

# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO<sub>x</sub>\_VOC62

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## HO + 1-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>			
$(1.5 \pm 0.1) \times 10^{-11}$	300	Pastrana and Carr, 1975	DF-RF (a)
$7.6 \times 10^{-12} \exp[(468 \pm 151)/T]$	298-424	Atkinson and Pitts, 1975	FP-RF (b)
$(3.53 \pm 0.36) \times 10^{-11}$	297.7		
$(2.94 \pm 0.14) \times 10^{-11}$	298	Ravishankara et al., 1978	FP-RF (c)
$(3.34 \pm 0.25) \times 10^{-11}$	297 ± 2	Nip and Paraskevopoulos, 1979	FP-RA (d)
$(3.0 \pm 0.4) \times 10^{-11}$	298	Biermann et al., 1982	DF-MS (e)
$1.6 \times 10^{-11}$	478	Liu et al., 1989	PR-RA (f)
$(7.71 \pm 1.06) \times 10^{-11}$	170	Sims et al., 1994	PLP-LIF (g)
$(3.49 \pm 0.11) \times 10^{-11}$	295		
$(3.30 \pm 0.12) \times 10^{-11}$	295		
$(5.80 \pm 1.51) \times 10^{-11}$	165 ± 14	Vakhtin et al., 2001, 2003	PLP-LIF (h)
$(8.13 \pm 2.10) \times 10^{-11}$	165 ± 14		
$(3.0 \pm 0.2) \times 10^{-11}$	296 ± 2		
<i>Relative Rate Coefficients</i>			
$4.08 \times 10^{-11}$	298	Morris and Niki, 1971a	DF-MS (i)
$2.83 \times 10^{-11}$	303	Wu et al., 1976	RR (j)
$3.21 \times 10^{-11}$	300	Barnes et al., 1982	RR (k)
$(3.13 \pm 0.08) \times 10^{-11}$	298 ± 2	Ohta, 1984	RR (l)
$(3.19 \pm 0.17) \times 10^{-11}$	295 ± 1	Atkinson and Aschmann, 1984	RR (m)

### Comments

- Experiments carried out at 1 Torr (1.3 mbar) of He diluent.
- Experiments carried out at 25 Torr (33 mbar) of Ar diluent.
- Rate coefficients measured at 3 and 20 Torr (4 and 27 mbar) of helium diluent, with rate coefficients of  $(2.96 \pm 0.19) \times 10^{-11}$  and  $(2.94 \pm 0.14) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. Value cited in the table is that at 20 Torr He.
- Experiments carried out at 55 Torr (73 mbar) of (91% H<sub>2</sub> + 9% N<sub>2</sub>O) diluent.
- 1-Butene was in ~10-fold excess of HO radical; concentrations, and the concentrations of 1-butene were monitored by photoionization mass spectrometry at  $m/z = 56$ . Experiments were carried out at ~2 Torr (~2.7 mbar) of He diluent.
- Rate coefficients measured over the temperature range 478-853 K at 760 Torr (1.013 bar) of Ar diluent. Data were presented graphically and not tabulated.
- Experiments at 295 K were carried out at total pressures of Ar diluent of 14 and 23 Torr (19 and 31 mbar), with respective rate coefficients of  $(3.49 \pm 0.11) \times 10^{-11}$  and  $(3.30 \pm 0.12) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Rate coefficients of  $(4.27 \pm 0.56) \times 10^{-10}$ ,  $(3.15 \pm 0.40) \times 10^{-10}$  and  $(2.73 \pm$

