$HO + CH_3C(O)CH_2OH \rightarrow CH_3C(O)CHOH + H_2O$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(3.0 \pm 0.3) \times 10^{-12}$	298	Dagaut et al., 1989	FP-RF (a)
$(2.8 \pm 0.2) \times 10^{-12}$	~298	Chowdhury et al., 2002	PLP-LIF (b)
$2.15 \times 10^{-12} \exp[(305 \pm 10)/T]$	233-363	Dillon et al., 2006	PLP-LIF (c)
$(5.95 \pm 0.50) \times 10^{-12}$	298		
$(3.17 \pm 0.22) \times 10^{-12}$	298	Butkovskaya et al., 2006	DF-CIMS (d)
$1.88 \times 10^{-11} \exp[-(545 \pm 60)/T]$	280-350	Baasandorj et al., 2009	DF-RF (e)
$(3.02 \pm 0.28) \times 10^{-12}$	298		
$1.77 \times 10^{-12} \exp[(353 \pm 36)/T]$	290-380	Vu et al., 2013	PLP-LIF (f)
$5.74 \pm 0.32 \times 10^{-12}$	301		
$1.75 \times 10^{-12} \exp[(367 \pm 51)/T]$	298-370	Bedjanian, 2020	DF-MS (g)
$6.03 \pm 0.91 \times 10^{-12}$	298		
Relative Rate Coefficients			
$(2.52 \pm 0.27) \times 10^{-12}$	298	Orlando et al., 1999	RR (h)
$(3.52 \pm 0.32) \times 10^{-12}$	298	Orlando et al., 1999	RR (i)
$(6.02 \pm 1.20) \times 10^{-12}$	301	Bedjanian, 2020	RR (j)
$(6.71 \pm 1.34) \times 10^{-12}$	290	Bedjanian, 2020	RR (k)

Comments

(a) Experiments carried out in Ar bath-gas, with HO ($10^{10} - 10^{11}$ molecule cm^{-3}) generated by the VUV photolysis of H$_2$O.

(b) HO generated by the 193 nm photolysis of a 2% mixture of CH$_3$C(O)CH$_2$OH in $10 - 90$ Torr Ar.

(c) HO radicals were generated by the photolysis of HONO at 351 nm or by the 248 nm photolysis of O$_3$ in the presence of CH$_4$. At 298 K, HO and DO radicals were also generated by the 248 nm photolysis of H$_2$O$_2$ and D$_2$O$_2$, respectively. The CH$_3$C(O)CH$_2$OH concentration was monitored in-situ by UV absorption at 184.9 nm using a cross section of 5.4×10^{-18} cm^2 molecule^{-1}. The rate coefficients were independent of pressure of He or N$_2$ 50 $- 200$ Torr ($67 - 267$ mbar) and of the HO radical generation method. At 298 K, the rate coefficients for reaction of HO and DO with CH$_3$C(O)CH$_2$OH agreed to within 10%.

(d) Experiments carried out at 200 Torr (267 mbar) pressure, HO was generated via reaction of F-atoms with H$_2$O and quantified by titration in reaction with NO$_2$. The CH$_3$C(O)CH$_2$OH concentration immediately prior to entering the reaction cell was monitored by UV absorption at 254 nm using a cross-section of 4.42×10^{-20} cm^2 molecule^{-1}, which is a factor

1.25 less than the present preferred value of 5.54×10^{-20} cm^2 molecule^{-1} (IUPAC, 2020). A rate coefficient of k(DO + CH$_3$C(O)CH$_2$OH) = $(4.08 \pm 0.31) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} was also measured. Reactants and products were monitored using negative and positive ion reactions with SF$_6^-$, O$_3^-$ and H$_3$O$^+$. The products observed were CH$_3$C(O)CHO, HC(O)OH, CH$_3$C(O)OH, HCHO, CO$_2$, HO$_2$ and CH$_3$C(O)O$_2$.

(e) Experiments at pressures of 2-5 Torr of He. HO ($< 3 \times 10^{11}$ molecule cm^{-3}) was generated by the reaction of H with NO$_2$. Careful conditioning of the flow-tube or addition of O$_2$ was necessary to minimize the hydroxyacetone-catalysed loss of HO on the wall. CH$_3$C(O)CH$_2$OH was monitored via absorption at 254 nm and converted to concentrations using a cross-section of 5.54×10^{-20} cm^2 molecule^{-1}, which agrees with the present IUPAC recommendation (IUPAC, 2020). k was independent of pressure between 2 and 5 Torr of He.

(f) Experiments in He bath-gas at pressures between 10 and 100 Torr He with HO ($1 - 4 \times 10^{10}$ molecule cm^{-3}) generated by the 248 nm photolysis of H$_2$O$_2$. The expression in the table refers to data obtained at 50 Torr. The temperature dependence of k is complex and at temperatures > ca. 400 K, the rate coefficient increases with increasing temperature. At pressures lower than ca. 40 Torr He, the rate coefficient at 301 K decreases with decreasing pressure.

