

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_21

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(CH=CH₂)(CH₃)COO (*Z*- and *E*-), (C(CH₃)=CH₂)CHO (*Z*- and *E*-) Reactions with SO₂, H₂O, (H₂O)₂ and thermal decomposition

Kinetics studies

Reference	Temp./K	Technique/Comments
<i>Relative Rate Studies</i>		
Sipilä et al., 2014	293	CIMS (a)
Newland et al., 2015	287-302	FTIR/UVF (b)
Nguyen et al., 2016	295	Multi-instrumented (c)

Comments

- (a) H₂SO₄ formation from SO₂ oxidation in the presence of isoprene and ozone was studied as a function of [SO₂] and relative humidity in a flow of synthetic air at 1 bar and 293 K. Propane was also present in the mixtures to scavenge HO radicals. NO₃⁻ chemical-ionization-atmospheric pressure interface-time-of-flight mass spectrometry (CI-APi-TOF MS) was used for the detection of sulfuric acid. Plots of H₂SO₄ formation rate vs. [SO₂] were fitted to determine the yield of sCIs produced from isoprene ozonolysis, where the sCIs comprise CH₂OO and the C₄ species identified above. The total yield was determined from [H₂SO₄]_{max}/Δ[isoprene]. [H₂SO₄]_{max} was the concentration measured at the high end of the applied [SO₂] range (2.4 × 10¹⁴ molecule cm⁻³), and the loss of isoprene, Δ[isoprene], was determined from initial [O₃], [isoprene], the rate coefficient for the O₃ + isoprene reaction, and the residence time in the flow tube (39.5 s). This results in a total sCI yield of 0.66 ± 0.29, based on $k(\text{O}_3 + \text{isoprene}) = 1.05 \times 10^{-14} \exp(-2000/T)$ (IUPAC current recommendation). The results were used to determine values of $k_{\text{loss}}/k(\text{sCI} + \text{SO}_2)$ at 10 % and 50 % RH. k_{loss} is the effective pseudo-first order loss rate of sCI, including thermal decomposition and the reaction with water vapour, given by $k_{\text{loss}} = k(\text{sCI} + \text{M}) + (k(\text{sCI} + \text{H}_2\text{O}) \times [\text{H}_2\text{O}])$. Measured values therefore represent weighted average rate constant ratios for the population of isoprene-derived sCIs. Values of $k_{\text{loss}}/k(\text{sCI} + \text{SO}_2) = (2.5 \pm 0.1) \times 10^{12} \text{ cm}^{-3}$ at 10 % RH and $k_{\text{loss}}/k(\text{sCI} + \text{SO}_2) = (2.1 \pm 0.5) \times 10^{13} \text{ cm}^{-3}$ at 50 % RH were determined, assuming a single sCI species model, although this did not provide a good description of the data obtained at 50 % RH. An expanded analysis, using a two sCI species model, provided a better description of the data at 50 % RH, with the two species accounting for 85 % and 15 % of the total. The corresponding rate coefficient ratios at 50 % RH, $k_{\text{loss}}/k(\text{sCI} + \text{SO}_2)$, were $3.3 \times 10^{13} \text{ cm}^{-3}$ for species 1 and $2.6 \times 10^{11} \text{ cm}^{-3}$ for species 2, consistent with substantially differing reactivities for the component sCIs. It was suggested that the much stronger [H₂O] dependence for species 1 could be consistent with it being CH₂OO.
- (b) SO₂ removal in the presence of isoprene and ozone, was measured as a function of humidity under atmospheric boundary layer conditions in a 200 m³ static chamber (EUPHORE) at 1 bar and 287-302 K. Cyclohexane was also present in the mixtures to scavenge HO radicals. Detection was by FTIR for organic species, and UV fluorescence for SO₂ and O₃. The SO₂ removal rate was observed to display a systematic dependence on [H₂O] over the range 0.4 – 21 × 10¹⁶ molecule cm⁻³. This confirmed significant reaction for at least some of the isoprene-derived sCIs with H₂O, as is expected in the case of CH₂OO. Under excess SO₂ conditions ([SO₂] ≈ 2.5 × 10¹³ molecule cm⁻³), the total isoprene ozonolysis sCI yield was calculated to be 0.56 ± 0.03. The data were analysed using a linear regression of the quantity [SO₂] × ((1/*f*) – 1) vs [H₂O], where *f* is the fraction of the sCIs produced that react with SO₂. This gave the rate constant ratio $k(\text{sCI} +$

