Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information:

Water vapour effects on secondary organic aerosol formation in isoprene ozonolysis

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In the supporting information, we show results from the negative ion- chemical ionization mass spectrometer (NI-CIMS) and scanning mobility particle sizer (SMPS) measurements for experiments conducted in the presence of dimethyl ether (DME) as an OH radical scavenger. Details for the NI-CI mass spectra peak attribution are also shown.

Figure S1 shows Cl^--CI mass spectra of gas-phase products from isoprene ozonolysis in the absence (black) and the presence (red) of DME as an OH scavenger under dry conditions at the reaction time of 1 hour.

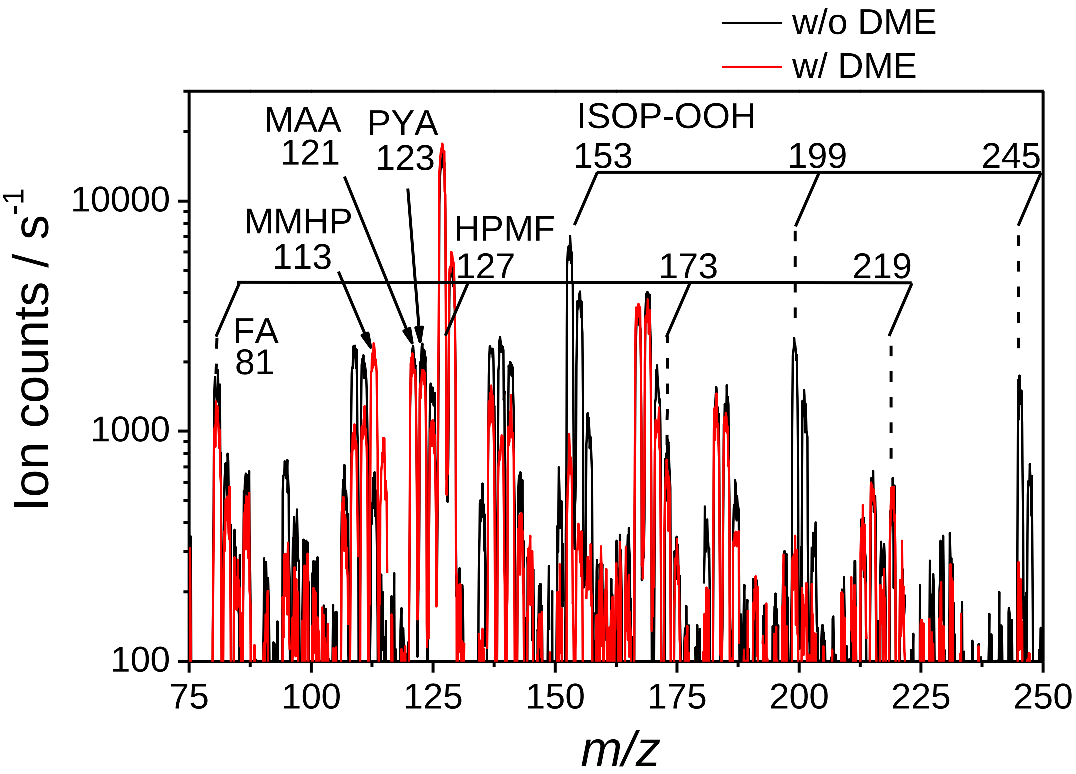

Figure S1. Cl$^-$-CI mass spectra of gas-phase products from isoprene ozonolysis under dry conditions in the absence (black) and the presence (red) of DME. FA, MAA, PYA, MMHP, HPMF, and ISOP-OOH denote formic acid, methacrylic acid, pyruvic acid, methoxymethyl hydroperoxide, hydroperoxymethyl formate, and isoprene-derived hydroperoxide, respectively. Spectra are obtained by subtracting a background spectra obtained before adding O_3 to initiate the reaction. The initial mixing ratios were [isoprene] = 2 ppmv, [O_3] = 4 ppmv, and [DME] = 700 ppmv, respectively.

The peak at *m/z* 113 was observed in the presence of OH scavengers shown in Fig. S1, indicating that they are attributed to methoxymethyl hydroperoxide (MMHP), an OH oxidation product of DME.[1, 2] The peaks at *m*/*z* 153, 199 and 245 are found to be largely decreased by the addition of DME in agreement with our attribution of these peaks to an isoprene-derived hydroperoxide (ISOP-OOH) and its oligomers with CH_2OO units.

