

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_22

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E-(CH=CH₂)(CH₃)COO + SO₂ → products

Rate coefficient data

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i> (4.2 ± 0.6) × 10 ⁻¹¹	298	Caravan et al., 2020	PLP-PIMS/UV-vis-A (a)

Comments

- (a) *Z*- and *E*-(CH=CH₂)(CH₃)COO (also referred to as *anti*- and *syn*- MVK oxide, respectively) were produced from the reaction of CH₂=CHC(CH₃)I with O₂, following the 248 nm or 266 nm photolysis of 1,3-diiodobut-2-ene/O₂ mixtures in He or N₂. Experiments were carried out using time-resolved UV/visible absorption spectroscopy (13 mbar He and 5.3 – 930 mbar N₂) and multiplexed photoionization mass spectrometry, MPIMS (13 mbar He). *Z*-(CH=CH₂)(CH₃)COO decomposes very rapidly via 1,5 ring-closure, allowing the specific investigation of the bimolecular kinetics of the reactions of *E*-(CH=CH₂)(CH₃)COO with added reagents. *k* was determined from the observed first order decay of *E*-(CH=CH₂)(CH₃)COO as a function of excess [SO₂]. The value of *k* was found to be independent of pressure over the range 400 – 930 mbar N₂, and those measurements form the basis of the value tabulated above. SO₃ was observed as a reaction product in MPIMS experiments carried out in 13 mbar He.

Preferred Values

Parameter	Value	T/K
<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	4.2 × 10 ⁻¹¹	298
<i>Reliability</i> Δ log <i>k</i>	± 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 C₁ – C₃ sCIs, for which the preferred values lie in the range 2.6 × 10⁻¹¹ to 1.55 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹. However, it is approaching a factor four lower than that for the di-substituted sCI, (CH₃)₂COO, which shows the highest reactivity with SO₂ studied to date. This suggests that the resonance stabilization of the Criegee functionality with

the vinyl substituent in the di-substituted E -(CH=CH₂)(CH₃)COO results in a lowering of reactivity towards SO₂. Caravan et al. (2020) also observed the production of SO₃ (13 mbar pressure, using PIMS), with a formation time constant that matched the removal of E -(CH=CH₂)(CH₃)COO, confirming that SO₃ 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=CH₂)(CH₃)COO with SO₂ 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 (CH₃)₂COO + SO₂ reaction. The chemically-activated secondary ozonide is calculated to decompose exclusively to SO₃ and CH₃C(O)CH=CH₂ (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., Trongsirawat, 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.