

Criegee Intermediates and their impacts on the troposphere

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Criegee intermediates (CIs), carbonyl oxides formed in ozonolysis of alkenes, play key roles in the troposphere. The decomposition of CIs can be a significant source of OH to the tropospheric oxidation cycle especially during nighttime and winter months. A variety of model-measurement studies have estimated surface-level stabilized Criegee intermediate (sCI) concentrations on the order of $1 \times 10^4 \text{ cm}^{-3}$ to $1 \times 10^5 \text{ cm}^{-3}$, which makes a non-negligible contribution to the oxidising capacity in the terrestrial boundary layer. The reactions of sCI with the water monomer and the water dimer have been found to be the most important bimolecular reactions to the tropospheric sCI loss rate, at least for the smallest carbonyl oxides; the products from these reactions (e.g. hydroxymethyl hydroperoxide, HMHP) are also of importance to the atmospheric oxidation cycle. The sCI can oxidise SO_2 to form SO_3 , which can go on to form a significant amount of H_2SO_4 which is a key atmospheric nucleation species and therefore vital to the formation of clouds. The sCI can also react with carboxylic acids, carbonyl compounds, alcohols, peroxy radicals and hydroperoxides, and the products of these reactions are likely to be highly oxygenated species, with low vapour pressures, that can lead to nucleation and SOA formation over terrestrial regions.

Environmental Impacts

Criegee intermediates (CI) have been elusive moieties in the gas-phase until recently but have extremely interesting kinetic and mechanistic properties. The paper reviews the concentrations of stabilized CI on regional and global scales, the unimolecular decomposition of CI and bimolecular reactions of stabilized CI with a series of compounds. The potential role of the products of these reactions in atmospheric chemistry have been discussed which can alter our thinking about the oxidising capacity of the Earth's atmosphere and the rate of generation of secondary organic aerosol (SOA).

Formation of Criegee Intermediates

The ozonolysis of alkenes proceeds *via* carbonyl oxide intermediates; Rudolph Criegee first proposed this scheme in 1949 in the aqueous phase.¹ The reaction proceeds in two distinct steps; the first being a 1,3-cycloaddition of ozone across a double bond to form a primary ozonide, followed by decomposition to a carbonyl and a carbonyl oxide (Figure 1), otherwise known as a Criegee intermediate (CI).² This mechanism is also followed in the gaseous phase, and therefore in the atmosphere.

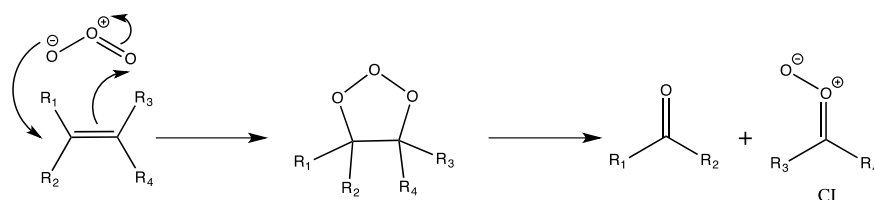


Figure 1 Formation of a primary ozonide followed by decomposition to a carbonyl and Criegee intermediate

The primary ozonide formed from the reaction of ozone with an alkene is very energy rich, and dissociates into a stable carbonyl compound and a vibrationally excited Criegee intermediate (CI*). The CI* can then either undergo unimolecular decomposition or can form a stabilised Criegee intermediate (sCI) *via* collisional relaxation.³

sCl can also be formed in the troposphere through radical-radical reactions (e.g. $\text{CH}_3\text{O}_2 + \text{BrO}^4$, $\text{CH}_3\text{O}_2 + \text{OH}^5$ and $\text{CH}_3\text{O}_2 + \text{Cl}^6$), but their contribution to the total sCl is negligible.

Unimolecular decomposition of Criegee Intermediates and formation of OH

The reaction of the alkenes with ozone can be the major chemical sink of alkenes in heavily polluted areas, depending on conditions. OH radicals can be produced from the ozonolysis of alkenes via either prompt formation from Cl^* or formation from the decomposition of sCl's at different species-dependent rates (Table 1). There has been an increasing amount of interest in Cl chemistry in recent years after the realisation that the decomposition of the Cl species can result in significant production of OH and HO_2 radicals which affects the oxidising capacity of the atmosphere.^{7,8} Experimental measurement of OH radical yields from alkene ozonolysis through Cl formation has historically proved to be difficult, because the OH radical formed quickly reacts with the original alkene or other decomposition products. In the past this has been circumvented by adding OH scavenger molecules (e.g. alkanes) to the reaction mixture, so that the rate of scavenger decay is indicative of OH concentration.⁹ However, newer experimental methods employ direct measurement by laser-induced fluorescence (LIF) spectroscopy.^{7,10-14} Production of the OH radical *via* the Cl decomposition is thought to occur mainly through the *syn*-conformation.¹⁵ This proceeds *via* isomerisation to a vinyl hydroperoxide, followed by the cleavage of the O-OH bond.¹⁶⁻¹⁷ The OH production from the *anti*-conformation is also possible via isomerization of the molecule to a carboxylic acid followed by cleavage of the C-OH bond.^{13,18}

Table 1 The first order rate coefficients for the total sCl loss

Species	Rate coefficient (s^{-1})		Reaction conditions (Pressure, p and Temperature, T)	References
	Experimental	Theoretical		
CH_2OO	0.33 0.19 ± 0.07 ^f 0.23 ± 0.12 ^f 11.6 ± 8.0 ⁵ 96-246 ⁵ 8-249 ⁵ 73-283 ⁵ 80-100 ^f 115 ± 20 ⁵ 44.8 ± 11.9 ^f	0.33 0.31	High p limit, T=298 K High p limit, T=298 K $p=760$ Torr, T=297 ± 1 K $p=760$ Torr, T=293 ± 0.5 K $p=7-30$ Torr, T=293 K $p=25$ Torr N_2 , T=297 K $p=50$ Torr N_2 , T=297 K $p=100$ Torr N_2 , T=297 K $p=50-200$ Torr, T=295 K $p=5.1$ Torr, T=295 K $p=760$ Torr, T=297 K	Olzmann et al. ¹⁷ Long et al. ¹⁹ Berndt et al. ²⁰ Berndt et al. ²⁰ Chhantyal-Pun et al. ²¹ Buras et al. ²² Buras et al. ²² Buras et al. ²² Liu et al. ²³ Sheps ²⁴ Ouyang et al. ²⁵
CH_3CHOO	≤ 20 ^f 288 ± 275(<i>syn</i>) ^f 3-30(<i>syn</i>) ^f ≤ 250 ⁵ 2.9 ± 0.9 ^f 76 ^f 2.5 ^f	67.2(<i>anti</i>) 24.2(<i>syn</i>) 55.4(<i>anti</i>) 328(<i>syn</i>) 166(<i>syn</i>)	High p limit, T=298 K High p limit, T=298 K High p limit, T=298 K High p limit, T=298 K High p limit, T=298 K $p=700$ Torr, T=300 K $p=760$ Torr, T=293-303 K $p=735$ Torr, T=293 K $p=4$ Torr, T=298 K $p=760$ Torr, T=293 ± 0.5 K $p=760$ Torr, T=298 K $p=758±4$ Torr, T=297±3 K	Kuwata et al. ²⁶ Kuwata et al. ²⁶ Long et al. ¹⁹ Long et al. ¹⁹ Fang et al. ²⁷ Herron et al. ²⁸ Newland et al. ²⁹ Novelli et al. ³⁰ Taatjes et al. ³¹ Berndt et al. ³² Fenske et al. ³³ Horie and Moortgat ³
$(\text{CH}_3)_2\text{COO}$	6.4 ± 0.9 ^{f,*} 2.7 ± 0.7 ^{f,*} 305 ± 70 ⁵ 361 ± 49 ^{5,**} 269 ± 82 ^{5,**} 916 ± 56 ^{5,**} 3.0 ± 0.4 ^f 151 ± 35 ^f	3.5 2.6 250 369	$p=100$ Torr $p=10$ Torr High p limit, T=298 K High p limit, T=298 K $p=10-100$ Torr, T=293 K $p=200$ Torr, T=298 K $p=200$ Torr, T=283 K $p=200$ Torr, T=323 K $p=760$ Torr, T=293 ± 0.5 K $p=760$ Torr, T=298-299 K	Kroll et al. ¹² Kroll et al. ¹² Olzmann et al. ¹⁷ Fang et al. ²⁷ Chhantyal-Pun et al. ²⁴ Smith et al. ³⁵ Smith et al. ³⁵ Smith et al. ³⁵ Berndt et al. ³² Newland et al. ²⁹
$\Sigma(\text{MVKOO} + \text{MACROO})$	26 ± 27 ^f		$p=760$ Torr, T=287-302 K	Newland et al. ²⁹
α -pinene sCl	<240 ± 44 (<i>syn</i>) ^f		$p=760$ Torr, T=287-302 K	Newland et al. ³⁶
β -pinene sCl	<170 ± 38 (<i>syn</i>) ^f		$p=760$ Torr, T=287-302 K	Newland et al. ³⁶
Limonene sCl	>130 ± 3 (<i>syn</i>) ^f		$p=760$ Torr, T=287-302 K	Newland et al. ³⁶

Note: the experimental first order rate coefficients include a component from wall loss of the Criegee intermediate in addition to unimolecular decomposition, *the wall loss was negligible in the work of Kroll et al.⁹ experiment because of using large diameter reactor, **the wall loss (assuming equal to thermal decomposition of CH_2OO) was accounted for in the work of Smith et al.³⁵. MVKOO represents methyl vinyl carbonyl oxide and MACROO represents methacrolein oxide which are isoprene derived sCl's. ⁵The values are from direct monitoring of the sCl decay, ^fThe values are from indirect sCl measurements.

