

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_AROM16

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

HO + C₆H₅NO₂ (nitrobenzene) → products

Rate coefficient data

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$6 \times 10^{-13} \exp[-(440 \pm 80)/T]$	259-362	Witte et al., 1986	FP-RF (a)
$(1.37 \pm 0.14) \times 10^{-13}$	299		
<i>Relative Rate Coefficients</i>			
$<6.4 \times 10^{-13}$	296 ± 2	Atkinson et al., 1987	RR (b)
$<8.3 \times 10^{-13}$	296 ± 2	Atkinson et al., 1987	RR (c)

Comments

- (a) At 100 Torr (133 mbar) of Ar diluent.
- (b) HO radicals generated by the photolysis of CH₃ONO in air at atmospheric pressure in a ~60 L Teflon chamber, with analyses of nitrobenzene and benzene (the reference compound) by GC. The measured rate coefficient ratio $k(\text{HO} + \text{nitrobenzene})/k(\text{HO} + \text{benzene}) < 0.53$ is placed on an absolute basis using a rate coefficient of $k(\text{HO} + \text{benzene}) = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (c) HO radicals generated by the dark reaction of O₃ + N₂H₄ in air at atmospheric pressure in a 5870 L reaction chamber. The concentrations of nitrobenzene and dimethyl ether (the reference compound) were monitored by FTIR spectroscopy, and the measured rate coefficient ratio $k(\text{HO} + \text{nitrobenzene})/k(\text{HO} + \text{dimethyl ether}) < 0.3$ is placed on an absolute basis using a rate coefficient of $k(\text{HO} + \text{dimethyl ether}) = 2.76 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).

Preferred Values

$k = 6.0 \times 10^{-13} \exp(-440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250-370 K.

$k = 1.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

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

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The upper limits to the rate coefficients obtained by Atkinson et al. (1987) are consistent with the absolute rate coefficients measured by Witte et al. (1986). The rate expression reported by Witte et al. (1986) is accepted as the preferred value. Since the Witte et al. (1986) study is the sole published study to

report rate coefficients for this reaction (rather than upper limits), correspondingly large uncertainties are given. The reaction proceeds mainly by HO radical addition to the aromatic ring (Witte et al., 1986).

References

- Atkinson, R., Tuazon, E. C., Wallington, T. J., Aschmann, S. M., Arey, J., Winer, A. M. and Pitts Jr., J. N.: Environ. Sci. Technol., 21, 64, 1987.
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Witte, F., Urbanik, E. and Zetzsch, C.: J. Phys. Chem., 90, 3251, 1986.