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Mechanistic insights into chloroacetic acid production from atmospheric multiphase volatile organic compound–chlorine chemistry

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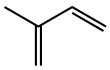
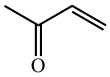
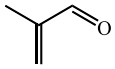
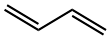
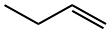
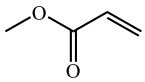
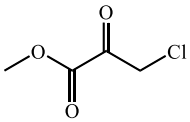
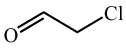
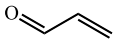
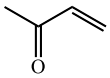
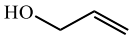
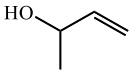
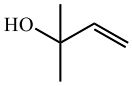
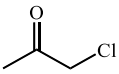
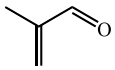
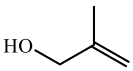
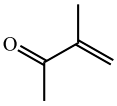
Table S1. Identified Cl-OVOCs and their precursors in previous VOC-Cl chamber experiments.

Cl-OVOCs	structure	precursor	structure	Ref.
formyl chloride		isoprene		(Orlando et al., 2003; Wennberg et al., 2018)
		methyl vinyl ketone		(Orlando et al., 2003)
		methacrolein		(Orlando et al., 2003)
		1,3-butadiene		(Orlando et al., 2003)
		1-butene		(Orlando et al., 2003)
		methyl acrylate		(Blanco et al., 2010)
		methyl 3-chloro-2-oxopropanoate		(Wennberg et al., 2018)
chloro-acetaldehyde		1-butene		(Orlando et al., 2003)
		acrolein		(Canosa-Mas et al., 2001)
		methyl vinyl ketone		(Canosa-Mas et al., 2001; Orlando et al., 2003)
		allyl alcohol		(Rodríguez et al., 2012)
		3-buten-2-ol		(Rodríguez et al., 2012)
		2-methyl-3-buten-2-ol		(Rodríguez et al., 2012)
chloroacetone		methacrolein		(Canosa-Mas et al., 2001; Kaiser et al., 2010; Orlando et al., 2003)
		2-methyl-2-propen-1-ol		(Rodríguez et al., 2012)
		3-methyl-3-buten2-one		(Wang et al., 2015)

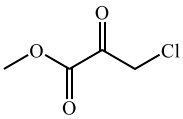
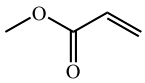
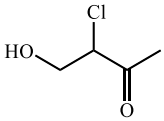
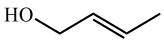
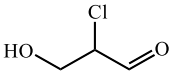
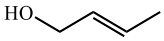
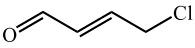
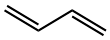
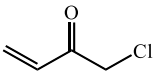
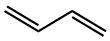
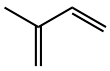
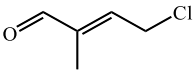
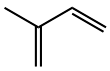
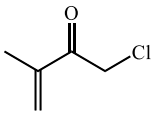
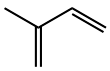
methyl 3-chloro-2-oxopropanoate		methyl acrylate		(Blanco et al., 2010)
3-choloro-4-hydroxy-2-butanone		crotyl alcohol		(Rodríguez et al., 2012)
2-chloro-propanal		crotyl alcohol		(Rodríguez et al., 2012)
4-chloro-crotonaldehyde		1,3-butadiene		(Orlando et al., 2003; Wang and Finlayson-Pitts, 2001)
chloro-methyl vinyl ketone		1,3-butadiene		(Wang and Finlayson-Pitts, 2001)
		isoprene		(Wennberg et al., 2018)
chloro-methylbutenal		isoprene		(Wennberg et al., 2018)
chloro-methylbutenone		isoprene		(Orlando et al., 2003; Wennberg et al., 2018)

Table S2. Input data of the chemical box model for the campaign-averaged conditions.

