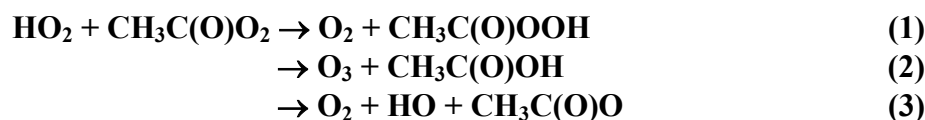


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC54

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$$\Delta H^\circ(1) = -180 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -132 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -13 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$4.3 \times 10^{-13} \exp[(1040 \pm 100)/T]$	253-368	Moortgat et al., 1989	FP-AS (a)
$(1.3 \pm 0.3) \times 10^{-11}$	298		
$3.9 \times 10^{-13} \exp[(1350 \pm 250)/T]$	269-363	Crawford et al., 1999	PLP-IR-AS (b)
$(4.4 \pm 1.6) \times 10^{-11}$	297		
$6.4 \times 10^{-13} \exp[(925 \pm 120)/T]$	273-403	Tomas et al., 2001	FP-AS (c)
$(1.51 \pm 0.07) \times 10^{-11}$	293		
$(1.50 \pm 0.08) \times 10^{-11}$	293	Le Crâne et al., 2006	FP-AS (d)
$(1.4 \pm 0.5) \times 10^{-11}$	298	Dillon and Crowley, 2008	PLP-LIF (e)
$(2.1 \pm 0.4) \times 10^{-11}$	298*	Groß et al., 2014	PLP-LIF-AS (f)
$(2.4 \pm 0.4) \times 10^{-11}$	293	Winiberg et al., 2016	UVP-FTIR-LIF (g)
<i>Branching Ratios</i>			
$k_1/k_2 \approx 3$	298	Niki et al., 1985	FTIR (h)
$k_2/k = 0.33 \pm 0.07$	253-368	Moortgat et al., 1989	FP-AS (i)
$k_1/k_2 = 3.3 \times 10^2 \exp[(-1430 \pm 480)/T]$	263-333	Horie and Moortgat, 1992	FTIR (j)
$k_1/k_2 = 2.7$	298		
$k_2/k = 0.12 \pm 0.04$	295	Crawford et al., 1999	PLP-FTIR (k)
$k_2/k = 0.20 \pm 0.02$	298-373	Tomas et al., 2001	FP-AS (l)
$k_1/k = 0.40 \pm 0.16$	298	Hasson et al., 2004	UVP-FTIR/HPLC (m)
$k_2/k = 0.20 \pm 0.08$			
$k_3/k = 0.40 \pm 0.16$			
$k_2/k = 0.20 \pm 0.01$	298	Le Crâne et al., 2006	FP-AS (n)
$k_3/k < 0.1$			
$k_1/k = 0.38 \pm 0.13$	296	Jenkin et al., 2007	UVP-FTIR (o)
$k_2/k = 0.12 \pm 0.04$			
$k_3/k = 0.43 \pm 0.10$			
$k_3/k = 0.5 \pm 0.2$	298	Dillon and Crowley, 2008	PLP-LIF (e)
$k_2/k = 0.16 \pm 0.08$	298*	Groß et al., 2014	PLP-LIF-AS (f)
$k_3/k = 0.61 \pm 0.09$			
$k_1/k = 0.37 \pm 0.10$	293	Winiberg et al., 2016	UVP-FTIR-LIF (g)
$k_2/k = 0.12 \pm 0.04$			
$k_3/k = 0.51 \pm 0.12$			

