

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation Data Sheet
CGI_14_(CH₃)₂COO + M

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(CH₃)₂COO (+ M) → products

Rate coefficient data

<i>k</i> / s ⁻¹	Temp /K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
370 ± 34 (263 mbar)	298	Huang et al., 2015	PLP-LPUVA (a)
269 ± 82	283	Smith et al., 2016	PLP-Slow Flow-LPUVA (b)
361±49 (131 - 263 mbar)	298		
628±60	310		
916±56	323		
305 ± 70 (13 - 131 mbar)	293	Chhantyal-Pun et al., 2017	PLP- PIMS/CRDS (c)
<i>Relative Rate Coefficients</i>			
3.0 ± 0.4	293	Berndt et al., 2012	RR-FTIR/ TDLS (d)
437 ± 44	278	Berndt et al., 2014	FT/CI-API-TOF MS (e)
643 ± 78	293		
1021 ± 105	303		
831 ± 185	293	Newland et al., 2014	RR-FTIR/UVA/ UV fluorescence (f)

Comments

- (a) (CH₃)₂COO was generated from 248 nm pulsed photolysis of a gaseous mixture consisting of 2,2-diiodopropane ((CH₃)₂CI₂), O₂, and buffer gas (N₂). (CH₃)₂CI₂ + hv → (CH₃)₂CI + I; (CH₃)₂CI + O₂ → (CH₃)₂COO + IO, at about 13 – 1030 mbar (10 - 770 Torr) total pressure and 298 K. (CH₃)₂COO was monitored by UV absorption in the region 300 – 450 nm. IO was also detected, which is formed from secondary chemistry of the reaction of iodo-alkyl radicals with O₂. First order decay plots in presence of added H₂O showed no significant dependence on [H₂O], but decay rate constants decreased with total [(CH₃)₂COO] to a limiting value at low initial radical concentration, when influence of radical-CI reactions is minimal. This limiting value of *k*_{dec} is attributed to thermal decomposition. The cited value was obtained by linear extrapolation of a plot of the pseudo-first order rate constants at 260 mbar to the limit at Abs((CH₃)₂COO) = 0.

- (b) $(\text{CH}_3)_2\text{COO}$ was generated from pulsed photolysis of a gaseous mixture consisting of 2,2-diiodopropane, $(\text{CH}_3)_2\text{CI}_2$, O_2 , and buffer gas (N_2) at 248 nm : $(\text{CH}_3)_2\text{CI}_2 + \text{h}\nu \rightarrow (\text{CH}_3)_2\text{CI} + \text{I}$; $(\text{CH}_3)_2\text{CI} + \text{O}_2 \rightarrow (\text{CH}_3)_2\text{COO} + \text{IO}$. Total pressure was 200 Torr; $(\text{CH}_3)_2\text{COO}$ was monitored by time-resolved UV absorption due to the $\tilde{\text{B}}(1\text{A}') \leftarrow \tilde{\text{X}}(1\text{A}')$ electronic transition. The amount of $(\text{CH}_3)_2\text{COO}$ formed was estimated using a cross-section $\sigma = 1.6 \times 10^{-17} \text{ cm}^2$ 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 $(\text{CH}_3)_2\text{COO}$ with other radical species produced following photolysis. The rate coefficients for thermal decomposition, k_d , were determined by optimised fitting of decay traces generated by numerical integration of a kinetics model to the experimental data, making use of an optimized value of the second order component, k_{second} , (mainly due to self-reaction), which was well defined in experiments at highest initial concentrations. The values of k_{dec} , increased significantly with temperature. A plot of $\log k_d$ derived from direct measurement of $(\text{CH}_3)_2\text{COO}$ in this work gives $E_a = 24.2 \pm 5.0 \text{ kJ mol}^{-1}$ for decomposition. $(\text{CD}_3)_2\text{COO}$ kinetics were also investigated using the precursor $(\text{CD}_3)_2\text{CI}_2$; k_d for $(\text{CD}_3)_2\text{COO}$ at 298 K was estimated to be $<100 \text{ s}^{-1}$, and no significant T dependence.
- (c) Acetone oxide, $(\text{CH}_3)_2\text{COO}$, was formed by laser photolysis of 2,2-diiodopropane 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 the acetone oxide removal without added reagents display a combination of first- and second-order decay kinetics, which were deconvolved to derive values for both the self-reaction of $(\text{CH}_3)_2\text{COO}$, k_{second} , and unimolecular thermal decay, k_{dec} . The cited value is a mean of 4 determinations of k_{dec} over the pressure range 13 - 131 mbar; both k_{dec} and k_{second} were independent of pressure in this range.
- (d) 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 . in a flow system, equipped with CIMS for detection of H_2SO_4 using NO_3^- as reagent ion. Total pressure = 1 bar; at RH: 50% . The time dependence of H_2SO_4 production after addition of different $[\text{SO}_2]$ allowed estimation of an upper limit to the decomposition of acetone oxide rate and a rate constant ratio $k_{\text{dec}}/k((\text{CH}_3)_2\text{COO} + \text{SO}_2) = (4.1 \pm 2.2) \times 10^{-4} \text{ molecule cm}^{-3}$ for reaction of $(\text{CH}_3)_2\text{COO}$ with SO_2 . Here, k_{loss} is equal to k_{dec} because the $\text{sCI} + \text{H}_2\text{O}$ reaction can be neglected as a significant removal process for $(\text{CH}_3)_2\text{COO}$.
- (e) $(\text{CH}_3)_2\text{COO}$ prepared by $\text{O}_3 + \text{TME}$ 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 effect of $[\text{H}_2\text{O}]$ (RH = 2 – 50%) on yield of H_2SO_4 was negligible, and it was deduced that thermal decomposition was the dominant reaction competing with $(\text{CH}_3)_2\text{COO} + \text{SO}_2$ reaction. A distinct temperature dependence of H_2SO_4 formation was observed, attributed to the thermal decomposition of $(\text{CH}_3)_2\text{COO}$, The IUPAC recommendation for $k((\text{CH}_3)_2\text{COO} + \text{SO}_2)$, i.e. $1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule s}^{-1}$ independent of temperature was used to obtain the listed values. An Arrhenius plot $\ln(k_{\text{dec}}/k((\text{CH}_3)_2\text{COO} + \text{SO}_2))$ vs. $1/T$, was linear, yielding $E_a(\text{dec}) - E_a(\text{SO}_2) = 44.0 \pm 1.2 \text{ kJ mol}^{-1}$.

