

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO₃_VOC7

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This data sheet updated: 29th October 2007 (with no revisions of the preferred values).

NO₃ + *n*-C₄H₁₀ → products

Rate coefficient data

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
≤2 x 10 ⁻¹⁷	298 ± 2	Wallington et al., 1986	FP-A (a)
(4.5 ± 0.6) x 10 ⁻¹⁷	298	Bagley et al., 1990	DF-A
(1.44 ± 0.12) x 10 ⁻¹⁶	333		
(4.6 ± 1.2) x 10 ⁻¹⁶	373		
(1.12 ± 0.12) x 10 ⁻¹⁵	423		
(3.2 ± 0.3) x 10 ⁻¹⁵	473		
(9.0 ± 0.4) x 10 ⁻¹⁵	523		
<i>Relative Rate Coefficients</i>			
(6.6 ± 1.7) x 10 ⁻¹⁷	296 ± 2	Atkinson et al., 1984	RR (b)

Comments

- (a) NO₃ radicals were generated by the flash photolysis of ClONO₂ at wavelengths >180 nm and monitored by optical absorption at 662 nm.
- (b) NO₃ radicals were produced by the thermal decomposition of N₂O₅, and the concentrations of *n*-butane and *n*-heptane (the reference organic) were measured by GC. A rate coefficient ratio of $k(\text{NO}_3 + n\text{-butane})/k(\text{NO}_3 + n\text{-heptane}) = 0.48 \pm 0.12$ was obtained and is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + n\text{-heptane}) = 1.37 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (Atkinson, 1991).

Preferred Values

$k = 4.6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.8 \times 10^{-12} \exp(-3280/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 290-430 K.

Reliability

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

$\Delta \log(E/R) = \pm 400$ K.

Comments on Preferred Values

The preferred values are based on the absolute rate coefficients measured by Bagley et al. (1990) over the temperature range 298-423 K (at temperatures above 423 K the Arrhenius plot exhibits upward curvature, especially above 473 K). A least-squares analysis of the 298-423 K rate coefficients of Bagley et al. (1990) results in the preferred Arrhenius expression. The

preferred rate coefficient at 298 K is at least a factor of 2 higher than the upper limit reported by Wallington et al. (1986), but is in agreement within the measurement uncertainties with the relative rate coefficient of Atkinson et al. (1984). At room temperature and below the reaction proceeds mainly by H-atom abstraction from the CH₂ groups (Bagley et al., 1990; Atkinson, 1991).

References

- Atkinson, R.: J. Phys. Chem. Ref. Data, 20, 459, 1991.
Atkinson, R., Plum, C. N., Carter, W. P. L., Winer, A. M. and Pitts Jr., J. N.: J. Phys. Chem., 88, 2361, 1984.
Bagley, J. A., Canosa-Mas, C., Little, M. R., Parr, A. D., Smith, S. J., Waygood, S. J. and Wayne, R. P.: J. Chem. Soc. Faraday Trans., 86, 2109, 1990.
Wallington, T. J., Atkinson, R., Winer, A. M. and Pitts Jr., J. N.: J. Phys. Chem., 90, 4640, 1986.