$\text{H}_2\text{O})/k(\text{sCI} + \text{SO}_2) = (3.1 \pm 0.5) \times 10^{-5}$ from the slope, and an estimate of $k(\text{sCI} + \text{M})/k(\text{sCI} + \text{SO}_2) = (3.0 \pm 3.2) \times 10^{11}$ molecule cm^{-3} from the intercept, where these values represent weighted average rate constant ratios for the population of isoprene-derived sCIs.

- (c) The product distribution from the reaction of O_3 with isoprene was investigated in the multi-instrumented Caltech dual 24 m^3 Teflon chamber at 1 bar and ~ 295 K. In most experiments, cyclohexane was also present in the mixtures to scavenge HO radicals. Experiments were carried out as a function of RH over the range 4 % to 76 %, in the absence or presence of SO_2 . The development of the system was monitored using GC-FID and FTIR for isoprene, methacrolein and methyl vinyl ketone, aerosol time-of-flight MS for H_2SO_4 , and commercial analysers for O_3 and trace NO and NO_2 . HCHO, HO and HO_2 were measured using LIF, and gas phase peroxides (e.g. H_2O_2 , HOCH_2OOH , CH_3OOH), acidic compounds (e.g. SO_2 , $\text{HC}(\text{O})\text{OH}$) and other polar organics (e.g. hydroxycarbonyls) using CIMS. The results obtained as a function of RH suggest that CH_2OO is the only sCI to react bimolecularly under the experimental conditions, and a yield of 0.61 ± 0.09 was determined. The yields of methacrolein (0.42 ± 0.06) and methyl vinyl ketone (0.18 ± 0.06) were relatively insensitive to humidity, suggesting that the C_4 CIs either have a low stabilization fraction, or that the C_4 sCIs produced decompose rapidly. A yield of 0.28 ± 0.05 was also determined for HO radicals. The results as a function of $[\text{SO}_2]$ yielded the rate coefficient ratio, $k(\text{sCI} + \text{SO}_2)/k(\text{sCI} + (\text{H}_2\text{O})_{n=1,2}) \approx (2.2 \pm 0.3) \times 10^4$. A comprehensive reaction mechanism was proposed which reproduces laboratory data over the wide range of relative humidity. The observations for HOCH_2OOH , HCHO, $\text{HC}(\text{O})\text{OH}$ and H_2O_2 were used to determine branching ratios for the reactions of CH_2OO with H_2O and $(\text{H}_2\text{O})_2$ (see data sheet CGI_4).