(f) The removal of SO₂ in the presence of 2-butene–ozone systems was measured as a function of humidity in [the EUPHORE simulation chamber](#), under atmospheric boundary layer conditions. SO₂ and O₃ [concentrations](#) were measured using conventional fluorescence and UV absorption monitors, respectively; [the alkene concentration](#) was determined via FTIR spectroscopy. The yield of (CH₃)₂COO from the TME + O₃ reaction was reported to be 0.32(±0.20). The observed SO₂ removal kinetics are consistent with the rate constant ratio: $k_{\text{dec}}/k((\text{CH}_3)_2\text{COO} + \text{SO}_2) = (63 \pm 14) \times 10^{11} \text{ molecule cm}^{-3}$. The cited value uses the IUPAC recommendation for $k((\text{CH}_3)_2\text{COO} + \text{SO}_2)$, i.e. $1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule s}^{-1}$.

Preferred Values

Parameter	Value	T/K
$k(\text{s}^{-1})$	$1.0 \times 10^7 \exp(-3020/T)$ 400	280 - 330 298

Reliability

$\Delta \log k$	0.1	298
$\Delta (E/R)$	±300	

Comments on Preferred Values

The unimolecular decay rate coefficient for thermal decomposition of (CH₃)₂COO (acetone oxide) has been determined in 3 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 near ambient temperatures from these studies are all consistent. The absence of pressure dependence over the range 13-130 mbar in the latter study at room temperature indicates the reaction is near its high pressure limit. The decomposition rate constant shows a substantial increase with temperature.

The relative rate determinations from ozonolysis of 2,3-dimethyl-2-butene (TME) using reaction of (CH₃)₂COO with SO₂ as a reference, do not show such consistency, The earlier data, indicated a very slow rate of decomposition but the more recent results give values of k_{dec} about a factor of 2 higher than the direct measurements at room temperature. The difficulty seems to lie in distinguishing the slow thermal decomposition from other pseudo first-order loss processes in these complex systems. However the temperature dependence of the ratio $k_{\text{dec}}/k_{\text{SO}_2}$ obtained by Berndt et al. (2014), which reflects the T-dependence of k_{dec} , supports the direct measurements of Smith et al. (2016), but gives a substantially higher activation energy (44.0±1.2 kJ mol⁻¹).

