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

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

**(CH3)2COO + H2O → products (1)**

**(CH3)2COO + (H2O)2 → products (2)**

## Rate coefficient data

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| *k*/cm3 molecule-1 s-1 | Temp./K | Reference | | Technique/Comments |
| *Absolute Rate Coefficients* |  | |  |  |
| *k*1 *<* 1.5 × 10-16 | 298 | Huang et al., 2015 | | PLP-LPUVA (a) |
| *k*2 *<* 1.3 × 10-13 | 298 |  | |  |
| *Relative Rate Coefficients* |  |  | |  |
| *k*1 = (6.4 ± 3.4) × 10−14 | 298 | Becker et al., 1993 | | RR-FTIR/ TDLS (b) |
| *k*1 < 6.9 × 10−16 | 293 | Berndt et al., 2014 | | FT/CI-APi-TOF MS(c) |
| *k*1 = (1.34 ± 0.39) × 10−14 | 298-299 | Newland et al., 2015 | | RR-FTIR/UVA/UVF (d) |

##### Comments

1. (CH3)2COO was generated from the 248 nm pulsed photolysis of a gaseous mixture consisting of (CH3)2CI2, O2 and buffer gas (N2) at 20 - 400 Torr total pressure. (CH3)2COO was monitored by UV absorption in the region 300 – 450 nm, corresponding to the B̃ (1A′) ← X̃(1A′) electronic transition (Liu et al., 2014). IO was also detected and is thought to be formed from a second channel of the (CH3)2CI2 + O2 reaction. The (CH3)2COO decay showed no dependence on [H2O] even at high concentrations (90% RH at 298 K), over a wide range of experimental conditions.
2. Study of the 2,3-dimethyl-but-2-ene + O3 reaction in the presence of 1 bar of synthetic air with and without added SO2. Yields of H2O2 (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*((CH3)2COO + SO2) = (4.1 ± 2.2) × 10-4 was reported. *k*1 is placed on an absolute basis using *k*((CH3)2COO + SO2) = 1.55 × 10-10 cm3 molecule-1 s-1 at 298 K (IUPAC, current recommendation).
3. (CH3)2COO prepared by the O3 + 2,3-dimethyl-but-2-ene reaction in the presence of SO2 and propane (HO radical scavenger) in a flow system, equipped with CIMS for detection of H2SO4 using NO3- as reagent ion. Total pressure = 1 bar. The yield of (CH3)2COO from the 2,3-dimethyl-but-2-ene + O3 reaction was reported to be 0.45 ± 0.20. The effect of [H2O] (RH = 2 – 50%) on yield of H2SO4 was very weak and only allowed determination of an upper limit rate coefficient ratio *k*1/*k*((CH3)2COO + SO2) < 4 × 10-6 at 293 K. A distinct temperature dependence of H2SO4 formation was observed, attributed to the thermal decomposition of (CH3)2COO, which is its dominant loss reaction in this system. The cited upper limit value of *k*1 uses *k*((CH3)2COO + SO2) = 4.23 × 10-13 exp(1760/*T*) cm3 molecule-1 s-1 (IUPAC, current recommendation).
4. The removal of SO2 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 SO2 and O3 abundance were measured using conventional fluorescence and UV absorption monitors, respectively; the alkene abundance was determined via FTIR spectroscopy. The yield of (CH3)2COO 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* ((CH3)2COO+SO2) = (8.7 ± 2.5) × 10-5. *k*1 is placed on an absolute basis using *k*((CH3)2COO + SO2) = 4.23 × 10-13 exp(1760/*T*) cm3 molecule-1 s-1 (IUPAC, current recommendation).

##### Preferred Values

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Parameter** | | **Value** | | **T/K** |
|  | |  | |  |
| *k*1/ cm3 molecule-1 s-1 | | < 1.5 × 10-16 | | 298 |
| *k*2/ cm3 molecule-1 s-1 | | < 1.3 × 10-13 | | 298 |
|  |  | |  | |

1. *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**

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