IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_AROM6

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

$NO_3 + C_6H_5OH$ (Phenol) $\rightarrow C_6H_5O + HNO_3$ (1)
$\rightarrow$ 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			
$(2.61 \pm 0.53) \times 10^{-12}$	300 ± 1	Carter et al., 1981	RR (a)
$(3.64 \pm 0.14) \times 10^{-12}$	294	Atkinson et al., 1984	RR (b)
$(4.78 \pm 0.52) \times 10^{-12}$	298 ± 1	Atkinson et al., 1984	RR (c)
$(3.92 \pm 0.25) \times 10^{-12}$	296 ± 2	Atkinson et al., 1992	RR (b)
$(5.81 \pm 1.13) \times 10^{-12}$	295 ± 2	Bolzacchini et al., 2001	RR (b)

Comments

(a) NO_3 radicals were generated from the reaction of O_3 with NO_2 in the presence of phenol and *cis*-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 *cis*-2-butene reacted with NO_3 radicals. The concentrations of phenol and *cis*-2-butene were monitored by GC. The derived rate coefficient ratio is placed on an absolute basis using a rate coefficient of $k(NO_3 + cis\text{-2-butene}) = 3.52 \times 10^{-13}$ 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 phenol and 2-methyl-2-butene (the reference compound) at atmospheric pressure of air. The concentrations of phenol and 2-methyl-2-butene were monitored by GC. The measured rate coefficient ratios of $k(NO_3 + \text{phenol})/k(NO_3 + \text{2-methyl-2-butene}) = 0.389 \pm 0.014$ (Atkinson et al., 1984), 0.418 ± 0.026 (Atkinson et al., 1992) and 0.62 ± 0.12 (Bolzacchini et al., 2001) are placed on an absolute basis using a rate coefficient of $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(c) NO_3 radicals were generated from the thermal decomposition of N_2O_5 at atmospheric pressure of air. The concentrations of phenol, N_2O_5 and NO_2 were monitored by FTIR spectroscopy. The rate coefficient for NO_3 + phenol 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 $K = 2.75 \times 10^{-11}$ cm^3 molecule^{-1} at 298 K (IUPAC, current recommendation).

Preferred Values

$k = 3.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

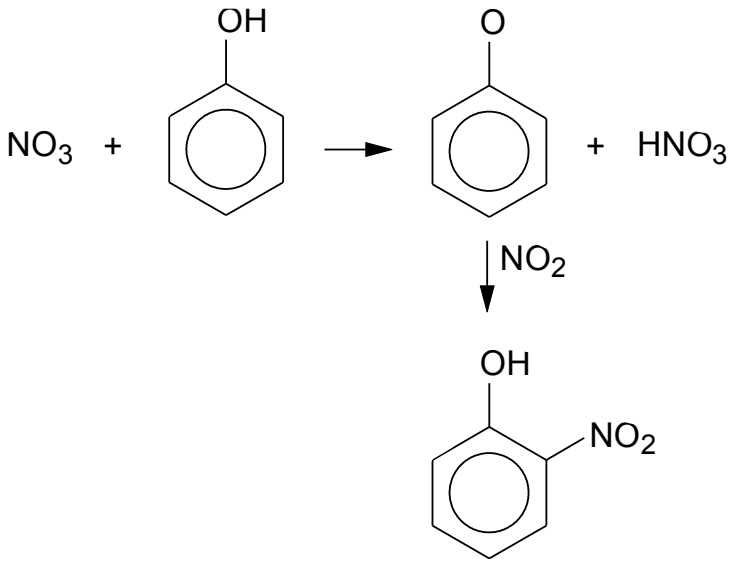
Reliability

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

Comments on Preferred Values

The reported rate coefficients are all from relative rate studies conducted at room temperature. 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 preferred value is based on the studies of Atkinson et al. (1984; 1992) in which the rate coefficients were measured relative to those for NO_3 + alkene (2-methyl-2-butene in both studies) and used the thermal decomposition of N_2O_5 to generate NO_3 radicals.

Atkinson et al. (1992) observed the formation of 2-nitrophenol in 25.1 ± 5.1% yield. 2-Nitrophenol formation is believed to arise from phenoxy + NO_2, and the measured 2-nitrophenol yield of Atkinson et al. (1992) therefore suggests that channel (1) accounts for at least 25 ± 5% of the overall reaction.



References

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