Parameter	Diurnal average[a]	Parameter	Diurnal average
T (K)	297.0 ± 1.0	propane (ppb)	1.0 ± 0.2
RH (%)	74.7 ± 5.0	isobutane (ppb)	0.39 ± 0.07
SO_2 (ppb)	2.7 ± 0.1	n-butane (ppb)	0.6 ± 0.1
CO (ppb)	264.8 ± 10.4	isopentane (ppb)	0.35 ± 0.07
NO (ppb)	0.33 ±0.24	n-pentane (ppb)	0.23 ± 0.03
NO_2 (ppb)	3.2 ± 0.7	2-methylpentane (ppb)	0.36 ± 0.08
N_2O_5 (ppb)	0.036 ± 0.029	n-hexane (ppb)	0.16 ± 0.05
HONO (ppb)	0.15 ± 0.03	cyclohexane (ppb)	0.022 ± 0.001
O_3 (ppb)	49.8 ± 9.9	acetylene (ppb)	1.3 ± 0.2
Sa (um^2 cm^{-3})	181.5 ± 23.2	ethene (ppb)	0.6 ± 0.1
$ClNO_2$ (ppb)	0.29 ± 0.23	propene (ppb)	0.10 ± 0.03
Cl_2 (ppb)	0.016 ± 0.014	isoprene (ppb)	0.17 ± 0.10
HOCl (ppb)	0.039 ± 0.019	α-pinene (ppb)	0.019 ± 0.007
BrCl (ppt)	0.64 ± 0.38	β-pinene (ppb)	0.010 ± 0.004
Br_2 (ppt)	3.1 ± 1.0	toluene (ppb)	0.36 ± 0.06
jNO_2 (10^{-3} s-1)	6.3[b]	benzene (ppb)	0.15 ± 0.02
methane	2000[c]	ethylbenzene (ppb)	0.05 ± 0.01
ethane (ppb)	1.7 ± 0.1	o-xylene (ppb)	0.04 ± 0.02

[a]Daily average ± standard deviation; [b]maximum value; [c]constant value.

Table S3. Branching ratios (Γ) and rate constants (k, 10^{-10} cm^3/molecule s) of alkene + $Cl^{\bullet}$ reactions.

VOC	*updated model*			*original model*	
	Γ	k	Reference	Γ	k
C_3H_6	α-C addition: 92% abstraction: 8%	2.93	(Kaiser and Wallington, 1996)	α-C addition: 40% β-C addition: 50% abstraction: 10%	2.70
C_5H_8	α-C addition: 85% abstraction: 15%	4.75	(Wennberg et al., 2018)	addition: 100%	4.75
MVK	α-C addition: 75% abstraction: 25%	2.20	(Orlando et al., 2003)	-	2.20
MACR	α-C addition: 86% abstraction: 14%	2.30	(Sun et al., 2014)	-	1.70

Table S4. QC-calculated energies of solvation and aqueous-phase reactions of OVOCs and their reactive uptake coefficients[1].

OVOC	ΔG_{sol}	$\Delta G^{\ddagger}_{hyd}$	$\Delta_r G_{hyd}$	$\Delta G'_{sol}$	λ	Ref.
formaldehyde	-1.30	41.84	0.17	-8.87	2.00×10^{-3}	(Iraci and Tolbert, 1997)
glyoxal	-2.68	41.73	0.35	-11.13	2.90×10^{-3}	(Liggio et al., 2005)
methylglyoxal	-3.30	42.75	1.80	-11.58	3.70×10^{-4}	(De Haan et al., 2018)
2-butanone	-3.43	46.30	7.47	-7.62	1.50×10^{-4}	(Schütze and Herrmann, 2004)
acetone	-3.55	47.84	7.93	-11.06	1.80×10^{-4}	(Schütze and Herrmann, 2004)
2,3-butanedione	-3.78	45.74	5.41	-8.10	8.00×10^{-5}	(Schütze and Herrmann, 2004)
formyl chloride	-1.14	28.79	-7.58	-9.04	2.34×10^{-2}	this work
chloro-acetaldehyde	-3.42	42.31	1.87	-10.92	8.23×10^{-4}	this work
chloro-acetone	-6.52	46.37	8.81	-8.40	7.07×10^{-5}	this work
cholro-butanedione	-4.27	39.58	1.85	-8.55	8.31×10^{-4}	this work
CMBO	-5.16	49.06	10.69	-10.13	3.63×10^{-5}	this work
CAA	-	-	-	-	7.05×10^{-5}	(Wang et al., 2020)

[1]ΔG_{sol} is solvation energy of OVOC, $\Delta G^{\ddagger}_{hyd}$ and $\Delta_r G_{hyd}$ are the Gibbs free energy changes between transition states and reactants and between products and reactants in the mono-hydration reactions of OVOC in the aqueous phase, respectively, $\Delta G'_{sol}$ is the evaporation energy of diol, λ is the reactive uptake coefficient from references and calculated in this work.

