

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC61

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HO + 2-Methylpropene → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$9.2 \times 10^{-12} \exp[(503 \pm 151)/T]$	297-424	Atkinson and Pitts, 1975	FP-RF (a)
$(5.07 \pm 0.51) \times 10^{-11}$	297.2		
<i>Relative Rate Coefficients</i>			
6.46×10^{-11}	298	Morris and Niki, 1971a	DF-MS (b)
5.01×10^{-11}	303	Wu et al., 1976	RR (c)
6.16×10^{-11}	300	Barnes et al., 1982	RR (d)
$(5.47 \pm 0.09) \times 10^{-11}$	298 ± 2	Ohta, 1984	RR (e)
$(5.23 \pm 0.25) \times 10^{-11}$	295 ± 1	Atkinson and Aschmann, 1984	RR (f)

Comments

- Experiments carried out at 25 Torr (33 mbar) of Ar diluent.
- A rate coefficient for HO + 2-methylpropene was obtained relative to that for propene at 1 Torr (1.3 mbar) He diluent by monitoring the decays of 2-methylpropene and propene and the respective average HO radical concentrations under identical experimental conditions. The rate coefficient ratio $k(\text{HO} + 2\text{-methylpropene})/k(\text{HO} + \text{propene}) = 3.8$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{propene}) = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ under the experimental condition used (Morris and Niki, 1971b).
- HO radicals were generated by the photolysis of organic-NO_x-O₂-air mixtures at atmospheric pressure. 2-Methylpropene and *cis*-2-butene (the reference compound) were measured by GC, and the measured rate coefficient ratio $k(\text{HO} + 2\text{-methylpropene})/k(\text{HO} + \textit{cis}\text{-2-butene}) = 0.92$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \textit{cis}\text{-2-butane}) = 5.45 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 303 K (IUPAC, current recommendation).
- HO radicals were generated by dark decomposition of HOONO₂ in the presence of NO at atmospheric pressure of N₂ or air. 2-Methylpropene and ethene (the reference compound) were monitored by GC, and the measured rate coefficient ratio $k(\text{HO} + 2\text{-methylpropene})/k(\text{HO} + \text{ethene}) = 7.3$ is placed on an absolute basis using a rate coefficient of $k(\text{HO} + \text{ethene}) = 8.44 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K and atmospheric pressure of air (Atkinson and Arey, 2003).
- HO radicals were generated by the photolysis of H₂O₂ at 253.7 nm in 760 Torr of N₂ or O₂ diluent in a quartz vessel. The concentrations of 2-methylpropene and 2-methyl-2-butene (the reference compound) were measured by GC during the experiments. The measured rate coefficient ratios $k(\text{HO} + 2\text{-methylpropene})/k(\text{HO} + 2\text{-methyl-2-butene}) = 0.63 \pm 0.01$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + 2\text{-methyl-2-butene}) = 8.69 \times 10^{-11}$ at 298 K and atmospheric pressure of air (Atkinson and Arey, 2003).
- HO radicals were generated by the photolysis of CH₃ONO in air at wavelengths >300 nm in a ~60 L Teflon chamber at atmospheric pressure of air. The concentrations of 2-methylpropene and propene (the reference compound) were monitored by GC during the experiments. The

measured rate coefficient ratio $k(\text{HO} + 2\text{-methylpropene})/k(\text{HO} + \text{propene}) = 1.95 \pm 0.09$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{propene}) = 2.68 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K and atmospheric pressure of air (Atkinson and Arey, 2003).

Preferred Values

$k = 9.4 \times 10^{-12} \exp(505/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 290-430 K

$k = 5.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

At room temperature, the absolute rate coefficient of Atkinson and Pitts (1975) and the relative rate coefficients of Wu et al. (1976), Barnes et al. (1982), Ohta (1984) and Atkinson and Aschmann (1984) are in reasonable agreement. Using propene as the reference compound, Atkinson and Aschmann (1984) measured rate coefficients for 1-butene, 3-methyl-1-butene, 2-methylpropene, *cis*-2-butene, *trans*-2-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, propadiene, 1,3-butadiene and isoprene at $295 \pm 1 \text{ K}$ and atmospheric pressure of air. These relative rate data for were fit by Atkinson (1989) to the absolute rate coefficients then available for propene, 1-butene, 3-methyl-1-butene, 2-methylpropene, *cis*-2-butene, *trans*-2-butene, 2-methyl-2-butene, propadiene and 1,3-butadiene (Atkinson and Pitts, 1975, 1978; Atkinson et al., 1977; Ravishankara et al., 1978; Nip and Paraskevopoulos, 1979; Tully and Goldsmith, 1985), using the observed temperature dependencies or $E/R = -500 \text{ K}$ to adjust the measured rate coefficients to 295 K. The result of this fitting procedure (Atkinson, 1989) was that for 2-methylpropene, $k = 5.23 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K. Combined with the temperature dependence of Atkinson and Pitts (1975), this leads to the preferred values.

At room temperature and below, the reaction proceeds dominantly by HO radical addition to the C=C bond. At elevated temperatures ($>650 \text{ K}$), the HO-2-methylpropene adducts decompose rapidly back to reactants and the observed reaction is then H-atom abstraction (Atkinson, 1989).

References

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- Recommendation
- Atkinson and Pitts (1975)
- ▲ Ohta (1984)
- ◆ Atkinson and Aschmann (1984)