Day-time OH radical production is dominated by the photolysis of ozone, but it has been widely documented in research that Cl decomposition is one of the important sources of atmospheric OH.^{27,30,37} The decomposition of Cl can be a major source of night-time OH and up to ~24% of daytime OH production.³⁸ The PUMA campaign³⁷ (an intensive field study in Birmingham, UK) has also shown that Cl decomposition is of large significance in OH winter concentrations. A 15-fold

decrease in OH production should be expected in the winter months at higher latitudes compared with the summer months, due to low UV intensity retarding the ozone photolysis pathway, but only a 2-fold decrease in OH concentration is seen due to the formation of OH through the efficient ozonolysis of alkenes.³⁷ Elshorbany et al.³⁹ also reported a significant daytime OH formation (24%) through ozone-alkene reactions in the urban area of Santiago, Chile. The ozonolysis of the alkenes increases with increasing temperature,⁴⁰ thus the largest production of OH through the formation of CIs is expected over tropical regions and alkene-abundant areas. We estimated the OH formation from the decomposition of CIs using a global atmospheric chemistry and transport model, STOCHEM-CRI (model description can be found in our previous publications⁴¹⁻⁴⁶ and found that in the terrestrial rainforest and boreal forest regions, up to 13% of OH radicals were formed via CI unimolecular decomposition (Figure 2). Thus, the amount of OH radicals produced from CI reactions in these areas can have a significant impact on the oxidizing capacity in the troposphere.

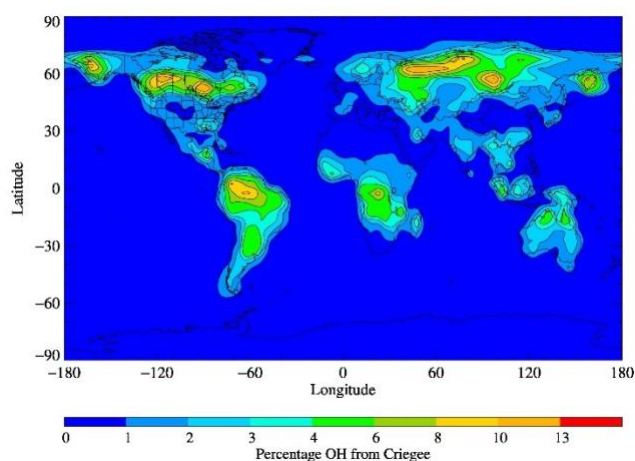


Figure 2 Estimation of the annual average percentage of OH formed from the CIs, simulated by the STOCHEM-CRI model.

Bimolecular reactions of Criegee Intermediates

Only a fraction of CI^* (termed as sCIs) formed survive to undergo bimolecular reaction. These occur when either the initial CI^* does not have sufficient energy to undergo unimolecular reaction or isomerisation, or the CI^* are stabilised by collisions with a bath gas, M , (e.g. N_2 in the atmosphere).^{11-12,47} sCIs can react with a variety of secondary compounds, 'Criegee scavengers', including: NO_x , SO_2 , CO , water, water dimer, alcohols, aldehydes and carboxylic acids. However, in the atmosphere it is likely that only water, SO_2 and NO_x are of any appreciable concentration to act as sCI sinks. Historically, research has focused on the reaction of sCIs with water and it was assumed that HCOOH production was the major reaction pathway.⁴⁸ However, recent findings^{21,23,24,25,31,34,49} have shown that rate constants for reaction with NO_2 , SO_2 and carboxylic acids are significantly higher than previously thought. The direct measurements (through photolytic generation of Criegee intermediates using diiodoalkanes), indirect determinations (via ozonolysis measurements), and computational calculations give a wide range of the rate coefficient values for the bimolecular reactions (see Tables 2-6). Gaining a quantifiable understanding of the products and their distributions from these bimolecular reactions are important as they may have significant impacts on the troposphere.^{42,50,51}

Table 2 Rate coefficient for the reaction of sCl₂ with water

Species	Rate coefficient (cm ³ s ⁻¹)		Temperature (K)	References						
	Experimental	Theoretical								
CH ₂ OO	$< 4 \times 10^{-15} \xi$ $(2.5 \pm 1.0) \times 10^{-17} \gamma, f$ $< 9 \times 10^{-17} \gamma, f$ $(1.3 \pm 0.4) \times 10^{-15} \gamma$ $< 1.5 \times 10^{-15} \xi$ $(3.2 \pm 1.2) \times 10^{-16} \gamma$ $(2.4 \pm 1.6) \times 10^{-16} \xi$	2.4×10^{-16} 3.7×10^{-16} 3.1×10^{-15} 5.9×10^{-17} 8.2×10^{-18}	298 298 298 298 298 297 295 298-303 298 297 ± 1 293	Long et al. ¹⁹ Lin et al. ⁵² Anglada et al. ⁵³ Anglada et al. ⁵⁴ Ryzhkov and Ariya ⁵⁵ Welz et al. ⁵⁶ Ouyang et al. ²⁵ Stone et al. ⁵⁷ Newland et al. ²⁷ Chao et al. ⁵⁸ Berndt et al. ²⁰ Sheps et al. ⁵⁰						
		<i>syn</i> -CH ₃ CHOO	$< 4 \times 10^{-15} \xi$ $< 2 \times 10^{-16} \xi$	5.7×10^{-20} 2.0×10^{-19} 2.1×10^{-18} 4.2×10^{-20} 1.2×10^{-20}	298 298 298 298 298 293	Long et al. ¹⁹ Lin et al. ⁵² Anglada et al. ⁵³ Anglada et al. ⁵⁴ Ryzhkov and Ariya ⁵⁵ Taatjes et al. ³¹ Sheps et al. ⁵⁹				
				<i>anti</i> -CH ₃ CHOO	$(2.3 \pm 2.1) \times 10^{-14} \gamma$ $(1.0 \pm 0.4) \times 10^{-14} \xi$ $(2.4 \pm 0.4) \times 10^{-14} \xi$ $(1.31 \pm 0.26) \times 10^{-14} \xi$	6.3×10^{-15} 3.4×10^{-14} 1.7×10^{-13} 2.5×10^{-15} 6.7×10^{-16}	298 298 298 298 298 297-302 298 293 298	Long et al. ¹⁹ Lin et al. ⁵² Anglada et al. ⁵³ Anglada et al. ⁵⁴ Ryzhkov and Ariya ⁵⁵ Newland et al. ²⁹ Taatjes et al. ³¹ Sheps et al. ⁵⁹ Lin et al. ⁶⁰		
						(CH ₃) ₂ COO	$(2.1 \pm 0.6) \times 10^{-15} \gamma$ $< 1.5 \times 10^{-16} \xi$	3.8×10^{-17} 7.5×10^{-19} 2.9×10^{-19}	298 298 298 298-303 298	Anglada et al. ⁵³ Anglada et al. ⁵⁴ Ryzhkov and Ariya ⁵⁵ Newland et al. ²⁹ Huang et al. ⁶¹

Note: ξ The values are from direct monitoring of the sCl decay, γ The values are from indirect sCl measurements. f the values from the experiments could not distinguish between the reaction with the water monomer or the dimer reaction.

