

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC64

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This data sheet created March 2009.

HO + *trans*-2-Butene → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(1.2 \pm 1) \times 10^{-11}$	300	Pastrana and Carr, 1975	DF-RA (a)
$1.12 \times 10^{-11} \exp[(549 \pm 151)/T]$	298-425	Atkinson and Pitts, 1975	FP-RF (b)
$(6.99 \pm 0.70) \times 10^{-11}$	297.8		
$(1.69 \pm 0.083) \times 10^{-10}$	170	Sims et al., 1994	PLP-LIF (c)
$(6.83 \pm 0.22) \times 10^{-11}$	295		
<i>Relative Rate Coefficients</i>			
7.14×10^{-11}	298	Morris and Niki, 1971a	DF-MS (d)
7.09×10^{-11}	303	Wu et al., 1976	RR (e)
$(5.96 \pm 0.31) \times 10^{-11}$	298 ± 2	Ohta, 1983	RR (f)
$(6.51 \pm 0.14) \times 10^{-11}$	295 ± 1	Atkinson and Aschmann, 1984	RR (g)
$(7.3 \pm 1.3) \times 10^{-11}$	297.4 ± 1.7	Edney et al., 1986	RR (h)
$(7.21 \pm 0.38) \times 10^{-11}$	298 ± 3	Rogers, 1989	RR (i)

Comments

- Experiments carried out at 1 Torr (1.3 mbar) of He diluent.
- Experiments carried out at 25 Torr (33 mbar) of Ar diluent.
- Experiments at 295 K were carried out at a total pressure of Ar diluent of 14 Torr (19 mbar). Rate coefficients of $(4.52 \pm 0.32) \times 10^{-10}$, $(4.03 \pm 0.44) \times 10^{-10}$ and $(3.17 \pm 0.24) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ were also measured at 23, 44 and 75 K, respectively.
- A rate coefficient for HO + *trans*-2-butene was obtained relative to that for propene at 1 Torr (1.3 mbar) He diluent by monitoring the decays of *trans*-2-butene and propene and the respective average HO radical concentrations under identical experimental conditions. The measured rate coefficient ratio $k(\text{HO} + \textit{trans}\text{-2-butene})/k(\text{HO} + \textit{propene}) = 4.2$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \textit{propene}) = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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. *trans*-2-Butene and *cis*-2-butene (the reference compound) were measured by GC, and the measured rate coefficient ratio $k(\text{HO} + \textit{trans}\text{-2-butene})/k(\text{HO} + \textit{cis}\text{-2-butene}) = 1.3$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \textit{cis}\text{-2-butene}) = 5.45 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 303 K (IUPAC, current recommendation).
- HO radicals were generated by the photolysis of H₂O₂ at 253.7 nm in 760 Torr of N₂ or O₂ diluent in a quartz vessel. The concentrations of *trans*-2-butene and *cis*-1,3-pentadiene (the reference compound) were measured by GC during the experiments. The measured rate coefficient ratios $k(\text{HO} + \textit{trans}\text{-2-butene})/k(\text{HO} + \textit{cis}\text{-1,3-pentadiene}) = 0.59 \pm 0.03$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \textit{cis}\text{-1,3-pentadiene}) = 1.01 \times 10^{-10}$ at 298 K and atmospheric pressure of air (Atkinson, 1989; 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 *trans*-2-butene and propene (the reference compound) were monitored by GC during the experiments. The measured rate coefficient ratio $k(\text{HO} + \textit{trans}\text{-2-butene})/k(\text{HO} + \textit{propene}) = 2.43 \pm 0.05$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \textit{propene}) = 2.68 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K and atmospheric pressure of air (Atkinson and Arey, 2003).