Preferred Values

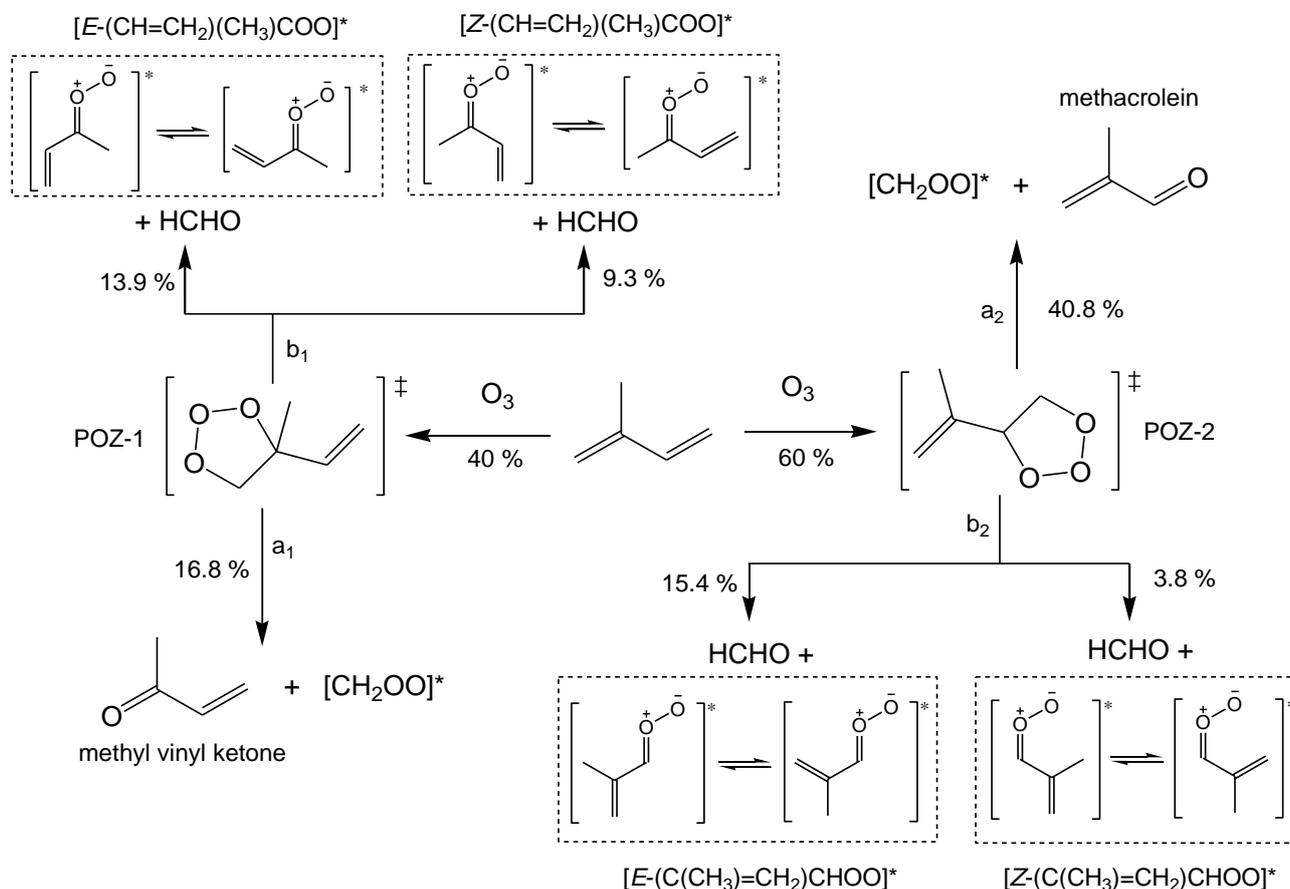
Parameter	$k_{298\text{ K}}$	$k(T)$	Note
$k(\text{sCI} + \text{SO}_2)/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$			
Z-(CH=CH ₂)(CH ₃)COO	4.2×10^{-11}		(a)
E-(CH=CH ₂)(CH ₃)COO	4.2×10^{-11}		(b)
Z-(C(CH ₃)=CH ₂)CHOO	2.6×10^{-11}		(c)
E-(C(CH ₃)=CH ₂)CHOO	1.4×10^{-10}		(d)
$k(\text{sCI} + \text{H}_2\text{O})/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$			
Z-(CH=CH ₂)(CH ₃)COO	1.79×10^{-18}	$2.21 \times 10^{-21} T^{2.27} \exp(-1858/T)$	(e)
E-(CH=CH ₂)(CH ₃)COO	7.89×10^{-20}	$7.07 \times 10^{-19} T^{1.46} \exp(-3132/T)$	(e)
Z-(C(CH ₃)=CH ₂)CHOO	1.19×10^{-19}	$2.24 \times 10^{-19} T^{1.65} \exp(-2989/T)$	(e)
E-(C(CH ₃)=CH ₂)CHOO	1.43×10^{-16}	$2.93 \times 10^{-19} T^{1.66} \exp(-973/T)$	(e)
$k(\text{sCI} + (\text{H}_2\text{O})_2)/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$			
Z-(CH=CH ₂)(CH ₃)COO	4.87×10^{-15}	$2.25 \times 10^{-21} T^{2.27} \exp(493/T)$	(e)
E-(CH=CH ₂)(CH ₃)COO	3.06×10^{-16}	$7.63 \times 10^{-19} T^{1.45} \exp(-675/T)$	(e)
Z-(C(CH ₃)=CH ₂)CHOO	4.39×10^{-16}	$2.42 \times 10^{-19} T^{1.64} \exp(-548/T)$	(e)
E-(C(CH ₃)=CH ₂)CHOO	2.79×10^{-13}	$3.24 \times 10^{-19} T^{1.65} \exp(1271/T)$	(e)
$k(\text{sCI} + \text{M})/\text{s}^{-1}$ (thermal decomposition)			
Z-(CH=CH ₂)(CH ₃)COO	1.36×10^4	$9.75 \times 10^8 T^{1.03} \exp(-5081/T)$	(e),(f)
E-(CH=CH ₂)(CH ₃)COO	5.13×10^1	$4.36 \times 10^{-67} T^{25.9} \exp(2737/T)$	(e)
Z-(C(CH ₃)=CH ₂)CHOO	1.40×10^4	$2.58 \times 10^9 T^{0.87} \exp(-5090/T)$	(e)
E-(C(CH ₃)=CH ₂)CHOO	3.02×10^1	$1.68 \times 10^{10} T^{1.02} \exp(-7732/T)$	(e)