Figure S2 shows Cl^--CI mass spectra of gas-phase products from isoprene ozonolysis in the presence of DME as an OH scavenger under dry (black) and humidified (red) conditions at the reaction time of 1 hour.

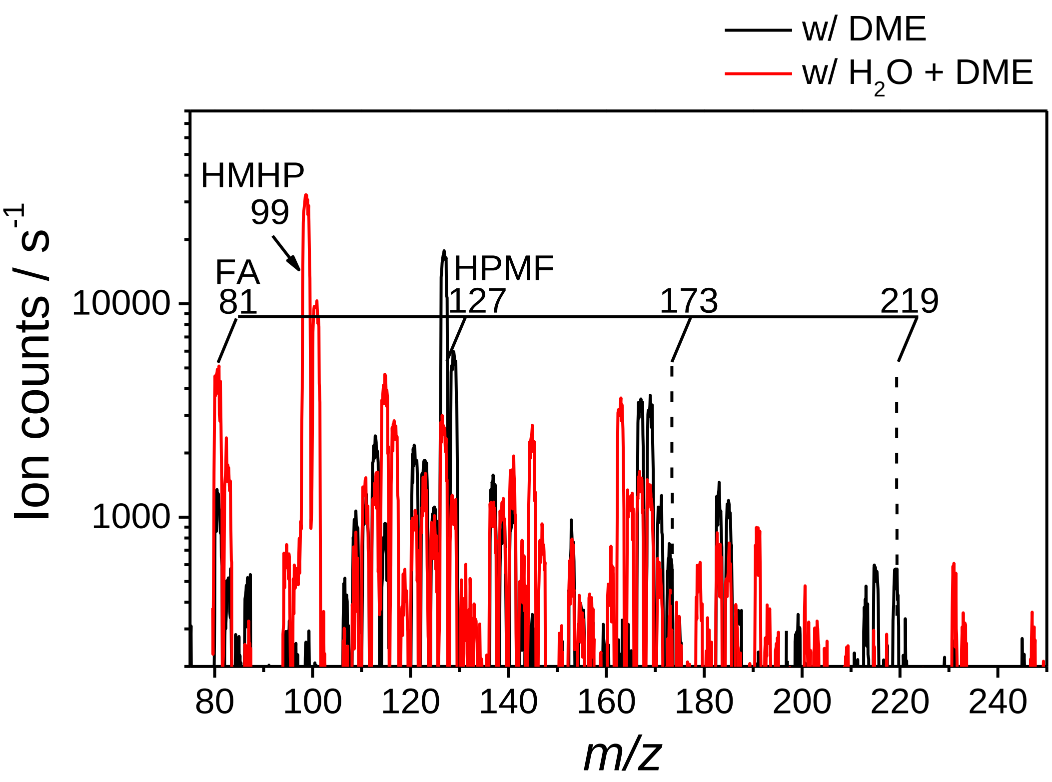

Figure S2. Cl^--CI mass spectra of gas-phase products from isoprene ozonolysis in the presence of DME under dry (black) and humidified (red) conditions. FA, HMHP, and HPMF denote formic acid, hydroxymethyl hydroperoxide and hydroperoxymethyl formate, respectively. Spectra are obtained by subtracting a background spectra obtained before adding O_3 to initiate the reaction. The initial mixing ratios were [isoprene] = 2 ppmv, [O_3] = 4 ppmv, and [DME] = 700 ppmv, respectively. RH was below 1% and 50% under dry and humidified conditions, respectively.

The peaks attributed to oligomeric hydroperoxides composed of CH_2OO units are reduced by the addition of water vapour. This water vapour effect is similar to that observed without DME shown in Fig. 1.

Figure S3 shows OH radical scavenger effect on SOA formation from isoprene ozonolysis.