- (h) HO radicals were generated by the photolysis of CH_3ONO in one atmosphere of air. The concentrations of *trans*-2-butene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \textit{trans}\text{-2-butene})/k(\text{HO} + \textit{propene})$ is placed on an absolute basis by use of a rate coefficient at 297 K and atmospheric pressure of air of $k(\text{HO} + \textit{propene}) = 2.65 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003).
- (i) HO radicals were generated by the photolysis of HONO in one atmosphere of air in a 600 L stainless steel cell. The concentrations of *trans*-2-butene and propene (the reference compound) were measured by FTIR spectroscopy. The measured rate coefficient ratio $k(\text{HO} + \textit{propene})/k(\text{HO} + \textit{trans}\text{-2-butene}) = 0.365 \pm 0.019$ is placed on an absolute basis by use of a rate coefficients at 298 K and atmospheric pressure of air of $k(\text{HO} + \textit{propene}) = 2.63 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003).

Preferred Values

$k = 1.0 \times 10^{-11} \exp(553/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 290-430 K

$k = 6.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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 coefficients of Atkinson and Pitts (1975), and Sims et al. (1994) and the relative rate coefficients of Wu et al. (1976), Ohta (1983), Atkinson and Aschmann (1984), Edney et al. (1986) and Rogers (1989) are in reasonable agreement, with that of Edney et al (1986) having a large associated uncertainty. 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 *trans*-2-butene, $k = 6.51 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K. Combined with the temperature dependence of Atkinson and Pitts (1975), this leads to the preferred values.

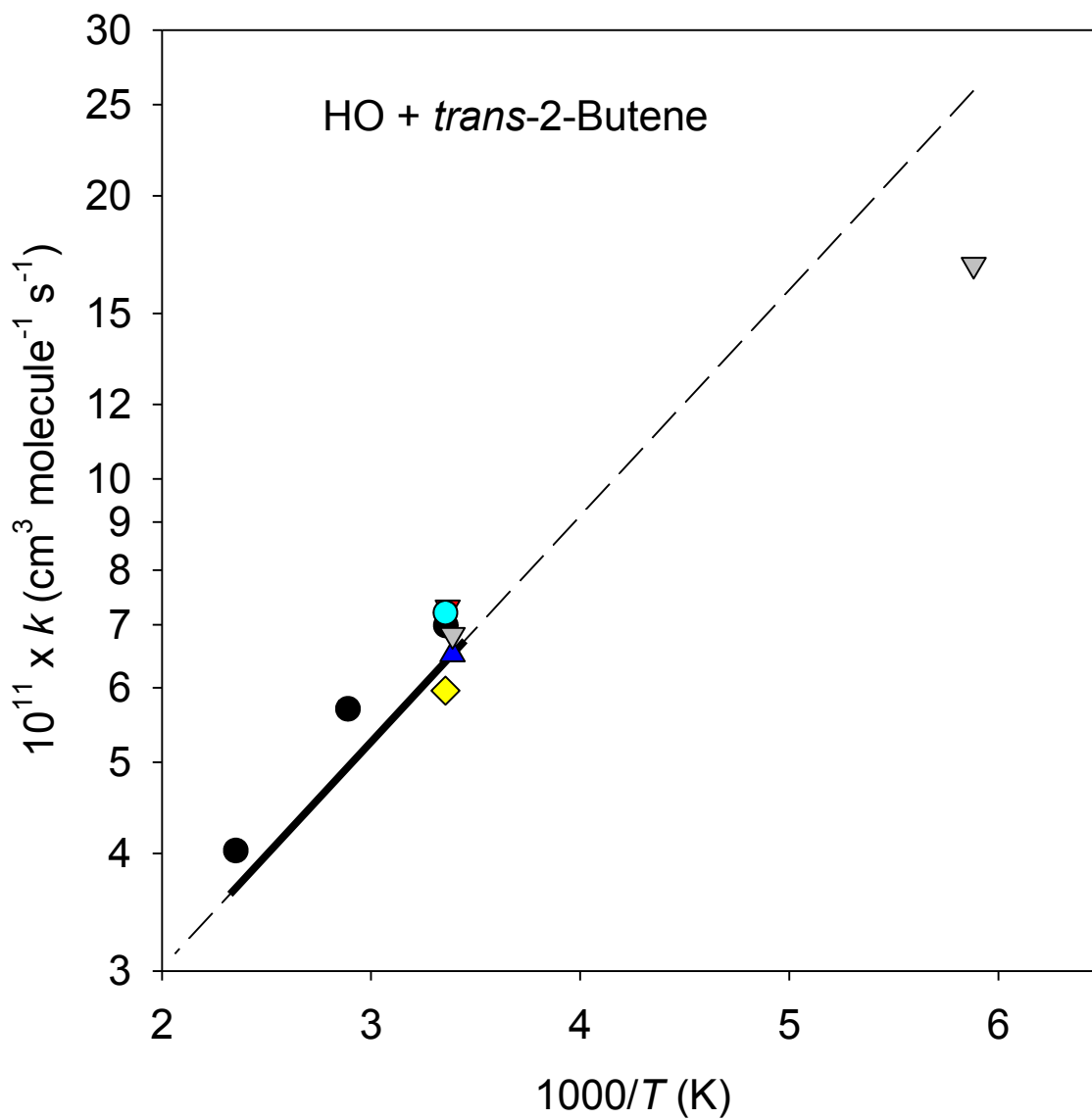
The more recent absolute rate coefficient of Sims et al. (1994) at 295 K is in good agreement with the preferred value. The preferred Arrhenius expression should not be used much below room temperature; clearly extrapolation to 170 K leads to overprediction of the measured rate coefficient of Sims et al. (1994). Rather, the expression of the form $k = a \exp(-bT)$ appears to give a reasonable fit, with $a = 6.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $b = 0.0076$, based on the preferred 295 K value and the 170 K rate coefficient of Sims et al. (1994).