Notes: ^a Based on 298 K IUPAC recommendation for E-(CH=CH₂)(CH₃)COO (see Note (b)), assumed here to be temperature independent over the range 287-302 K; ^b IUPAC recommendation, based on Caravan et al. (2020) (see data sheet CGI_22), assumed here to be temperature independent over the range 287-302 K; ^c Based on the 298 K IUPAC recommendation for Z-CH₃CHOO (see data sheet CGI_15), assumed here to be temperature independent over the range 287-302 K; ^d Based on the 298 K IUPAC recommendation for E-CH₃CHOO (see data sheet CGI_15), assumed here to be temperature independent over the range 287-302 K; ^e Adopted from the theoretical/SAR methods reported by Vereecken et al. (2017), as presented in Supplement Tables 31, 35 and 40 of that paper; ^f Exponent of pre-exponential factor changed from 9 to 8 for consistency with 298 K rate coefficient reported by Vereecken et al. (2017).

Comments on Preferred Values

The reaction of O₃ with isoprene results in the formation CH₂OO and the C₄ species, Z-(CH=CH₂)(CH₃)COO, E-(CH=CH₂)(CH₃)COO, Z-(C(CH₃)=CH₂)CHOO and E-(C(CH₃)=CH₂)CHOO. The rate coefficient ratios reported in the studies of Sipilä et al. (2014), Newland et al. (2015) and Nguyen et al. (2016) (see comments (a)-(c)) are therefore weighted averages for the population of sCIs under the studied conditions. The three studies demonstrate that the chemistry of the system is strongly dependent on both [SO₂] and [H₂O]. This confirms significant reaction for at least some of the isoprene-derived sCIs with SO₂ and H₂O (and/or (H₂O)₂); as indeed is well established from direct kinetics studies in the case of CH₂OO and E-(CH=CH₂)(CH₃)COO (see data sheets CGI_1, CGI_4 and CGI_22). However, the results of Sipilä et al. (2014) at 50 % relative humidity and theoretical predictions (e.g. Vereecken et al., 2017) indicate that the reactivity of the set of C₁ and C₄ sCIs likely varies considerably from one species to another, such that the system cannot be interpreted consistently in terms of bulk or averaged rate parameters. In addition, the results suggest that the sCI population is dominated by CH₂OO, precluding reliable analytical extraction of kinetic data for the C₄ isomers. An explicit appraisal of the system has therefore been carried out, with most parameters either inferred from those for the simpler C₂ sCIs, or adopted from theoretical studies. This analysis forms the basis of the preferred values tabulated above, and is explained and justified in the following paragraphs.

The initial formation mechanism for the excited Criegee intermediates (CIs) is shown in the schematic below, with their resultant yields (Y_{CI}) also given in the table below. The contributions assigned to the channels are taken from Nguyen et al. (2016), and are based on a combination of their results and information from the literature. The CIs either decompose promptly, or are stabilized to form the corresponding sCIs. The fractional stabilization (F_{stab}) applied to the CIs is based on the species-dependent values calculated for atmospheric pressure in the theoretical study of Zhang et al. (2002), resulting in the sCI yields (Y_{sCI}) shown in the table below.



