IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_AROM3

This data sheet last evaluated September 2008; last change in preferred values September 2008.

NO_3 + *m*-$CH_3C_6H_4OH$ (*m*-cresol) → $CH_3C_6H_4O$ + HNO_3 (1)
→ other products (2)

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(8.10 \pm 1.16) \times 10^{-12}$	300 ± 1	Carter et al., 1981	RR (a)
$(1.66 \pm 0.18) \times 10^{-11}$	298 ± 1	Atkinson et al., 1984	RR (b)
$\sim 1.33 \times 10^{-11}$	298 ± 1	Atkinson et al., 1984	RR (c)
$(9.74 \pm 0.47) \times 10^{-12}$	296 ± 2	Atkinson et al., 1992	RR (d)

Comments

(a) NO_3 radicals were generated from the reaction of O_3 with NO_2 in the presence of *m*-cresol and 2-methyl-2-butene (the reference compound) at atmospheric pressure of air. The contribution of the O_3 reaction was taken into account in estimating the amount of 2-methyl-2-butene reacted with NO_3 radicals. The concentrations of *m*-cresol and 2-methyl-2-butene were monitored by GC. The derived rate coefficient ratio is placed on an absolute basis using a rate coefficient of $k(NO_3$ + 2-methyl-2-butene) = 9.37×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(b) NO_3 radicals were generated from the thermal decomposition of N_2O_5 in the presence of *m*-cresol and phenol (the reference compound) at atmospheric pressure of air. The concentrations of *m*-cresol and phenol were monitored by FTIR spectroscopy. The measured rate coefficient ratio of $k(NO_3$ + *m*-cresol)/$k(NO_3$ + phenol) = 4.36 ± 0.46 is placed on an absolute basis using a rate coefficient of $k(NO_3$ + phenol) = 3.8×10^{-12} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(c) NO_3 radicals were generated from the thermal decomposition of N_2O_5 at atmospheric pressure of air. The concentrations of *m*-cresol, N_2O_5 and NO_2 were monitored by FTIR spectroscopy. The rate coefficient for NO_3 + *m*-cresol was measured relative to the equilibrium coefficient K for the reactions $NO_2 + NO_3 \leftrightarrow N_2O_5$. The experimental data are placed on an absolute basis by use of an equilibrium coefficient of K = 2.75 x 10^{-11} cm^3 molecule^{-1} at 298 K (IUPAC, current recommendation). Evidence for secondary reactions removing *m*-cresol observed.

(d) NO_3 radicals were generated from the thermal decomposition of N_2O_5 in the presence of *m*-cresol and 2-methyl-2-butene (the reference compound) at atmospheric pressure of air. The concentrations of *m*-cresol and 2-methyl-2-butene were monitored by GC. The measured rate coefficient ratio of $k(NO_3$ + *m*-cresol)/$k(NO_3$ + 2-methyl-2-butene) = 1.04 ± 0.05 is placed on an absolute basis using a rate coefficient of $k(NO_3$ + 2-methyl-2-butene) = 9.37×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

Preferred Values

$k = 1.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

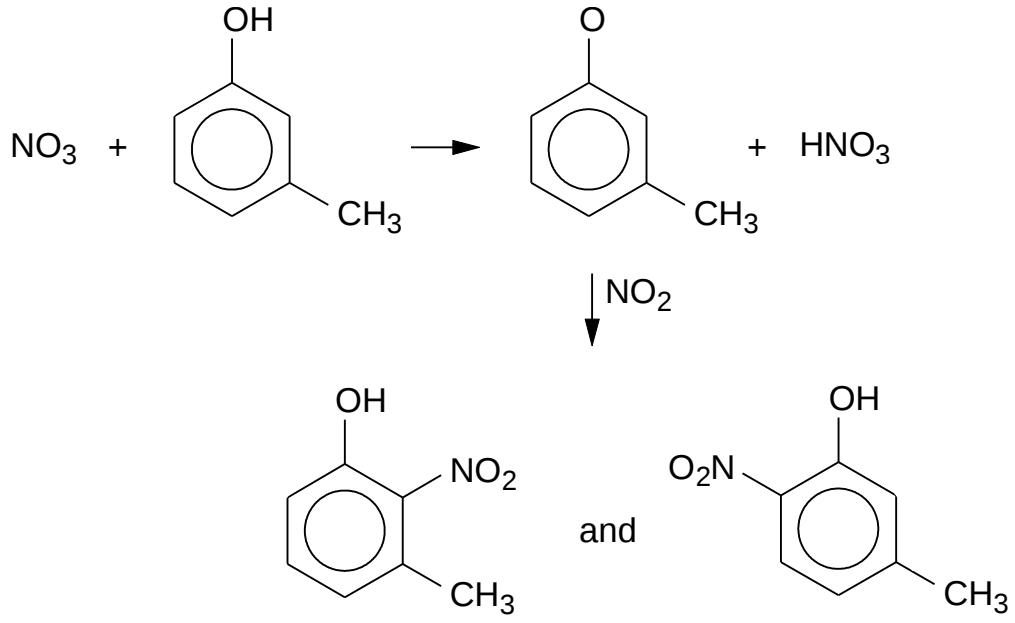
Reliability

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

Comments on Preferred Values

The reported rate coefficients are all from relative rate studies conducted at room temperature, and range over a factor of 2. The rate coefficient of Carter et al. (1981) and that of Atkinson et al. (1984) relative to the equilibrium constant for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions are subject to significant uncertainties because of the concurrent reaction of O_3 with 2-methyl-2-butene in the Carter et al. (1981) study and the uncertainties in the equilibrium constant for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions in the Atkinson et al. (1984) study. The rate coefficient measured by Atkinson et al. (1984) relative to NO_3 + phenol is a factor of 1.7 higher than that of Atkinson et al. (1992), possibly due to difficulties in determining the small amounts of phenol reacted (Atkinson et al., 1984). The preferred value is based on the study of Atkinson et al. (1992) in which the rate coefficient was measured relative to that for NO_3 +-methyl-2-butene (a fairly reliably known rate coefficient) and used the thermal decomposition of N_2O_5 to generate NO_3 radicals. The approximate (and potentially upper limit) rate coefficient of Atkinson et al. (1984) measured relative to the equilibrium constant for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions is in reasonable agreement with the preferred value, as is that of Carter et al. (1981).

Atkinson et al. (1992) observed the formation of 3-methyl-2-nitrophenol and 5-methyl-2-nitrophenol in 16.8 ± 2.9% and 19.6 ± 3.6% yields, respectively. 3- and 5-Methyl-2-nitrophenol formation is believed to arise from methylphenoxy + NO_2, and the measured 3- and 5-methyl-2-nitrophenol yields of Atkinson et al. (1992) therefore suggest that channel (1) accounts for at least 36 ± 5% of the overall reaction.



References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.

Atkinson, R., Aschmann, S. M., Arey, J.: Environ. Sci. Technol., 26, 1397, 1992.

Atkinson, R., Carter, W. P. L., Plum, C. N., Winer, A. M. and Pitts Jr., J. N.: Int. J. Chem. Kinet., 16, 887, 1984.

Carter, W. P. L., Winer, A. M. and Pitts Jr., J. N.: Environ. Sci. Technol., 15, 829, 1981.
IUPAC: http://iupac.pole-ether.fr (2013).