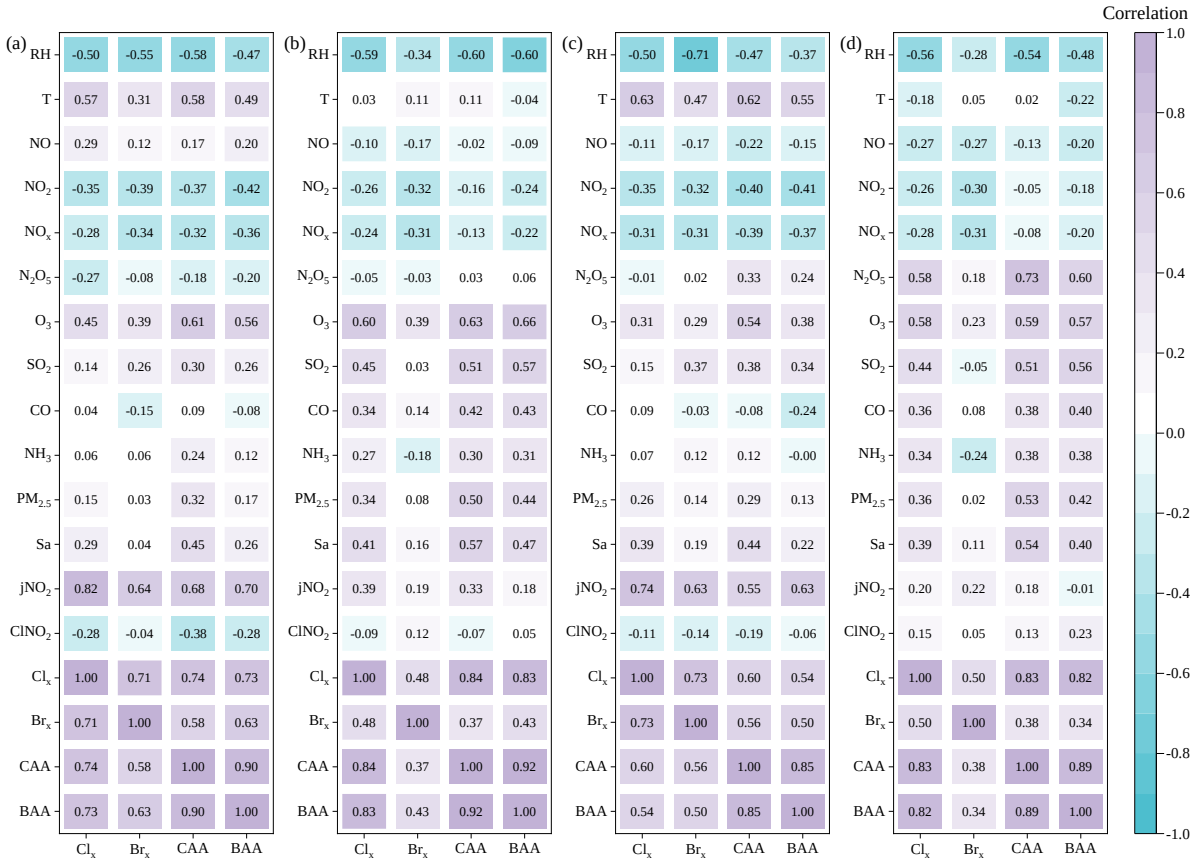


Figure S1. The correlation coefficients between important meteorological factors and CAA concentration (a) during all day in 2020, (b) during all day in 2021, (c) during 10:00 – 14:00 in 2020 and (d) during 10:00 – 14:00 in 2021. $Cl_x = 2 \times Cl_2 + HOCl + BrCl$, and $Br_x = 2 \times Br_2 + BrCl$. All data are 1-h averages.

