

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI\_30

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

### $E\text{-(CH=CH}_2\text{)(CH}_3\text{)COO + HC(O)OH} \rightarrow \text{products}$

#### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i> $(3.1 \pm 0.1) \times 10^{-10}$	298	Caravan et al., 2020	PLP-PIMS/UV-vis-A (a)

#### Comments

- (a) *Z*- and *E*-(CH=CH<sub>2</sub>)(CH<sub>3</sub>)COO (also referred to as *anti*- and *syn*- MVK oxide, respectively) were produced from the reaction of CH<sub>2</sub>=CHC(CH<sub>3</sub>)I with O<sub>2</sub>, following the 248 nm or 266 nm photolysis of 1,3-diiodobut-2-ene/O<sub>2</sub> mixtures in He or N<sub>2</sub>. Experiments were carried out using time-resolved UV/visible absorption spectroscopy and multiplexed photoionization mass spectrometry, MPIMS (13 mbar He). *Z*-(CH=CH<sub>2</sub>)(CH<sub>3</sub>)COO decomposes very rapidly via 1,5 ring-closure, allowing the specific investigation of the bimolecular kinetics of the reactions of *E*-(CH=CH<sub>2</sub>)(CH<sub>3</sub>)COO with added reagents. The tabulated value of *k* was determined from the observed first order decay of *E*-(CH=CH<sub>2</sub>)(CH<sub>3</sub>)COO as a function of excess [HC(O)OH] at a pressure of 13 mbar He in UV/visible absorption spectroscopy experiments. Product masses consistent with formation of hydroperoxybut-3-en-2-yl formate were observed in the MPIMS experiments.

#### Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3.1 \times 10^{-10}$	298
<i>Reliability</i> $\Delta \log k$	$\pm 0.3$	298

#### Comments on Preferred Values

The preferred value of *k* is based on the determination reported in the sole kinetics study of Caravan et al. (2020). The value of *k*, near the gas kinetic limit, is comparable with those reported for the simple C<sub>1</sub> – C<sub>3</sub> sCIs, for which the preferred values lie in the range  $1.1 \times 10^{-10}$  to  $5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

High-level theoretical calculations, also reported by Caravan et al. (2020), predict that the reaction proceeds via effectively barrierless insertion of *E*-(CH=CH<sub>2</sub>)(CH<sub>3</sub>)COO into HC(O)OH, leading to

formation of hydroperoxybut-3-en-2-yl formate (HPBF). Consistent with this, Caravan et al. (2020) observed product masses compatible with the formation of HPBF in PIMS experiments at 13 mbar pressure.  $k$  was calculated to be pressure- and temperature-dependent over the tropospheric range, with the value at 1 bar well described by the expression  $7.7 \times 10^6 T^{-5.86} \exp(-1170/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  ( $4.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K). The preferred value of  $k$  is based on the experimental measurement at 13 mbar, but with uncertainty bounds that encompass the calculated 1 bar value.

## References

Caravan, R. L., Vansco, M. F., Au, K., Khan, M. A. H., Li, Y.-L. Winiberg, F. A. F., Zuraski, K., Lin, Y.-H., Chao, W., Trongsiwat, N., Walsh, P. J., Osborn, D. L., Percival, C. J., Lin, J.-J. M., Shallcross, D. E., Sheps, L., Klippenstein, S. J., Taatjes, C. A., and Lester, M. I.: Proc. Nat. Acad. Sci., 117 (18), 9733, doi: 10.1073/pnas.1916711117, 2020.