IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_14

$(CH_3)_2COO + M \rightarrow$ products

Rate coefficient data

k/ s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
370 ± 34	298	Huang et al., 2015	PLP-LPUVA (a)
269 ± 82	283	Smith et al., 2016	PLP-Slow Flow-LPUVA (b)
361 ± 49	298		
628 ± 60	310		
916 ± 56	323		
305 ± 70	293	Chhantyal-Pun et al., 2017	PLP- PIMS/CRDS (c)
Relative Rate Coefficients			
605 ± 109	293	Berndt et al., 2012	RR-FTIR/ TDLS (d)
416 ± 121	278	Berndt et al., 2014	FT/CI-APi-TOF MS (e)
722 ± 52	293		
2449 ± 865	323		
4280 ± 544	343		
929 ± 220	298-299	Newland et al., 2015	RR-FTIR/UVA/UVF (f)

Comments

(a) $(CH_3)_2COO$ was generated from 248 nm pulsed photolysis of a gaseous mixture consisting of 2,2-diiodopropane $((CH_3)_2CI_2)$, O_2 and buffer gas (N_2), $(CH_3)_2CI_2 + h\nu \rightarrow (CH_3)_2CI + I$, at about 13 – 1030 mbar (10 - 770 Torr) total pressure and 298 K. $(CH_3)_2COO$ was monitored by UV absorption in the region 300 – 450 nm. IO was also detected, which is formed from the second channel, $(CH_3)_2CI + O_2 \rightarrow (CH_3)_2COO + IO$. First order decay rate constants decreased with total $[(CH_3)_2COO]$ to a limiting value at low initial radical concentration, when influence of radical-CI reactions is minimal. We infer this limiting value to be due to thermal decomposition. The cited value of k was obtained by linear extrapolation of a plot of the pseudo-first order rate constants at 267 mbar (200 Torr) to the limit at zero absorption from $(CH_3)_2COO$.

(b) $(CH_3)_2COO$ was generated from pulsed photolysis of a gaseous mixture consisting of 2,2-diiodopropane, $(CH_3)_2CI_2$, O_2, and buffer gas (N_2) at 248 nm, $(CH_3)_2CI_2 + h\nu \rightarrow (CH_3)_2CI + I$, at a total pressure of 200 Torr. $(CH_3)_2COO$ was monitored by time-resolved UV absorption due to the $\tilde{B}$ $(1A') \leftarrow \tilde{X}(1A')$ electronic transition. The amount of $(CH_3)_2COO$ formed was estimated using a cross-section $\sigma = 1.6 \times 10^{-17}$ cm^2 at 340 nm. Kinetic decays were recorded in the temperature range 283-323 K. The decay kinetics exhibited a complex mixed first and second order form, due to thermal decomposition, self-reaction and reaction of $(CH_3)_2COO$ with other radical species produced following photolysis. k was determined by numerical simulation, making use of an optimized value of the second order component (mainly due to self-reaction), which was well defined in experiments at the highest initial concentrations. The values of k increased significantly with temperature. The results are consistent with $k = 7.25 \times 10^6 \exp[-(2919 \pm 604)/T]$. $(CD_3)_2COO$

kinetics were also investigated using the precursor $(CD_3)_2CI_2$. k for $(CD_3)_2COO$ at 298 K was estimated to be <100 s^{-1}, with no significant T dependence.

(c) $(CH_3)_2COO$ was formed by laser photolysis of $(CH_3)_2CI_2$ in the presence of O_2 and characterized by synchrotron photoionization mass spectrometry; and also by cavity ringdown ultraviolet absorption spectroscopy. Cavity ringdown measurements of $(CH_3)_2COO$ loss without added reagents display a combination of first- and second-order decay kinetics, which were deconvolved to derive values for both the $(CH_3)_2COO$ self-reaction rate constant, and the unimolecular thermal decay constant, k. The cited value is a mean of four determinations of k over the pressure range 13 - 131 mbar. Both k and the self-reaction rate constant were independent of pressure in this range.