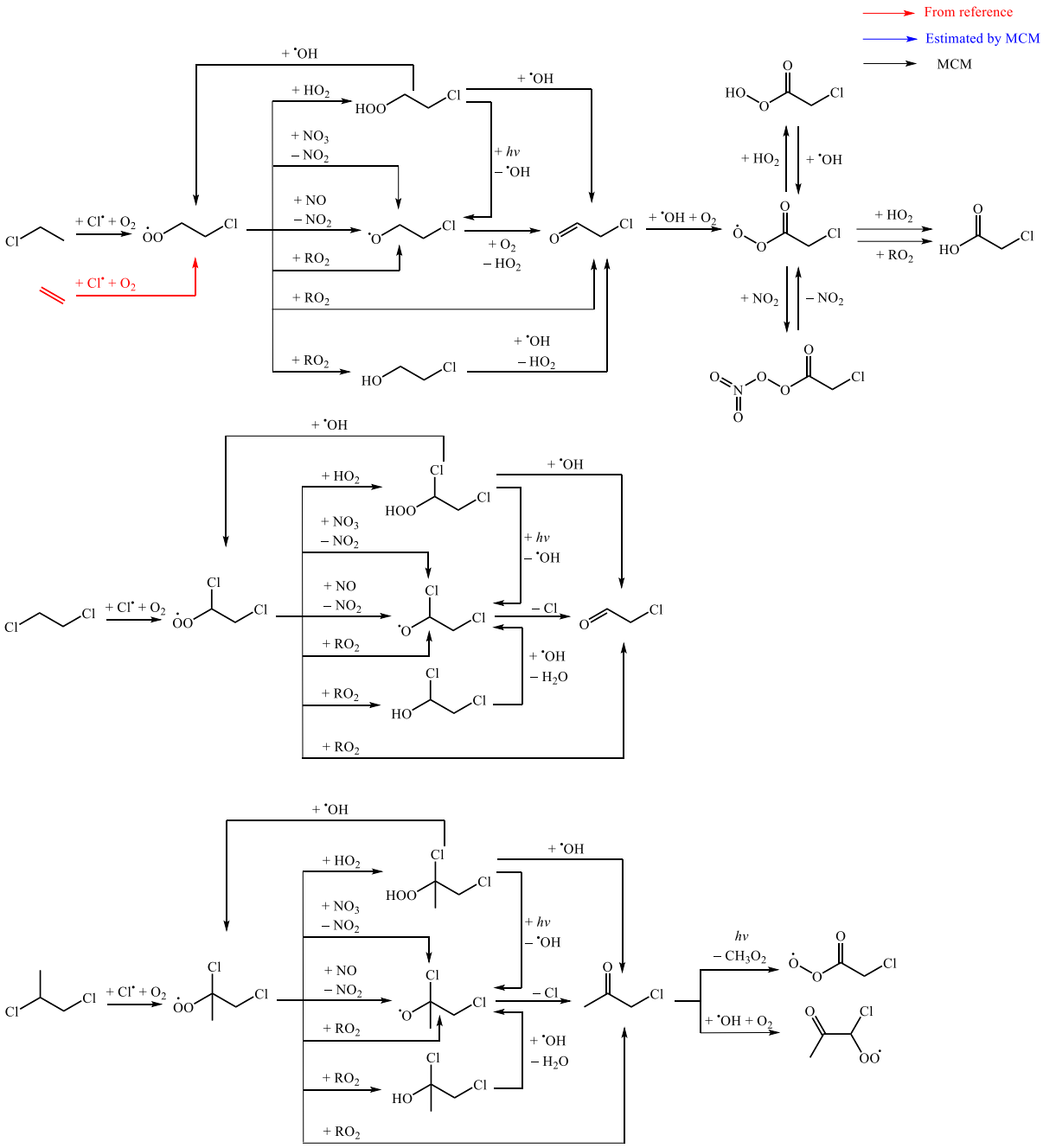


Figure S2. The primary reaction mechanisms of Cl• with 1-chloroethane (C_2H_5Cl), 1,2-dichloroethane ($C_2H_4Cl_2$), 1,2-dichloropropane ($C_3H_6Cl_2$), and ethene (C_2H_4).