Table 3 Rate coefficient for the reaction of sCl₂ with water dimer

(H ₂ O) ₂	Rate coefficient (cm ³ s ⁻¹)		Temperature (K)	References		
	Experimental	Theoretical				
CH ₂ OO	$(7.5 \pm 0.4) \times 10^{-12} \gamma$ $(6.5 \pm 0.8) \times 10^{-12} \xi$ $(7.4 \pm 0.6) \times 10^{-12} \xi$ $(4.0 \pm 1.2) \times 10^{-12} \xi$ $(8.2 \pm 0.8) \times 10^{-12} \gamma$ $(6.6 \pm 0.7) \times 10^{-12} \xi$	5.4×10^{-12} $(1.2-1.4) \times 10^{-12}$	298 298 300 298 298 294 298 ± 2 293	Lin et al. ⁵² Ryzhkov and Ariya ⁵⁵ Liu et al. ⁶² Chao et al. ⁵⁸ Smith et al. ⁶³ Lewis et al. ⁶⁴ Yajima et al. ⁶⁵ Sheps et al. ⁵⁰		
			<i>syn</i> -CH ₃ CHOO	2.6×10^{-14} $(1.0-1.2) \times 10^{-15}$	298 298	Lin et al. ⁵² Ryzhkov and Ariya ⁵⁵
					<i>anti</i> -CH ₃ CHOO	1.6×10^{-11} $(1.0-2.8) \times 10^{-12}$
			(CH ₃) ₂ COO	$(6.5-10.2) \times 10^{-17}$		

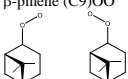
Note: ξ The values are from direct monitoring of the sCl decay, γ The values are from indirect sCl measurements.

Table 4 Rate coefficient for the reaction of sCl₂ with NO₂

NO ₂	Rate coefficient (cm ³ s ⁻¹)		Temperature (K)	References		
	Experimental	Theoretical				
CH ₂ OO	$(7 + 3/-2) \times 10^{-12} \xi$ $(1.5 \pm 0.5) \times 10^{-12} \gamma$	4.4×10^{-12}	298 295 298	Welz et al. ⁵⁶ Stone et al. ⁵⁷ Vereeken and Nguyen ⁶⁶		
			CH ₃ CHOO (<i>syn and anti</i>)	$(2.0 \pm 1.0) \times 10^{-12} \xi$ $(1.7 \pm 0.3) \times 10^{-12} \xi$	298 298	Taatjes et al. ³¹ Caravan et al. ⁶⁷
					(CH ₃) ₂ COO	$\leq 5 \times 10^{-12} \xi$

Note: ξ The values are from direct monitoring of the sCl decay, γ The values are from indirect sCl measurements.

Table 5 Rate coefficient for the reaction of sCIs with SO₂

SO ₂	Rate coefficient (cm ³ s ⁻¹)		Temperature (K)	References
	Experimental	Theoretical		
CH ₂ OO		4.0×10^{-10}	298	Kurtén et al. ⁶⁸ Kuwata et al. ⁶⁹ Welz et al. ⁵⁶ Chhantyal-Pun et al. ²¹ Stone et al. ⁵⁷ Sheps ²⁴ Liu et al. ²³ Berndt et al. ⁷⁰
		$(3.68 \pm 0.02) \times 10^{-11}$	298	
		$(3.9 \pm 0.7) \times 10^{-11}$ ξ	298	
		$(3.80 \pm 0.04) \times 10^{-11}$ ξ	293	
		$(3.42 \pm 0.42) \times 10^{-11}$ γ	295	
		$(4.1 \pm 0.3) \times 10^{-11}$ ξ	295	
		$(3.53 \pm 0.29) \times 10^{-11}$ γ	295	
		$(3.3 \pm 0.9) \times 10^{-11}$ γ	295 ± 2	
<i>syn</i> -CH ₃ CHOO	$(2.4 \pm 0.3) \times 10^{-11}$ ξ		298	Taatjes et al. ³¹ Sheps et al. ⁵⁹
	$(2.9 \pm 0.3) \times 10^{-11}$ ξ		293	
<i>anti</i> -CH ₃ CHOO	$(6.7 \pm 1.0) \times 10^{-11}$ ξ		298	Taatjes et al. ³¹ Sheps et al. ⁵⁹
	$(22.0 \pm 2.0) \times 10^{-11}$ ξ		293	
<i>syn- and anti</i> -CH ₂ CHOO	$(1.4 \pm 0.4) \times 10^{-13}$ γ		293 ± 0.5	Berndt et al. ³²
(CH ₃) ₂ COO		4.0×10^{-10}	298	Kurtén et al. ⁶⁸ Chhantyal-Pun et al. ³⁴ Huang et al. ⁶¹ Berndt et al. ³²
		$(7.3 \pm 0.5) \times 10^{-11}$ ξ	298	
		$(13.2 \pm 1.3) \times 10^{-11}$ ξ	298	
		$(7.7 \pm 1.4) \times 10^{-13}$ γ	293 ± 0.5	
β -pinene (C ₉)OO		4.0×10^{-11} γ	298 ± 0.5	Ahrens et al. ⁷¹
				

Note: ξ The values are from direct monitoring of the sCI decay, γ The values are from indirect sCI measurements.