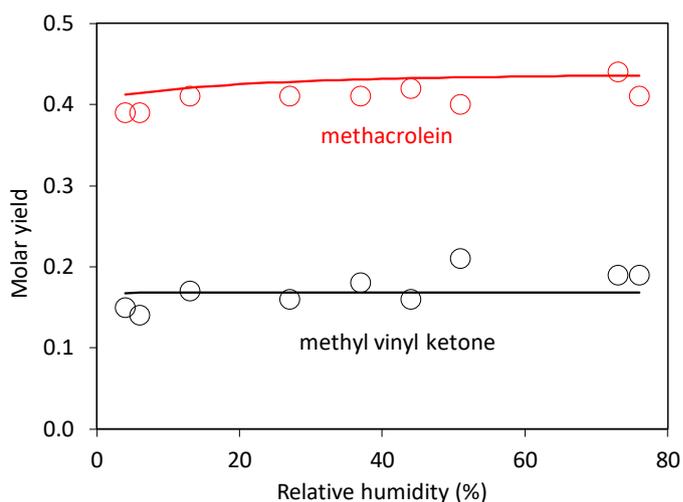
sCI	Y_{CI}	F_{stab}	Y_{sCI}
CH ₂ OO	0.576	0.95	0.547
Z-(CH=CH ₂)(CH ₃)COO	0.093	0.34	0.032
E-(CH=CH ₂)(CH ₃)COO	0.139	0.54	0.075
Z-(C(CH ₃)=CH ₂)CHOO	0.038	0.37	0.014
E-(C(CH ₃)=CH ₂)CHOO	0.154	0.20	0.031

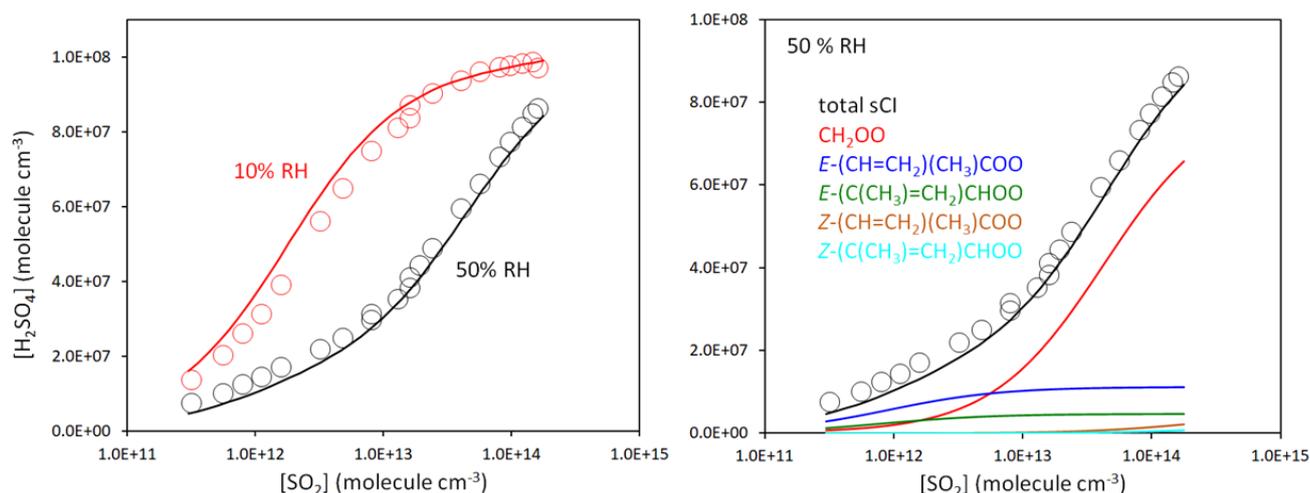
The resultant total sCI yield, 0.70, is higher than those reported by Sipilä et al. (2014) and Newland et al. (2015). However, Z-(CH=CH₂)(CH₃)COO and Z-(C(CH₃)=CH₂)CHOO are calculated to decompose very rapidly (Vereecken et al., 2017), such that they are barely scavenged over the reported range of experimental conditions in most studies. The total yield of the remaining sCIs (which likely contribute to the bimolecular reactivity of the system) is about 0.65. This is in acceptable agreement with the adjusted yield of 0.66 ± 0.29 , based on the results of Sipilä et al. (2014) (see comment (a)), and 0.56 ± 0.03 , reported by Newland et al. (2015). The calculated yield of CH₂OO is about 0.55, which also agrees with the Nguyen et al. (2016) value of 0.61 ± 0.09 . Based on this information, we recommend a total sCI yield of 0.65 ± 0.10 .