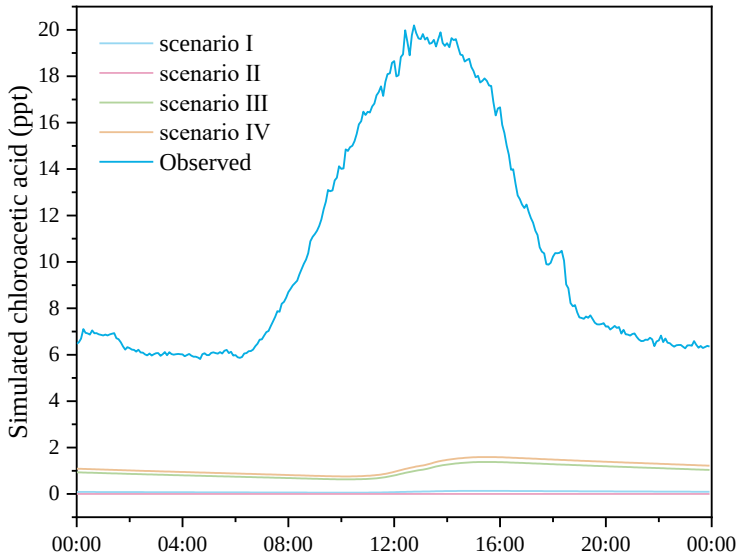


Figure S3. Box model-simulated and observed diurnal profiles of chloroacetic acid in different scenarios. The simulated result of scenario II is close to zero.

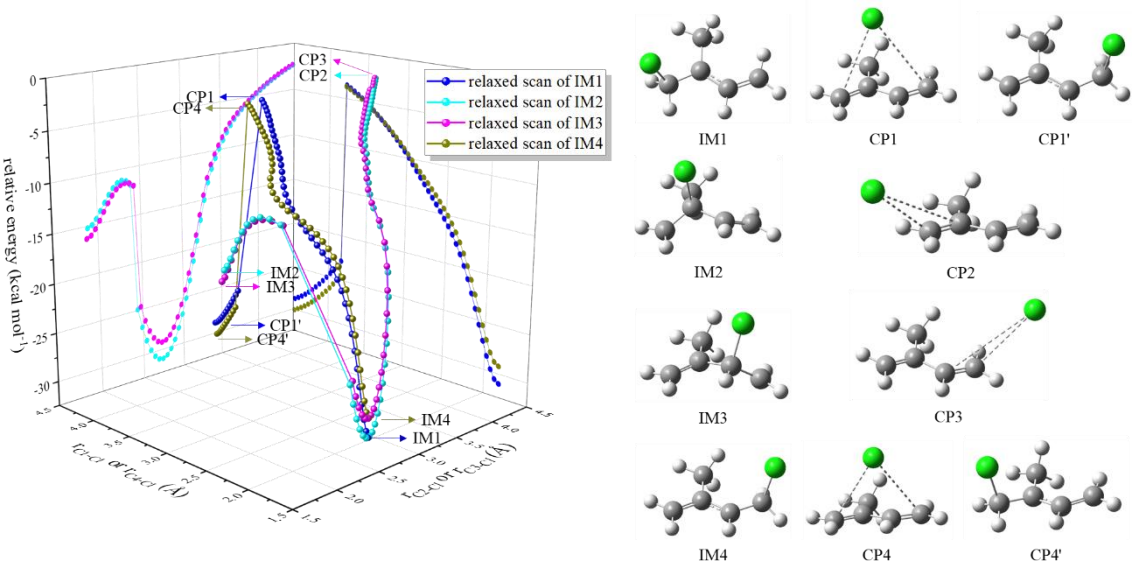


Figure S4. Relaxed scan of Cl• addition to isoprene. IM1, IM2, IM3, and IM4 are intermediates for Cl• addition to 1-, 2-, 3-, and 4-positions of isoprene, and CP1 – CP4, CP1' and CP4' are derived from scans of IM1 – IM2 in terms of bond lengths (r) of C-Cl as variables, respectively. Scanned potential energy surfaces of IM1 – IM4 take the total energy of the reactants Cl• + isoprene as zero for reference. The relative energies of IM1 and IM4 are lowest. A relaxed scan of IM1 reveals a minimum energy path (MEP): CP1' ← CP1 ← IM1, where CP1' approximates IM4. The relaxed scan of IM4 also reveals interconversion between IM1 and IM4, but the energy barriers are too high to be difficult to occur. The relaxed scans of IM2 and IM3 reveal the MEP of IM2 ← IM1 ← CP2 and IM3 ← IM4 ← CP3. Saddle points of IM2 and IM3 are difficult to reach due to their conversion to IM1 and IM4 passing through low-energy barriers. Thus, Cl• prefers to add to 1- and 4-positions of isoprene.