Table 6 Rate coefficients for the reaction of sCIs with other species

Reaction	Rate coefficient (cm ³ s ⁻¹)		Temperature (K)	References
	Experimental	Theoretical		
CH ₂ OO + CH ₃ CHO	1.0×10^{-12} γ		298	Fenske et al. ³³ Taatjes et al. ⁷² Stone et al. ⁵⁷ Elsamra et al. ⁷³
CH ₂ OO + CH ₂ CHO	$(9.4 \pm 0.7) \times 10^{-13}$ ξ		293	
CH ₂ OO + CH ₂ CHO	$(1.48 \pm 0.04) \times 10^{-12}$ γ		295	
CH ₂ OO + CH ₂ CHO	$(3.0 \pm 0.6) \times 10^{-13}$ ξ		298	
CH ₂ OO + HCOOH	$(1.1 \pm 0.7) \times 10^{-10}$ ξ		298	Welz et al. ⁴⁹ Chhantyal-Pun et al. ²⁴ Welz et al. ⁴⁹ Welz et al. ⁴⁹ Chhantyal-Pun et al. ²⁴
CH ₂ OO + HCOOH	$(1.14 \pm 0.07) \times 10^{-10}$ ξ		294	
<i>syn</i> -CH ₃ CHOO + HCOOH	$(2.5 \pm 0.3) \times 10^{-10}$ ξ		298	
<i>anti</i> -CH ₃ CHOO + HCOOH	$(5.0 \pm 3.0) \times 10^{-10}$ ξ		298	
(CH ₃) ₂ COO + HCOOH	$(3.3 \pm 0.3) \times 10^{-10}$ ξ		294	
(CH ₃) ₂ COO + HCOOH	$(3.0 \pm 0.2) \times 10^{-10}$ ξ		294	
CH ₂ OO + CH ₂ COOH	$(1.3 \pm 0.1) \times 10^{-10}$ ξ		298	Welz et al. ⁴⁹ Chhantyal-Pun et al. ²⁴ Berndt et al. ⁷⁰ Welz et al. ⁴⁹ Welz et al. ⁴⁹ Chhantyal-Pun et al. ²⁴ Chhantyal-Pun et al. ²⁴ Chhantyal-Pun et al. ²⁴ Chhantyal-Pun et al. ²⁴ Chhantyal-Pun et al. ²⁴ Chhantyal-Pun et al. ²⁴ Chhantyal-Pun et al. ²⁴ Chhantyal-Pun et al. ²⁴ Chhantyal-Pun et al. ²⁴ Chhantyal-Pun et al. ²⁴ Chhantyal-Pun et al. ²⁴
CH ₂ OO + CH ₂ COOH	$(1.47 \pm 0.07) \times 10^{-10}$ ξ		294	
CH ₂ OO + CH ₂ COOH	$(1.25 \pm 0.3) \times 10^{-10}$ ξ		295	
<i>syn</i> -CH ₃ CHOO + CH ₂ COOH	$(1.7 \pm 0.5) \times 10^{-10}$ ξ		298	
<i>anti</i> -CH ₃ CHOO + CH ₂ COOH	$(2.5 \pm 0.6) \times 10^{-10}$ ξ		298	
(CH ₃) ₂ COO + CH ₂ COOH	$(3.3 \pm 0.3) \times 10^{-10}$ ξ		294	
(CH ₃) ₂ COO + CH ₂ COOH	$(3.4 \pm 0.3) \times 10^{-10}$ ξ		294	
CH ₂ OO + CF ₃ COOH	$(3.4 \pm 0.3) \times 10^{-10}$ ξ		294	
CH ₂ OO + CClF ₂ COOH	$(3.34 \pm 0.16) \times 10^{-10}$ ξ		294	
CH ₂ OO + CF ₂ CF ₂ COOH	$(4.48 \pm 0.23) \times 10^{-10}$ ξ		294	
CH ₂ OO + Pyruvic acid	$(0.2 \pm 0.02) \times 10^{-10}$ ξ		294	
(CH ₃) ₂ COO + CF ₃ COOH	$(3.4 \pm 0.3) \times 10^{-10}$ ξ		294	
(CH ₃) ₂ COO + CClF ₂ COOH	$(3.9 \pm 0.2) \times 10^{-10}$ ξ		294	
(CH ₃) ₂ COO + CF ₂ CF ₂ COOH	$(4.4 \pm 0.2) \times 10^{-10}$ ξ		294	
(CH ₃) ₂ COO + Pyruvic acid	$(0.9 \pm 0.1) \times 10^{-10}$ ξ		294	
CH ₂ OO + NO	$< 6.0 \times 10^{-14}$ ξ		298	Welz et al. ⁵⁶ Stone et al. ⁵⁷
CH ₂ OO + NO	$< 2.0 \times 10^{-13}$ γ		295	
CH ₂ OO + CO		2.0×10^{-21}	298	Vereecken et al. ⁷⁶ Vereecken et al. ⁷⁶ Vereecken et al. ⁷⁶ Vereecken et al. ⁷⁶ Vereecken et al. ⁷⁶
<i>syn</i> -CH ₃ CHOO + CO		7.0×10^{-21}	298	
<i>anti</i> -CH ₃ CHOO + CO		8.0×10^{-20}	298	
(CH ₃) ₂ COO + CO		3.0×10^{-20}	298	
CH ₂ OO + CH ₃ COCH ₃	$(2.3 \pm 0.3) \times 10^{-13}$ ξ		293	
CH ₂ OO + CH ₃ COCH ₃	$(1.2 \pm 0.2) \times 10^{-12}$ ξ		298	Elsamra et al. ⁷³
CH ₂ OO + O ₃		4.0×10^{-13}	298	Vereecken et al. ⁷⁶ Vereecken et al. ⁷⁶ Vereecken et al. ⁷⁶ Vereecken et al. ⁷⁶ Vereecken et al. ⁷⁶
<i>syn</i> -CH ₃ CHOO + O ₃		3.0×10^{-14}	298	
<i>anti</i> -CH ₃ CHOO + O ₃		3.0×10^{-12}	298	
(CH ₃) ₂ COO + O ₃		8.0×10^{-14}	298	
(CH ₃) ₂ COO + O ₃		8.0×10^{-14}	298	
CH ₂ OO + HOOH		3.0×10^{-13}	298	Vereecken et al. ⁷⁶ Vereecken et al. ⁷⁶ Vereecken et al. ⁷⁶
CH ₂ OO + CH ₂ OOH		6.0×10^{-12}	298	
(CH ₃) ₂ COO + CH ₂ OOH		8.0×10^{-13}	298	
CH ₂ OO + ethene	7×10^{-16} ξ		298	Buras et al. ⁷⁷
CH ₂ OO + propene	18×10^{-16} ξ		298	Buras et al. ⁷⁷
CH ₂ OO + isobutene	14×10^{-16} ξ		298	Buras et al. ⁷⁷
CH ₂ OO + 1-butene	15×10^{-16} ξ		298	Buras et al. ⁷⁷
CH ₂ OO + 2-butene	7×10^{-16} ξ		298	Buras et al. ⁷⁷
CH ₂ OO + isoprene	$(1.5 \pm 0.1) \times 10^{-15}$ ξ		295	Decker et al. ⁷⁸ Decker et al. ⁷⁸
	$(23 \pm 2) \times 10^{-15}$ ξ		536	
CH ₂ OO + CH ₂ OO	7.4×10^{-11} ξ		293	Chhantyal-Pun et al. ²¹ Ting et al. ⁷⁹ Su et al. ⁸⁰ Buras et al. ⁷⁷ Buras et al. ⁷⁷ Buras et al. ⁷⁷
CH ₂ OO + CH ₂ OO	$8.0 \pm 4.0 \times 10^{-11}$ ξ		295	
CH ₂ OO + CH ₂ OO	2.4×10^{-10} ξ		298	
CH ₂ OO + CH ₂ OO	6.0×10^{-11} ξ		297	
CH ₂ OO + CH ₂ OO	2.2×10^{-10} ξ		343	
CH ₂ OO + CH ₂ OO	$1.7 \pm 0.2 \times 10^{-13}$ ξ		298	
CH ₂ OO + H ₂ S			298	Smith et al. ⁸¹
CH ₂ OO + HNO ₂	5.4×10^{-10} ξ		295	Foreman et al. ⁸² Raghunath et al. ⁸³ Foreman et al. ⁸²
CH ₂ OO + HNO ₂		5.1×10^{-10}	295	
CH ₂ OO + HCl	4.6×10^{-11} ξ		295	
CH ₃ (CH ₂) ₁₁ CHOO + HCOOH	1.1×10^{-10} ξ		296 ± 3	Tobias and Ziemann ⁸⁴
CH ₃ (CH ₂) ₁₁ CHOO + C ₆ H ₁₃ COOH	2.8×10^{-10} ξ		296 ± 3	Tobias and Ziemann ⁸⁴
CH ₃ (CH ₂) ₁₁ CHOO + HCHO	4.4×10^{-11} ξ		296 ± 3	Tobias and Ziemann ⁸⁴
CH ₃ (CH ₂) ₁₁ CHOO + CH ₃ CH(OH)CH ₃	8.3×10^{-13} ξ		296 ± 3	Tobias and Ziemann ⁸⁴
CH ₃ (CH ₂) ₁₁ CHOO + CH ₃ CH(OH)CH ₃	3.6×10^{-13} ξ		296 ± 3	Tobias and Ziemann ⁸⁴
CH ₂ OO + CH ₃ OH	$3.7 \pm 1.4 \times 10^{-21}$ T^2 $\exp(1710 \pm 103/T)$ ξ			McGillen et al. ⁵¹
CH ₂ OO + C ₂ H ₅ OH	$4.2 \pm 2.2 \times 10^{-21}$ T^2 $\exp(1717 \pm 145/T)$ ξ			McGillen et al. ⁵¹
(CH ₃) ₂ COO + CH ₃ OH	6.1×10^{-22} $T^{3/2}$ $\exp(5852/T)$ -5.8×10^{16} $T^{3/2}$ $\exp(-3741/T)$ ξ			McGillen et al. ⁵¹
CH ₂ OO + CF ₃ C(O)CF ₃	$(3.0 \pm 0.3) \times 10^{-11}$ ξ		293	Taatjes et al. ⁷²

Note: ξ The values are from direct monitoring of the sCI decay, γ The values are from indirect sCI measurements, ³⁴we assume the rate coefficient of CH₃(CH₂)₁₁CHOO + HCOOH as 1.1×10^{-10} cm³ s⁻¹ (for CH₂OO literature) and estimate the rate coefficients of the reaction of CH₃(CH₂)₁₁CHOO with C₆H₁₃COOH, HCHO, CH₃CH(OH)CH₃ and CH₃OH using the relative rate constants table from Tobias and Ziemann.⁸⁴

The high concentration of water vapour in the lower troposphere (1.3×10^{17} to 8.3×10^{17} molecule cm^{-3})⁶¹ makes it likely that the reaction of water with sCl_s will be a dominant chemical sink. The energy barrier of the sCl + H₂O reaction is reduced dramatically when interacting with a water dimer, as opposed to a monomer. Even though these dimers make up a small percentage (<1%) of water vapour, the reduced activation energy significantly increases the rate of the reaction.^{52,55} Using the tropospheric water concentration estimated by Huang et al.⁶¹, the tropospheric water dimer concentrations at 298 K are calculated to be in the range of 3.5×10^{13} to 1.4×10^{15} molecule cm^{-3} . The median rate coefficients for reaction with water and water dimer extracted from the reported values in Tables 2 and 3 are 3.2×10^{-16} and 5.4×10^{-12} $\text{cm}^3 \text{s}^{-1}$ leading to loss rates at the surface of 40-270 s^{-1} and 190-7780 s^{-1} by water and water dimer, respectively. One of the main products of the reaction, sCl + water or water dimer is found to be hydroxymethyl hydroperoxide (HMHP).^{50,85,86} The global atmospheric chemistry and transport model study estimated the levels of HMHP in the range of 10-200 ppt (Figure 3) with the highest peak found in terrestrial rain-forest regions.⁵⁰ However, HMHP itself can undergo decomposition to formic acid contributing to the acidity of precipitation.⁸⁷ It is known that HMHP has various toxic effects on plant cells and enzymes.⁸⁸⁻⁸⁹ sCl formed from large functionalized or cyclic alkenes can react with water to form lower vapour pressure products (e.g. production of pinic acid from β -pinene suggested by Docherty and Ziemann⁹ that are thought to be important species acting as Cloud Condensation Nuclei (CCN).

