Supporting Information

Role of atomic chlorine in atmospheric volatile organic compound oxidation and secondary organic aerosol formation: a review

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Text S1 Estimation of Cl exposure

The Cl concentration is calculated based on the reaction rate constants and the variation in the concentration of VOCs. As VOC is consumed during the reaction, the concentration of Cl decreases. Therefore, different levels of precursor compounds result in varying exposure to Cl.

$$\frac{d[VOC]}{dt} = -k_{Cl} \times [Cl] \times [VOC] \quad (1)$$

The reaction rate constant between VOC and Cl atoms (k_{Cl}) leads to the following integrated equation (2):

$$\ln\left(\frac{[anisole]_0}{[anisole]_t}\right) = k_{Cl} \times [Cl] \times t \quad (2)$$

Cl exposure at each condition can be calculated using equation (3):

$$Cl_{exp} = \int_0^t [Cl]dt = \frac{1}{k_{Cl}} \times ln\left(\frac{[VOC]_0}{[VOC]_t}\right) \quad (3)$$

Table S1 Category, number, median and mean values of organic compounds.

Category	Number	Median value (cm^3 $molecule^{-1}$ s^{-1})	Mean value (cm^3 $molecule^{-1}$ s^{-1})
Alkane	40	3.08×10^{-10}	3.24×10^{-10}
Alkene	37	4.11×10^{-10}	4.36×10^{-10}
Alkyne	2	5.00×10^{-10}	5.00×10^{-10}
Aromatic compound	48	2.06×10^{-10}	2.15×10^{-10}
Alcohol	63	2.74×10^{-10}	2.57×10^{-10}
Ether	40	1.98×10^{-10}	2.37×10^{-10}
Aldehyde	28	1.88×10^{-10}	1.90×10^{-10}
Ketone	37	1.47×10^{-10}	1.59×10^{-10}
Ester	84	9.01×10^{-11}	1.21×10^{-10}
Carboxylic acid	3	1.90×10^{-13}	1.64×10^{-12}
Nitrogen compound	53	2.20×10^{-11}	8.60×10^{-11}
Sulfur compound	14	2.42×10^{-10}	2.74×10^{-10}
Halogenated compound	267	2.30×10^{-12}	3.84×10^{-11}

Table S2 Summary of key missing pathways in Cl-initiated oxidation within current chemical mechanism (MCM).

VOCs	Absence of key Cl pathways	Existing constraints	Priority
Alkanes	Reaction with Cl is assumed to be similar to that with OH	Chlorinated organics were observed, which likely originated from Cl addition to the double bond present on the heterogeneously produced dihydrofurans.[1]	medium
Alkenes	Cl addition; subsequent RO_2 chemistry	The Cl addition pathway is predominant, leading to organochlorine formation.[2] Reaction mechanism for isoprene have been elucidated, but precise branching ratios and product yields remain poorly constrained.[3]	high
Aromatics	Ring-retaining; subsequent RO_2 chemistry	Cl-initiated oxidation of aromatics predominantly proceeds via ring-retaining pathways.[4] Reaction mechanisms for toluene, m-xylene, and ethylbenzene have been elucidated, but precise branching ratios and product yields remain poorly constrained.[5-7]	high
All	RO_2 + Cl/ClO reactions; secondary Cl/OH production	RO_2 + Cl/ClO reactions are critical RO_2 loss pathways.[8,9] OH-isoprene chemistry is an integral part of high-NO_x Cl-isoprene oxidation chemistry, accounting for up to 40% of total isoprene oxidation.[3]	high

Table S3 Comparison of SOA yields from VOC oxidation initiated by Cl atoms versus OH radicals.