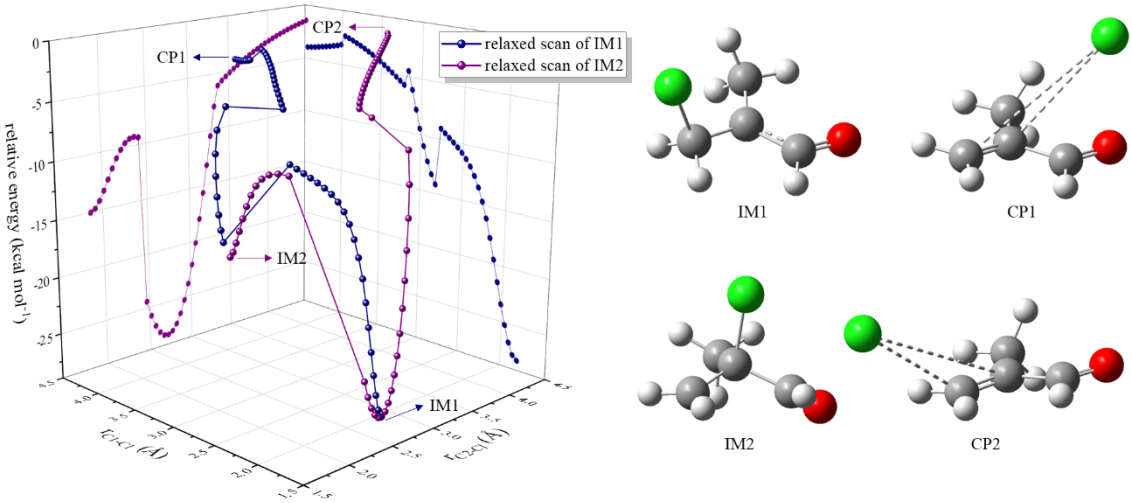


Figure S5. Relaxed scan of Cl• addition to methacrolein (MACR). Similar to the Cl• addition of propene.

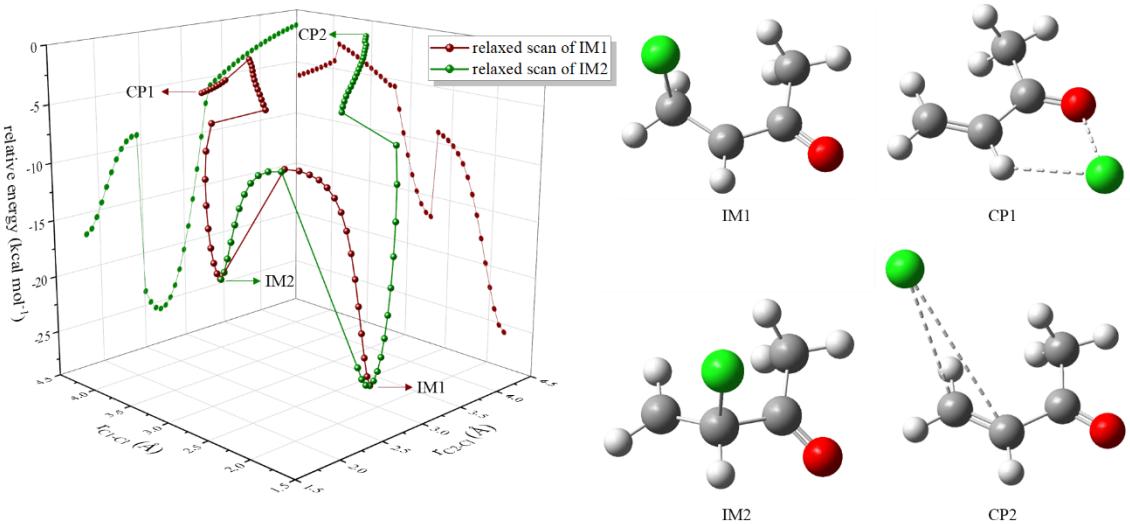


Figure S6. Relaxed scan of Cl• addition to methyl vinyl ketone (MVK). Similar to the Cl• addition of propene.