Comments

- (a) Flash photolysis of Cl_2 in the presence of $\text{CH}_3\text{CHO}-\text{CH}_3\text{OH}-\text{N}_2$ mixtures at total pressures of 800 mbar to 866 mbar (600 Torr to 650 Torr). $[\text{CH}_3\text{C}(\text{O})\text{O}_2]$ was monitored by UV absorption over the wavelength range 195 nm to 280 nm and the absorption cross-section measured relative to $\Delta(\text{HO}_2) = 5.3 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 210 nm. Rate coefficients were derived from a computer simulation of absorption traces at a range of wavelengths, based on a mechanism including secondary removal of $\text{CH}_3\text{C}(\text{O})\text{O}_2$. The mechanism assumed that the $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2$ reaction proceeds by channels (1) and (2).
- (b) Pulsed laser photolysis of $\text{Cl}_2-\text{CH}_3\text{OH}-\text{CH}_3\text{CHO}-\text{O}_2-\text{N}_2$ mixtures at a total pressure of about 67 mbar (50 Torr). The progress of the reaction was followed by time-resolved UV absorption measurements over the range 200 nm to 300 nm and by monitoring $[\text{HO}_2]$ by infrared laser diode absorption at 1117.5 cm^{-1} . Because of the difficulty of deconvoluting the UV spectra, values of k were determined from the infrared measurements by fitting the $[\text{HO}_2]$ profiles using a detailed mechanism. The mechanism assumed that the $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2$ reaction proceeds by channels (1) and (2).
- (c) Flash photolysis of $\text{Cl}_2-\text{CH}_3\text{CHO}-\text{CH}_3\text{OH}-\text{O}_2-\text{N}_2$ mixtures. The progress of the reaction was followed by time-resolved UV absorption measurements at 207 nm and 250 nm. Values of k were derived by simulation of the absorption measurements at 207 nm, using a detailed chemical mechanism. The mechanism assumed that the $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2$ reaction proceeds by channels (1) and (2).
- (d) Re-evaluation of the room temperature results of Tomas et al. (2001) using cross-sections recommended by Tyndall et al. (2001), with the assumption that the $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2$ reaction proceeds by channels (1) and (2). Inclusion of channel (3) in the reaction mechanism, with $k_3/k = 0.4$, resulted in an optimised $k = (2.20 \pm 0.07) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, but a stated poorer description of the data.
- (e) Pulsed laser photolysis of $\text{Cl}_2-\text{CH}_3\text{CHO}-\text{CH}_3\text{OH}-\text{O}_2-\text{N}_2$ mixtures to generate the reagent radicals with HO_2 in large excess. The production and removal of HO radicals, formed in channel (3), was followed using direct detection by LIF. k and k_3/k were determined simultaneously from simulation of the time dependence of the HO radical concentration, using a detailed chemical mechanism. No systematic dependence on total pressure over the range 100 to 705 mbar was observed.
- (f) Pulsed laser photolysis of $\text{Cl}_2-\text{CH}_3\text{CHO}-\text{CH}_3\text{OH}-\text{O}_2-\text{N}_2$ mixtures at room temperature. Experiments performed with initial $[\text{HO}_2]/[\text{CH}_3\text{C}(\text{O})\text{O}_2]$ in the range 0.9-47.0 at total pressures over the range 133 to 677 mbar, with the time dependence of the reagent radical concentrations monitored using UV absorption. The formation of O_3 (by channel (2)) and HO radicals (by channel (3)) was monitored using UV absorption and LIF, respectively. k , k_2/k and k_3/k were determined from simulation of the system using a detailed mechanism, with the errors in the optimised parameters assessed using a Monte Carlo approach. Values of k_3/k of 0.63 ± 0.09 , 0.60 ± 0.09 , and 0.54 ± 0.08 reported at 133, 266 and 677 mbar, respectively, with the final reported value tabulated above based on the mean of all determinations. The reaction of $\text{CH}_3\text{C}(\text{O})\text{O}_2$ with DO_2 was also investigated at 133 and 266 mbar by substituting the reagent CH_3OH with CH_3OD , leading to an identical value of k , but a larger value of $k_3/k = (0.80 \pm 0.14)$.
- (g) UV irradiation of $\text{Cl}_2-\text{CH}_3\text{CHO}-\text{CH}_3\text{OH}-\text{air}$ mixtures in a stainless steel chamber at a total pressure of 1 bar. The chamber was equipped with an FTIR detection system for organic reagents and products and O_3 , and a LIF based FAGE system for detection of HO and HO_2 . Experiments were performed with HO_2 in excess over $\text{CH}_3\text{C}(\text{O})\text{O}_2$ ($[\text{CH}_3\text{OH}]/[\text{CH}_3\text{CHO}]$ in the range 1.5-5.6) and the initial time development of the system ($< 50\%$ depletion of CH_3CHO) was characterised. Values of k , k_1/k , k_2/k and k_3/k were derived simultaneously from optimised simulation of the system over the range of studied conditions using a detailed chemical mechanism.
- (h) FTIR study of irradiated $\text{Cl}_2-\text{HCHO}-\text{CH}_3\text{CHO}-\text{O}_2$ mixtures. The branching ratio was based on the analysis of the products $\text{CH}_3\text{C}(\text{O})\text{OOH}$, $\text{CH}_3\text{C}(\text{O})\text{OH}$ and O_3 , with the assumption that the reaction proceeds via channels (1) and (2).

