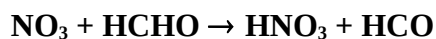


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO<sub>3</sub>\_VOC10

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet updated: 18<sup>th</sup> October 2007 (with revision of the preferred values).



$$\Delta H^\circ = -57.1 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(5.8 \pm 0.4) \times 10^{-16}$	$300 \pm 1$	Cantrell et al., 1985	(a)
$(5.2 \pm 0.9) \times 10^{-16}$	$298 \pm 2$	Doussin et al., 2003	(b)
<i>Relative Rate Coefficients</i>			
$(4.75 \pm 0.39) \times 10^{-16}$	$298 \pm 1$	Atkinson et al., 1984	(c,d)
$(7.2 \pm 1.1) \times 10^{-16}$	$298 \pm 2$	Cantrell et al., 1985	(d,e)
$(1.15 \pm 0.24) \times 10^{-15}$	$295 \pm 2$	Hjorth et al., 1988	(c,d,e,f)

### Comments

- (a) NO<sub>3</sub> radicals were generated *in situ* from the reaction NO<sub>2</sub> + O<sub>3</sub> → NO<sub>3</sub> + O<sub>2</sub>. NO<sub>3</sub> radical concentrations were measured by differential optical absorption spectroscopy (DOAS), and the rate coefficient derived from the concentrations of reactants and products measured by FTIR absorption spectroscopy and by DOAS (for the NO<sub>3</sub> radical and NO<sub>2</sub>). The cited error is two standard deviations of the four measurements of the rate coefficient using this experimental technique.
- (b) NO<sub>3</sub> radicals were generated *in situ* from the reaction NO<sub>2</sub> + O<sub>3</sub> → NO<sub>3</sub> + O<sub>2</sub>, in the presence of CH<sub>3</sub>CHO. NO<sub>3</sub> radical concentrations were measured by optical absorption at 662 nm, and the rate coefficient derived from the concentrations of reactants and products measured by FTIR absorption spectroscopy and (for the NO<sub>3</sub> radical) optical absorption using computer modeling.
- (c) NO<sub>3</sub> radicals were generated by the thermal decomposition of N<sub>2</sub>O<sub>5</sub>.
- (d) Relative to the equilibrium coefficient *K* for the reactions NO<sub>2</sub> + NO<sub>3</sub> ↔ N<sub>2</sub>O<sub>5</sub>. The experimental data are placed on an absolute basis by use of an equilibrium coefficient of *K* = 2.75 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> at 298 K and 4.01 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> at 295 K (IUPAC, current recommendation).
- (e) NO<sub>3</sub> radicals were generated *in situ* from the reaction NO<sub>2</sub> + O<sub>3</sub> → NO<sub>3</sub> + O<sub>2</sub>.
- (f) Note that while the equilibrium coefficient used in the data analysis of Hjorth et al. (1988) was stated to be from Graham and Johnston (1978) (3.43 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> at 295 K), the value used (Hjorth et al., 1988) was 1.88 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup>.

### Preferred Values

$$k = 5.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

*Reliability*

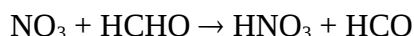
$\Delta \log k = \pm 0.20$  at 298 K.

#### *Comments on Preferred Values*

The relative rate coefficients measured by Atkinson et al. (1984), Cantrell et al. (1985) and Hjorth et al. (1988) disagree by up to a factor of 2.4 when a consistent temperature-dependent equilibrium coefficient for the  $\text{NO}_2 + \text{NO}_3 \leftrightarrow \text{N}_2\text{O}_5$  reactions is used to place the rate coefficients on an absolute basis. The rate coefficients obtained by Cantrell et al. (1985) and Doussin et al. (2003) from experiments in which  $\text{NO}_3$  radicals were measured directly by optical absorption (and hence derivation of the rate coefficient does not involve the equilibrium coefficient for the  $\text{NO}_2 + \text{NO}_3 \leftrightarrow \text{N}_2\text{O}_5$  reactions) fall within the range of the relative rate coefficients of Atkinson et al. (1984) and Cantrell et al. (1985).

Accordingly, the preferred value of  $k = 5.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K is based on the absolute rate measurements of Cantrell et al. (1985) and Doussin et al. (2003). While no temperature dependence of the rate coefficient has been measured to date, by analogy with the  $\text{NO}_3$  radical reaction with  $\text{CH}_3\text{CHO}$  a pre-exponential factor of  $\sim 2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is expected, and hence  $k(\text{NO}_3 + \text{HCHO}) \sim 2 \times 10^{-12} \exp(-2440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

D and  $^{18}\text{O}$  isotope effects have been measured by D'Anna et al. (2003) and Fielberg et al. (2004). This reaction proceeds by H-atom abstraction.



#### **References**

- Atkinson, R., Plum, C. N., Carter, W. P. L., Winer, A. M. and Pitts Jr., J. N.: *J. Phys. Chem.* 88, 1210, 1984.
- Cantrell, C. A., Stockwell, W. R., Anderson, L. G., Busarow, K. L., Perner, D., Schmeltekopf, A., Calvert, J. G. and Johnston, H. S.: *J. Phys. Chem.* 89, 139, 1985.
- D'Anna, B., Bakken, V., Beukes, J. A., Nielsen, C. J., Brudnik, K. and Jodkowski, J. T.: *Phys. Chem. Chem. phys.* 5, 1790, 2003.
- Doussin, J. F., Picquet-Varrault, B., Durand-Jolibois, R., Loirat, H. and Carlier, P.: *J. Photochem. Photobiol. A: Chem.* 157, 283, 2003.
- Fielberg, K. L., Johnson, M. S. and Nielsen, C. J.: *J. Phys. Chem. A* 108, 7393, 2004.
- Graham, R. A. and Johnston, H. S.: *J. Phys. Chem.* 82, 254, 1978.
- Hjorth, J., Ottobriini, G. and Restelli, G.: *J. Phys. Chem.* 92, 2669, 1988.
- IUPAC, <http://iupac.pole-ether.fr>, 2013.