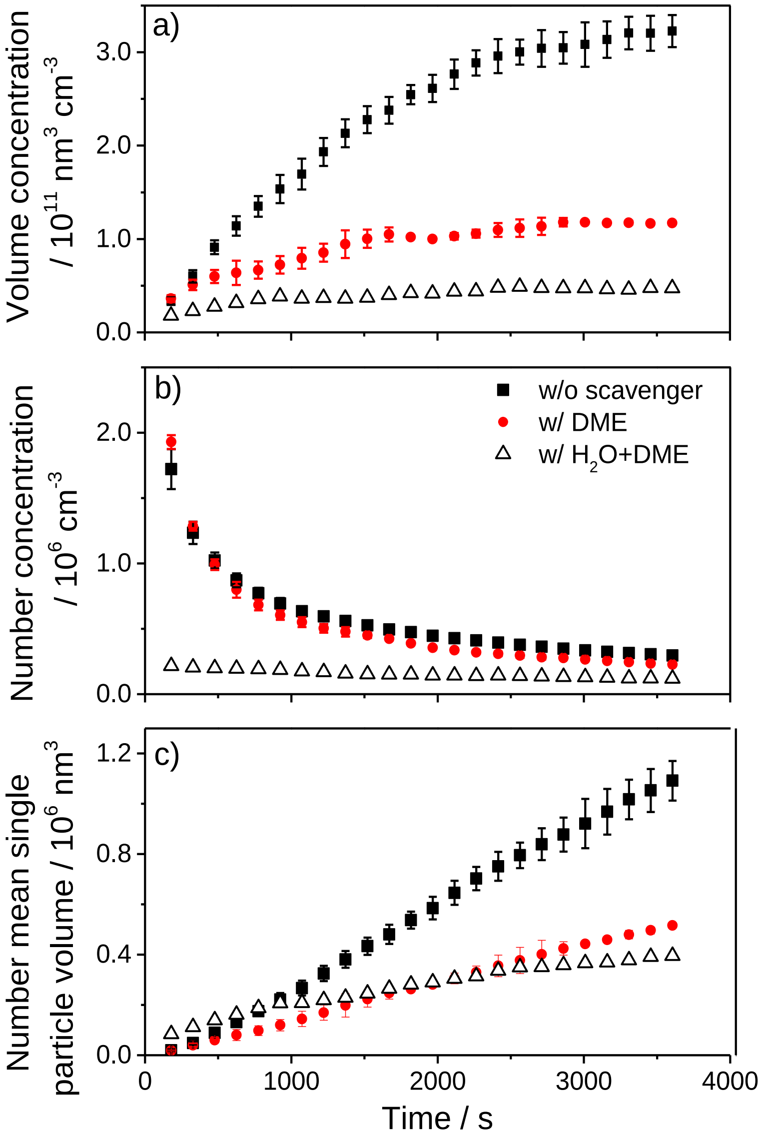

Figure S3. Panels a), b) and c) show the total particle volume concentration, total particle number concentration and the number mean single particle volume (volume concentration / number concentration) in isoprene ozonolysis without scavengers (black squares), with

DME (red circles) and with H_2O (RH50%) + DME (open triangles). The initial mixing ratios were [isoprene] = 2 ppmv, [O_3] = 4.0 - 4.5 ppmv, and [DME] = 700 ppmv, respectively. Error bars indicate one standard deviation of replicate experiments.

Figures S3(a) and S3(b) show that the addition of DME under dry conditions does not affect the particle number concentration but reduces the particle volume concentration. Then the addition of water vapour in the presence of DME largely suppresses both the number and volume concentrations of the particles.

Figure S4 shows that the saturated vapour concentrations, $C°$, estimated by the non-linear group-contribution expression[3] along with those obtained experimentally for selected oligomeric hydroperoxides from PTR-MS measurements of gas- and particle-phase components[4]. They are found to agree fairly well with each other.

