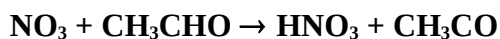


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO<sub>3</sub>\_VOC11

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 no revisions to the preferred values).



$$\Delta H^\circ = -53.0 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.44 \times 10^{-12} \exp[-(1860 \pm 300)/T]$ $(2.74 \pm 0.33) \times 10^{-15}$	264-374 298	Dlugokencky and Howard, 1989	F-LIF (a)
$6.2 \times 10^{-11} \exp[-(2826 \pm 866)/T]$ $(3.2 \pm 0.8) \times 10^{-15}$	298-433 298 ± 2	Cabañas et al., 2001	DF-LIF (b)
$(2.1 \pm 0.7) \times 10^{-15}$	298 ± 2	Doussin et al., 2003	(c)
$(2.6 \pm 0.5) \times 10^{-15}$	300 ± 3	Bossmeyer et al., 2006	DOAS/GC (d)
<i>Relative Rate Coefficients</i>			
$(2.06 \pm 0.52) \times 10^{-15}$	300	Morris and Niki, 1974	RR (e)
$(1.97 \pm 0.42) \times 10^{-15}$	298 ± 1	Atkinson et al., 1984	RR (e)
$(2.55 \pm 0.49) \times 10^{-15}$	299 ± 1	Cantrell et al., 1986	RR (e)
$(2.62 \pm 0.29) \times 10^{-15}$	298 ± 2	D'Anna et al., 2001a,b	RR (f)

### Comments

- NO<sub>3</sub> radicals were generated by the thermal dissociation of N<sub>2</sub>O<sub>5</sub> in a flow system. Initial NO<sub>3</sub> radical concentrations were  $(0.6\text{-}3.0) \times 10^{10} \text{ molecule cm}^{-3}$ .
- Initial NO<sub>3</sub> radical concentrations were  $(0.6\text{-}3.0) \times 10^{12} \text{ molecule cm}^{-3}$ .
- NO<sub>3</sub> radicals were generated *in situ* from the reaction  $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$ , 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.
- Carried out in the EUPHORE chamber at atmospheric pressure of air. NO<sub>3</sub> radical concentrations measured by DOAS, and CH<sub>3</sub>CHO concentrations by GC.
- The cited rate coefficients are relative to the equilibrium coefficient  $K$  for the reactions  $\text{NO}_2 + \text{NO}_3 \leftrightarrow \text{N}_2\text{O}_5$ , with values of  $K = 2.75 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$  at 298 K,  $2.43 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$  at 299 K and  $2.15 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$  at 300 K (IUPAC, current evaluation) being used to place the measured rate coefficient ratios on an absolute basis.
- NO<sub>3</sub> radicals were generated by the thermal dissociation of N<sub>2</sub>O<sub>5</sub>. Experiments were carried out in 1 atmosphere of air with measurements of acetaldehyde and 1-butene (the reference compound) by FTIR spectroscopy. The measured rate coefficient ratio  $k(\text{NO}_3 + \text{acetaldehyde})/k(\text{NO}_3 + 1\text{-butene}) = 0.194 \pm 0.021$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{NO}_3 + 1\text{-butene}) =$

$1.35 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (Atkinson, 1997). Experiments with acetaldehyde- $d_1$  ( $\text{CH}_3\text{CDO}$ ) yielded a rate coefficient ratio  $k(\text{NO}_3 + \text{CH}_3\text{CHO})/k(\text{NO}_3 + \text{CH}_3\text{CDO}) = 2.37 \pm 0.08$  at  $298 \pm 2 \text{ K}$  (D'Anna et al., 2001a).

### Preferred Values

$k = 2.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.4 \times 10^{-12} \exp(-1860/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 260-380 K.

#### Reliability

$\Delta \log k = \pm 0.15$  at 298 K.