In the following analysis, the rate coefficients shown above in the table of preferred values were applied to the C₄ sCI isomers, along with the IUPAC recommendations for CH₂OO given in data sheets CGI_1, CGI_4 and CGI_13, and for the E-(CH=CH₂)(CH₃)COO + SO₂ reaction given in data sheet CGI_22. Those for the other C₄ sCI + SO₂ reactions were inferred from the recommendation for E-(CH=CH₂)(CH₃)COO, in the case of its stereoisomer Z-(CH=CH₂)(CH₃)COO; and from the recommendations for Z- and E-CH₃CHOO, in the cases of the C₄ mono-substituted isomers Z- and E-(C(CH₃)=CH₂)CHOO. The reactions were assumed to proceed via a single channel in each case, producing SO₃ and either methyl vinyl ketone or methacrolein. The rate coefficients for unimolecular decomposition of the C₄ sCIs and their reactions with H₂O and (H₂O)₂ were adopted from the theoretical/SAR study of Vereecken et al. (2017). The concentrations of (H₂O)₂ were calculated using the equilibrium constants reported by Ruscic (2013). The aim of this analysis is to show that the results reported by Sipilä et al. (2014), Newland et al. (2015) and Nguyen et al. (2016) as a function of [SO₂] and [H₂O] can be recreated acceptably using these parameters.

The pathway contributions shown in the above schematic result in primary yields of 40.8 % for methacrolein and 16.8 % for methyl vinyl ketone. These agree with those reported (e.g. Aschmann and Atkinson, 1994; Grosjean et al., 1993; Rickard et al., 1999; Nguyen et al., 2016), which lie in the range 32-44 % for methacrolein and 13-18 % for methyl vinyl ketone. Nguyen et al. (2016) showed that the yields are relatively insensitive to humidity, consistent with limited secondary formation from the reactions of the C₄ sCIs with H₂O or (H₂O)₂. The adjacent plot shows the calculated maximum dependence of the yields on relative humidity at 295 K (lines), compared with the Nguyen et al. (2016) data (points), based on assuming the H₂O and (H₂O)₂ reactions form methacrolein or methyl vinyl ketone exclusively.

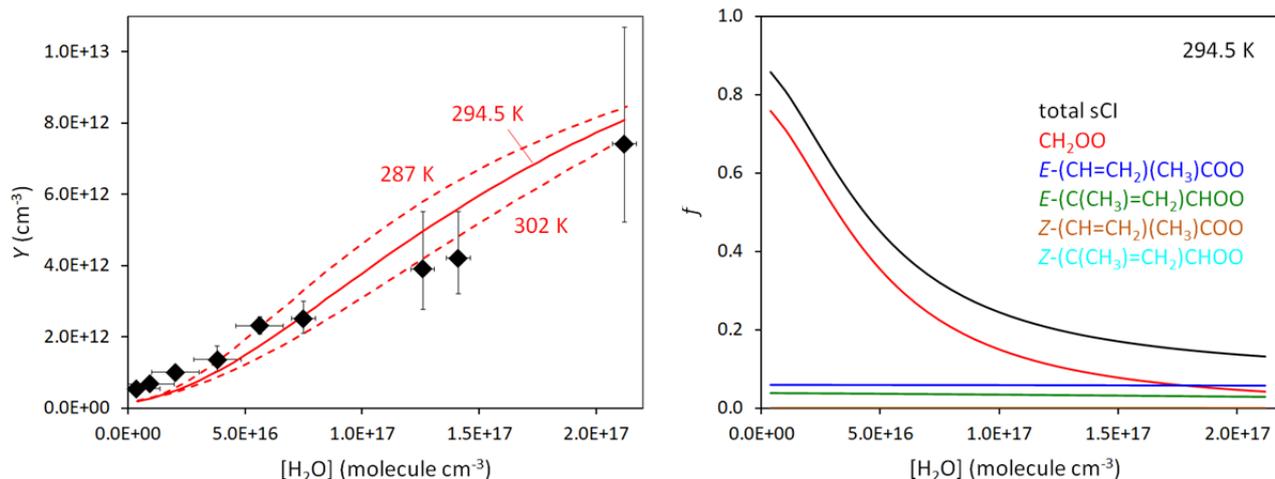
The calculated yield of methyl vinyl ketone is completely insensitive to relative humidity because thermal decomposition of Z- and E-(CH=CH₂)(CH₃)COO dominates over the water reactions under all conditions, as is also the case for Z-(C(CH₃)=CH₂)CHOO. The small dependence simulated for methacrolein (leading to a maximum secondary yield of 2.7 % at 76 % relative humidity) results from E-(C(CH₃)=CH₂)CHOO being significantly scavenged by reactions with both H₂O and (H₂O)₂.





