IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC39

HO + C$_2$H$_5$ONO$_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
4.7 x 10^{-14} exp[(716 ± 138)/T]	298-373	Nielsen et al., 1991	PR-RA (a)
(5.3 ± 0.6) x 10^{-13}	298 ± 2		
3.68 x 10^{-12} exp(-1077/T)	223-394	Talukdar et al., 1997	PLP-LIF (b)
+ 5.32 x 10^{-14} exp(126/T)			
(1.80 ± 0.12) x 10^{-13}	298		
3.30 x 10^{-12} exp[-(699 ± 140)/T]	298-373	Shallcross et al., 1997	DF-RF (c)
(3.30 ± 0.68) x 10^{-13}	298		
Relative Rate Coefficients			
(4.9 ± 2.1) x 10^{-13}	303 ± 2	Kerr and Stocker, 1986	RR (d)
(4.2 ± 0.3) x 10^{-13}	298 ± 2	Nielsen et al., 1991	RR (e)
(2.2 ± 0.8) x 10^{-13}	304 ± 6	Kakesu et al., 1997	RR (f)

Comments

(a) Conducted at 1 bar Ar.

(b) Extensive study of the reactions of ethyl nitrate with HO radicals (223-394 K), H^{18}O radicals (300 K) and DO radicals (229-378 K). HO, H^{18}O and DO radicals were produced from the pulsed laser photolysis of HONO at 355 nm, of O$_3$-H$_2^{18}$O mixtures at 248 nm, and of DONO at 355 nm, respectively. The diluent gas and total pressures were He [67-400 mbar (50-300 Torr)], N$_2$ [400 mbar (300 Torr)], SF$_6$ [267 mbar (200 Torr)] or He-SF$_6$ [133-400 mbar (100- 300 Torr)], and O$_2$ partial pressures of 67 mbar (50 Torr) were used in certain experiments. No effects on the measured rate coefficients were observed on varying the total pressure, the diluent gas, or the partial pressure of O$_2$. The measured rate coefficients for the reactions of the H^{18}O and DO radicals with ethyl nitrite were 11-16% higher than that for the HO radical reaction, and no formation of HO radicals was observed in the H^{18}O and DO radical reactions.

(c) The rate coefficient at 298 K was measured over the pressure range 5.7-27 mbar (4.3-19.9 Torr) of He, with no effect of pressure being observed. The rate coefficients at 313 K and 373 K were measured over the pressure range 1.3-4.0 mbar (1-3 Torr) of He.

(d) HO radicals generated by photolysis of HONO-air mixtures at atmospheric pressure. The concentrations of ethyl nitrate and ethene (the reference organic) were measured by GC. The measured rate coefficient ratio of k(HO + ethyl nitrate)/k(HO + ethene) = 0.059 ± 0.025 is placed on an absolute basis by use of a rate coefficient k(HO + ethene) = 8.32 x 10^{-12} cm^3 molecule^{-1} s^{-1} at 303 K and atmospheric pressure of air (Atkinson, 1997).

(e) HO radicals were generated by photolysis of CH$_3$ONO-NO-air mixtures at atmospheric pressure. The concentrations of ethyl nitrate and 2-methylpropane (the reference organic) were measured by

GC, and the measured rate coefficient ratio 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} (Atkinson, 2003).

(f) Relative rate method. HO radicals were generated by the photolysis of O_3-H_2O-O_2 mixtures at atmospheric pressure at ~290-310 nm. The concentrations of ethyl nitrate and the reference compounds ethane and 2-methylpropane were measured by GC. The measured rate coefficient ratios are placed on an absolute basis by use of rate coefficients of k(HO + ethane) = 6.9 x 10^{-12} exp(-1000/T) cm^3 molecule^{-1} s^{-1} and k(HO + 2-methylpropane) = 1.17 x 10^{-17} T^2 exp(213/T) cm^3 molecule^{-1} s^{-1} (Atkinson, 2003; IUPAC, 2007). The cited rate coefficient is the unweighted average with a two standard deviation error limit.

Preferred Values

k = 1.8 x 10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K.
k = 6.7 x 10^{-13} exp(-395/T) cm^3 molecule^{-1} s^{-1} over the temperature range 230-300 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 400$ K.

Comments on Preferred Values
There are serious discrepancies between the absolute and relative rate studies of Kerr and Stocker (1986) and Nielsen et al. (1991) carried out at ~1 bar total pressure and the absolute rate and the relative rate studies of Talukdar et al. (1997) and Kakesu et al. (1997), respectively, in both the room temperature rate coefficient (Nielsen et al., 1991; Talukdar et al., 1997; Kerr and Stocker, 1986; Kakesu et al., 1997) and the temperature dependence (Nielsen et al., 1991; Talukdar et al., 1997). The positive temperature-dependence observed by Talukdar et al. (1997) is supported, qualitatively, by the low-pressure absolute rate study of Shallcross et al. (1997), although the rate coefficients of Shallcross et al. (1997) are a factor of ~1.8 higher than those of Talukdar et al. (1997). The reasons for these discrepancies are not known, but we favour the results of the extensive Talukdar et al. (1997) study which are consistent with H- (or D-) atom abstraction. The study of Talukdar et al. (1997) showed no effect of total pressure, diluent gas [ranging from 67 mbar (50 Torr) of He to 267 mb (200 Torr) of SF_6 or 400 mbar (300 Torr) N_2] or the presence or absence of O_2 at a partial pressure of 67 mbar (50 Torr) on the measured rate coefficients.

While the study of Talukdar et al. (1997) was not carried out in air at 1 bar pressure, the data obtained strongly suggest that the rate coefficient is consistent with an H-atom abstraction process and that the measured rate coefficients should be appropriate for atmospheric purposes. The Arrhenius plots of the HO and DO radical reactions exhibit significant curvature (Talukdar et al., 1997). The preferred values are based on a unit-weighted least-squares fit of the 233-298 K rate coefficients of Talukdar et al. (1997) to the Arrhenius expression, $k = A$ exp (-B/T). Large uncertainty limits are assigned because of the discrepancies between the various studies (Kakesu et al., 1997; Kerr and Stocker, 1986; Nielsen et al., 1991; Shallcross et al., 1997; Talukdar et al., 1997) noted above. Further absolute rate studies conducted at atmospheric pressure of air are required.

References

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