(g) Experiments at pressures of ca. 2 Torr of He. HO ($1.5 - 3.5 \times 10^{11}$ molecule cm^{-3}) was generated by the reaction of H with NO$_2$. Wall losses of HO, inferred from plots of first-order loss constant versus [CH$_3$C(O)CH$_2$OH] were much larger than those derived from [HO] decays in the absence of CH$_3$C(O)CH$_2$OH. The temperature dependence is complex: At T < 370 K a negative dependence on temperature is observed. The expression for k listed in the table was derived from an unweighted fit to the authors data at 298, 330, 336 and 370 K.

(h) HO radicals were generated by the photolysis of methyl nitrite in synthetic air at 1 bar total pressure. Hydroxyacetone and methanol (the reference compound) were monitored by FTIR spectroscopy. The measured rate coefficient ratios k(HO + CH$_3$C(O)CH$_2$OH)/k(HO + methanol) = 2.8 ± 0.3 is placed on an absolute basis using k(HO + methanol) = 9.0×10^{-13} cm^3 molecule^{-1} s^{-1} (IUPAC, 2020).

(i) HO radicals were generated by the photolysis of methyl nitrite in synthetic air at 1 bar total pressure. Hydroxyacetone and ethanol (the reference compound) were monitored by FTIR spectroscopy. The measured rate coefficient ratio k(HO + hydroxyacetone)/k(HO + ethanol) = 1.1 ± 0.1 is placed on an absolute basis using k(HO + ethanol) = 3.2×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K, respectively (IUPAC, 2020).

(j) At 2 Torr He, 250 – 750 K. Relative to HO + Br$_2$. k(HO + CH$_3$C(O)CH$_2$OH) / k(HO + Br$_2$) was derived from the yield of HOBr (monitored by MS) for different [CH$_3$C(O)CH$_2$OH] and fixed initial HO and Br$_2$ and placed on an absolute basis using k(HO + Br$_2$) = 2.16×10^{-11} exp(207/T) (Bedjanian et al., 2019). Experiments at 1, 5, and 10.4 Torr of He yielded very similar values for k (6.06, 6.44, and 5.84×10^{-12} cm^3 molecule^{-1} s^{-1}, respectively).

(k) At 2.1 Torr He, 290 and 320 K. Relative to HO + heptane. k(HO + CH$_3$C(O)CH$_2$OH) / k(HO + heptane) was derived from changes in concentration (monitored by MS) of CH$_3$C(O)CH$_2$OH and heptane and placed on an absolute basis using k(HO + heptane) = 3.75×10^{-16} T$^{1.65}$ exp(101/T) (Morin et al, 2015). Experiments at 1.45, 3.25, and 7.6 Torr of He result in very similar values of k = 6.22, 5.98, and 5.87×10^{-12} cm^3 molecule^{-1} s^{-1}, respectively.

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	5.9×10^{-12}	298
k /cm^3 molecule^{-1} s^{-1}	$2.0 \times 10^{-12}\exp(320/T)$	230-380
Reliability		
$\Delta \log k$ ± 0.2		298
$\Delta E/R$ ± 50		230-380

Comments on Preferred Values

The several absolute and relative rate studies of the kinetics of this reaction are generally not in good agreement, delivering inconsistent results on the room temperature value of k, the sign of its temperature dependence and the existence of a pressure dependence at low pressures. The poor agreement is related to difficulties in handling CH$_3$C(O)CH$_2$OH, which has a large affinity for surfaces but is also tied to the detailed reaction mechanism (see below).

The Arrhenius plot at the end of this datasheet illustrates the divergence in values of k in the atmospherically relevant temperature range (T < 380 K) where two groupings can be observed. Five datasets indicate a rate coefficient at room temperature which is close to 3×10^{-12} cm^3 molecule^{-1} s^{-1} (Dagaut et al., 1989; Orlando et al., 1999; Chowdhury et al., 2002; Butkovskaya et al., 2006; Baasandorj et al., 2009) with one of these studies determining a positive dependence on temperature at low pressure (Baasandorj et al., 2009).

A second set of experiments (Dillon et al., 2006; Vu et al., 2013; Bedjanian 2020) indicate that the room temperature rate coefficient is close to 6×10^{-12} cm^3 molecule^{-1} s^{-1} with k increasing with decreasing temperature in the range 230-400 K. The results of Vu et al., (2013) and Bedjanian (2020) also show that the rate coefficient increases with increasing temperature above 400 K, though Bedjanian (2020) could not confirm the pressure dependence (at room temperature) observed at pressures under 40 Torr He reported by Vu et al. (2013).

