IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, Data Sheet CGI_19_$(CH_3)_2COO + H_2O$

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$(CH_3)_2COO + H_2O \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp /K	Reference	Technique/Comments
Absolute Rate Coefficients			
$< 1.5 \times 10^{-16}$	298	Huang et al., 2015	PLP-LPUVA (a)
Relative Rate Coefficients			
1.5×10^{-14}	298	Becker et al., 1993	RR-FTIR/ TDLS (b)
$< 5.2 \times 10^{-16}$	278-343	Berndt et al., 2014	FT/CI-APi-TOF MS(c)
$< 1.1 \times 10^{-14}$	293	Newland et al., 2014	RR-FTIR/UVA/ UVfluorescence

Comments

(a) $(CH_3)_2COO$ was generated from the 248 nm pulsed photolysis of a gaseous mixture consisting of 1,1 di-iodoacetone $(CH_3)_2CI_2$, O_2, and buffer gas (N_2) at 20 - 400 Torr total pressure. $(CH_3)_2COO$ was monitored by UV absorption in the region 300 – 450 nm, corresponding to the $\tilde{B}$ (1A′) ← $\tilde{X}$(1A′) electronic transition (Liu et al., 2014). IO was also detected and is thought to be formed in secondary chemistry following the reaction $(CH_3)_2CI_2 + O_2$. For $(CH_3)_2COO$ the decay showed no dependence on water vapour even at high $[H_2O]$ (90% RH at 298 K), over a wide range of experimental conditions.

(b) Study of the 2,3-dimethyl-2-butene (TME) + O_3 reaction in the presence of 1 bar of synthetic air with and without added SO_2; H_2O_2 yields were measured by tunable diode laser absorption spectroscopy or by FTIR spectroscopy. The reported rate constant ratio $k / k_{SO2} = (4.1 \pm 2.2) \times 10^{-4}$ for reaction of $(CH_3)_2COO$ with H_2O and SO_2, which gave the cited value using the IUPAC recommended value of k_{SO2} at 1 bar pressure.

(c) $(CH_3)_2COO$ prepared by O_3 + TME reaction in the presence of SO_2 in a flow system, equipped with CIMS for detection of H_2SO_4 using NO_3^- as reagent ion. Total pressure = 1 bar. The yield of $(CH_3)_2COO$ from the TME + O_3 reaction was reported to be 0.45(±0.20). The effect of $[H_2O]$ (RH = 2 – 50%) on yield of H_2SO_4 was very weak and only allowed determination of an upper limit rate coefficient ratio $k((CH_3)_2COO + H_2O)/k((CH_3)_2COO + SO_2) = 4 \times 10^{-6}$ at 293 K. A distinct temperature dependence of H_2SO_4 formation was observed, attributed to the thermal decomposition of $(CH_3)_2COO$, which is its dominant loss reaction in this system. The cited value uses the IUPAC recommendation for $k((CH_3)_2COO+SO_2)$, i.e. 1.3×10^{-10} cm^3molecule s^{-1} to evaluate the upper limit.

(d) The removal of SO_2 in the presence of 2-butene–ozone systems was measured as a function of humidity in EUPHORE simulation chamber, under atmospheric boundary layer conditions. SO_2 and O_3 abundance were measured using conventional fluorescence and UV absorption monitors, respectively; alkene abundance was determined via FTIR spectroscopy. The yield of $(CH_3)_2COO$ from the TME + O_3 reaction was reported to be 0.32(±0.20). The observed SO_2 removal kinetics are consistent with the rate constant ratio: $k((CH_3)_2COO+H_2O)/k((CH_3)_2COO+SO_2)$ = (8.7 ± 2.5) x 10^{-5}. The cited value uses the IUPAC recommendation for $k((CH_3)_2COO + SO_2)$, i.e. 1.3 x10^{-10} cm^3molecule s^{-1}.

Preferred Values

Parameter	Value	T/K
k/cm^3 molecule^{-1} s^{-1}	$< 1.5 \times 10^{-16}$	298

Reliability

$\Delta \log k$	0.5	298

Comments on Preferred Values

All studies point to a slow reaction of $(CH_3)_2COO$ (acetone oxide) with H_2O. The relative rate determinations from ozonolysis of 2,3-dimethyl-2-butene (TME) do not show much consistency, however. The difficulty seems to lie in distinguishing the slow reaction with water from the thermal decomposition and other pseudo first-order loss processes, which have similar, system dependent, rates. The direct kinetic study of Huang et al.(2015) offers the most definitive picture which shows no dependence of the pseudo first order decay constant on water vapour over a wide range of conditions. These data form the basis of the preferred values for $(CH_3)_2COO$ (acetone oxide) reaction with H_2O are based on the study of Huang et al (2015).

Quantum chemical studies predict that $(CH_3)_2COO$ (acetone oxide) reacts with H_2O. $(CH_3)_2COO$ is significantly less reactive than *anti*-CH_3CHOO towards, e.g., H_2O (Anglada et al., 2011) and alkenes (Vereecken et al, 2014).

References

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