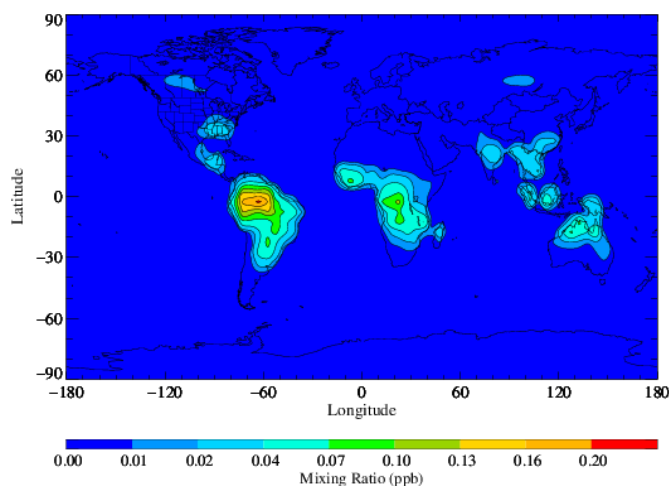


Figure 3 The estimated annual average surface HMHP produced from the sCl + water reaction simulated by the STOCHEM-CRI model (Adapted from Sheps et al.⁵⁰).

A theoretical study⁹⁰ showed that, for CH₂OO and *anti*-CH₃CHOO, reaction with water and water dimer dominated the loss processes, even in a relatively low humidity environment such as Mexico City. Literature has shown that the rate coefficients for the reaction of sCl + water have a large dependence on the conformation of the sCl being considered, *anti*-sCl_s are thought to react up to 5 orders of magnitude faster than *syn*-sCl_s (see Table 2). Despite the slow reaction of *syn*-sCl_s, they can go on to provide a source of OH radicals.⁵⁴ Alkene ozonolysis favours *syn*-formation and therefore these reactions can provide an essential source of atmospheric OH, and recent work^{53,91} confirms this OH production pathway. For *anti*-CH₃CHOO, the median rate coefficient for reaction with water is 1.31×10^{-14} $\text{cm}^3 \text{s}^{-1}$ leading to loss rate coefficients near Earth's surface of between $(1.7-10.8) \times 10^3 \text{s}^{-1}$, which greatly exceeds all estimates of the rate coefficient for unimolecular loss. For *syn*-CH₃CHOO the median rate coefficient for reaction with water is 2.0×10^{-19} $\text{cm}^3 \text{s}^{-1}$ leading to loss rates at the surface between approximately $2.6 \times 10^{-2} \text{s}^{-1}$ and $1.7 \times 10^{-1} \text{s}^{-1}$ which is far smaller than estimates of the rate coefficients for unimolecular loss. For (CH₃)₂COO, the median rate coefficient for reaction with water is 3.8×10^{-17} $\text{cm}^3 \text{s}^{-1}$ leading to loss rates at the surface between 10-30 s^{-1} which is similar to the rate coefficients for unimolecular loss, making both loss processes comparable. Therefore, for the few sCl_s where data have been collected for both reactions, reaction with either the water monomer or dimer seems to be a dominant loss process. However, a much larger dataset, with larger sCl_s, is needed to establish a more general prediction.

Although reactions with the water monomer and dimer may dominate removal of sCl, and thus other reaction pathways are of marginal importance in determining atmospheric sCl concentration, sCl can be substantial contributors to

formation or removal of other species, particularly if sCl reactions can compete with reactions of OH. The oxidation of NO *via* sCl to NO₂ is slow ($6.0 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$), which, along with the low tropospheric concentrations relative to water vapour, mean that this pathway is rarely considered to be of major importance.⁹⁰ This is supported in the work by Welz et al.⁵⁶ that shows even with $[\text{NO}] = 5 \times 10^{15} \text{ cm}^{-3}$ no increase in the decay rate of the CH₂OO was observable. However, the oxidation of NO₂ *via* sCl was found to be much faster than the reaction of NO + sCl (Table 4). Experiments have struggled to accurately ascertain information about the oxidation products of the reaction. Indirect kinetic measurements^{25,92} suggested NO₃ formation from sCl+NO₂ under ambient atmospheric boundary layer conditions. However, Caravan et al.⁶⁷ demonstrated the formation of a Criegee-NO₂ adduct and found limited evidence for the NO₃ production channel (upper limit of 30%) in their direct measurement technique. The adduct formation as a competitor of NO₃ production makes the reaction of sCl + NO₂ a small contribution on NO₃ concentration, unless the adduct in turn generates NO₃ on longer kinetic timescales or through subsequent reactions.⁶⁷

Oxidation of SO₂ by sCl was believed to be of little tropospheric importance until relatively recently. Measurement of sCl oxidation of SO₂ can be difficult because the OH radicals resulting from Cl decomposition can also compete. However, recently the direct kinetic measurement studies^{21,23,31,34,56,57} showed that reaction rate constants for these reactions are up to 4 orders of magnitude larger than previously thought³³ and an order of magnitude larger than those reported for NO₂ for all sCl studied (Table 5). The global atmospheric chemistry and transport model STOCHEM-CRI has been integrated showing that the oxidation of SO₂ by sCl is more significant (by up to 100%) in the terrestrial rain-forests and high latitude boreal forests compared with its oxidation by OH (Figure 4). The values are comparable with the study⁹³ who predicted up to 75% gas phase formation of H₂SO₄ from sCl +SO₂ relative to OH +SO₂ in the equatorial region. However, the modelling study of Sarwar et al.⁹⁴ showed that the oxidation of SO₂ by sCl has little impact on H₂SO₄ formation but decreasing the rate coefficient of the reaction of sCl with H₂O in the model can enhance the H₂SO₄ formation. The model has a limited number of alkenes producing limited sCls, the loss processes detailed in Table 2-3 may play different roles for more complex sCls. Thus, the main challenges facing accurate model predictions of steady state sCl and its impact on the troposphere is the many decades of uncertainty associated with the rate coefficients for water vapour.

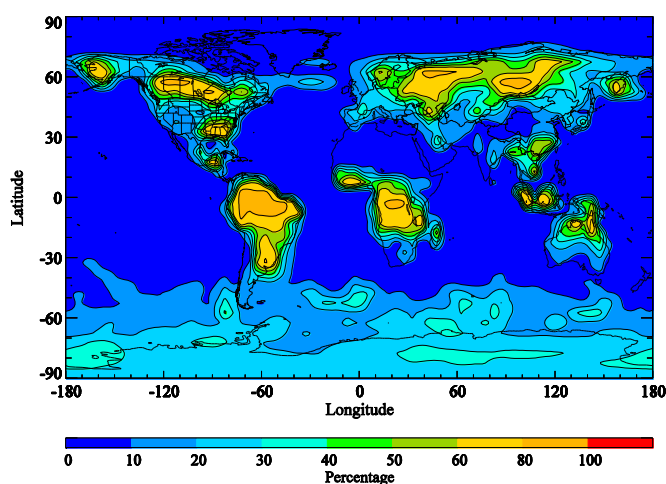


Figure 4 The estimated percent contribution of the gas phase oxidation process of SO₂+sCl compared with the gas phase oxidation process of SO₂ +OH simulated by the STOCHEM-CRI model.

The SO₃ formed in these reactions^{31,56,71} reacts with water vapour on very fast time-scales to form H₂SO₄.^{32,95-97} Mauldin et al.⁹⁸ inferred the presence of sCl by investigating H₂SO₄ produced from the reaction, sCl+SO₂, this formation path had significance to reduce the discrepancy between measured and model H₂SO₄. Further study has shown that the oxidation of SO₂ by sCl can rival the OH oxidation pathway in heavily polluted urban environments,⁴² accounting for as much as 33-46% of H₂SO₄ production at ground level.⁹⁹

Recent direct kinetic studies of the reaction of Criegee intermediates with organic acids have identified rate coefficients that are substantially higher,^{73-75,100} than previous estimates based on theoretical calculations and/or end-product

analysis (see Table 6), high enough that these reactions can potentially have significant impacts on the loss of sCl. The first order rate coefficient ratio of the reactions $\text{sCl} + \text{acids}$ is found to be one order magnitude higher relative to the reaction $\text{sCl} + \text{SO}_2$. It has been noted^{30,101-103} that because of the very fast reaction of organic acids with sCl, they can be used to trap sCl in laboratory and field experiments. Recently, Chhantyal-Pun et al.⁷⁴ reported structure-specific rate coefficients for the reactions of various Criegee intermediates with different organic acids. Chhantyal-Pun et al.⁷⁵ also found that these reactions show relatively small temperature dependence over the temperature range found in lower troposphere. Incorporating these reactions of Criegee intermediates with organic acids in the STOCHEM-CRI model^{175,104} shows that loss of acids by sCl exceeds 60% of their total loss in South America, South Africa, Australia and parts of south East Asia resulting in large reductions of the life-time and burden of acetic acid in these regions (Figure 5).

