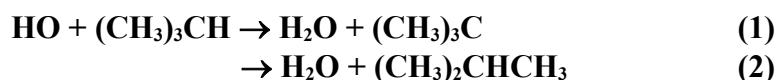


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC60

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This data sheet created March 2009.



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>			
$(2.13 \pm 0.12) \times 10^{-12}$	297 ± 1	Greiner, 1967	FP-KS
$8.7 \times 10^{-12} \exp[-(387 \pm 63)/T]$	297-498	Greiner, 1970	FP-KS
$(2.67 \pm 0.17) \times 10^{-12}$	298		
$(2.70 \pm 0.20) \times 10^{-12}$	267	Trevor et al., 1982	PLP-RF
3.6×10^{-12}	298		
$(3.62 \pm 0.40) \times 10^{-12}$	324		
$(1.83 \pm 0.34) \times 10^{-12}$	296	Böhland et al., 1984	PLP-LMR
$(1.9 \pm 0.3) \times 10^{-12}$	295	Schmidt et al., 1985	PLP-LIF
$4.31 \times 10^{-17} T^{1.80} \exp(175/T)$	293-864	Tully et al., 1986a	PLP-LIF
$(2.19 \pm 0.11) \times 10^{-12}$	293		
$(2.09 \pm 0.42) \times 10^{-11}$	1146 ± 15	Bott and Cohen, 1989	SH-RA
$(2.11 \pm 0.09) \times 10^{-12}$	~298	Schiffman et al., 1991	PLP-IR
$9.32 \times 10^{-18} T^2 \exp[(274 \pm 16)/T]$	231-372	Talukdar et al., 1994	PLP-LIF
$(2.10 \pm 0.16) \times 10^{-12}$	298		
$(2.09 \pm 0.06) \times 10^{-12}$	300	Donahue et al., 1998	DF-LIF
$(2.38 \pm 0.07) \times 10^{-12}$	325		
$(2.47 \pm 0.09) \times 10^{-12}$	340		
$(2.62 \pm 0.08) \times 10^{-12}$	375		
$(2.72 \pm 0.14) \times 10^{-12}$	390		
<i>Relative Rate Coefficients</i>			
1.9×10^{-11}	793	Baldwin and Walker, 1964	RR (a)
9.9×10^{-12}	753	Baker et al., 1970; Baldwin and Walker, 1979	RR (a)
$(3.43 \pm 0.86) \times 10^{-12}$	298	Gorse and Volman, 1972/73, 1974	RR (b)
$(7.88 \pm 0.44) \times 10^{-12}$	653	Hucknall et al., 1975	RR (c)
2.2×10^{-12}	303	Wu et al., 1976	RR (d)
$(2.19 \pm 0.05) \times 10^{-12}$	300 ± 1	Darnall et al., 1978	RR (e)
$(2.06 \pm 0.05) \times 10^{-12}$	297 ± 2	Atkinson et al., 1984	RR (f)
$(2.17 \pm 0.31) \times 10^{-12}$	297.8 ± 0.4	Edney et al., 1986	RR (e)
$6.33 \times 10^{-21} T^{3.125} \exp(540/T)$	229-403	Wilson et al., 2006	RR (g)
2.09×10^{-12}	298		

Comments

- (a) Derived from the effects of the addition of small amounts of 2-methylpropane to slowly reacting mixtures of H₂ + O₂. The loss of H₂ 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 2-methylpropane was measured by GC. The rate coefficient ratios $k(\text{HO} + 2\text{-methylpropane})/k(\text{HO} + \text{H}_2) = 20$ at 793 K (Baldwin and Walker, 1964) and 12.6 at 753 K (Baker et al., 1970; Baldwin and Walker, 1979) are 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 and $9.62 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 793 K (Atkinson, 2003).