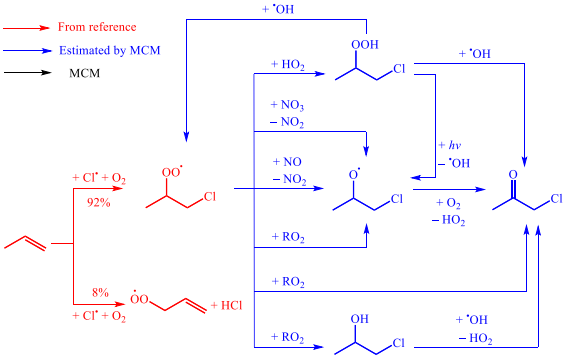


Figure S7. Proposed the primary reaction mechanisms of Cl• with propene (C_3H_6).

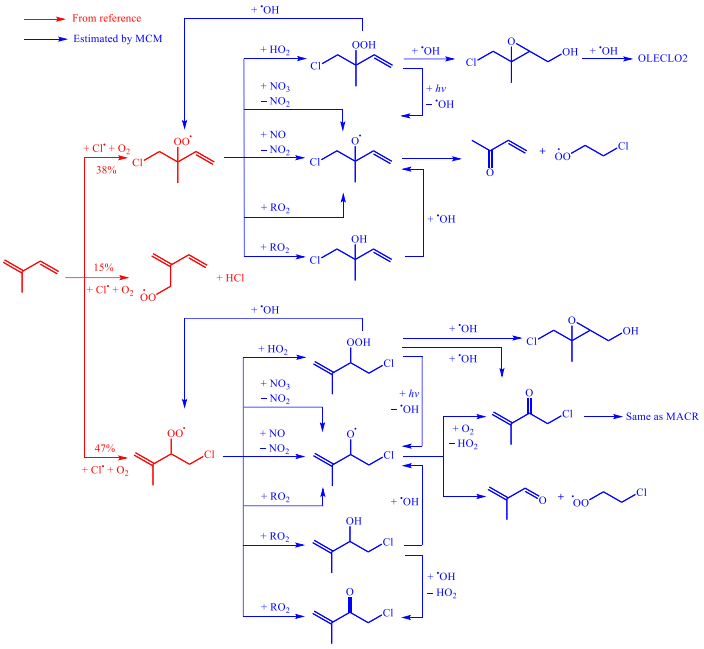


Figure S8. Proposed the primary reaction mechanisms of Cl• with isoprene (C_5H_8).

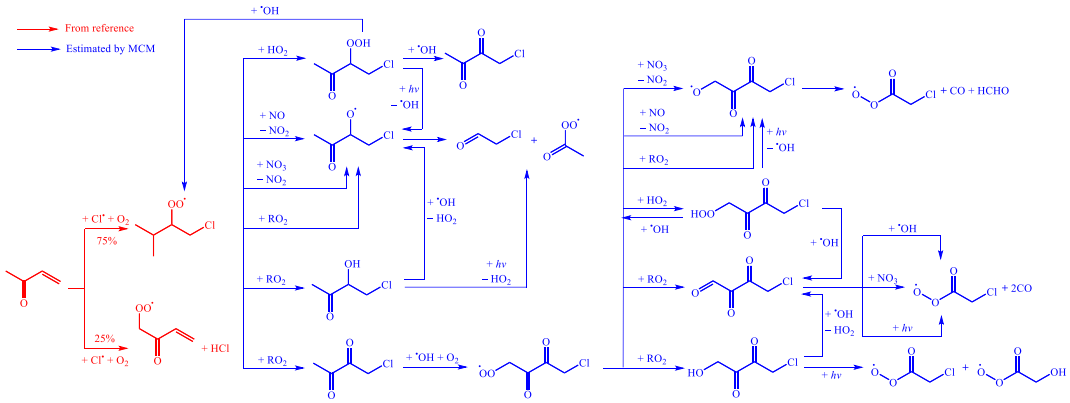


Figure S9. Proposed the primary reaction mechanisms of Cl• with methyl vinyl ketone (MVK).

