

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx80

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NO₃ + C₂HCl₃ → products

Rate coefficient data

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
4.0 x 10 ⁻¹³ exp (-2030/ <i>T</i>)	278-368	Noremsaune et al., 1997	DF-Vis (a)
(4.43 ± 0.32) x 10 ⁻¹⁶	295		
<i>Relative Rate Coefficients</i>			
(2.9 ± 0.2) x 10 ⁻¹⁶	298	Atkinson et al., 1987	RR (b)
(3.8 ± 0.4) x 10 ⁻¹⁶	298	Noremsaune et al., 1997	RR (c)
(4.7 ± 1.1) x 10 ⁻¹⁶	298	Noremsaune et al., 1997	RR (d)
(3.6 ± 0.9) x 10 ⁻¹⁶	298	Chew et al., 1998	RR (e)

Comments

- NO₃ was generated by F + HNO₃ and detected by optical absorption in a multi-pass cell. Experiments conducted under pseudo-first order conditions.
- The relative decay rates of C₂HCl₃ and C₂H₄ were monitored in N₂O₅-NO₂-organic-air mixtures at one atmosphere total pressure of air to obtain: $k(\text{NO}_3 + \text{C}_2\text{HCl}_3)/k(\text{NO}_3 + \text{C}_2\text{H}_4) = (1.37 \pm 0.08)$. This rate coefficient ratio was placed on an absolute basis using $k(\text{NO}_3 + \text{C}_2\text{H}_4) = 2.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).
- NO₃ was formed in the thermal decomposition of N₂O₅ in mixtures containing C₂HCl₃ and ethene as reference reactant at total pressures of 1013 mbar N₂. The addition of ethane as Cl atom scavenger had no effect. $k(\text{NO}_3 + \text{C}_2\text{HCl}_3)/k(\text{NO}_3 + \text{C}_2\text{H}_4)$ was measured to be (1.79 ± 0.18). This was placed on an absolute basis using $k(\text{NO}_3 + \text{C}_2\text{H}_4) = 2.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).
- NO₃ was formed in the thermal decomposition of N₂O₅ in mixtures containing C₂HCl₃ and C₂H₃Cl as reference reactant at total pressures of 1013 mbar N₂. Addition of ethane as Cl atom scavenger had no effect. $k(\text{NO}_3 + \text{C}_2\text{HCl}_3)/k(\text{NO}_3 + \text{C}_2\text{H}_3\text{Cl})$ was measured to be (1.3 ± 0.04). This was placed on an absolute basis using $k(\text{NO}_3 + \text{C}_2\text{H}_3\text{Cl}) = (3.7 \pm 0.8) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Noremsaune et al., 1997).
- NO₃ was formed in the thermal decomposition of N₂O₅ in mixtures containing C₂HCl₃ and 2,3-dimethylbutane as reference reactant at total pressures of 990 mbar air. Depletion of reactants was monitored by GC-FID. Addition of ethane as Cl and OH atom scavenger. $k(\text{NO}_3 + \text{C}_2\text{HCl}_3)/k(\text{NO}_3 + 2,3\text{-dimethylbutane})$ was measured to be (0.82 ± 0.21). This was placed on an absolute basis using $k(\text{NO}_3 + 2,3\text{-dimethylbutane}) = 4.39 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

$k = 3.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 3.2 \times 10^{-13} \exp(-2030/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270-370 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred value is derived from the relative rate coefficients measured by Atkinson et al. (1987), and Noremsaune et al. (1997) determined relative to ethene, and Chew et al. (1998) relative to 2,3-dimethylbutane. The temperature dependence is based on the result of Noremsaune et al. (1997), the only measurement over a range of temperatures. Their A-factor has been modified to reproduce the recommended rate constant at 298 K. There are several product channels open, resulting in formation of trichloroepoxyethane, dichloroacetylchloride, chloroformyl and carbonylchloride (Noremsaune et al., (1995), Perez-Casany et al., (2000)).

References

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Chew, A. A., Atkinson, R. and Aschmann, S. M.: *J. Chem. Soc. Faraday Trans.*, 94, 1083, 1998.

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