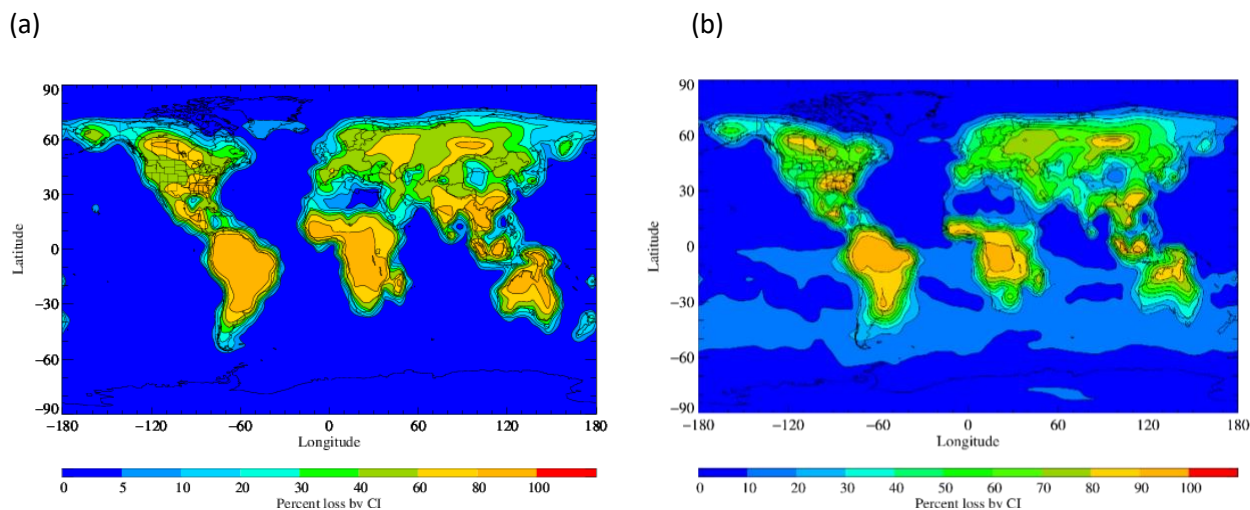


Figure 5 The estimated annual average (a) CH_3COOH , (b) CF_3COOH loss contribution by sCl simulated by the STOCHEM-CRI model (Adapted from Khan et al.¹⁰⁴ and Chhantyal-Pun et al.⁷⁵)

The rate coefficients for reactions of sCl with methanol and ethanol (Table 6) are ~ 1000 times smaller than those for carboxylic acid reactions. In terms of loss of methanol and ethanol, the reactions with sCl are of minor importance, but they may be significant in the formation of gas-phase species e.g. α -alkoxyalkyl hydroperoxides (AAAH).⁵¹ The STOCHEM-CRI model study suggests that up to 20 ppt of AAAH may be formed in terrestrial regions (Figure 6) where there are large emissions of alcohols and the precursors to sCl. The formation of larger, more functionalized organic hydroperoxides derived from the reactions of more complicated sCl, alcohols, or the secondary oxidation of primary AAAHs may be significant in terms of the formation of secondary organic aerosol (SOA) in the troposphere.⁵¹

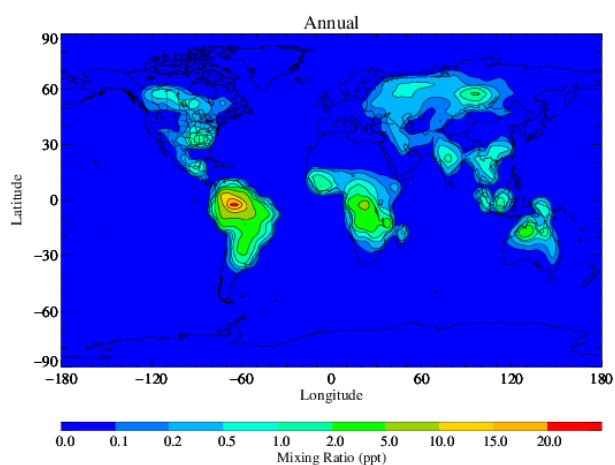


Figure 6 The estimated annual average of α -alkoxyalkyl hydroperoxide (AAAH) level from the reaction of sCl with methanol, simulated by STOCHEM-CRI (Adapted from McGillen et al.⁵¹).

Estimation of regional and global sCI

sCIs are difficult to measure in the atmosphere due to their low steady state concentration, which is controlled by the slow rate of formation by ozonolysis and fast rate of destruction by various reactions (bimolecular or unimolecular). However, because the trace gases (e.g. O_3 , unsaturated VOCs) that contribute to formation of sCI have been measured (National Environmental Technology Centre (NETCEN) data archive, <http://uk-air.defra.gov.uk>), a reasonable estimate of sCI can be made using the steady state approximation.¹⁰⁵ The levels of VOCs are high in the urban atmosphere because of their emissions from transport and other combustion sources, and these VOCs can then take part in photochemical ozone production in the downwind urban plume.¹⁰⁶⁻¹⁰⁷ The elevated concentrations of ozone and increased levels of VOCs (e.g. alkenes) can lead to the formation of substantial sCI in the urban environment. The ozonolysis reactions of available 9 alkenes in the NETCEN data set, and an additional 43 alkenes modelled using information given by the Air Quality Improvement Research Program (AQIRP), give estimates of sCI concentrations of UK environments (e.g. $660 \pm 650 \text{ cm}^{-3}$ for London Eltham, $1960 \pm 2390 \text{ cm}^{-3}$ for London Marylebone Road and $590 \pm 440 \text{ cm}^{-3}$ for Harwell). The estimated sCI concentrations have a diurnal cycle with peaks during the afternoon, yearly cycle with peaks in Spring and weekly cycle with peaks on Sunday (see Figure 7). The sCI levels are predicted to be larger in the day time due to higher levels of VOCs, O_3 and higher temperature throughout the day. Moreover, the increased levels of O_3 along with higher temperature in spring months lead to an overall increase in sCI production in Spring. The variation of sCI between weekdays and weekend is not significant, although slightly higher levels are expected in the weekend because the lower traffic (i.e., low NO_x emissions) increases the VOC/ NO_x ratio resulting in higher O_3 production. Using the estimated levels of urban sCI, the oxidation rate of $SO_2 + sCI$ (37.6 Gg/yr) in urban areas is non-negligible compared with the most conventional oxidation rate of $SO_2 + OH$ (0.64 Tg/yr) in urban areas.¹⁰⁵

Thus, these sCI reactions can alter the oxidizing capacity of the urban troposphere.

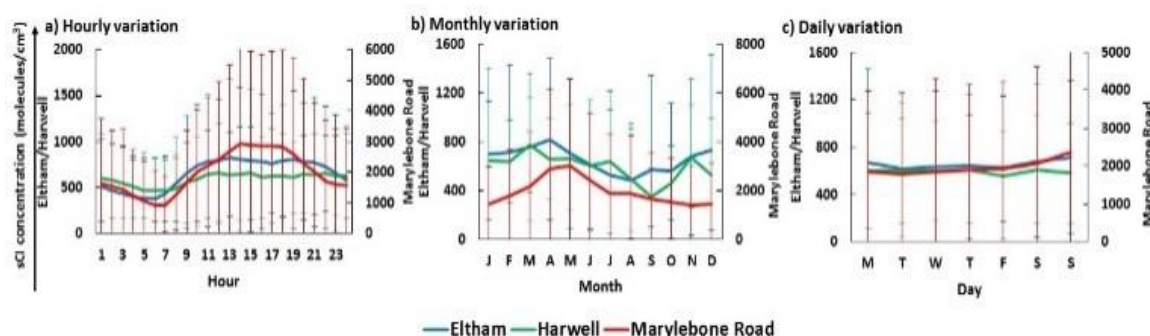


Figure 7 The hourly, monthly, and daily estimated sCI concentrations in the two urban sites and one rural site of UK (Adapted from Khan et al.¹⁰⁵). The error bars represent ± 1 SD of the whole data series.

