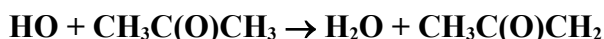


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC19

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 no revision of the preferred values).



$$\Delta H^\circ = -87.8 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.7 \times 10^{-12} \exp[-(600 \pm 75)/T]$	240-440	Wallington and Kurylo, 1987	FP-RF
$(2.16 \pm 0.16) \times 10^{-13}$	296		
$(8.80 \pm 1.32) \times 10^{-12}$	1217	Bott and Cohen, 1991	SH-RA
$1.25 \times 10^{-12} \exp[-(561 \pm 57)/T]$	243-372	Le Calvé et al., 1998	PLP-LIF
$(1.84 \pm 0.24) \times 10^{-13}$	298		
$8.8 \times 10^{-12} \exp[-(1320 \pm 163)/T] + 1.7 \times 10^{-14} \exp[(423 \pm 109)/T]$	202-395	Wollenhaupt et al., 2000	PLP-LIF/RF
$(1.73 \pm 0.09) \times 10^{-13}$	298		
$(1.73 \pm 0.05) \times 10^{-13}$	298	Vasvári et al., 2001	DF-RF
1.38×10^{-13}	199-383	Gierczak et al., 2003	PLP-LIF/DF-CIMS (a)
$+ 3.86 \times 10^{-11} \exp(-1997/T)$			
$(1.77 \pm 0.18) \times 10^{-13}$	298		
$3.99 \times 10^{-24} T^{4.00} \exp[(453 \pm 44)/T]$	298-832	Yamada et al., 2003	PLP-LIF
$(1.56 \pm 0.08) \times 10^{-13}$	298		
$4.90 \times 10^{-11} \exp(-2297/T)$	982-1300	Vasudevan et al., 2005	SH-RA (b)
$3.92 \times 10^{-12} \exp[-(938 \pm 70)/T]$	271-402	Davis et al., 2005	DF-RF/LIF (c)
$(1.73 \pm 0.06) \times 10^{-13}$	300 ± 2		
<i>Relative Rate Coefficients</i>			
$(2.7 \pm 0.1) \times 10^{-13}$	303 ± 2	Kerr and Stocker, 1986	RR (d)
$(2.17 \pm 0.04) \times 10^{-13}$	298 ± 2	Carr et al., 2003	RR (e)
$1.39 \times 10^{-12} \exp[-(604 \pm 44)/T]$	253-373	Raff et al., 2005	RR (f)
1.83×10^{-13}	298		

Comments

- Rate coefficients for the reaction of HO radicals with acetone were shown to be independent of pressure over the range 1.1 Torr (1.5 mbar) of He diluent to 490 Torr (653 mbar) of SF₆ diluent. Rate coefficients were also measured for the reactions HO + CD₃C(O)CD₃ (211-383 K), DO + CD₃C(O)CD₃ (213-324 K), H¹⁸O + CH₃C(O)CH₃ (240-296 K) and DO + CH₃C(O)CH₃ (223-296 K) over the indicated temperature ranges. The measured H/D isotope effect, $k(\text{HO} + \text{CH}_3\text{C}(\text{O})\text{CH}_3)/k(\text{HO} + \text{CD}_3\text{C}(\text{O})\text{CD}_3)$, increased from 5.9 ± 0.9 at 298 K to 8.6 ± 0.8 at 212 K.
- HO radicals were generated by shock-heating of *tert*-butyl hydroperoxide and monitored by laser absorption at 306.7 nm. A fit of the absolute rate data of Wallington and Kurylo (1987), Bott and Cohen (1991), Le Calvé et al. (1998), Wollenhaupt et al. (2000), Gierczak et al. (2003) and

Vasudevan et al. (2005) and the relative rate data of Tranter et al. (2001) to a multi-parameter expression yielded $k = \{1.33 \times 10^{-13} + 1.01 \times 10^{-15} T^{1.41} \exp(-1289/T)\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 199-1300 K.

- c) Rate coefficients were also measured for the reaction $\text{HO} + \text{CD}_3\text{C}(\text{O})\text{CD}_3$ over the temperature range 258-369 K, and for $\text{DO} + \text{CH}_3\text{C}(\text{O})\text{CH}_3$ and $\text{DO} + \text{CD}_3\text{C}(\text{O})\text{CD}_3$ at $300 \pm 2 \text{ K}$.
- d) HO radicals were generated by the photolysis of HONO in air, and the concentrations of acetone and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{acetone})/k(\text{HO} + \text{ethene}) = 0.032 \pm 0.001$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{ethene}) = 8.32 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 303 K and atmospheric pressure (Atkinson, 1997).
- e) HO radicals were generated by the photolysis of O_3 at 254 nm in the presence of H_2O . The diluent gas was O_2 and the total pressure was 730-760 Torr (973-1013 mbar). The concentrations of acetone and 1,2-dichloroethane (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{acetone})/k(\text{HO} + 1,2\text{-dichloroethane}) = 0.94 \pm 0.015$ was placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + 1,2\text{-dichloroethane}) = 2.31 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Carr et al., 2003).
- f) HO radicals were generated by the photolysis at $<315 \text{ nm}$ of $\text{O}_3\text{-O}_2\text{-H}_2\text{O-He}$ mixtures at 735-750 Torr (980-1000 mbar) total pressure in 0.16 or 0.50 L quartz reaction vessels. The concentrations of acetone and CH_3CHF_2 (the reference compound) were measured by MS. The measured rate coefficient ratios of $k(\text{HO} + \text{acetone})/k(\text{HO} + \text{CH}_3\text{CHF}_2)$ are placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{CH}_3\text{CHF}_2) = 2.80 \times 10^{-18} T^2 \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation). Rate coefficients were also measured for the reaction of HO radicals with $\text{CD}_3\text{C}(\text{O})\text{CD}_3$, relative to those for CH_2F_2 , over the temperature range 293-373 K. Use of $k(\text{HO} + \text{CH}_2\text{F}_2) = 4.80 \times 10^{-18} T^2 \exp(-1080/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation) leads to $k(\text{HO} + \text{CD}_3\text{C}(\text{O})\text{CD}_3) = 5.06 \times 10^{-13} \exp(-819/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 293-373 K. Acetic acid was observed as a product of the reaction of HO radicals with $\text{CH}_3\text{C}(\text{O})\text{CH}_3$, but was attributed mainly or wholly to secondary chemistry.

