

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

Data Sheet oIOx5; VII.A4.2

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The citation for the preferred values in this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>.

This datasheet last evaluated: June 2014; last change in preferred values: June 2014



Rate coefficient data ($k = k_1 + k_2 + k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(1.47 \pm 0.08) \times 10^{-12}$	298	Carl and Crowley (2001)	PLP-RF (a)
$1.65 \times 10^{-11} \exp[-(780 \pm 90)/T]$	300-370	Zhang et al. (2012)	FP-RF (b)
$(1.24 \pm 0.06) \times 10^{-12}$	300		
<i>Relative Rate Coefficients</i>			
$(1.8 \pm 0.3) \times 10^{-12}$	298	Cotter et al. (2003)	DF-RF (c)

Comments

- (a) HO radicals were generated by the two photon 439.44 nm (Nd-YAG pumped dye laser) photolysis of NO_2 (generating $\text{O}(^1\text{D})$ and $\text{O}(^3\text{P})$ atoms) in the presence of H_2 . Experiments were conducted in 20 Torr (27 mbar) of argon diluent. HO radicals were monitored using resonance fluorescence at 308 nm.
- (b) HO radicals were generated by the VUV flash photolysis of H_2O in 188 Torr (250 mbar) of helium diluent. HO radicals were monitored using resonance fluorescence at 308 nm.
- (c) HO radicals were generated by the reaction of H atoms with NO_2 in 1.5 or 5.0 Torr (2.0 or 6.7 mbar) of helium diluent at $298 \pm 2 \text{ K}$. There was no discernable effect of total pressure over the range studied. It is possible that the measured rate coefficient is an overestimation of $k(\text{HO} + \text{C}_3\text{H}_7\text{I})$ because of additional loss of HO radicals via reaction with products of the $\text{HO} + \text{C}_3\text{H}_7\text{I}$ reaction. While secondary chemistry should manifest itself in curvature of the first order ($\ln([\text{HO}]_0/[\text{HO}]_t)$ versus time) plots, Cotter et al. (2003) calculated that such curvature would be not be discernable given the data scatter. Cotter et al. (2003) estimated that correction of the rate coefficient for possible additional loss of HO radicals via secondary reactions would lower the rate coefficient to $1.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.86 \times 10^{-11} \exp(-780)/T$	290 -380
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.36×10^{-12}	298
<i>Reliability</i>		
$\Delta \log k$	0.08	298

Comments on Preferred Values

Recognizing the possible contribution of secondary loss of HO radicals, Cotter et al. (2003) considered their rate coefficient determination to be an upper limit. The value derived by Cotter et al. (2003) corrected for possible secondary reactions is consistent, within the likely combined experimental uncertainties, with that from Carl and Crowley (2001) and Zhang et al. (2012). The results from Carl and Crowley (2001) and Zhang et al. (2012) are in good agreement within the likely combined uncertainties. Our recommended value at 298 K is the average from Carl and Crowley (2001) and Zhang et al. (2012). The temperature dependence is taken from a fit to the work by Zhang et al. (2012) with the A-factor adjusted to reproduce the recommended value at 298 K.

References

- Carl, S. A., and Crowley, J. N.: Atmos. Chem. Phys., 1, 1, 2001.
 Cotter, E. S. N., Canosa-Mas, C.E., Manners, C. R., Wayne, R. P., and Shallcross, D. E.: Atmos. Environ., 37, 1125, 2003.
 Zhang, S., Strekowski, R.S., Monod, A., Bosland, L., and Zetzsch, C.: J. Phys. Chem. A, 116, 9497, 2012.