The expression for the recommended values of k_{dec} is obtained by an Arrhenius fit to the data from the three cited direct kinetic studies, which are plotted in Fig 1. The value of k_{dec} at 298 K (398 s⁻¹) is in good agreement with the unimolecular reaction rate coefficient 369 s⁻¹ at 298 K, calculated by Liu et al. (2014), using master-equation calculations and RRKM theory. Smith et al. (2016) reported theoretical calculations of k_{dec} for (CH₃)₂COO and (CD₃)₂COO which show a strong

temperature dependence, with theoretical Arrhenius activation energies of 35.5 and 56.4 kJmol⁻¹ respectively. The theoretical and experimental $k_{\text{dec}}(T)$ values are consistent with each other for (CH₃)₂COO, and the experimentally observed slower decomposition of (CD₃)₂COO is predicted. All of these values are an order of magnitude larger than the unimolecular decay rate coefficient value for decomposition of CH₂OO, $11.6 \pm 8.0 \text{ s}^{-1}$. Tunnelling through the barrier, computed from high level electronic structure theory, which is experimentally validated, makes a significant contribution to the decay rate (Fang et al, 2016).

The quantum chemical studies predict that decomposition of (CH₃)₂COO (acetone oxide) occurs via a 1-4 H-atom transfer to form 2-hydroperoxypropene. This process is exothermic and HO is produced in its subsequent decomposition. UV depletion studies coupled with photoionization mass spectrometry have shown relative yields of the HO radical to be greater from (CH₃)₂COO than from CH₂OO (Fang et al. 2016). These observations suggest that facile intramolecular hydrogen transfer leads to a [faster](#) unimolecular [decomposition](#) rate [for](#) (CH₃)₂COO than [for](#) CH₂OO.

References

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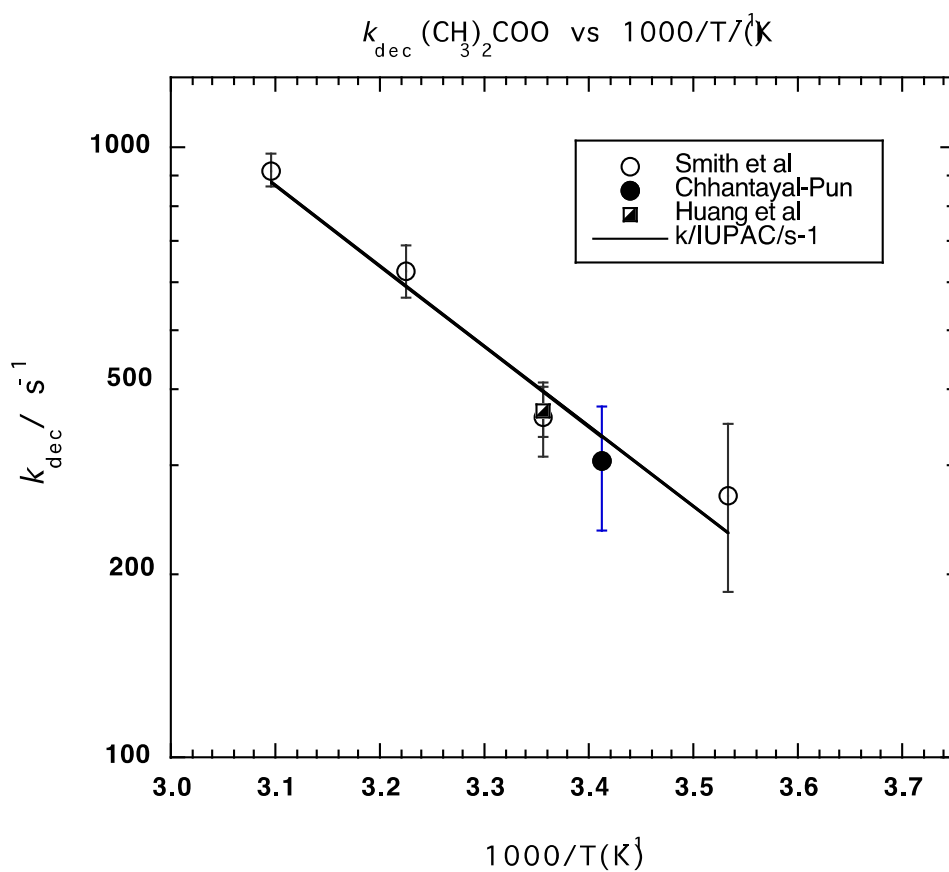


Fig 1 Plot of rate coefficient for decomposition of $(\text{CH}_3)_2\text{COO}$ measured in direct experiments; errors are experimental errors cited by authors.