The dependence of H_2SO_4 formation as a function of $[\text{SO}_2]$ was calculated for the conditions of the experiments reported by Sipilä et al. (2014), i.e. at 293 K and either 10 % or 50 % relative humidity. The above figure compares the results of the calculations (lines) with the Sipilä et al. (2014) data (points). The observations at both 10 % and 50 % relative humidity are well recreated, given the uncertainty bounds on the applied parameters. The right-hand panel shows the calculated contributions of the five sCI species to H_2SO_4 formation at 50 % relative humidity. This shows that the total formation is dominated by the contributions from CH_2OO , $E\text{-(CH=CH}_2\text{)(CH}_3\text{)COO}$ and $E\text{-(C(CH}_3\text{)=CH}_2\text{)CHOO}$ across the $[\text{SO}_2]$ range, with $Z\text{-(CH=CH}_2\text{)(CH}_3\text{)COO}$ also making a small contribution at the high end of the range. Of the three main contributors, it is noted that CH_2OO accounts for about 84 % of combined sCI yield of this subset, with $E\text{-(CH=CH}_2\text{)(CH}_3\text{)COO}$ and $E\text{-(C(CH}_3\text{)=CH}_2\text{)CHOO}$ collectively accounting for the remaining 16 %. This is therefore fully consistent with the two species model of Sipilä et al. (2014), and their differential relative reactivities with SO_2 and H_2O , which was based on 85 % and 15 % contributors (see comment (a)).

The influence of $[\text{H}_2\text{O}]$ on the removal of SO_2 (initially 50 ppb) was also calculated for conditions representative of those reported by Newland et al. (2015). The experiments were carried out at ambient temperatures, reported to be in the range 287-302 K, such that there was likely temperature variability in this range both between and within experiments. The calculations were therefore performed for the mid-range temperature (294.5 K) and the extreme temperatures. The left-hand panel below shows the calculated $[\text{H}_2\text{O}]$ dependence of the function Y (lines) compared with the Newland et al. (2015) data (points). Y is defined as $[\text{SO}_2] \times ((1/f) - 1)$ (Newland et al., 2015), where f is the fraction of sCIs removed by reaction with SO_2 . The observed dependence therefore results from a reduction in f as $[\text{H}_2\text{O}]$ increases. In a single sCI system, and assuming the sCI does not react significantly with $(\text{H}_2\text{O})_2$, the plot would be expected to be linear with a slope $k(\text{sCI} + \text{H}_2\text{O})/k(\text{sCI} + \text{SO}_2)$ and an intercept of $k(\text{sCI} + \text{M})/k(\text{sCI} + \text{SO}_2)$, and this was the basis of the Newland et al. (2015) analysis. However, the calculated dependence is not linear, resulting from the differing relative reactivities of the component sCIs with SO_2 and H_2O , and the role of the $(\text{H}_2\text{O})_2$ reactions. The initial increase and upward curvature at low $[\text{H}_2\text{O}]$ in the calculated dependence of Y results mainly from the impact of increased loss of CH_2OO via reaction with H_2O and, particularly, $(\text{H}_2\text{O})_2$. This is also illustrated in the right-hand panel, which shows that the calculated variation in f at low $[\text{H}_2\text{O}]$ for the set of sCIs is dominated by the decrease in the CH_2OO contribution. By the mid-range $[\text{H}_2\text{O}]$, less than 20 % of CH_2OO is reacting with SO_2 , and $(\text{H}_2\text{O})_2$ is its major reaction partner. As a result, the contributions of $E\text{-(CH=CH}_2\text{)(CH}_3\text{)COO}$ and $E\text{-(C(CH}_3\text{)=CH}_2\text{)CHOO}$ to f become increasingly important. These sCIs react significantly (about 50 % and 80 %, respectively) with SO_2 for the whole range of conditions, and their contributions show little or no dependence on $[\text{H}_2\text{O}]$. They therefore have an important influence on the $[\text{H}_2\text{O}]$ dependence of Y towards the high end of the $[\text{H}_2\text{O}]$ range, because of their much slower relative reactivity with H_2O and