The pulsed photolysis method offers advantages over the use of low-pressure flow tubes when dealing with reactions of HO with molecules that have a large affinity for surfaces and, for the purpose of atmospheric modelling our preferred values (230 – 380 K) are based on the absolute results of Dillon et al. (2006) and Vu et al. (2013), noting that the rate coefficients obtained by Bedjanian (2020) at low pressure by both absolute and relative methods are in excellent agreement with both. It is not clear why the flash-photolysis study of Dagaut (1989) returns a lower value at room temperature, though the lack of experimental details makes it difficult to identify potential sources of uncertainty in this study. The main focus of the experiments of Chowdhury et al. (2002), who examined photo-fragments from CH$_3$C(O)CH$_2$OH excitation at 193 nm, was not the kinetics of the reaction and the large intercepts on their plot of first order decay rate constant of [HO] versus [CH$_3$C(O)CH$_2$OH] may indicate a complex chemical system due to the presence of organic radicals. The study of Butkovskaya (2006), obtained at 200 Torr, focussed on the formation of products rather than the rate coefficient and the significant inverse kinetic isotope effect (k(DO) / k(HO) = 1.3), which is not consistent with the data of Dillon et al. (2006) may indicate secondary HO formation e.g. in the presence of O$_2$ in their system. Note that use of the preferred value for the absorption cross-section of CH$_3$C(O)CH$_2$OH at 254 nm, would

result in an increase in the rate coefficient for DO + $CH_3C(O)CH_2OH$ to a value of 5.1×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K, which is only 30% lower than that reported for DO + $CH_3C(O)CH_2OH$ by Dillon et al (2006).
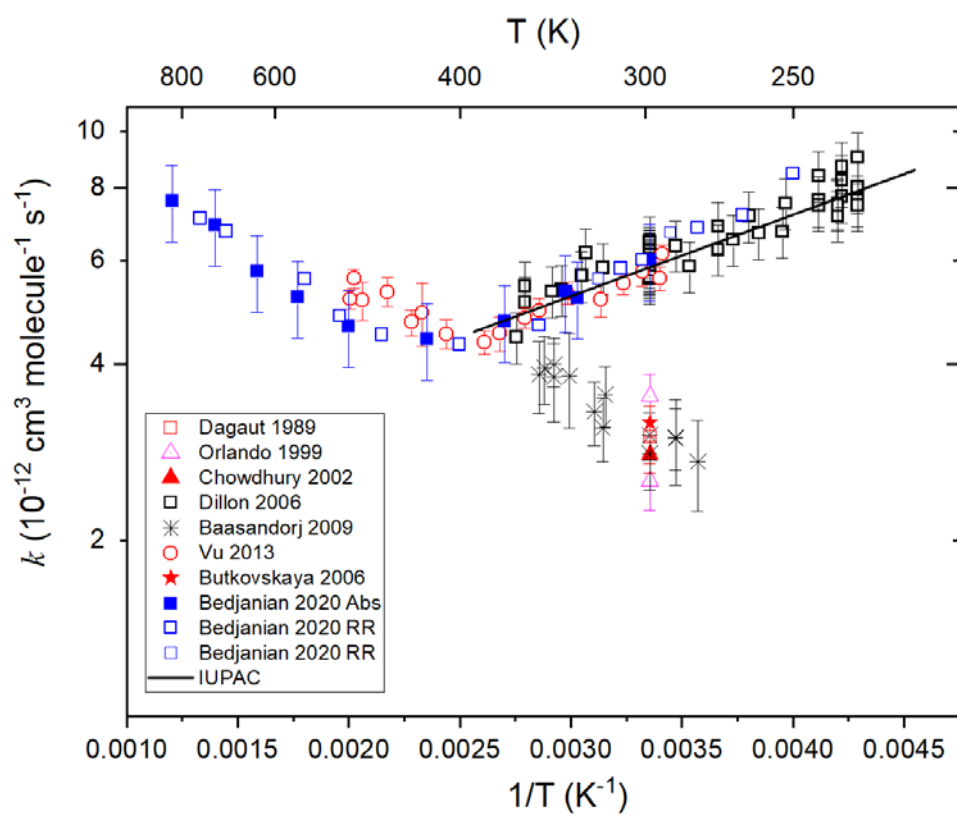
The difference in results to the relative rate study of Orlando et al (1999) at 1 bar in air is perhaps the most difficult to explain. Their relative data show considerable scatter, and the use of two different reference reactants did not result in a consistent value of k, which together may indicate variable wall losses of $CH_3C(O)CH_2OH$. However, this would appear insufficient to account for a factor two in the rate coefficient and a further relative rate study at atmospheric pressure of air is desirable.

Theoretical studies (Dillon et al., 2006; Galano, 2006; Vu et al., 2013) of the reaction between HO and $CH_3C(O)CH_2OH$ indicate the formation of a hydrogen-bonded pre-reaction that, together with a submerged transition state (to product $CH_3C(O)CHOH$) leads to the complex temperature dependence observed. Based on their own data and those of Dillon et al (2006) and Vu et al (2013), Bedjanian (2020) report a parameterisation ($k = 4.4 \times 10^{-20}$ $T^{2.63}$exp(1110/T) cm^3 molecule^{-1} s^{-1}) that can be used over the temperature range 230-830 K.

At room temperature, formation of $CH_3C(O)CHOH$ is expected to account for > 99% of the overall reaction (Galano, 2006), with abstraction of H atoms from the -CH_3 and -OH groups insignificant.

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Rate coefficients for HO + CH₃C(O)CH₂OH. The solid, black line represents the IUPAC preferred values.