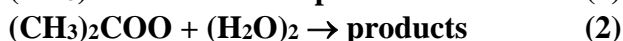
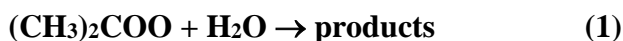


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_19

Datasheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission. The citation for this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, (<http://iupac.pole-ether.fr>).

This datasheet last evaluated: February 2020; last change in preferred values: February 2020



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_1 < 1.5 \times 10^{-16}$	298	Huang et al., 2015	PLP-LPUVA (a)
$k_2 < 1.3 \times 10^{-13}$	298		
<i>Relative Rate Coefficients</i>			
$k_1 = (6.4 \pm 3.4) \times 10^{-14}$	298	Becker et al., 1993	RR-FTIR/ TDLS (b)
$k_1 < 6.9 \times 10^{-16}$	293	Berndt et al., 2014	FT/CI-API-TOF MS(c)
$k_1 = (1.34 \pm 0.39) \times 10^{-14}$	298-299	Newland et al., 2015	RR-FTIR/UVA/UVF (d)

Comments

- (a) $(\text{CH}_3)_2\text{COO}$ was generated from the 248 nm pulsed photolysis of a gaseous mixture consisting of $(\text{CH}_3)_2\text{Cl}_2$, O_2 and buffer gas (N_2) at 20 - 400 Torr total pressure. $(\text{CH}_3)_2\text{COO}$ was monitored by UV absorption in the region 300 – 450 nm, corresponding to the $\tilde{\text{B}}(1\text{A}') \leftarrow \tilde{\text{X}}(1\text{A}')$ electronic transition (Liu et al., 2014). IO was also detected and is thought to be formed from a second channel of the $(\text{CH}_3)_2\text{Cl}_2 + \text{O}_2$ reaction. The $(\text{CH}_3)_2\text{COO}$ decay showed no dependence on $[\text{H}_2\text{O}]$ even at high concentrations (90% RH at 298 K), over a wide range of experimental conditions.
- (b) 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 . Yields of H_2O_2 (a product of the title reaction) were measured by tunable diode laser absorption spectroscopy or by FTIR spectroscopy. The reported rate constant ratio $k_1/k((\text{CH}_3)_2\text{COO} + \text{SO}_2) = (4.1 \pm 2.2) \times 10^{-4}$ was reported. k_1 is placed on an absolute basis using $k((\text{CH}_3)_2\text{COO} + \text{SO}_2) = 1.55 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).
- (c) $(\text{CH}_3)_2\text{COO}$ prepared by the $\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}$ 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 yield of $(\text{CH}_3)_2\text{COO}$ from the 2,3-dimethyl-but-2-ene + O_3 reaction was reported to be 0.45 ± 0.20 . The effect of $[\text{H}_2\text{O}]$ (RH = 2 – 50%) on yield of H_2SO_4 was very weak and only allowed determination of an upper limit rate coefficient ratio $k_1/k((\text{CH}_3)_2\text{COO} + \text{SO}_2) < 4 \times 10^{-6}$ at 293 K. A distinct temperature dependence of H_2SO_4 formation was observed, attributed to the thermal decomposition of $(\text{CH}_3)_2\text{COO}$, which is its dominant loss reaction in this system. The cited upper limit value of k_1 uses $k((\text{CH}_3)_2\text{COO} + \text{SO}_2) = 4.23 \times 10^{-13} \exp(1760/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).
- (d) The removal of SO_2 during the ozonolysis of 2,3-dimethyl-but-2-ene was measured as a function of humidity in EUPHORE simulation chamber, under atmospheric boundary layer conditions. Cyclohexane was also present to scavenge HO radicals. The SO_2 and O_3 abundance were measured using conventional fluorescence and UV absorption monitors, respectively; the alkene abundance was determined via FTIR spectroscopy. The yield of $(\text{CH}_3)_2\text{COO}$ from the 2,3-dimethyl-but-2-ene +

O₃ reaction was reported to be 0.32 ± 0.20 . The observed SO₂ removal kinetics are consistent with the rate constant ratio: k_1/k_2 ((CH₃)₂COO+SO₂) = $(8.7 \pm 2.5) \times 10^{-5}$. k_1 is placed on an absolute basis using $k((\text{CH}_3)_2\text{COO} + \text{SO}_2) = 4.23 \times 10^{-13} \exp(1760/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

Preferred Values

Parameter	Value	T/K
$k_1/ \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$< 1.5 \times 10^{-16}$	298
$k_2/ \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$< 1.3 \times 10^{-13}$	298

Comments on Preferred Values

All studies point to a slow reaction of (CH₃)₂COO with H₂O. The relative rate determinations from ozonolysis of 2,3-dimethyl-2-butene do not show much consistency, however. The difficulty seems to lie in distinguishing the slow reaction with water from 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 [H₂O] over a wide range of conditions, which precludes any significant reaction with either monomer or dimer. These data form the basis of the preferred upper limit values for k_1 and k_2 .

Quantum chemical studies predict that (CH₃)₂COO is significantly less reactive with H₂O than *E*-CH₃CHOO (Anglada et al., 2011). This is consistent with experimental observations, as reflected in the IUPAC recommended rate coefficients for the two species.

References

- Anglada, J.M., Gonzalez, J., and Torrent-Sucarrat, M.: Phys. Chem. Chem. Phys., 13, 13034, 2011.
- Becker, K. H., Brockmann, K. J. and Bechara, J.: Atmos. Environ. A, 27(1), 57, 1993.
- Berndt, T., Jokinen, T., Sipilä, M., Mauldin, R. L., Herrmann, H., Stratmann, F., Junninen, H. and Kulmala, M.: Atmos. Environ., 89, 603, 2014.
- Huang, H.-L., Chao, W. and Lin, J. J.-M.: Proc. Natl. Acad. Sci., 112(35), 10857, doi: 10.1073/pnas.1513149112, 2015.
- Newland, M. J., Rickard, A. R., Alam, M. S., Vereecken, L., Muñoz, A., Rodenas, M. and Bloss, W. J.: Phys. Chem. Chem. Phys., 17, 4076, 2015.