- $0.16) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  were also measured at 23, 44 and 75 K, respectively.
- (h) Rate coefficients of  $(1.74 \pm 0.28) \times 10^{-10}$ ,  $(1.24 \pm 0.27) \times 10^{-10}$  and  $(1.68 \pm 0.40) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  were also measured at  $96 \pm 4$ ,  $103 \pm 9$  and  $110 \pm 7$  K, respectively. The rate coefficient cited in the table for  $296 \pm 2$  K is an average value of five measurements made over the pressure range 0.88-102 Torr (1.2-136 mbar) of  $\text{N}_2$  diluent gas; no pressure dependence was observed over this pressure range.
- (i) A rate coefficient for HO + 1-butene was obtained relative to that for propene at 1 Torr (1.3 mbar) He diluent by monitoring the decays of 1-butene and propene and the respective average HO radical concentrations under identical experimental conditions. The rate coefficient ratio  $k(\text{HO} + 1\text{-butene})/k(\text{HO} + \text{propene}) = 2.4$  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).
- (j) HO radicals were generated by the photolysis of organic- $\text{NO}_x$ - $\text{O}_2$ -air mixtures at atmospheric pressure. 1-Butene and *cis*-2-butene (the reference compound) were measured by GC, and the measured rate coefficient ratio  $k(\text{HO} + 1\text{-butene})/k(\text{HO} + \textit{cis}\text{-2-butene}) = 0.52$  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).
- (k) HO radicals were generated by dark decomposition of  $\text{HOONO}_2$  in the presence of NO at atmospheric pressure of  $\text{N}_2$  or air. 1-Butene and ethene (the reference compound) were monitored by GC, and the measured rate coefficient ratio  $k(\text{HO} + 1\text{-butene})/k(\text{HO} + \text{ethene}) = 3.8$  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).
- (l) HO radicals were generated by the photolysis of  $\text{H}_2\text{O}_2$  at 253.7 nm in 760 Torr of  $\text{N}_2$  or  $\text{O}_2$  diluent in a quartz vessel. The concentrations of 1-butene and propene (the reference compound) were measured by GC during the experiments. The measured rate coefficient ratios  $k(\text{HO} + \text{propene})/k(\text{HO} + 1\text{-butene}) = 0.84 \pm 0.02$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO} + \text{propene}) = 2.63 \times 10^{-11}$  at 298 K and atmospheric pressure of air (Atkinson and Arey, 2003).
- (m) HO radicals were generated by the photolysis of  $\text{CH}_3\text{ONO}$  in air at wavelengths  $>300$  nm in a  $\sim 60$  L Teflon chamber at atmospheric pressure of air. The concentrations of 1-butene and propene (the reference compound) were monitored by GC during the experiments. The measured rate coefficient ratio  $k(\text{HO} + 1\text{-butene})/k(\text{HO} + \text{propene}) = 1.19 \pm 0.06$  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

$k = 6.6 \times 10^{-12} \exp(465/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 290-430 K

$k = 3.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

#### Reliability

$\Delta \log k = \pm 0.08$  at 298 K.

$\Delta(E/R) = \pm 150$  K.

#### Comments on Preferred Values

At room temperature, the absolute rate coefficients of Atkinson and Pitts (1975), Ravishankara et al. (1978), Biermann et al. (1982), Sims et al. (1994) and Vakhtin et al. (2001, 2003) 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, with the relative rate studies of Ohta (1984) and Atkinson and Aschmann (1984) obtaining identical rate coefficient ratios of  $k(\text{HO} + 1\text{-butene})/k(\text{HO} + \text{propene}) = 1.19 \pm 0.03$  at  $298 \pm 2$  K and  $1.19 \pm 0.06$  at  $295 \pm 1$  K, respectively. 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  $295 \pm 1$  K and atmospheric pressure of air. These relative rate data 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  $E/R = -500$  K to adjust the measured rate coefficients to 295 K. The result of this fitting procedure (Atkinson, 1989) was that for 1-butene,  $k = 3.19 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 295 K. Combined with the temperature dependence of Atkinson and Pitts (1975), this leads to the preferred values.