- (i) Derived from the same experiments as in Comment (a) by making allowance for absorption by O₃ product.
- (j) FTIR study of irradiated CH₃C(O)C(O)CH₃ in the presence of Ar-O₂ mixtures at total pressures of 973 mbar to 1026 mbar (730 Torr to 770 Torr). The reaction products CO₂, CO, HCHO, HCOOH, CH₃C(O)OH, CH₃C(O)OOH, CH₃OH, H₂O₂ and O₃ were analysed by matrix-isolation FTIR spectroscopy combined with a molecular-beam sampling technique. The branching ratio, k_1/k_2 , was derived from the yields of CH₃C(O)OOH and O₃ which are believed to be formed uniquely from channels (1) and (2) respectively.
- (k) UV irradiation of Cl₂-CH₃CHO-CH₃OH-air mixtures in a smog chamber fitted with an FTIR detection system. Branching ratios were derived from the yields of CH₃C(O)OOH and CH₃C(O)OH which gave $k_2/k = 0.10 \pm 0.02$ at 295 K. Branching ratios were also derived from the O₃ yields determined from the kinetics traces at long reaction times in experiments performed to obtain the rate coefficient [see Comment (b)]. These experiments gave $k_2/k = 0.16 \pm 0.04$ at 295 K. The value cited in the Table is a weighted mean of values from all of the experiments. The O₃ yield measurements suggest only a small increase in k_2/k as temperature is lowered from 359 K to 265 K.
- (l) Branching ratio was derived from the residual absorption at 240 nm (attributed to O₃) at long reaction times in experiments described in Comment (c). There was no detectable change in k_2/k with change in temperature from 298 K to 373 K.
- (m) Continuous photolysis of Cl₂ in the presence of CH₃CHO-CH₃OH-O₂-N₂ mixtures at a total pressure of 1066 mbar (800 Torr). Yields of CH₃OOH and CH₃C(O)OOH (by HPLC) and CH₃OOH, CH₃C(O)OOH, CH₃C(O)OH and CO₂ (by FTIR) were measured as a function of the initial concentration ratio [CH₃OH]₀/[CH₃CHO]₀ over the range 0 to 5, corresponding to conditions over which dominant removal of CH₃C(O)O₂ changes from its self reaction to the reaction with HO₂. The results were analysed by simulation using a detailed chemical mechanism taking account of the sequential formation of CH₃O₂ in the system. A value of $k = 2.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reported to provide the best description of the data in conjunction with the reported final branching ratios.
- (n) Flash photolysis of Cl₂-CH₃CHO-CH₃OH-O₂-N₂ mixtures. Channel (3) was investigated through addition of benzene to scavenge HO, using absorption of the product HOC₆H₆ radicals at 290 nm as the diagnostic. Upper limit value of k_3/k determined from simulation of the kinetic absorption traces at 290 nm using a detailed chemical mechanism. k_2/k was derived from the residual absorption at 240 nm (attributed to O₃) at long reaction times in the absence of benzene, with the assumption that the CH₃C(O)O₂ + HO₂ reaction proceeds by channels (1) and (2).
- (o) UV irradiation of Cl₂-CH₃CHO-CH₃OH-air mixtures in a smog chamber fitted with an FTIR detection system, at a total pressure of 930 mbar. Channel (3) was investigated through addition of variable quantities of benzene to scavenge HO, using the formation of phenol as the diagnostic, based on a phenol yield of 0.531 ± 0.066 (Volkamer et al., 2002). k_1/k , k_2/k and k_3/k derived from optimised simulation of CH₃C(O)OOH, CH₃C(O)OH and phenol formation, respectively, for a range of conditions, using a detailed chemical mechanism. Additional evidence for production of HO in the system was derived from examination of the relative removal of the reagents, CH₃CHO and CH₃OH, as a function of [benzene].

