

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI\_19

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This datasheet created: September 2015

### (CH<sub>3</sub>)<sub>2</sub>COO + H<sub>2</sub>O → products

#### Rate coefficient data

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

#### Comments

- (a) (CH<sub>3</sub>)<sub>2</sub>COO was generated from pulsed photolysis of a gaseous mixture consisting of 1,1 di-iodoacetone (CH<sub>3</sub>)<sub>2</sub>CI<sub>2</sub>, O<sub>2</sub>, and buffer gas (N<sub>2</sub>) at 248 nm (KrF excimer laser) via the established preparation method: (CH<sub>3</sub>)<sub>2</sub>CI<sub>2</sub> + hv → (CH<sub>3</sub>)<sub>2</sub>CI + I; (CH<sub>3</sub>)<sub>2</sub>CI + O<sub>2</sub> → (CH<sub>3</sub>)<sub>2</sub>COO + IO (2, 30), at 20 - 400 Torr total pressure. (CH<sub>3</sub>)<sub>2</sub>COO was monitored by UV absorption in the region 300 – 450 nm, corresponding to the  $\tilde{B}(1A') \leftarrow \tilde{X}(1A')$  electronic transition (Liu et al., 2014). A continuous probe light beam multipassed (x6 to x8) the long axis of the 76 cm photolysis and was detected on a time-gated iCCD spectrometer. (CH<sub>3</sub>)<sub>2</sub>COO kinetics observed by recording the time-resolved UV absorption spectrum. IO was also detected and is thought to be formed in secondary chemistry following the reaction (CH<sub>3</sub>)<sub>2</sub>CI<sub>2</sub> + O<sub>2</sub>. For (CH<sub>3</sub>)<sub>2</sub>COO the decay showed no dependence on water vapour even at high [H<sub>2</sub>O] (90% RH at 298 K), over a wide range of experimental conditions. The estimated upper limit is based on variability of 223 data points.
- (b) Study of the 2,3-dimethyl-2-butene (TME) + O<sub>3</sub> reaction in the presence of 1 bar of synthetic air with and without added SO<sub>2</sub>; H<sub>2</sub>O<sub>2</sub> yields were measured by tunable diode laser absorption spectroscopy or by FTIR spectroscopy. The reported rate constant ratio k/k<sub>SO2</sub> = (4.1 ± 2.2) × 10<sup>-4</sup> for reaction of (CH<sub>3</sub>)<sub>2</sub>COO with H<sub>2</sub>O and SO<sub>2</sub> gave the cited value using the IUPAC recommended value of k<sub>SO2</sub> at 1 bar pressure.
- (c) (CH<sub>3</sub>)<sub>2</sub>COO prepared by O<sub>3</sub> + TME reaction in the presence of SO<sub>2</sub> in a flow system, equipped with CIMS for detection of H<sub>2</sub>SO<sub>4</sub> using NO<sub>3</sub><sup>-</sup> as reagent ion. Total pressure = 1 bar. The yield of (CH<sub>3</sub>)<sub>2</sub>COO from the TME + O<sub>3</sub> reaction was reported to be 0.45(±0.20). The effect of [H<sub>2</sub>O] (RH = 2 – 50%) on yield of H<sub>2</sub>SO<sub>4</sub> was very weak and only allowed determination of an upper limit rate coefficient

ratio  $k((\text{CH}_3)_2\text{COO} + \text{H}_2\text{O})/k((\text{CH}_3)_2\text{COO} + \text{SO}_2) = 4 \times 10^{-6}$  at 293 K. A distinct temperature dependence of  $\text{H}_2\text{SO}_4$  formation was observed, attributed to the thermal decomposition of  $(\text{CH}_3)_2\text{COO}$ , which is the dominant first order loss of the CI in this system. The cited value uses the IUPAC recommendation for  $k((\text{CH}_3)_2\text{COO} + \text{SO}_2)$ , i.e.  $1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule s}^{-1}$  to evaluate the upper limit.

- (d) The removal of  $\text{SO}_2$  in the presence of 2-butene–ozone systems was measured as a function of humidity in EUPHORE simulation chamber, under atmospheric boundary layer conditions.  $\text{SO}_2$  and  $\text{O}_3$  abundance were measured using conventional fluorescence and UV absorption monitors, respectively; alkene abundance was determined via FTIR spectroscopy. The yield of  $(\text{CH}_3)_2\text{COO}$  from the TME +  $\text{O}_3$  reaction was reported to be  $0.32(\pm 0.20)$ . The observed  $\text{SO}_2$  removal kinetics are consistent with the rate constant ratio:  $k((\text{CH}_3)_2\text{COO} + \text{H}_2\text{O})/k((\text{CH}_3)_2\text{COO} + \text{SO}_2) = (8.7 \pm 2.5) \times 10^{-5}$ . 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
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$< 1.5 \times 10^{-16}$	298
<i>Reliability</i>		
$\Delta \log k$	0.5	298

### Comments on Preferred Values

All studies point to a slow reaction of  $(\text{CH}_3)_2\text{COO}$  (acetone oxide) with  $\text{H}_2\text{O}$ . 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  $(\text{CH}_3)_2\text{COO}$  (acetone oxide) reaction with  $\text{H}_2\text{O}$  are based on the study of Huang et al (2015).

Quantum chemical studies predict that  $(\text{CH}_3)_2\text{COO}$  (acetone oxide) reaction with  $\text{H}_2\text{O}$ . In the case of  $(\text{CH}_3)_2\text{COO}$  is significantly less reactive than *anti*- $\text{CH}_3\text{CHOO}$  towards, e.g.,  $\text{H}_2\text{O}$  (Anglada et al., 2011) and alkenes (Vereecken et al, 2014).

### References

J. H. Kroll, S. R. Sahay, J. G. Anderson, K. L. Demerjian and N. M. Donahue, J. Phys. Chem. **105**, 4446, (2001).

K. H. Becker, K. J. Brockmann, and J. Bechara, Atmos. Environ., 27A **57**, 1993.

Liu, F., Beames J. M., Green, A.M., Lester, M. I., UV spectroscopic characterization of dimethyl- and ethyl-substituted carbonyl oxides. J Phys Chem A 118(12):2298–2306, 2014.

Berndt T, et al. (2014) H<sub>2</sub>SO<sub>4</sub> formation from the gas-phase reaction of stabilized Criegee intermediates with SO<sub>2</sub>: Influence of water vapour content and temperature. Atmos Environ 89:603–612.

Vereecken L, Harder H, Novelli A (2012) The reaction of Criegee intermediates with NO, RO<sub>2</sub>, and SO<sub>2</sub>, and their fate in the atmosphere. Phys Chem Chem Phys 14(42): 14682–14695.

Liu F, Beames JM, Green AM, Lester MI (2014) UV spectroscopic characterization of dimethyl- and ethyl-substituted carbonyl oxides. J Phys Chem A 118(12):2298–2306.