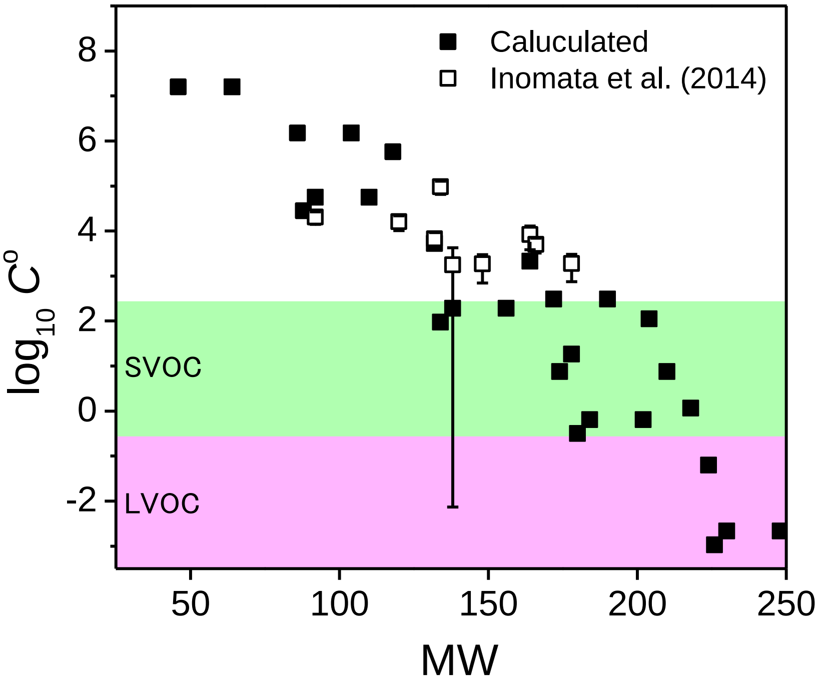

Figure S4 Saturated vapour pressures, *C*°, calculated by non-linear group-contribution expression[3] of C_1 and C_4 sCI oligomers and primary products of isoprene ozonolysis. Experimental *C*° of sCI oligomers by Inomata et al.[4] are also shown. The green and pink regions indicate semi volatile and low-volatility organic compounds (SVOC and LVOC), separately.

Table SI summarised the experimental conditions.

Table SI Summary of the experimental conditions

[isoprene] / ppmv*	$[O_3]$ / ppmv	DME	RH
2	4.3	None	< 1%
2	4.0	None	< 1%
2	4.4	None	< 1%
2	4.3	None	< 1%
2	4.3	None	< 1%
2	4.4	None	< 1%
2	4.0	None	< 1%
2	4.0	None	< 1%
2	4.3	None	18%
2	3.7	None	35%
2	4.2	None	60%
2	4.1	None	60%
2	4.1	None	60%
2	3.7	None	69%
2	4.3	700 ppmv	< 1%
2	4.3	700 ppmv	< 1%
2	4.0	700 ppmv	< 1%
2	4.5	700 ppmv	50%

*estimated from the flow rate and introduction period of isoprene/N_2 gas.

Table SII summarises the attribution of observed peaks in the gas and particle phase analysis by Cl^--CIMS. Simple formation schemes of the products as well as their abbreviation are also shown in the supporting material of our previous work.[4]

Table SII Summary of peak attributions

m/z	MW	w/o scavenger[a]	w/ DME[a]	w/ H_2O[a]	attribution [b,c]
81(83)	46	○	○	○	FA
95(97)	60	○	D	○	AA, glycol aldehyde
99(101)	64	-	-	○	HMHP
107(109)	72	○	○	-	acrylic acid
109(111)	74	○	D	○	propanoic acid
111(113)	76	○	○	○	glycolic acid
113(115)	78	-	○	-	MMHP
115(117)	80	-	-	○	HPMP
117(119)	82	-	-	○	HMHP•H_2O
121(123)	86	○	○	D	MAA
123(125)	88	○	○	D	PYA
127(129)	92	○	○	D	HPMF
137(139)	102	○	D	D	HPMVK
139(141)	104	○	D	○	HPMGLY
145(147)	110	-	-	○	HMHP-C_1 sCI
153(155)	118	○	D	○	ISOP-OOH
155(157)	120	○	-	○	MVK-OOH, MACR-OOH,
167(169)	132	○	○	D	MAA-C_1 sCI, FA-C_4 sCIs
169(171)	134	○	○	D	PYA-C_1 sCI
173(175)	138	○	○	-	HPMF-C_1 sCI
183(185)	148	○	○	D	HPMVK-C_1 sCI,
185(187)	150	○	○	D	HPMGLY-C_1 sCI,

199(201)	164	○	-	D	ISOP-OOH-(C_1 sCI)$_2$,
215(217)	180	○	○	-	PYA -(C_1 sCI)$_2$
245(247)	210	○	-	-	ISOP-OOH-(C_1 sCI)$_2$

[a] D: decrease of peak intensity.

[b] FA: formic acid, AA: acetic acid, MMHP: methoxymethyl hydroperoxide, HPMP: hydroperoxymethyl hydroperoxide, MAA: methacrylic acid, MVK: methyl vinyl ketone, MACR: methacrolein, PYA: pyruvic acid, HPMF: hydroperoxymethyl formate, HPMVK: hydroperoxymethyl vinyl ketone, HPMGLY: hydroperoxymethyl glyoxal, X-OOH: X-derived hydroperoxide, X-(C_mCI)$_n$: oligomeric hydroperoxide from X.

[c] from refs. 4-8

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