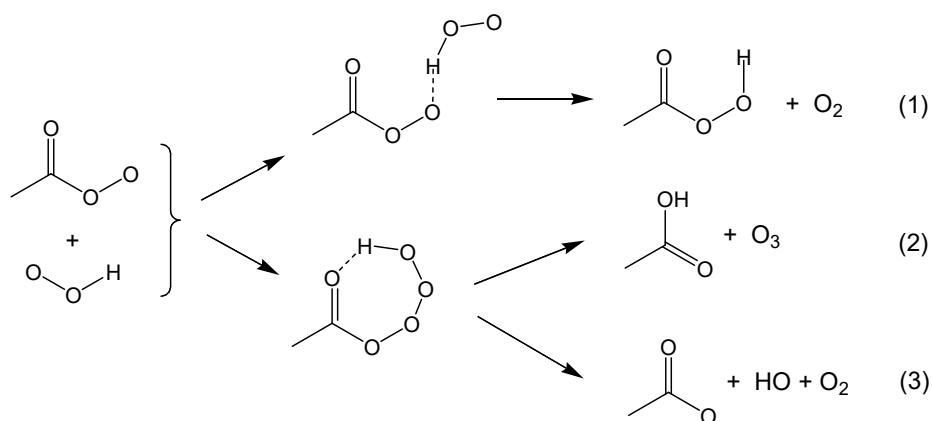
Preferred Values

Parameter	Value	T/K
k	$2.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	298
k	$3.14 \times 10^{-12} \exp(580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	250-300
k_1/k	0.37	298
k_2/k	0.13	298
k_3/k	0.50	298
k_1/k_2	$3.4 \times 10^2 \exp(-1430/T)$	250-340
k_3/k_2	$2.34 \times 10^4 \exp(-2600/T)$	250-300
<i>Reliability</i>		
$\Delta \log k$	± 0.2	298
$\Delta E/R$	$\pm 400 \text{ K}$	
$\Delta k_1/k$	± 0.1	298
$\Delta k_2/k$	± 0.1	298
$\Delta k_3/k$	± 0.1	298
$\Delta (E_1/R - E_2/R)$	$\pm 500 \text{ K}$	
$\Delta (E_3/R - E_2/R)$	$\pm 3000 \text{ K}$	