- (b) HO radicals were generated by the photolysis of H_2O_2 at 254 nm in $\text{H}_2\text{O}_2\text{-CO-O}_2\text{-2-methylpropane}$ mixtures at total pressures of 16-21 Torr (21-28 mbar) (Gorse and Volman, 1972/73). The effect of varying the 2-methylpropane concentration on the CO_2 production rate was investigated (Gorse and Volman, 1972/73), and a rate coefficient ratio of $k(\text{HO} + 2\text{-methylpropane})/k(\text{HO} + \text{CO}) = 23.5$ derived (Gorse and Volman, 1974). This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{CO}) = 1.46 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation, using $M = \text{N}_2$).
- (c) HO radicals were generated by the decomposition of H_2O_2 in a boric acid-coated reaction vessel, and the concentrations of 2-methylpropane and propane (the reference compound) were measured by GC. The measured rate coefficient ratios of $k(\text{HO} + 2\text{-methylpropane})/k(\text{HO} + \text{propane}) = 1.28 \pm 0.07$ 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, current recommendation).
- (d) HO radicals were generated by the photolysis of organic- $\text{NO}_x\text{-O}_2\text{-air}$ mixtures at atmospheric pressure. 2-Methylpropane and *cis*-2-butene (the reference compound) were measured by GC, and the measured rate coefficient ratio $k(\text{HO} + 2\text{-methylpropane})/k(\text{HO} + \textit{cis}\text{-2-butene}) = 0.04$ 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).
- (e) HO radicals were generated by the photolysis of CH_3ONO in one atmosphere of air. The concentrations of 2-methylpropane and *n*-butane (the reference compound) were measured by GC. The measured rate coefficient ratios $k(\text{HO} + 2\text{-methylpropane})/k(\text{HO} + \textit{n}\text{-butane})$ are placed on an absolute basis by use of rate coefficients of $k(\text{HO} + \textit{n}\text{-butane}) = 2.34 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and $2.37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K (IUPAC, current recommendation).
- (f) HO radicals were generated by the photolysis of CH_3ONO in one atmosphere of air. The concentrations of 2-methylpropane and *n*-butane (the reference compound) were measured by GC. The measured rate coefficient ratio $k(\text{HO} + 2\text{-methylpropane})/k(\text{HO} + \textit{n}\text{-butane}) = 0.886 \pm 0.021$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \textit{n}\text{-butane}) = 2.33 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K (IUPAC, current recommendation).
- (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 2-methylpropane and *n*-butane (the reference compound) were measured by GC/MS. The measured rate coefficient ratios $k(\text{HO} + 2\text{-methylpropane})/k(\text{HO} + \textit{n}\text{-butane})$ are placed on an absolute basis using a rate coefficient of $k(\text{HO} + \textit{n}\text{-butane}) = 2.03 \times 10^{-17} T^2 \exp(78/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

Preferred Values

$$k = 2.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 5.4 \times 10^{-12} \exp(-285/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 210\text{-}300 \text{ K.}$$

Reliability

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

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

Comments on Preferred Values

The preferred values are based on the absolute rate coefficients of Tully et al. (1986a), Bott and Cohen (1989), Talukdar et al. (1994) and Donahue et al. (1998) and the relative rate coefficients of Baker et al. (1970) [as re-evaluated by Baldwin and Walker (1979)], Hucknall et al. (1975), Atkinson et al. (1984) [which is taken to supersede the earlier study of Darnall et al. (1978)] and Wilson et al. (2006). The three parameter expression, $k = CT^2 \exp(-D/T)$, was fitted to the rate coefficients from these studies, resulting in $k = 1.17 \times 10^{-17} T^2 \exp(213/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 210-1150 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 250 K and is derived from the three parameter expression with $A = C e^2 T^2$ and $B = D + 2T$. The preferred values are in good agreement with the room temperature absolute and relative rate coefficients of Greiner (1967, 1970), Böhland et al. (1984), Schmidt et al. (1985), Schiffman et al. (1991), Wu et al. (1976), Darnall et al. (1978) and Edney et al. (1986), which were not used in the evaluation of the rate coefficient.

Tully et al. (1986a) also measured rate coefficients for the reaction of the HO radical with 2-methylpropane-d₁, 2-methylpropane-d₉ and 2-methylpropane-d₁₀. Combining their rate coefficients for 2-methylpropane, 2-methylpropane-d₁, 2-methylpropane-d₉ and 2-methylpropane-d₁₀ with the deuterium isotope ratio $k_{\text{H}}/k_{\text{D}}$ for -CH₃/-CD₃ groups obtained from the 2,2-dimethylpropane (neopentane) reaction (Tully et al., 1985, 1986b), Tully et al. (1986a) derived rate coefficients for H-atom abstraction from the primary C-H bonds of the three CH₃ groups ($3k_{\text{primary}}$) and from the tertiary C-H bond in the CH group (k_{tertiary}), of $3k_{\text{primary}} = 3.81 \times 10^{-16} T^{1.53} \exp(-391/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ($6.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K) and $k_{\text{tertiary}} = 9.52 \times 10^{-14} T^{0.51} \exp(-32/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ($1.56 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K).

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- Recommendation
- Tully et al. (1986a)
 - ▼ Bott and Cohen (1989)
 - Talukdar et al. (1994)
 - ◆ Donahue et al. (1998)
 - ▲ Baker et al. (1970), Baldwin and Walker (1979)
 - ◆ Hucknall et al. (1975)
 - Atkinson et al. (1984)
 - ▽ Wilson et al. (2006)