In the 3-D chemistry and transport model STOCHEM-CRI study, the Criegee field was generated using ozonolysis reactions of six alkenes (ethene, propene, *trans*-but-2-ene, isoprene, α -pinene and β -pinene) and their losses by water, water dimer and unimolecular decomposition. Based on the availability of experimental measurements and quantum calculations of the loss processes of different sCIs,⁵¹ the Criegee field was created where the levels of sCI range from near zero up to levels approaching $6.0 \times 10^5 \text{ cm}^{-3}$, with the highest levels predicted to be over regions of high biogenic emissions of reactive (unsaturated) hydrocarbons, e.g. the Amazon rain forest (see Figure 8a). A similar spatial distribution of sCI was shown by Vereecken et al.⁹³ with the peak sCI concentrations below $1.0 \times 10^5 \text{ cm}^{-3}$. The Criegee chemistry used in STOCHEM-CRI is different from that of Vereecken et al.⁹³ (e.g. Vereecken et al. assigned rapid 1,5-ring closure for the isoprene-derived Criegee intermediates, MVKOO and MACROO during unimolecular decomposition) which can explain the higher sCI concentration estimation in our study. The zonal plot from STOCHEM-CRI study shows that sCI levels estimated are highest (up to $7.0 \times 10^4 \text{ cm}^{-3}$) in the tropics and fall dramatically with altitude (Figure 8b). The ozone levels are higher in the upper troposphere, but the alkene levels decrease with altitude because of their short lifetimes (typically days to hours). In addition, the decreased rate coefficients of the ozonolysis reactions because of the decreasing temperature further from the surface reduce the formation of sCI in the upper troposphere.

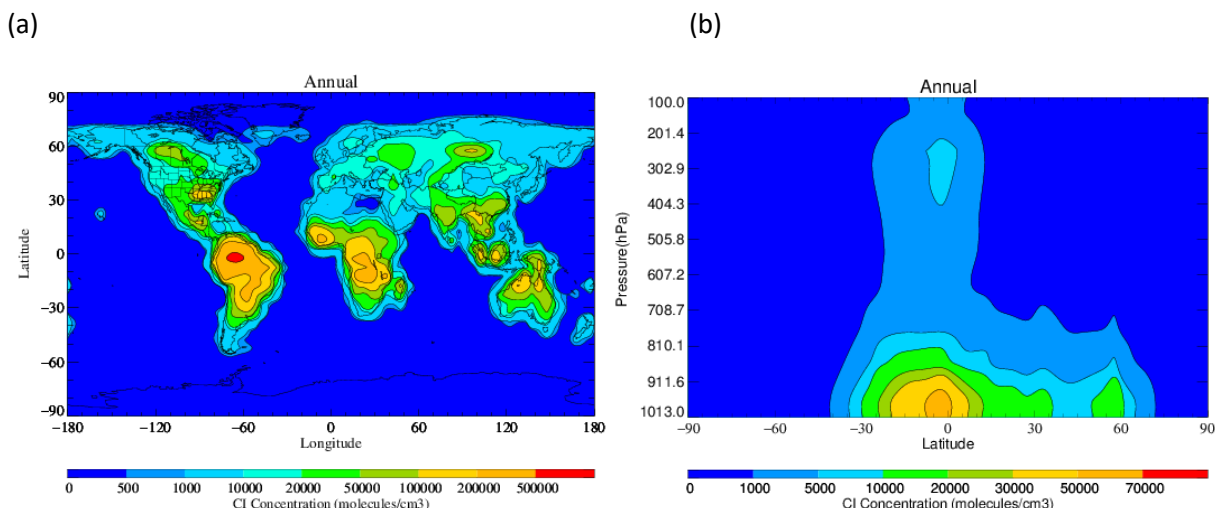


Figure 8 An estimate of annual average (a) surface levels (b) zonal levels of sCl derived using the global model, STOCHEM-CRI.

A variety of theoretical and field studies have also estimated levels of sCl using available measurements of alkenes and ozone. Vereecken et al.⁹⁰ estimated isoprene and monoterpene derived sCl_s to be $1.2 \times 10^4 \text{ cm}^{-3}$ and $7.1 \times 10^2 \text{ cm}^{-3}$, respectively at the tropical forest of Surinam using the steady state approximation. An indirect measurement, where the oxidation of SO₂ to H₂SO₄ in the presence of an OH scavenger is used to quantify the oxidant, gave sCl concentrations of $\sim 5.0 \times 10^4 \text{ cm}^{-3}$ (with an order of magnitude uncertainty) for the boreal forest and rural environments of Finland and Germany.¹⁰⁸ However, the wall loss of sCl was not considered in their study which gives their estimate as a lower limit. Kim et al.¹⁰⁹ estimated peak sCl levels of $\sim 5.5 \times 10^4 \text{ cm}^{-3}$ at $\sim 5 \text{ pm}$ downwind of the Dallas-Fort Worth, Texas conurbation, which are very similar to the study⁹⁹ who predicted sCl levels up to $\sim 5 \times 10^4 \text{ cm}^{-3}$ in Hyytiälä, Finland, and Hohenpeissenberg, Germany. Bonn et al.¹¹⁰ found sCl levels in the range of $2 \times 10^4 \text{ cm}^{-3}$ to $4 \times 10^5 \text{ cm}^{-3}$ during the day over the period August to September in the Mt. Kleiner Feldberg region in central Germany. In all cases, the oxidation of SO₂ by sCl at these calculated levels form an additional amount of H₂SO₄ which brings models into better agreement with measurements. However, Berresheim et al.¹¹¹ potentially detected sCl in the atmosphere at Mace Head in Ireland, using a CIMS-HO (HO instrument using Chemical Ionisation Mass Spectrometry) and found that the oxidation of SO₂ by sCl at Mace Head, Ireland can increase the H₂SO₄ concentrations by only 5-30% which is very small with respect to the average factor of 4.7 required to match the observed H₂SO₄ concentration. Analysis of all reported estimated sCl_s levels gives a reasonable amount of sCl $\sim (1-5) \times 10^4 \text{ cm}^{-3}$ over the terrestrial boundary layer. However, direct measurements of sCl would be required for quantifying the changes of the tropospheric oxidizing capacity due to sCl_s; failing that, more complete *in situ* measurements of the available alkene concentration can be used to calculate the sCl levels in different environments.^{42,105} Detection of sCl in the atmosphere may soon become possible by direct measurement techniques such as near-UV cavity ringdown spectroscopy,²¹ UV-Vis spectroscopy,^{58,64} IR spectroscopy,¹¹² Proton transfer reaction time of flight mass spectrometry (PTR-TOF-MS),¹¹³⁻¹¹⁴ or chemical ionisation mass spectrometry (CIMS).^{70,115} However, it should be noted that direct measurements will represent a significant analytical challenge as a result of the low concentration of sCl_s that are predicted in the atmosphere.

Potential importance of sCl on the troposphere

sCl_s are important in the oxidative capacity and aerosol formation in the troposphere, and the high reactivity of sCl towards many key trace gas species (e.g. water vapour, SO₂, NO₂ and carboxylic acids) implies a greater role of sCl_s in atmospheric chemistry than thought a decade ago. If we consider the level of sCl in the terrestrial boundary layer of the order of $1 \times 10^4 \text{ cm}^{-3}$ and the level of OH is of $1 \times 10^6 \text{ cm}^{-3}$, ~ 10 -fold larger k_{sCl} than k_{OH} is sufficient for the loss rate via reaction with sCl to compete with the loss by reaction with OH. The ratio of loss rates (Table 7) shows that some of the species (e.g. HNO₃, HCOOH, CH₃COOH, CF₃COOH, CF₃COCF₃, and pyruvic acid) where k_{sCl} is more than 100-fold higher than k_{OH} resulting in the dominance of removal by sCl over OH. Thus, sCl makes a significant contribution to the oxidising

capacity in the terrestrial boundary layer by reducing the estimated lifetime of these species and may lead to products that are condensable.⁴⁹

For species such as HCl and SO₂, loss via reaction with OH and sCl are found to be comparable (Table 6). However, in the presence of higher sCl production, e.g., because of increased alkenes levels and increased temperature, oxidation of SO₂ by sCl can be of greater significance. Both field studies^{98-100,108,116} and modelling studies^{42,117-119} suggest that sCl could make a significant contribution (10-70%) to SO₂ oxidation (i.e., H₂SO₄ formation), but the extent of that contribution varies from study to study because of the different environmental conditions. The formation of H₂SO₄ from sCl is atmospherically important because it can act as a CCN through the formation of secondary organic aerosol (SOA)¹²⁰ and can also acidify rain. The conversion of SO₂ into H₂SO₄ has been the focus of many research works, and understanding how H₂SO₄ influences cloud and SOA formation is of vital importance when modelling the direct and indirect effect of sCl.¹²¹

Table 7 Relative oxidation rates of some selected species by OH and sCl considering the concentrations of OH and sCl are 1×10^6 and $1 \times 10^4 \text{ cm}^{-3}$ respectively. Note: only CH₂OO is considered in the calculation.