(d) Study of the 2,3-dimethyl-but-2-ene + O_3 reaction in the presence of 1 bar of synthetic air with and without added SO_2, in a flow system, at 1 bar pressure and 50 % RH. Either propane or butane were also present to scavenge HO radicals. Formation of H_2SO_4 from the reaction of $(CH_3)_2COO$ with SO_2 was monitored with CIMS, using NO_3^- as reagent ion. The time dependence of H_2SO_4 production after addition of different $[SO_2]$ allowed estimation of $k_{loss} = (3.0 \pm 0.4)$ s^{-1} for $(CH_3)_2COO$, and a rate constant ratio $k_{loss}/k((CH_3)_2COO + SO_2) = (3.9 \pm 0.7) \times 10^{12}$ molecule cm^{-3}; where k_{loss} is the total first-order loss rate due to decomposition and reaction with H_2O. Because the (slow) reaction of $(CH_3)_2COO$ with H_2O can be neglected as a significant removal process for $(CH_3)_2COO$ under the experimental conditions, we infer that of $k_{loss} = k$. The tabulated value of k is based on the rate constant ratio, which agrees well with that reported in a subsequent study (Berndt et al., 2014). k is placed on an absolute basis using $k((CH_3)_2COO + SO_2) = 4.23 \times 10^{-13} \exp(1760/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation); although it is noted that the resultant value is not in good agreement with their reported absolute estimate.

(e) $(CH_3)_2COO$ prepared by O_3 + 2,3-dimethyl-but-2-ene reaction in the presence of SO_2 and propane (HO radical scavenger) in a flow system, equipped with CIMS for detection of H_2SO_4 using NO_3^- as reagent ion. Total pressure = 1 bar. The effect of $[H_2O]$ (RH = 2 – 50%) on yield of H_2SO_4 was negligible, and it was deduced that thermal decomposition was the dominant reaction competing with $(CH_3)_2COO + SO_2$ reaction. A distinct temperature dependence of H_2SO_4 formation was observed over the studied range (278–343 K), attributed mainly to the thermal decomposition of $(CH_3)_2COO$. The reported values of $k/k((CH_3)_2COO + SO_2)$ were placed on an absolute basis using $k((CH_3)_2COO + SO_2) = 4.23 \times 10^{-13} \exp(1760/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation). An Arrhenius plot of the resultant values of k vs. $1/T$, is linear, yielding a value of $E_a \approx 29$ kJ mol^{-1}.

(f) The removal of SO_2 in the presence of 2,3-dimethyl-but-2-ene/ozone systems was measured as a function of humidity in the EUPHORE simulation chamber, under atmospheric boundary layer conditions. Cyclohexane was also present to scavenge HO radicals. SO_2 and O_3 concentrations were measured using conventional fluorescence and UV absorption monitors, respectively; the alkene concentration was determined via FTIR spectroscopy. The yield of $(CH_3)_2COO$ from the 2,3-dimethyl-but-2-ene + O_3 reaction was reported to be (0.32 ± 0.20). The observed SO_2 removal kinetics are consistent with the rate constant ratio: $k/k((CH_3)_2COO + SO_2) = (6.3 \pm 1.4) \times 10^{12}$ molecule cm^{-3}. The tabulated value of k was placed on an absolute basis using $k((CH_3)_2COO + SO_2) = 4.23 \times 10^{-13} \exp(1760/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Parameter	Value	T/K
$k/$ s^{-1}	400	298
$k/$ s^{-1}	7.2×10^6 exp(-2920/T)	280-330
Reliability		
$\Delta \log k$	± 0.2	298
$\Delta (E/R)$	± 700	280-330

Comments on Preferred Values

k has been determined in three direct studies; by Huang et al. (2015) at 298 K, by Smith et al. (2016), who also reported a temperature dependence study over the range 283–323 K, and by Chhantyal-Pun et al. (2017) at 293 K. The results at near ambient temperatures from these studies are all consistent, and the absence of pressure dependence over the range 13-130 mbar (Chhantyal-Pun et al., 2017) indicates the measurements were made at the high-pressure limit. The decomposition rate constant shows a substantial increase with temperature. The preferred values of k are based on a fit to all the direct data, with E/R constrained to a value of 2920 K, based on the activation energy reported by Smith et al. (2016).