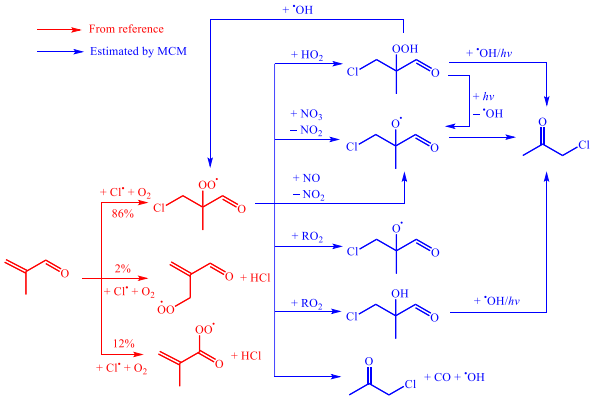


Figure S10. Proposed the primary reaction mechanisms of Cl• with methacrolein (MACR).

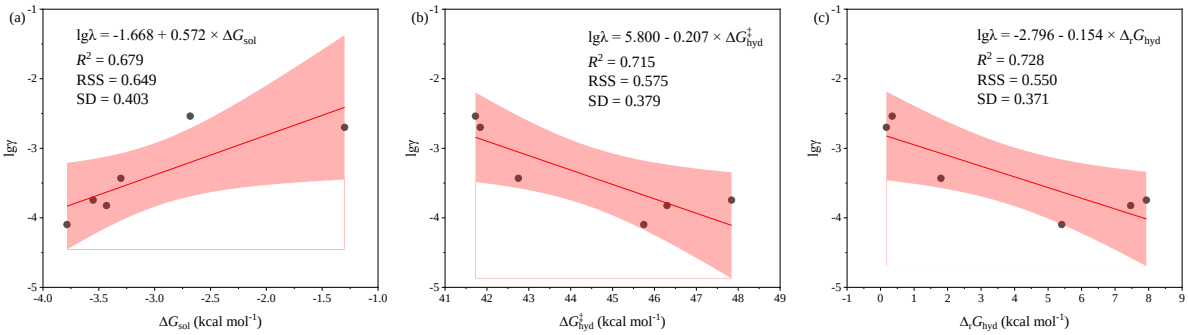


Figure S11. Linear relationships between Gibbs free energy of diol reactions and reactive uptake coefficients of carbonyls. (a) ΔG_{sol} as the solvation energy of carbonyls; (b) $\Delta G^{\ddagger}_{hyd}$ and (c) $\Delta_r G_{hyd}$ as the Gibbs free energy barriers and changes in the hydration reactions of carbonyls; λ as the reactive uptake coefficients; R^2 as the coefficient of determination; RSS as the residual sum of squares; SD as the standard deviation.

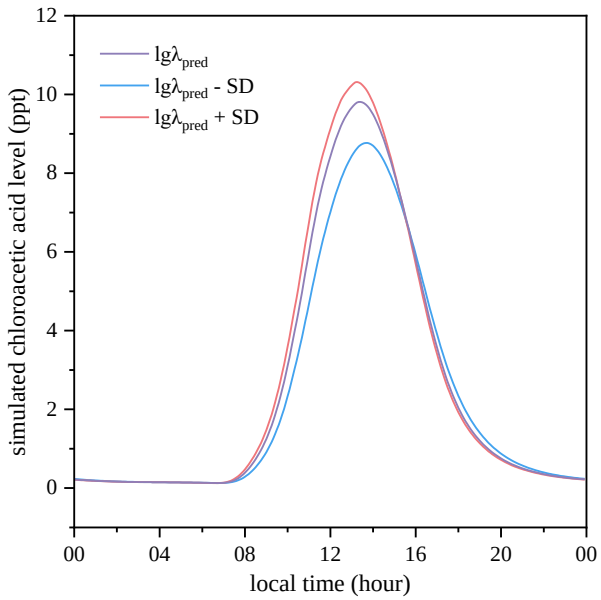


Figure S12. Sensitivity testing of the effects of reactive uptake coefficients of Cl-OVOCs on simulated chloroacetic acid and Cl-OVOC levels using our updated model. λ_{pred} are the predicted reactive uptake coefficients of Cl-OVOCs according to the linear relationship model between $\Delta_r G_{hyd}$ and lgλ, and SD is the standard deviation.

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