Preferred Values

$k = 1.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = \{8.8 \times 10^{-12} \exp(-1320/T) + 1.7 \times 10^{-14} \exp(423/T)\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 195-440 K.

Reliability

$\Delta \log k = \pm 0.08$ over the temperature range 195-440 K.

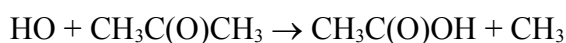
Comments on Preferred Values

The absolute rate studies of Wallington and Kurylo (1987), Bott and Cohen (1991), Le Calvé et al. (1998), Wollenhaupt et al. (2000), Vasvári et al. (2001), Gierczak et al. (2003), Yamada et al. (2003), Vasudevan et al. (2005) and Davis et al. (2005) lead to a generally consistent temperature-dependent set of rate coefficients for the reaction of HO radicals with acetone over the range 199-1300 K, and the relative rate coefficients measured by Raff et al. (2005) over the temperature range 253-373 K are also in good agreement with these absolute studies. In particular, the rate coefficients of Wollenhaupt et al. (2000) and Gierczak et al. (2003) are in excellent agreement over the temperature range common to both studies (202-383 K), and the low temperature ($<240 \text{ K}$) data of Wollenhaupt et al. (2000) have been confirmed by Gierczak et al. (2003). In these studies of Wollenhaupt et al. (2000) and Gierczak et al. (2003), the concentration of acetone in the flow stream was measured by UV absorption. The preferred rate expression uses the non-linear least-squares analysis presented by Wollenhaupt et al. (2000), which leads to a generally excellent fit of the rate coefficients of

Wallington and Kurylo (1987), Le Calvé et al. (1998), Wollenhaupt et al. (2000), Gierczak et al. (2003) and Davis et al. (2005) over the range 199-440 K. Note that the temperature-dependence of the rate coefficient for this reaction at ≤ 200 K is not well established, and the preferred expression should not be used below 195 K.

The measured deuterium isotope effect, $k(\text{HO} + \text{CH}_3\text{C}(\text{O})\text{CH}_3)/k(\text{HO} + \text{CD}_3\text{C}(\text{O})\text{CD}_3)$, is substantial, being 5.9 ± 0.9 (Gierczak et al., 2003), 6.8 ± 1.0 (Yamada et al., 2003), 5.65 (Raff et al., 2005) and 5.2 ± 0.6 (Davis et al., 2005) at 298-300 K, increasing to 8.6 ± 0.8 at 212 K (Gierczak et al., 2003). The magnitude of this deuterium isotope effect indicates that the rate-determining step involves C-H (or C-D) bond breakage.

Products of this reaction have been investigated by Wollenhaupt and Crowley (2000), Vasvári et al. (2001), Vandenberg et al. (2002), Tyndall et al. (2002), Turpin et al. (2003, 2006) and Talukdar et al. (2003), with conflicting results in some cases. Wollenhaupt and Crowley (2000) measured the amount of CH_3 radicals formed in the pathway



by converting methyl radicals to methoxy radicals by reaction with NO_2 and monitoring CH_3O by LIF, and concluded that the channel forming $\text{CH}_3\text{C}(\text{O})\text{OH} + \text{CH}_3$ accounted for $\sim 50\%$ of the overall reaction at 298 K and $\sim 30\%$ at 233 K. Vasvári et al. (2001) used a DF system with LIF detection of HO radicals and $\text{CH}_3\text{C}(\text{O})\text{CH}_2$ radicals to obtain a branching ratio for the H-atom abstraction pathway of 0.50 ± 0.04 at 298 K, apparently consistent with the data of Wollenhaupt and Crowley (2000). However, Vandenberg et al. (2002), Tyndall et al. (2002), Talukdar et al. (2003) and Turpin et al. (2006) measured upper limits to acetic acid formation of $<5\%$ at 298 K (Vandenberg et al., 2002), $<10\%$ at 296 K and 251 K (Tyndall et al., 2002), and $<1\%$ over the range 237-353 K (Talukdar et al., 2003). Furthermore, Talukdar et al. (2003) and Turpin et al. (2003) measured yields of $\text{CH}_3\text{C}(\text{O})\text{CH}_2$ radicals of $96 \pm 11\%$, independent of temperature over the range 242-350 K, and $90 \pm 10\%$ at 298 K, respectively. The results of these recent product studies of Vandenberg et al. (2002), Tyndall et al. (2002), Turpin et al. (2003) and Talukdar et al. (2003), together with the large deuterium isotope effect observed by Gierczak et al. (2003), Yamada et al. (2003) and Raff et al. (2005) and the lack of a pressure dependence (Gierczak et al., 2003), indicate that the reaction proceeds by H-atom abstraction.

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- \triangle Wallington and Kurylo (1987)
- \blacklozenge Le Calve et al. (1998)
- \bullet Wollenhaupt et al. (2000)
- \blacktriangledown Vasvari et al. (2001)
- \blacksquare Gierczak et al. (2003)
- \blacktriangle Yamada et al. (2003)
- \circ Davis et al. (2005)
- Recommendation

