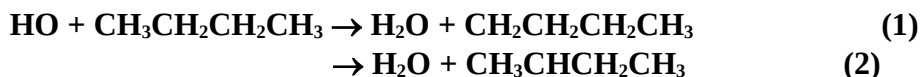


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC7

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet last evaluated December 2007 (with revision of the preferred values).



$$\Delta H^\circ(1) = -72.4 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -86.6 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.41 \times 10^{-11} \exp[-(524 \pm 93)/T]$	298-495	Greiner, 1970	FP-KS
$(2.56 \pm 0.08) \times 10^{-12}$	298		
$(2.35 \pm 0.35) \times 10^{-12}$	298	Stuhl, 1973	FP-RF
$(4.22 \pm 0.17) \times 10^{-12}$	298	Gordon and Mulac, 1975	PR-RA
$(4.15 \pm 0.17) \times 10^{-12}$	381		
$(4.98 \pm 0.17) \times 10^{-12}$	416		
$1.76 \times 10^{-11} \exp[-(559 \pm 151)/T]$	298-420	Perry et al., 1976	FP-RF
$(2.72 \pm 0.27) \times 10^{-12}$	298		
$(2.67 \pm 0.22) \times 10^{-12}$	297 ± 2	Paraskevopoulos and Nip, 1980	FP-RA
$(2.3 \pm 0.3) \times 10^{-12}$	295	Schmidt et al., 1985	PLP-LIF
$2.34 \times 10^{-17} T^{1.95} \exp(134/T)$	294-509	Droege and Tully, 1986	PLP-LIF
$(2.42 \pm 0.10) \times 10^{-12}$	294		
$(2.25 \pm 0.10) \times 10^{-12}$	297 ± 2	Abbatt et al., 1990	DF-LIF
$(2.32 \pm 0.08) \times 10^{-12}$	~298	Schiffman et al., 1991	PLP-IR
$2.04 \times 10^{-17} T^2 \exp[(85 \pm 8)/T]$	231-378	Talukdar et al., 1994	PLP-LIF
$(2.459 \pm 0.018) \times 10^{-12}$	299		
$(2.43 \pm 0.07) \times 10^{-12}$	300	Donahue et al., 1998	DF-LIF
$(2.74 \pm 0.08) \times 10^{-12}$	325		
$(2.87 \pm 0.09) \times 10^{-12}$	340		
$(3.48 \pm 0.10) \times 10^{-12}$	375		
$(3.54 \pm 0.11) \times 10^{-12}$	390		
$(2.6 \pm 0.5) \times 10^{-12}$	300	Chuong and Stevens, 2002	DF-LIF
$(2.6 \pm 0.2) \times 10^{-12}$	300		
$(1.00 \pm 0.03) \times 10^{-12}$	185	Donahue and Clarke, 2004	DF-LIF (a)
$(1.14 \pm 0.04) \times 10^{-12}$	195		
$(1.21 \pm 0.08) \times 10^{-12}$	205		
$(1.36 \pm 0.04) \times 10^{-12}$	215		
$(1.45 \pm 0.04) \times 10^{-12}$	225		
$(1.64 \pm 0.13) \times 10^{-12}$	235		
$(1.77 \pm 0.08) \times 10^{-12}$	245		
$(1.74 \pm 0.05) \times 10^{-12}$	255		
$(1.95 \pm 0.06) \times 10^{-12}$	265		
$(2.07 \pm 0.07) \times 10^{-12}$	275		
$(2.17 \pm 0.06) \times 10^{-12}$	285		
$(2.54 \pm 0.08) \times 10^{-12}$	295		

Relative Rate Coefficients

9.9×10^{-12}	753	Baker et al., 1970; Baldwin and Walker, 1979	RR (b)
$(9.3 \pm 0.8) \times 10^{-12}$	653	Hucknall et al, 1975	RR (c)
$(2.52 \pm 0.25) \times 10^{-12}$	299 ± 2	Atkinson et al., 1981	RR (d)
$(2.71 \pm 0.32) \times 10^{-12}$	295 ± 1	Atkinson and Aschmann, 1984	RR (d)
$(2.70 \pm 0.34) \times 10^{-12}$	300 ± 2	Barnes et al., 1986	RR (e)
$(2.36 \pm 0.04) \times 10^{-12}$	300	Behnke et al., 1988	RR (f)
$1.39 \times 10^{-11} \exp(-526/T)$	235-361	DeMore and Bayes, 1999	RR (g)
2.33×10^{-12}	298		

