IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC38

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

HO + CH$_3$ONO$_2$ $\rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(3.4 \pm 0.4) \times 10^{-14}$	298	Gaffney et al., 1986	DF-RF (a)
$8.8 \times 10^{-15} \exp[(1050 \pm 180)/T]$	298-393	Nielsen et al., 1991	PR-RA (b)
$(3.2 \pm 0.5) \times 10^{-13}$	298 ± 2		
$8.2 \times 10^{-13} \exp[-(1020 \pm 60)/T]$	221-414	Talukdar et al., 1997	PLP-LIF (c)
$(2.36 \pm 0.16) \times 10^{-14}$	298		
$4.1 \times 10^{-13} \exp[-(604 \pm 121)/T]$	298-423	Shallcross et al., 1997	DF-RF (d)
$(4.7 \pm 1.0) \times 10^{-14}$	298		
Relative Rate Coefficients			
$(3.8 \pm 1.0) \times 10^{-13}$	303 ± 2	Kerr and Stocker, 1986	RR (e)
$(3.1 \pm 0.7) \times 10^{-13}$	298 ± 2	Nielsen et al., 1991	RR (f)
$(3.0 \pm 0.7) \times 10^{-14}$	307 ± 3	Kakesu et al., 1997	RR (g)

Comments

(a) Conducted at 2.6-4.2 mbar (2.0-3.2 Torr) of He.

(b) Conducted at 1 bar Ar.

(c) In addition to measuring rate coefficients for the reaction of the HO radical with CH$_3$ONO$_2$, rate coefficients were measured for the reactions of the HO radical with CD$_3$ONO$_2$ (298-409 K), the DO radical with CH$_3$ONO$_2$ (246-353 K) and the H^{18}O radical with CH$_3$ONO$_2$ (253-298 K). HO, H^{18}O and DO radicals were generated by the pulsed laser photolysis of HONO at 355 nm and of O$_3$-H$_2$O mixtures at 266 nm, photolysis of O$_3$-H$_2$^{18}O mixtures at 266 nm, and photolysis of DONO at 355 nm and of O$_3$-D$_2$O mixtures at 266 nm, respectively. The diluent gas pressure was varied from 67 mbar (50 Torr) He plus 67 mbar (50 Torr) SF$_6$ to 133 mbar (100 Torr) He and to 400 mbar (300 Torr) SF$_6$, and up to 67 mbar (50 Torr) of O$_2$ was included in certain experiments. No effect of total pressure, nature of the diluent gas, or presence of O$_2$ on the measured rate coefficients was observed. The rate coefficients for the reactions of the H^{18}O radical with CH$_3$ONO$_2$ were essentially identical to those for the corresponding HO radical reaction, while the measured rate coefficients for the DO radical reaction were ~10-20% higher than the HO radical reaction. No evidence for formation of HO radicals was observed from these H^{18}O and DO radical reactions. The rate coefficients for the reaction of the HO radical with CD$_3$ONO$_2$ were a factor of 3-4 lower than those for HO + CH$_3$ONO$_2$ over the temperature range studied (298-409 K).

(d) The rate coefficient at 298 K was measured over the pressure range 2.7-27 mbar (2-20 Torr) of He, with no effect of pressure being observed. Rate coefficients at 333-423 K were measured over the pressure range 1.3-4.0 mbar (1-3 Torr) of He.

(e) HO radicals were generated from the photolysis of HONO-air mixtures at atmospheric pressure. The concentrations of methyl nitrate and ethene (the reference compound) were measured by GC.

The measured rate coefficient ratio of k(HO + methyl nitrate)/k(HO + ethene) = 0.046 ± 0.011 placed on an absolute basis by use of k(HO + ethene) = 8.32 x 10^{-12} cm^3 molecule^{-1} s^{-1} at 303 K and one atmosphere of air (Atkinson, 1997).

(f) HO radicals generated by the photolysis of CH$_3$ONO-NO-air mixtures at atmospheric pressure. The decays of CH$_3$ONO$_2$ and (CH$_3$)$_3$CH (the reference compound) were measured by GC. The rate coefficient ratio was placed on an absolute basis by use of k(HO + (CH$_3$)$_3$CH) = 2.12 x 10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson, 2003).

(g) HO radicals were generated by photolysis of O$_3$-H$_2$O-O$_2$ mixtures at atmospheric pressure at ~290-310 nm. Methyl nitrate and the reference compounds (methane, ethane and HFC-152a) were monitored by GC. The measured rate coefficient ratios are placed on an absolute basis by use of rate coefficients of k(HO + CH$_4$) = 1.85 x 10^{-12} exp(-1690/T) cm^3 molecule^{-1} s^{-1}, k(HO + C$_2$H$_6$) = 6.9 x 10^{-12} exp(-1000/T) cm^3 molecule^{-1} s^{-1} and k(HO + CH$_3$CHF$_2$) = 1.0 x 10^{-12} exp(-990/T) cm^3 molecule^{-1} s^{-1} (IPUPAC, 2007). The cited rate coefficient is the unweighted average, with a two standard deviation error limit.

Preferred Values

k = 2.3 x 10^{-14} cm^3 molecule^{-1} s^{-1} at 298 K.
k = 4.0 x 10^{-13} exp(-845/T) cm^3 molecule^{-1} s^{-1} over the temperature range 220-300 K.

Reliability
Δlog k = $^{+0.5}_{-0.2}$ at 298 K.
Δ(*E/R*) = ± 400 K.

Comments on Preferred Values

There are serious discrepancies between the room temperature rate coefficients of Gaffney et al. (1986), Talukdar et al. (1997) and Kakesu et al. (1997) and those of Kerr and Stocker (1986) and Nielsen et al. (1991), of a factor of ~10. Additionally, the temperature dependencies of Nielsen et al. (1991) and Talukdar et al. (1997) differ by ~2000 K. 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 ~1.3-2.0 higher than those of Talukdar et al. (1997) over the temperature range 298-423 K. The reasons for these various discrepancies are not presently known, but we favour the results of the Talukdar et al. (1997) study which are consistent with H- (or D-) atom abstraction to form H$_2$O + CH$_2$ONO. The extensive absolute study of Talukdar et al. (1997) shows no effect of the measured rate coefficient on pressure or diluent gas (133 mbar He to 400 mbar SF$_6$) nor on the presence or absence of up to 67 mbar of O$_2$. The experiments of Talukdar et al. (1997) on the reactions HO + CH$_3$ONO$_2$, H^{18}O + CH$_3$ONO$_2$, DO + CH$_3$ONO$_2$ and HO + CH$_3$ONO$_2$ show no formation of HO radicals from the H^{18}O and DO radical reactions with CH$_3$ONO$_2$, and the deuterium isotope effect of k_H/k_D ~4 at 298 K is totally consistent with H- (or D-) atom abstraction.

The preferred values are obtained from a unweighted least-squares analysis of the 221-298 K rate coefficients of Talukdar et al. (1997). Because of the significant discrepancies between the various studies (Gaffney et al., 1986; Kakesu et al., 1997; Kerr and Stocker, 1986; Nielsen et al., 1991; Shallcross et al., 1997; Talakdar et al., 1997), large uncertainty limits are assigned to the 298 K rate coefficient and the temperature dependence. Clearly, further absolute rate studies at atmospheric pressure of air are needed.

References

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