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

#### Comments on Preferred Values

The rate coefficients measured relative to the equilibrium coefficient for the reactions  $\text{NO}_2 + \text{NO}_3 \leftrightarrow \text{N}_2\text{O}_5$  are subject to significant uncertainties arising from uncertainties in the equilibrium coefficient for these reactions. The relative rate coefficients of Morris and Niki (1974), Atkinson et al. (1984) and Cantrell et al. (1986) are therefore not used in the evaluation of the rate coefficient for this reaction, although they are in agreement with the absolute room temperature rate coefficients of Dlugokencky and Howard (1989), Doussin et al. (2003) and Bossmeyer et al. (2006). The room temperature rate coefficient of D'Anna et al. (2001a,b), determined relative to that for the reaction of  $\text{NO}_3$  radicals with 1-butene is in (1989), is in excellent agreement with the absolute rate coefficient measured by Dlugokencky and Howard (1989), as are the recent absolute rate coefficients obtained by Doussin et al. (2003) and Bossmeyer et al. (2006) from simultaneous measurements of  $\text{NO}_3$  radical and  $\text{CH}_3\text{CHO}$  concentrations in environmental chambers. The absolute study of Cabañas et al. (2001) employed much higher initial  $\text{NO}_3$  radical concentrations than did Dlugokencky and Howard (1989), by a factor of  $\sim 100$ , and the measured rate coefficients of Cabañas et al. (2001) are significantly less precise and show a significantly higher temperature dependence. The preferred 298 K values is based on the room temperature rate coefficients of Dlugokencky and Howard (1989), D'Anna et al. (2001a,b), Doussin et al. (2003) and Bossmeyer et al. (2006), noting that the rate coefficient of Doussin et al. (2003) has a high associated uncertainty. The temperature dependence is that of Dlugokencky and Howard (1989), with the A-factor being adjusted to fit the 298 K preferred value.

D'Anna et al. (2001a, 2003) measured deuterium isotope effects at  $298 \pm 2 \text{ K}$  of  $k(\text{NO}_3 + \text{CH}_3\text{CHO})/k(\text{NO}_3 + \text{CD}_3\text{CHO}) = 1.19 \pm 0.11$  (D'Anna et al., 2003),  $k(\text{NO}_3 + \text{CH}_3\text{CHO})/k(\text{NO}_3 + \text{CH}_3\text{CDO}) = 2.37 \pm 0.08$  (D'Anna et al., 2001a) and  $k(\text{NO}_3 + \text{CH}_3\text{CHO})/k(\text{NO}_3 + \text{CD}_3\text{CDO}) = 2.51 \pm 0.09$  (D'Anna et al., 2003), indicates that, as expected, the reaction proceeds by H- (or D-) atom abstraction from the  $-\text{CHO}$  (or  $-\text{CDO}$ ) group.

### References

- Atkinson, R.: J. Phys. Chem. Ref. Data 26, 215, 1997.  
Atkinson, R., Plum, C. N., Carter, W. P. L., Winer, A. M. and Pitts Jr., J. N.: J. Phys. Chem. 88, 1210, 1984.  
Bossmeyer, J., Brauers, T., Richter, C., Rohrer, F., Wegener, R. and Wahner, A.: Geophys. Res. Lett. 33, L18810, doi: 10.1029/2006GL026778, 2006.  
Cabañas, B., Martín, P., Salgado, S., Ballesteros, B. and Martínez, E.: J. Atmos. Chem. 40, 23, 2001.  
Cantrell, C. A., Davidson, J. A., Busarow, K. L., and Calvert, J. G.: J. Geophys. Res. 91, 5347, 1986.  
D'Anna, B., Langer, S., Ljungström, E., Nielsen, C. J. and Ullerstam, M.: Phys. Chem. Chem. Phys. 3, 1631, 2001a.

D'Anna, B., Andresen, Ø., Gefen, Z. and Nielsen, C. J.: Phys. Chem. Chem. Phys. 3, 3057, 2001b.  
D'Anna, B., Bakken, V., Beukes, J. A., Nielsen, C. J., Brudnik, K. and Jodkowski, J. T.: Phys. Chem. Chem. Phys. 5, 1790, 2003.  
Dlugokencky, E. J. and Howard, C. J.: J. Phys. Chem. 93, 1091, 1989.  
Doussin, J. F., Picquet-Varrault, B., Durand-Jolibois, R., Loirat, H. and Carlier, P.: J. Photochem. Photobiol. A: Chem. 157, 283, 2003.  
IUPAC, <http://iupac.pole-ether.fr>, 2013.  
Morris Jr., E. D. and Niki, H.: J. Phys. Chem. 78, 1337, 1974.