APPENDIX 1 example data sheets

A1 IUPAC Data Sheet HOx_VOC63 (HO + *cis*-2-Butene → products)

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
1.04×10^{-11} exp[$(488 \pm 151)/T$]	298-425	Atkinson and Pitts, 1975	FP-RF (a)
$(5.37 \pm 0.54) \times 10^{-11}$	297.6		
$(4.26 \pm 0.25) \times 10^{-11}$	298	Ravishankara et al., 1978	FP-RF (b)
$(1.30 \pm 0.13) \times 10^{-10}$	170	Sims et al., 1994	PLP-LIF (c)
$(6.18 \pm 0.57) \times 10^{-11}$	295		
Relative Rate Coefficients			
6.12×10^{-11}	298	Morris and Niki, 1971a	DF-MS (d)
$(5.3 \pm 1.1) \times 10^{-11}$	305 ± 2	Lloyd et al., 1976	RR (e)
$(6.0 \pm 1.2) \times 10^{-11}$	305 ± 2	Winer et al., 1976	RR (f)
$(5.47 \pm 0.18) \times 10^{-11}$	298 ± 2	Ohta, 1984	RR (g)
$(5.71 \pm 0.14) \times 10^{-11}$	295 ± 1	Atkinson and Aschmann, 1984	RR (h)

Comments

(a) Experiments carried out at 25 Torr (33 mbar) of Ar diluent.

(b) Rate coefficients measured at 3 and 20 Torr (4 and 27 mbar) of helium diluent, with rate coefficients of $(4.32 \pm 0.41) \times 10^{-11}$ and $(4.26 \pm 0.25) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively. Value cited in the table is that at 20 Torr He.

(c) Experiments at 295 K were carried out at a total pressure of Ar diluent of 14 Torr (19 mbar). Rate coefficients of $(3.89 \pm 0.23) \times 10^{-10}$, $(3.28 \pm 0.33) \times 10^{-10}$ and $(3.02 \pm 0.14) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} were also measured at 23, 44 and 75 K, respectively.

(d) A rate coefficient for HO + *cis*-2-butene was obtained relative to that for propene at 1 Torr (1.3 mbar) He diluent by monitoring the decays of *cis*-2-butene and propene and the respective average HO radical concentrations under identical experimental conditions. The rate coefficient ratio k(HO + *cis*-2-butene)/k(HO + propene) = 3.6 is placed on an absolute basis by use of a rate coefficient of k(HO + propene) = 1.7×10^{-11} cm^3 molecule^{-1} s^{-1} under the experimental condition used (Morris and Niki, 1971b).

(e) HO radicals generated by the photolysis of organic-NO_x mixtures at atmospheric pressure in a 5870 L reaction chamber, with analyses of *cis*-2-butene and *n*-butane (the reference compound) by GC. The measured rate coefficient ratio k(HO + *cis*-2-butene)/k(HO + *n*-butane) = 21.8 ± 4.4 is placed on an absolute basis using a rate coefficient of k(HO + *n*-butane) = 2.44×10^{-12} cm^3 molecule^{-1} s^{-1} at 305 K (IUPAC, current recommendation).

(f) HO radicals generated by the photolysis of organic-NO_x mixtures at atmospheric pressure in a 5870 L reaction chamber, with analyses of *cis*-2-butene and 2-methylpropene (the reference compound) by GC. The measured rate coefficient ratio k(HO + *cis*-2-butene)/k(HO + 2-methylpropene) = 1.22 ± 0.25 is placed on an absolute basis using a rate coefficient of k(HO + 2-methylpropene) = 4.92×10^{-11} cm^3 molecule^{-1} s^{-1} at 305 K (IUPAC, current recommendation).

(g) HO radicals were generated by the photolysis of H_2O_2 at 253.7 nm in 760 Torr of N_2 or O_2 diluent in a quartz vessel. The concentrations of *cis*-2-butene and 2-methyl-2-butene (the reference compound) were measured by GC during the experiments. The measured rate coefficient ratio *k*(HO + *cis*-2-butene)/*k*(HO + 2-methyl-2-butene) = 0.63 ± 0.02 is placed on an absolute basis by use of a rate coefficient of *k*(HO + 2-methyl-2-butene) = 8.69×10^{-11} at 298 K and atmospheric pressure of air (Atkinson and Arey, 2003).