Reactor	Reaction system	Oxidant	T (K)	RH (%)	Seed	SOA yield (%)	Reference
Chamber	Octane + NO_x	Cl	298	<5	$(NH_4)_2SO_4$	16−28	[1]
		OH	298	<1	Dioctyl sebacate	4−4.2	[10]
	Decane + NO_x	Cl	298	<5	$(NH_4)_2SO_4$	45−84	[1]
		OH	293	<10	$(NH_4)_2SO_4$	9.6−25.4	[11]
	Dodecane + NO_x	Cl	298	<5	$(NH_4)_2SO_4$	110−165	[1]
		OH	298	N/A	$(NH_4)_2SO_4$	22−62	[12]
	Butylcyclohexane + NO_x	Cl	N/A	<5	$(NH_4)_2SO_4$	165−75	[13]
		OH	298	<1	Dioctyl sebacate	38.3−38.5	[10]
	Hexylcyclohexane + NO_x	Cl	298	< 5	$(NH_4)_2SO_4$	69−78	[14]
		OH	N/A	N/A	$(NH_4)_2SO_4$	46−61	[12]
	Hexylcyclohexane	Cl	298	< 5	$(NH_4)_2SO_4$	43−47	[14]
		OH	N/A	N/A	$(NH_4)_2SO_4$	30−44	[12]
	Isoprene	Cl	298	< 5	$(NH_4)_2SO_4$	17−36	[2]
		OH	N/A	50	$(NH_4)_2SO_4$	4.8−14.7	[15]
	α-pinene	Cl	N/A	N/A	N/A	1.5−7.8	[16]
		OH	N/A	N/A	N/A	0.2−4.2	
	β-pinene	Cl	N/A	N/A	N/A	2.7−8.9	
		OH	N/A	N/A	N/A	1.8−7.1	
	D-limonene	Cl	N/A	N/A	N/A	0.8−3.5	
		OH	N/A	N/A	N/A	3.3−12	
	Toluene + NO_x	Cl	N/A	<5	$(NH_4)_2SO_4$	17−22	[7]
		OH	298	<5	$(NH_4)_2SO_4$	8−12.8	[17]
	Toluene	Cl	N/A	<5	$(NH_4)_2SO_4$	33−67	[7]
		OH	298	<5	$(NH_4)_2SO_4$	29.8−30.8	[17]
	m-xylene	Cl	298	30	$(NH_4)_2SO_4$	8.7−8.9	[6]
		OH	298	30	$(NH_4)_2SO_4$	4.4−4.6	
	Ethylbenzene + NO_x	Cl	N/A	0−60	$(NH_4)_2SO_4$	55−67	[5]
		OH	300	<0.5	none	1.3−16.7	[18]
	Naphthalene	Cl	293	<1	N/A	86−96	[19]
		OH	294−297	<5	N/A	8−16	[20]
	Acenaphthylene	Cl	293	<1	N/A	78−92	[19]
		OH	294−297	<5	N/A	2−12	[20]
	Acenaphthene	Cl	293	<1	N/A	89−107	[19]
		OH	294−297	<5	N/A	4−11	[20]
	1-methylnaphthalene + NO_x	Cl	N/A	N/A	none	54−55	[21]
		OH	N/A	N/A	none	43−45	
	Anisole	Cl	298	<20	none	20−66.2	[22]
		OH	N/A	38.5	none	11.9−34.2	[23]
OFR	Dodecane	Cl	299.1	1.2	none	110−250	[24]
		OH	299.2	30.9	none	18−91	[23]

D_5	Cl	294	35	none	10−270	[9]
	OH	300	41	none	2−150	
α-pinene	Cl	301	1.4	none	22−47	[24]
	OH	301.8	28.2	none	11−31	
Isoprene	Cl	299.5	4	none	1.1−21	
	OH	300.2	43.3	none	3.1−40	
Toluene	Cl	299.9	1.1	none	8.3−64	
	OH	299.2	31.7	none	9.8−56	

N/A: not available

Table S4 Cl-initiated SOA mass yield parameterization.

Precursor	SOA yield under low-NO_x conditions[a]		SOA yield under high-NO_x conditions		Reference
	Median (%)	Interquartile range[b] (%)	Median (%)	Interquartile range (%)	
Octane	N/A[c]	N/A	24	6	[1]
Decane	163	82	80	34	[1,13]
Dodecane	152.5	87.9	N/A	N/A	[1]
Butylcyclohexane	170	/[d]	103	18	[13]
Hexylcyclohexane	47.4	2.1	82.3	7.4	
Heptylcyclohexane	71.7	23.8	95.8	7.9	[14]
Octylcyclohexane	97.9	11.6	110.5	5	
Isoprene	18	13.1	N/A	N/A	[2,24]
β-pinene	16.8	3.9	N/A	N/A	
α-pinene	21.5	13	N/A	N/A	[16]
D-limonene[e]	22	2	7.7	0.4	
Toluene	36	37.5	19.5	/	[7,24]
m-xylene	8.8	/	4.5	/	[6]
Ethylbenzene	N/A	N/A	5.9	0.7	[5]
Anisole	25.7	16	21.3	2.1	[22]
1-methylnaphthalene	59.5	9.5	55	9.5	[21]
Naphthalene	91	/	N/A	N/A	
Acenaphthylene	85	/	N/A	N/A	[19]
Acenaphthene	98	/	N/A	N/A	
D_5	121.5	107.1	N/A	N/A	[9]

[a] High- and low-NO_x conditions refer to experiments conducted in the presence and absence of added NO_x, respectively. For precursors lacking sufficient data to distinguish between high- and low-NO_x conditions, the same parameter values can be applied under both environmental conditions.[25,26]

[b] Interquartile range of all Cl-SOA yield data for each precursor.

[c] N/A: not available.

[d] With fewer than three data points, the interquartile range cannot be calculated.

[e] High-level limonene data are used for the parameterization under low-NO_x conditions, while low-level limonene data are applied for high-NO_x conditions.[26]

Table S5 Estimating Cl exposure in smog chamber experiment of Cl-oxidized anisole.

VOC_0[a] ($ug\ m^{-3}$)	VOCr[b] ($ug\ m^{-3}$)	Reaction time (min)	SOA yield (%)	Cl exposure (molecules cm^{-3} s)
4595.5	2013.7		20	5.39×10^{9}
3582.7	1944.4		25.7	7.31×10^{9}
2846.5	1859.1	120	31.1	9.89×10^{9}
1829.3	1444		46.7	1.46×10^{10}
883.4	874.4		66.2	4.29×10^{10}

[a] The concentration of anisole before the start of the reaction.

[b] The total concentration of anisole consumed in the reaction.

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