

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI\_22

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



### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4.2 \pm 0.6) \times 10^{-11}$	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 (13 mbar He and 5.3 – 930 mbar N<sub>2</sub>) 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.  $k$  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 [SO<sub>2</sub>]. The value of  $k$  was found to be independent of pressure over the range 400 – 930 mbar N<sub>2</sub>, and those measurements form the basis of the value tabulated above. SO<sub>3</sub> was observed as a reaction product in MPIMS experiments carried out in 13 mbar He.

### Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$4.2 \times 10^{-11}$	298
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.2$	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 is comparable with those reported for the simple C<sub>1</sub> – C<sub>3</sub> sClIs, for which the preferred values lie in the range  $2.6 \times 10^{-11}$  to  $1.55 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . However, it is approaching a factor four lower than that for the di-substituted sCI, (CH<sub>3</sub>)<sub>2</sub>COO, which shows the highest reactivity with SO<sub>2</sub> studied to date. This suggests that the resonance stabilization of the Criegee functionality with

the vinyl substituent in the di-substituted *E*-(CH=CH<sub>2</sub>)(CH<sub>3</sub>)COO results in a lowering of reactivity towards SO<sub>2</sub>. Caravan et al. (2020) also observed the production of SO<sub>3</sub> (13 mbar pressure, using PIMS), with a formation time constant that matched the removal of *E*-(CH=CH<sub>2</sub>)(CH<sub>3</sub>)COO, confirming that SO<sub>3</sub> is a direct product of the reaction.

High-level theoretical calculations, also reported by Caravan et al. (2020), predict that the reaction of *E*-(CH=CH<sub>2</sub>)(CH<sub>3</sub>)COO with SO<sub>2</sub> proceeds via effectively barrierless formation of a chemically-activated secondary ozonide. However, the transition state is calculated to be at higher energy than those for simple sCIs, as a result of the resonance stabilization, consistent with the lower rate coefficient compared with the (CH<sub>3</sub>)<sub>2</sub>COO + SO<sub>2</sub> reaction. The chemically-activated secondary ozonide is calculated to decompose exclusively to SO<sub>3</sub> and CH<sub>3</sub>C(O)CH=CH<sub>2</sub> (methylvinyl ketone, MVK) at 13 mbar. This product channel is also calculated to dominate at 300 K and atmospheric pressure, with 5 % formation of the thermalized secondary ozonide.

## 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., Trongsiriwat, 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.