**IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI\_14**

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**(CH3)2COO + M → 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

1. (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 + hν → (CH3)2CI+ I, 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 the second channel, (CH3)2CI+ O2 → (CH3)2COO + IO. First order 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. 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 (CH3)2COO.
2. (CH3)2COO was generated from pulsed photolysis of a gaseous mixture consisting of 2,2-diiodopropane, (CH3)2CI2, O2, and buffer gas (N2) at 248 nm, (CH3)2CI2 + hν → (CH3)2CI+ I, at a total pressure of 200 Torr. (CH3)2COO was monitored by time-resolved UV absorption due to the B̃ (1A′) ← X̃(1A′) electronic transition. The amount of (CH3)2COO formed was estimated using a cross-section  = 1.6 × 10−17 cm2 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 (CH3)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 × 106 exp[-(2919 ± 604)/*T*)]. (CD3)2COO kinetics were also investigated using the precursor (CD3)2CI2. *k* for (CD3)2COO at 298 K was estimated to be <100 s−1, with no significant *T* dependence.
3. (CH3)2COO was formed by laser photolysis of (CH3)2CI2  in the presence of O2 and characterized by synchrotron photoionization mass spectrometry; and also by cavity ringdown ultraviolet absorption spectroscopy. Cavity ringdown measurements of (CH3)2COO loss without added reagents display a combination of first- and second-order decay kinetics, which were deconvolved to derive values for both the (CH3)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.
4. 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, in a flow system, at 1 bar pressure and 50 % RH. Either propane or butane were also present to scavenge HO radicals. Formation of H2SO4 from the reaction of (CH3)2COO with SO2 was monitored with CIMS, using NO3- as reagent ion. The time dependence of H2SO4 production after addition of different [SO2] allowed estimation of *k*loss = (3.0 ± 0.4) s-1 for (CH3)2COO, and a rate constant ratio *k*loss/*k*((CH3)2COO + SO2) = (3.9 ± 0.7) × 1012 molecule cm-3; where *k*loss is the total first-order loss rate due to decomposition and reaction with H2O. Because the (slow) reaction of (CH3)2COO with H2O can be neglected as a significant removal process for (CH3)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*((CH3)2COO + SO2) = 4.23 × 10-13 exp(1760/*T*) cm3 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.
5. (CH3)2COO prepared by 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 effect of [H2O] (RH = 2 – 50%) on yield of H2SO4 was negligible, and it was deduced that thermal decomposition was the dominant reaction competing with (CH3)2COO + SO2 reaction. A distinct temperature dependence of H2SO4 formation was observed over the studied range (278-343 K), attributed mainly to the thermal decomposition of (CH3)2COO. The reported values of *k*/*k*((CH3)2COO + SO2) were 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). An Arrhenius plot of the resultant values of *k* vs. 1/*T*, is linear, yielding a value of *E*a ≈ 29 kJ mol-1.
6. The removal of SO2 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. 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 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*/*k*((CH3)2COO + SO2) = (6.3 ± 1.4) × 1012 molecule cm-3. The tabulated value of *k* was 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*/ s-1 | 400 | 298 |
| *k*/ s-1 | 7.2 × 106 exp(-2920/*T*) | 280-330 |

*Reliability*

|  |  |  |
| --- | --- | --- |
|  log *k* | ± 0.2 | 298 |
|  (*E*/*R*) | ± 700 | 280-330 |

1. *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 (CH3)2COO with SO2 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 × 108 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 (CH3)2COO + SO2 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 (CH3)2COO and (CD3)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 (CH3)2COO, and the experimentally observed slower decomposition of (CD3)2COO is predicted.

The quantum chemical studies predict that decomposition of (CH3)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 (CH3)2COO than from CH2OO (Fang et al. 2016). These observations confirm that the facile 1,4 intramolecular hydrogen transfer leads to much faster unimolecular decomposition rate for (CH3)2COO compared with CH2OO, for which the mechanism is unavailable.

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Arrhenius plot of *k*((CH3)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 ×106 exp(-2920/*T*) s-1. The broken line is a fit to the relative rate data, *k* = 1.11 × 108 exp(-3500/*T*) s-1.