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

References

Atkinson, R.: J. Phys. Chem. Ref. Data, Monograph 1, 1, 1989.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Atkinson, R. and Aschmann, S. M.: Int. J. Chem. Kinet., 16, 1175, 1984.
Atkinson, R. and Pitts Jr., J. N.: J. Chem. Phys., 63, 3591, 1975.
Atkinson, R. and Pitts Jr., J. N.: J. Chem. Phys., 68, 2992, 1978.
Atkinson, R., Perry, R. A. and Pitts Jr., J. N.: J. Chem. Phys., 67, 3170, 1977.
Edney, E. O., Kleindienst, T. E. and Corse, E. W.: Int. J. Chem. Kinet., 18, 1355, 1986.
IUPAC: <http://iupac.pole-ether.fr>, 2013.
Morris Jr., E. D. and Niki, H.: J. Phys. Chem., 75, 3640, 1971a.
Morris Jr., E. D. and Niki, H.: J. Am. Chem. Soc., 93, 3570, 1971b.
Nip, W. S. and Paraskevopoulos, G.: J. Chem. Phys., 71, 2170, 1979.
Ohta, T.: J. Phys. Chem., 87, 1209, 1983.
Pastrana, A. V. and Carr Jr., R. W.: J. Phys. Chem., 79, 765, 1975.
Ravishankara, A. R., Wagner, S., Fischer, S., Smith, G., Schiff, R., Watson, R. T., Tesi, G. and Davis, D. D.: Int. J. Chem. Kinet., 10, 783, 1978.
Rogers, J. D.: Environ. Sci. Technol., 23, 177, 1989.
Sims, I. R., Smith, I. W. M., Bocherel, P., Defrance, A., Travers, D. and Rowe, B. R.: J. Chem. Soc. Faraday Trans., 90, 1473, 1994.
Tully, F. P. and Goldsmith, J. E. M.: Chem. Phys. Lett., 116, 345, 1985.
Wu, C. H., Japar, S. M. and Niki, H.: J. Environ. Sci. Health, A11, 191, 1976.

- Extrapolation of recommendation
- Recommendation
- Atkinson and Pitts (1975)
- ▼ Edney et al. (1986)
- ◆ Ohta (1984)
- ▲ Atkinson and Aschmann (1984)
- Rogers (1989)
- ▽ Sims et al. (1994)



- Recommendation
- Atkinson and Pitts (1975)
- ▼ Edney et al. (1986)
- ◆ Ohta (1984)
- ▲ Atkinson and Aschmann (1984)
- Rogers (1989)
- ▽ Sims et al. (1994)