The relative rate determinations from ozonolysis of 2,3-dimethyl-but-2-ene, using reaction of $(CH_3)_2COO$ with SO_2 as a reference, are also in good agreement; but consistently give values of k over a factor of 2 higher than the direct measurements at room temperature. The temperature dependence of k inferred from the data of Berndt et al. (2014) (see comment (e)) supports the direct measurements of Smith et al. (2016), and gives a comparable, but slightly higher, activation energy. An analysis of the indirect data alone provides a value $k = 1.11 \times 10^8$ exp(-3500/T) s^{-1}, with a value 880 s^{-1} at 298 K. The origins of this consistent discrepancy between the direct and relative rate determinations are currently unclear, although it is noted that the mechanism and products of the reference $(CH_3)_2COO + SO_2$ reaction are not fully characterized at atmospheric pressure (see data sheet CGI_18).
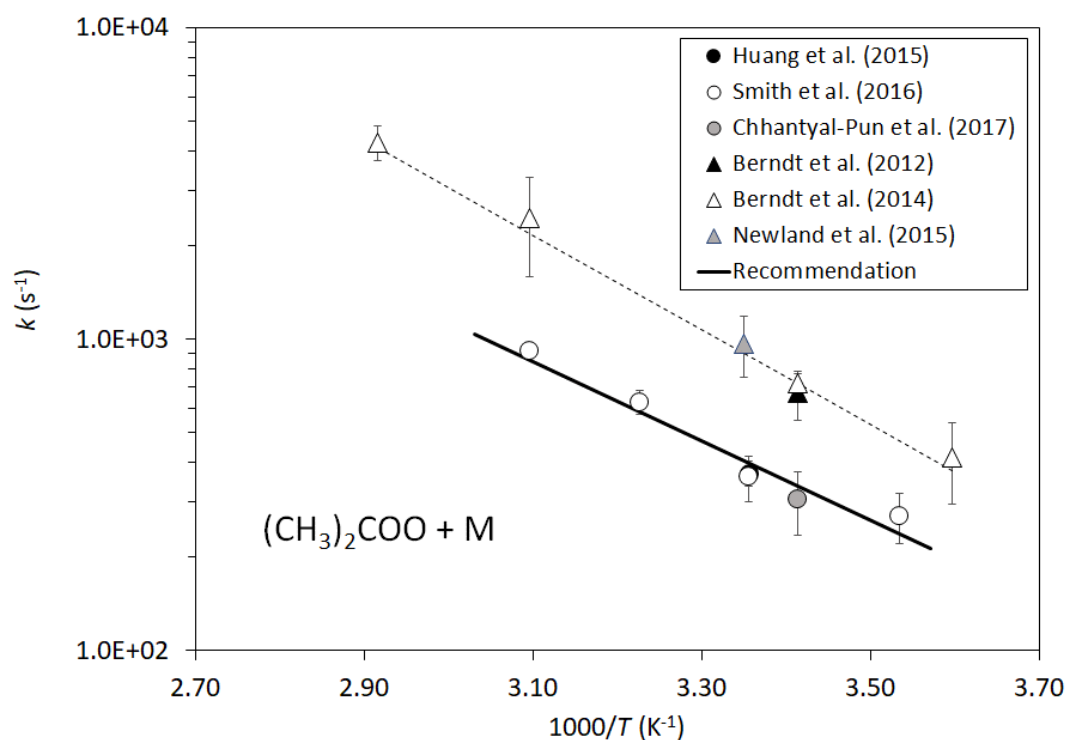
The preferred value of k at 298 K is in good agreement with the value of 369 s^{-1} calculated by Liu et al. (2014), using master-equation calculations and RRKM theory. Smith et al. (2016) reported theoretical calculations for $(CH_3)_2COO$ and $(CD_3)_2COO$ which show a strong temperature dependence in k, with Arrhenius activation energies of 35.5 and 56.4 kJ mol^{-1} respectively. The theoretical and experimental temperature dependences are consistent for $(CH_3)_2COO$, and the experimentally observed slower decomposition of $(CD_3)_2COO$ is predicted.

The quantum chemical studies predict that decomposition of $(CH_3)_2COO$ occurs via a 1,4 H-atom transfer to form the vinyl hydroperoxide intermediate, 2-hydroperoxypropene. This process is exothermic, and HO is produced from its subsequent decomposition. UV depletion studies coupled with photoionization mass spectrometry have shown relative yields of the HO radical to be greater from $(CH_3)_2COO$ than from CH_2OO (Fang et al. 2016). These observations confirm that the facile 1,4 intramolecular hydrogen transfer leads to much faster unimolecular decomposition rate for $(CH_3)_2COO$ compared with CH_2OO, for which the mechanism is unavailable.

References

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Arrhenius plot of $k((CH_3)_2COO + M)$. Direct determinations are shown as circlular points; relative rate determinations are shown as triangular points. The displayed errors are the experimental limits cited by the authors (but do not include uncertainty in the reference reaction for the relative rate studies). The full line is the IUPAC recommendation, $k = 7.2 \times 10^6 \exp(-2920/T)$ s^{-1}. The broken line is a fit to the relative rate data, $k = 1.11 \times 10^8 \exp(-3500/T)$ s^{-1}.