The preferred values are based on the study of Alvarado et al. (1998) carried out in a large volume Teflon chamber in which no wall losses of pinonaldehyde were observed.

References

- Alvarado, A., Arey, J. and Atkinson, R.: J. Atmos. Chem., 31, 281, 1998.
Atkinson, R.: J. Phys. Chem. Ref. Data, 20, 459, 1991.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Glasius, M., Calogirou, A., Jensen, N. R., Hjorth, J. and Nielsen, C. J.: Int. J. Chem. Kinet., 29, 527, 1997.
Hallquist, M., Wängberg, I. and Ljungström, E.: Environ. Sci. Technol., 31, 3166, 1997.
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