IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC42

This data sheet last evaluated: 30th July 2007; no revision of preferred values.

HO + 1-$C_4H_9ONO_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(1.74 ± 0.19) x 10^{-12}	298 ± 2	Nielsen et al., 1991	PR-RA (a)
Relative Rate Coefficients			
(1.31 ± 0.10) x 10^{-12}	299 ± 2	Atkinson et al., 1982	RR (b,c)
(1.65 ± 0.18) x 10^{-12}	298 ± 2	Atkinson and Aschmann, 1989	RR (b,d)
(1.47 ± 0.08) x 10^{-12}	298 ± 2	Nielsen et al., 1991	RR (b,e)

Comments

(a) Carried out at a total pressure of 1 bar Ar.

(b) HO radicals were generated by the photolysis of CH_3ONO in air at atmospheric pressure (0.97 bar to 1.0 bar). The concentrations of 1-butyl nitrate and the reference organic were measured by GC.

(c) The measured rate coefficient ratio of k(HO + 1-butyl nitrate)/k(HO + cyclohexane) = 0.187 ± 0.014 is placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane) = 7.00 x 10^{-12} cm^3 molecule^{-1} s^{-1} at 299 K (Atkinson, 2003). Experiments were carried out in an ~75 liter Teflon chamber, and the data were interpreted as involving concurrent photolysis of 1-butyl nitrate.

(d) Experiments were carried out in a 6400 liter Teflon chamber, and irradiations were also carried out in the absence of CH_3ONO, allowing the photolysis rate to be accurately allowed for in the data analysis. The measured rate coefficient ratio of k(HO + 1-butyl nitrate)/k(HO + cyclohexane) = 0.237 ± 0.025 is placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane) = 6.97 x 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003). These data supersede those of Atkinson et al. (1982).

(e) The measured rate coefficient ratio k(HO + 1-butyl nitrate)/k(HO + 2-methylpropane) is placed on an absolute basis by use of a rate coefficient of k(HO + 2-methylpropane) = 2.12 x 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003).

Preferred Values

k = 1.6 x 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The absolute and relative rate coefficients of Atkinson and Aschmann (1989) (which supersedes the earlier data of Atkinson et al., 1982) and Nielsen et al. (1991) are in good agreement. The preferred value is an average of the absolute and relative rate constants of Atkinson and Aschmann (1989) and Nielsen et al., (1991). By analogy with the reaction of the HO radical with 2-propyl nitrate (IUPAC, 2007), the temperature dependence of the rate coefficient at temperatures below 300 K is likely to be small.

References

Atkinson, R.: Atmos. Chem. Phys. 3, 2233, 2003.

Atkinson, R. and Aschmann, S. M.: Int. J. Chem. Kinet. 21, 1123, 1989.

Atkinson, R., Aschmann, S. M., Carter, W. P. L. and Winer, A. M.: Int. J. Chem. Kinet. 14, 919, 1982.

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Nielsen, O. J., Sidebottom, H. W., Donlon, M. and Treacy, J.: Chem. Phys. Lett. 178, 163, 1991.