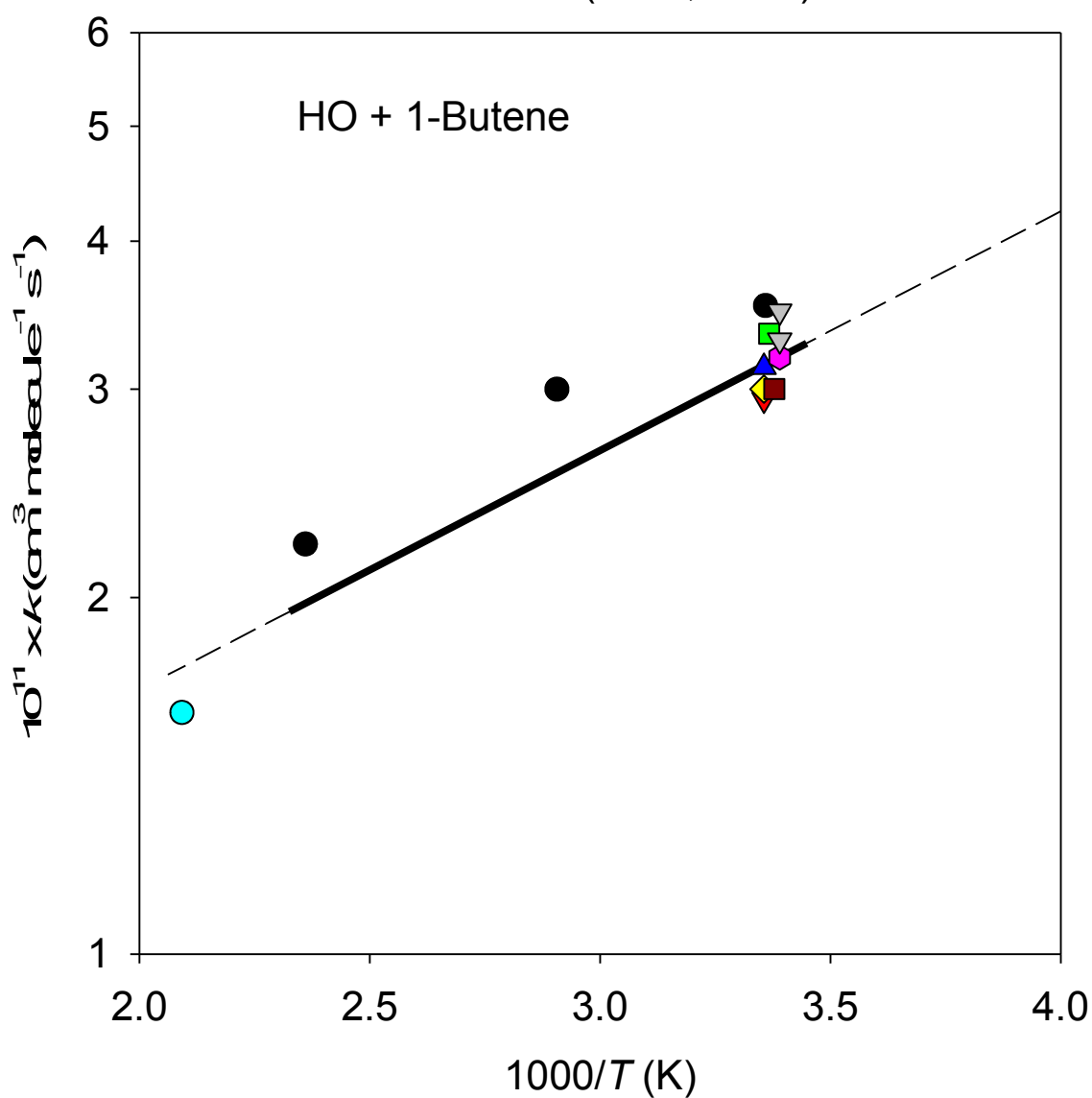
The more recent absolute rate coefficients of Sims et al. (1994) and Vakhtin et al. (2001, 2003) at 295-296 K are in good agreement with the preferred value, and the 478 K rate coefficient of Liu et al. (1989) is in good agreement with extrapolation of the recommended rate expression. The preferred Arrhenius expression should not be used much below room temperature; clearly extrapolation to 165-170 K leads to overprediction of the measured rate coefficients of Sims et al. (1994) and Vakhtin et al. (2001, 2003). Rather, the expression of the form  $k = a \exp(-bT)$  appears to give a reasonable fit, with  $a = 2.56 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $b = 0.00705$  (Atkinson and Arey, 2003).

At room temperature and below, the reaction proceeds by HO radical addition to the C=C bond, with H-atom abstraction accounting for <10% of the overall reaction at room temperature (Atkinson et al., 1985). At elevated temperatures (>650 K), the HO-1-butene adducts decompose rapidly back to reactants and the observed reaction is then H-atom abstraction (Atkinson, 1989).

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