Comments

- (a) Indicated errors are one standard deviation. Overall uncertainties were assessed to be $\pm 7.5\%$ for temperatures >250 K and $\pm 10\%$ for temperatures <250 K.
- (b) Derived from the effects of the addition of small amounts of *n*-butane to slowly reacting mixtures of $\text{H}_2 + \text{O}_2$. The loss of H_2 was followed by monitoring the pressure change due to the reaction $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$, and the loss of *n*-butane was measured by GC. The rate coefficient ratio $k(\text{HO} + n\text{-butane})/k(\text{HO} + \text{H}_2) = 13.2$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{H}_2) = 7.87 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 753 K (Atkinson, 2003).
- (c) HO radicals were generated by the decomposition of H_2O_2 in a boric acid-coated reaction vessel, and the concentrations of *n*-butane and propane (the reference compound) were measured by GC. The measured rate coefficient ratios of $k(\text{HO} + n\text{-butane})/k(\text{HO} + \text{propane}) = 1.54 \pm 0.13$ is placed on an absolute value using a rate coefficient of $k(\text{HO} + \text{propane}) = 6.16 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 653 K (IUPAC, 2004).
- (d) HO radicals were generated by the photolysis of CH_3ONO in one atmosphere of air. The concentrations of *n*-butane and propene (the reference compound) were measured by GC. The measured rate coefficient ratios of $k(\text{HO} + n\text{-butane})/k(\text{HO} + \text{propene}) = 0.0962 \pm 0.0093$ at 299 ± 2 K (Atkinson et al., 1981) and 0.101 ± 0.012 at 295 ± 1 K (Atkinson and Aschmann, 1984) are placed on an absolute value using a rate coefficient of $k(\text{HO} + \text{propene}) = 4.85 \times 10^{-12} \exp(504/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at atmospheric pressure of air (Atkinson, 1997).
- (e) HO radicals were generated by the photolysis of H_2O_2 in air at atmospheric pressure, and the concentrations of *n*-butane and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + n\text{-butane})/k(\text{HO} + \text{ethene}) = 0.32 \pm 0.04$ is placed on an absolute basis by use of 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, 1997).
- (f) HO radicals were generated by the photolysis of NO_x -organic-air mixtures at atmospheric pressure. The concentrations of *n*-butane and *n*-octane (the reference compound) were measured by GC, and the measured rate coefficient ratio of $k(\text{HO} + n\text{-butane})/k(\text{HO} + n\text{-octane})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + n\text{-octane}) = 8.15 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K (Atkinson, 2003).
- (g) HO radicals were generated by the photolysis of H_2O at 185 nm or, at low temperatures, by the photolysis of N_2O at 185 nm in the presence of H_2 . The concentrations of *n*-butane and propane (the reference compound) were measured by GC. The measured rate coefficient ratios $k(\text{HO} + n\text{-butane})/k(\text{HO} + \text{propane})$ are placed on an absolute basis using a rate coefficient of $k(\text{HO} + \text{propane}) = 1.65 \times 10^{-17} T^2 \exp(87/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2004).

Preferred Values

$k = 2.35 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 9.8 \times 10^{-12} \exp(-425/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 180-300 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.

$$\Delta(E/R) = \pm 100 \text{ K.}$$

Comments on Preferred Values

The preferred values are based on the absolute rate coefficients of Droege and Tully (1986), Abbatt et al. (1990), Talukdar et al. (1994), Donahue et al. (1998) and Donahue and Clarke (2004) and the relative rate coefficients of DeMore and Bayes (1999). An Arrhenius plot of the rate coefficients from these studies (Droege and Tully, 1986; Abbatt et al., 1990; Talukdar et al., 1994; Donahue et al., 1998; DeMore and Bayes, 1999; Donahue and Clarke, 2004), plus the higher temperature relative rate data of Baker et al. (1970) [as re-evaluated by Baldwin and Walker (1979)] and Hucknall et al. (1975), is clearly curved (see Arrhenius plot).

The rate coefficients from the studies of Droege and Tully (1986), Abbatt et al. (1990), Talukdar et al. (1994), Donahue et al. (1998), DeMore and Bayes (1999) and Donahue and Clarke (2004) are fitted to the three parameter expression, $k = CT^2 \exp(-D/T)$, resulting in $k = 2.03 \times 10^{-17} T^2 \exp(78/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 185-509 K. This expression also fits the higher temperature rate coefficient of Hucknall et al. (1975) extremely well. An Arrhenius fit, $k = A \exp(-B/T)$, of the rate coefficients from these studies of Droege and Tully (1986), Abbatt et al. (1990), Talukdar et al. (1994), Donahue et al. (1998), DeMore and Bayes (1999) and Donahue and Clarke (2004) at temperatures ≤ 300 K results in $k = 9.82 \times 10^{-12} \exp(-427/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. As shown in the Arrhenius plot, this is an excellent representation of the rate coefficients from these studies at ≤ 300 K, and is the recommended Arrhenius expression. The preferred values are in good agreement with the room temperature absolute and relative rate coefficients of Greiner (1970), Stuhl (1973), Perry et al. (1976), Paraskevopoulos and Nip (1980), Schmidt et al. (1985), Schiffman et al. (1991), Atkinson et al. (1981), Atkinson and Aschmann (1984), Barnes et al. (1986), Behnke et al. (1988) and Chuong and Stevens (2002), which were not used in the evaluation of the rate coefficient.

Note that the Arrhenius expression derived from the 3-parameter fit, centered at 225 K with $A = C e^2 T^2$ and $B = D + 2T$, of $k = 7.59 \times 10^{-12} \exp(-372/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ results in predicted rate coefficients 8% lower at 300 K and 5% higher at 180 K than those calculated from the preferred Arrhenius fit of the rate coefficients at ≤ 300 K.

Droege and Tully (1986) also measured rate coefficients for the reaction of the HO radical with n-butane-d₁₀, and derived a value of $k_1/k_2 = 1.035 \exp(-536/T)$, leading to $k_1 = 3.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and $k_2 = 2.00 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

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- Baldwin and Walker (1979)
- ▼ Hucknall et al. (1975)
- Droege and Tully (1986)
- ◆ Abbatt et al. (1990)
- ▲ Talukdar et al. (1994)
- ◆ Donahue et al. (1998)
- DeMore and Bayes (1999)
- ▼ Donahue and Clark (2004)
- 3-Parameter fit (see text)
- Recommended Arrhenius fit