(h) HO radicals were generated by the photolysis of CH_3ONO in air at wavelengths >300 nm in a ~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*(HO + *cis*-2-butene)/*k*(HO + propene) = 2.13 ± 0.05 is placed on an absolute basis by use of a rate coefficient of *k*(HO + propene) = 2.68×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 295 K and atmospheric pressure of air (Atkinson and Arey, 2003).

Preferred Values

$k = 1.1 \times 10^{-11} \exp(485/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 290-430 K
$k = 5.6 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta(E/R) = \pm 200$ 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 Lloyd et al. (1976), Winer et al. (1976), Ohta (1984) and Atkinson and Aschmann (1984) are in reasonable agreement, with those of Lloyd et al. (1976) and Winer et al. (1976) having large associated uncertainties. The absolute rate coefficient of Ravishankara et al. (1978) is ~20% lower, possibly because of wall losses of *cis*-2-butene in the static reaction vessel used (Atkinson, 1989). 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 ± 1 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 $E/R = -500$ K to adjust the measured rate coefficients to 295 K. The result of this fitting procedure (Atkinson, 1989) was that for *cis*-2-butene, $k = 5.71 \times 10^{-11}$ cm^3 $molecule^{-1}$ 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 agreement with the preferred value within the experimental uncertainties. 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 $a = 4.0 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} and $b = 0.0066$, based on the preferred 295 K rate coefficient 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 K), the HO-*cis*-2-butene adduct is expected to decompose rapidly back to reactants and the observed reaction is then H-atom abstraction (Atkinson, 1989).

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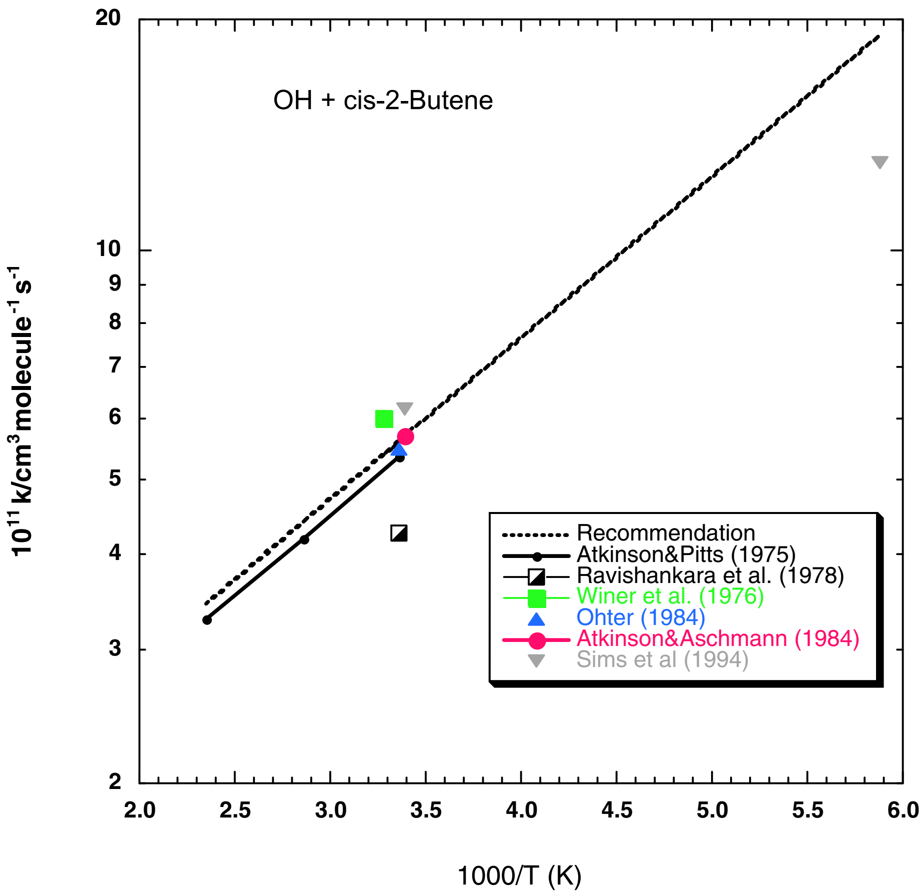
Figure A1 Arrhenius plot of data for HO + cis-2-butene reaction



APPENDIX 2 – Published Evaluations

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