IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC48

This data sheet last evaluated: 2nd August 2007; no revision of preferred values.

HO + CH_2=C(CH_3)C(O)ONO_2 (MPAN) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
(3.33 ± 0.40) x 10^{-12}	298 ± 2	Grosjean et al., 1993	RR (a)
(3.76 ± 0.58) x 10^{-11}	275 ± 3	Orlando et al., 2002	RR (b,c)
(2.88 ± 0.46) x 10^{-11}	275 ± 3	Orlando et al., 2002	RR (b,d)

Comments

(a) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by the photolysis (using natural sunlight) of ethyl nitrite-air mixtures, and the concentrations of CH_2=C(CH_3)C(O)ONO_2 (MPAN) and 1-butyl nitrate (the reference compound) were measured by GC with electron capture detection. The measured rate coefficient ratio of k(HO + MPAN)/k(HO + 1-butyl nitrate) = 2.08 ± 0.25 is placed on an absolute basis by use of a rate coefficient of k(HO + 1-butyl nitrate) = 1.6 x 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

(b) Relative rate method carried out in synthetic air at 0.93-0.97 bar. HO radicals were generated by the photolysis of ethyl nitrite-NO-air mixtures, and the concentrations of CH_2=C(CH_3)C(O)ONO_2 (MPAN) and ethene and propene (the reference compounds) were measured by *in situ* FTIR spectroscopy. Experiments were carried out at 275 ± 3 K to decrease the rate of thermal decomposition of MPAN (IUPAC, 2007) in the presence of NO. The measured rate coefficient ratios of k(HO + MPAN)/k(HO + ethene) = 3.9 ± 0.6 and k(HO + MPAN)/k(HO + propene) = 0.95 ± 0.15 are placed on an absolute basis by use of rate coefficients at 275 K and atmospheric pressure of air of k(HO + ethene) = 9.64 x 10^{-12} cm^3 molecule^{-1} s^{-1} and k(HO + propene) = 3.03 x 10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson, 1997).

(c) Relative to HO + ethene.

(d) Relative to HO + propene.

Preferred Values

k = 2.9 x 10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = {}^{+0.2}_{-0.5}$ at 298 K.

Comments on Preferred Values

The rate coefficients measured in the two studies of Grosjean et al. (1993) and Orlando et al. (2002) disagree by a factor of ~10, for reasons which are not known. The reaction of HO radicals with CH_2=C(CH_3)C(O)ONO_2 is expected to proceed almost exclusively by initial HO radical addition to the C=C bond (Grosjean et al., 1993; Orlando et al., 2002), and is

expected to have a small (and probably negative) temperature dependence at around room temperature. Support for the Orlando et al. (2002) study arises from the structurally similar compound $CH_2=C(CH_3)C(O)OCH_3$ having a rate coefficient for it's HO radical reaction of $(2.6 \pm 0.5) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K (Saunders et al., 1994), which is similar to that measured by Orlando et al. (2002) for HO + MPAN. Accordingly, the preferred value is based on the rate coefficients measured by Orlando et al. (2002) at 275 K, adjusted to 298 K using the temperature dependence observed for HO + propene (Atkinson, 1997), and with appropriately large and asymmetric uncertainties. Formaldehyde and hydroxyacetone have been observed as products of this reaction (Grosjean et al., 1993; Orlando et al., 2002).

References

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