Comments on Preferred Values

Several studies have clearly demonstrated the participation of reaction channels (1) and (2), with reasonably consistent relative values (k_1/k_2), lying in the approximate range 2–3 (average 2.8) at room temperature, being reported in studies where both channels have been measured (Niki et al., 1985; Horie and Moortgat, 1992; Hasson et al., 2004; Jenkin et al., 2007; Winiberg et al., 2016). The product yields measured in the studies of Hasson et al. (2004) and Jenkin et al. (2007), and their dependence on reagent conditions, provided indirect evidence for the participation of the HO radical-forming channel (3), which has more recently been confirmed by the direct detection of HO in the studies of Dillon and Crowley (2008), Groß et al. (2014) and Winiberg et al. (2016). The values of the branching ratio k_3/k reported in these studies are in relatively good agreement, and the preferred value at 298 K is based on the average of these determinations. Dillon and Crowley (2008) and Groß et al. (2014) report no significant dependence of pressure on the value of k_3/k over the range 100-700 mbar (although the data from those studies, and the entire dataset, can support a small systematic reduction in k_3/k with increasing pressure). The balance of the reaction is divided between channels (1) and (2) in accordance with the average relative value of k_1/k_2 indicated above, to yield the preferred values of k_1/k and k_2/k at 298 K, with the resultant value of k_2/k also being in agreement with the determination of Groß et al. (2014). The values of k_2/k in the earlier studies of Moorgat et al. (1989), Crawford et al. (1999), Tomas et al. (2001) and Le Crâne et al. (2006) did not take account of the impact of reagent radical regeneration via channel (3), and cannot be used without re-analysis of the original data.

Theoretical studies have determined that the formation of $\text{CH}_3\text{C}(\text{O})\text{OOH}$ and O_2 via channel (1) occurs by hydrogen atom migration from HO_2 to the terminal peroxy oxygen in $\text{CH}_3\text{C}(\text{O})\text{O}_2$ (Hasson et al., 2005), analogously to the dominant formation of ROOH and O_2 from the reactions of HO_2 with alkyl peroxy radicals (Vereecken and Francisco, 2012; and references therein). This is illustrated in the schematic below. Channels (2) and (3) proceed via formation of a common hydrogen-bonded tetroxide intermediate, which is not available for simple alkyl peroxy radicals. The calculations of Hasson et al. (2005) suggest that the importance of channel (3) increases relative to channel (2) as temperature increases.



The laboratory results of Horie and Moortgat (1992) indicate that k_1/k_2 possesses a strong temperature dependence. This forms the basis of the preferred temperature coefficient for this branching ratio, with the pre-exponential factor adjusted slightly to return the preferred ratio at 298 K. In the absence of laboratory temperature dependence studies of channel (3), the preferred temperature dependence of k_3/k_2 is based on the results of the theoretical calculations of Hasson et al. (2005) between 250 K and 300 K at atmospheric pressure, which also qualitatively recreate the temperature dependence in k_1/k_2 (at 250 K, this procedure results in $k_1/k_2 = 0.394$, $k_2/k_1 = 0.354$ and $k_3/k_1 = 0.252$). Further temperature dependence studies of the product channel branching ratios are required to confirm, and reduce the uncertainties in, the preferred values.

The preferred value of k at 298 K is based on the recent determinations of Groß et al. (2014) and Winiberg et al. (2016), which took account of (and quantified) the importance of channel (3) in their analyses. It is noted that the studies of Hasson et al. (2004) and Le Crâne et al. (2006) also indicate that the same value of k provides the best description of their data when a significant (40 %) contribution of channel (3) is included in the analysis (see comments (d) and (m)).

The measurements of k in the earlier temperature dependence studies are expected to be subject to systematic errors, because reagent radical regeneration via channel (3) was not taken into account in the analyses. Assuming that those studies were effectively partially “blind” to channel (3), comparison of our current preferred value at 298 K with that recommended previously when channel (3) was not taken into account ($1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; Atkinson et al., 2006) suggests that the measured value included only about 27 % of channel (3). Making the approximation that the same is true across the temperature range 250–300 K, our previous preferred temperature dependence ($E/R = -980 \text{ K}$) has been corrected using the preferred temperature-dependent branching ratios, resulting in a revised value of $E/R = -580 \text{ K}$. The assigned wide reliability limits reflect that the preferred value is based on the above assumption, and that the preferred temperature dependence of k_3/k_2 is itself provisional. Clearly, further temperature dependence studies of k and the product channel branching ratios are required.

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