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

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

NO_3 + Pinonaldehyde → products

Rate coefficient data

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

Comments

(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in N_2O_5-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 $k(NO_3 + \text{pinonaldehyde})/k(NO_3 + \text{propene})$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + \text{propene}) = 9.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

(b) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in N_2O_5-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 $k(NO_3 + \text{pinonaldehyde})/k(NO_3 + \text{1-butene})$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + \text{1-butene}) = 1.38 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 300 K (Atkinson and Arey, 2003).

(c) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in N_2O_5-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 $k(NO_3 + \text{pinonaldehyde})/k(NO_3 + \text{propene}) = 2.09 \pm 0.54$, $k(NO_3 + \text{pinonaldehyde})/k(NO_3 + \text{1-butene}) = 1.64 \pm 0.40$ and $k(NO_3 + \text{pinonaldehyde})/k(NO_3 + \text{thiophene}) = 0.49 \pm 0.11$ are placed on an absolute basis by use of rate coefficients at 296 K of $k(NO_3 + \text{propene}) = 9.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation), $k(NO_3 + \text{1-butene}) = 1.32 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003) and $k(NO_3 + \text{thiophene}) = 3.93 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} (Atkinson, 1991).

(d) Relative to $k(NO_3 + \text{propene})$.

(e) Relative to $k(NO_3 + \text{1-butene})$.

(f) Relative to $k(NO_3 + \text{thiophene})$.

Preferred Values

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

Reliability

$\Delta \log k = \pm 0.25$ at 298 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

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