$(\text{H}_2\text{O})_2$, compared with CH_2OO . The overall effect of the contributions from CH_2OO , $E\text{-(CH=CH}_2\text{)(CH}_3\text{)COO}$ and $E\text{-(C(CH}_3\text{)=CH}_2\text{)CHOO}$ is therefore a reduction in the slope of the $[\text{H}_2\text{O}]$ dependence towards the high end of the studied range.

The calculated dependence of Y on $[\text{H}_2\text{O}]$ provides an acceptable description of the Newland et al. (2015) data, although the calculated values are systematically below the observations at low $[\text{H}_2\text{O}]$. It is noted that Newland et al. (2015) applied a correction to account for reaction of sCIs with organic acids formed as products, and also interpreted the intercept of their plot in terms of sCI removal by thermal decomposition and other unaccounted for loss processes. The possible influence of other loss processes (e.g. reaction of sCIs with other reaction products) is not factored into the calculations presented here, and this may explain the small systematic difference at low $[\text{H}_2\text{O}]$. The sCI population average thermal decomposition rate at the low end of the $[\text{H}_2\text{O}]$ range is calculated to be about 6 s^{-1} , consistent with the value $\leq 12 (\pm 12) \text{ s}^{-1}$, derived by Newland et al. (2015) from the intercept of their linear regression analysis. This increases to over 50 s^{-1} at the high end of the $[\text{H}_2\text{O}]$ range, mainly due to the preferential increased removal of CH_2OO (which has a very low decomposition rate) by bimolecular reaction with H_2O and $(\text{H}_2\text{O})_2$.

The inferred or adopted parameters recommended here therefore provide an acceptable description of the $\text{O}_3 + \text{isoprene}$ observations reported by Sipilä et al. (2014), Newland et al. (2015) and Nguyen et al. (2016), although the data can support some tolerance in the absolute and relative parameter values. Measurements of speciated sCI yields, and further direct kinetics studies of the rate coefficients and product channels for the reactions of the C_4 sCI isomers, would therefore clearly be valuable. This is particularly important for $E\text{-(CH=CH}_2\text{)(CH}_3\text{)COO}$ and $E\text{-(C(CH}_3\text{)=CH}_2\text{)CHOO}$, for which bimolecular and unimolecular reactions are calculated to be competitive within the range of reported experimental conditions, and also for some tropospheric conditions. In this respect, Barber et al. (2018) and Vansco et al. (2018; 2019) have characterized the formation and UV-visible spectrum of Z - and $E\text{-(CH=CH}_2\text{)(CH}_3\text{)COO}$ from the photolysis of 1,3-di-iodobut-2-ene, and Z - and $E\text{-(C(CH}_3\text{)=CH}_2\text{)CHOO}$ from the photolysis of 1,3-di-iodo-2-methylprop-1-ene, providing methods for direct kinetics investigations of these isomers; as recently applied to the $E\text{-(CH=CH}_2\text{)(CH}_3\text{)COO} + \text{SO}_2$ reaction by Caravan et al. (2020). Barber et al. (2018) also report HO formation from the thermal decomposition of $E\text{-(CH=CH}_2\text{)(CH}_3\text{)COO}$, compatible with the expected pathway involving 1,4 H-atom transfer from the $-\text{CH}_3$ group to form a vinyl hydroperoxide intermediate, and at a rate that is consistent with theory.

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