Species	Rate coefficient of the reaction species + OH, k_{OH} ($\text{cm}^3 \text{ s}^{-1}$)	Rate coefficient of the reaction species + sCl, k_{sCl} ($\text{cm}^3 \text{ s}^{-1}$)	$k_{sCl}[sCl]/k_{OH}[OH]$
HNO ₃	1.5×10^{-13} (Atkinson et al. ¹²²)	5.4×10^{-10} (Foreman et al. ⁸²)	36
HCOOH	4.5×10^{-13} (Atkinson et al. ¹²³)	1.1×10^{-10} (Welz et al. ⁴⁹)	2.5
CH ₃ COOH	8.0×10^{-13} (Atkinson et al. ¹²³)	1.3×10^{-10} (Welz et al. ⁴⁹)	1.6
CF ₃ COOH	1.4×10^{-13} (Atkinson et al. ¹²³)	3.4×10^{-10} (Chhantyal-Pun et al. ⁷⁵)	24.3
HCl	8.0×10^{-13} (Atkinson et al. ¹²³)	4.6×10^{-11} (Foreman et al. ⁸²)	0.6
NO ₂	4.1×10^{-11} (Atkinson et al. ¹²²)	7.0×10^{-12} (Welz et al. ⁴⁹)	0.002
SO ₂	1.3×10^{-12} (Atkinson et al. ¹²²)	3.8×10^{-11} (Chhantyal-Pun et al. ²¹)	0.3
CH ₃ CHO	1.6×10^{-11} (Atkinson et al. ¹²³)	1.5×10^{-12} (Stone et al. ⁵⁷)	0.001
CH ₃ COCH ₃	2.2×10^{-13} (Atkinson et al. ¹²³)	1.2×10^{-12} (Elsamra et al. ⁷²)	0.06
CH ₃ OH	9.0×10^{-13} (Atkinson et al. ¹²³)	1.0×10^{-13} (McGillen et al. ⁵¹)	0.001
C ₂ H ₅ OH	3.2×10^{-12} (Atkinson et al. ¹²³)	1.2×10^{-13} (McGillen et al. ⁵¹)	0.0004

For some other species (e.g. CH₃OH, C₂H₅OH, CH₃CHO), k_{OH} is higher than k_{sCl} resulting in the dominance of removal by OH over sCl. However, this type of species, especially with a C=O, C-O-O-H, C-O-H and C-O-O moieties, can react with sCl to form adducts.³⁵ Synchrotron-based photoionization mass spectrometry measurements demonstrate that the adduct products formed from the reactions of sCl and organic acids, such adducts will have low vapour pressures and high O:C ratios which may lead to condensation of organic species and secondary organic aerosol (SOA) formation.^{49,74} Therefore, even though these reactions only represent a small fraction of the loss compared with the loss by OH, it may be important because of its contribution to SOA formation, with associated impacts on air quality and climate.

There are laboratory¹²⁴⁻¹²⁵ and chamber studies¹²⁶ that showed that reactions between sCl and RO₂ (peroxy radicals) and organic hydroperoxides (ROOH) can form addition products (Figure 9).

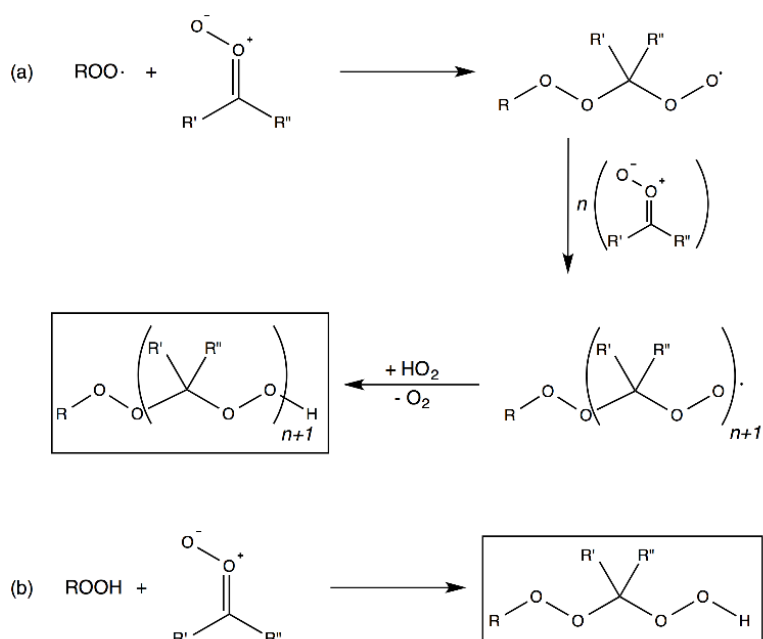


Figure 9 Mechanism for the sequential addition of sCl to (a) peroxy radical and (b) an organic hydroperoxide

Global model studies suggest that the highest concentrations of RO_2 up to 50 pptv⁴⁴ and ROOH up to 8 ppbv⁴⁵ are found in Amazon rainforest region, where the concentration of sCl is also found to be greatest. So, the oxidations of RO_2 and ROOH by sCl may be prominent in these regions, and if the products of these reactions are the adducts shown in Figure 9, these reactions may be significant for SOA formation. However, the large uncertainties of both rate coefficients and the product branching make quantification of these reaction channels difficult. Nevertheless, global model estimates of the distribution of $[\text{sCl}][\text{RO}_2]$ and $[\text{sCl}][\text{ROOH}]$ shows that elevated $[\text{sCl}][\text{RO}_2]$ and $[\text{sCl}][\text{ROOH}]$ exist over the tropical regions (Figure 10 and 11). In summary, the oxidation of VOCs by sCl is likely to yield highly oxygenated species which can lead to nucleation and the formation of SOA and the extent to which these reactions are affecting the regional and global climate is still to be determined.

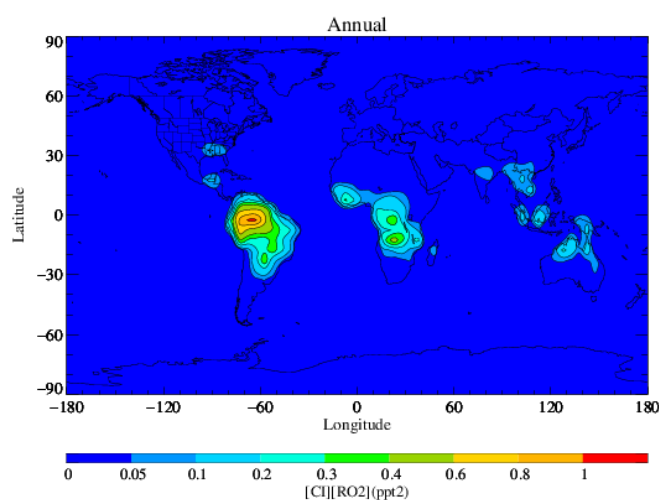


Figure 10 Annual average surface estimate of the product $[\text{sCl}][\text{RO}_2]$ using fields derived from the STOCHEM-CRI global model.

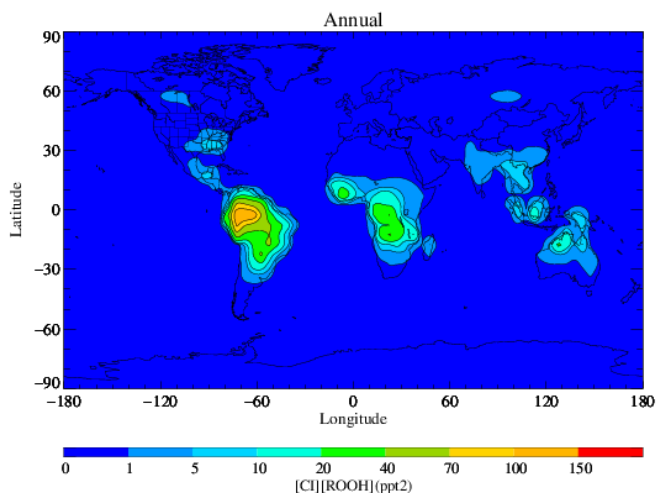


Figure 11 Annual average surface estimate of the expression $[sCl][ROOH]$ using fields derived from the STOCHEM-CRI global model.

Conclusions

The oxidation of alkenes via reaction with ozone act as a major sink for alkenes in the troposphere and has been established to yield Criegee intermediates. The unimolecular decomposition of these species is thought to be contributed to the formation of OH which is significant in the tropospheric oxidation cycle during nighttime and winter months. A variety of model-measurement studies estimated the surface levels of the Criegee intermediates in the order of 10^4 cm^{-3} to 10^5 cm^{-3} , the peak level was found over regions of high biogenic emissions e.g. the Amazon rain forest. The direct detection of Criegee intermediate and measurements of the reaction kinetics of Criegee with several important tropospheric species, NO_2 , SO_2 , water, water dimer, carboxylic acid, alcohols, aldehydes, ketones suggest that Criegee reactions are important in terms of the product information and their tropospheric distribution. The potential role of these intermediates in atmospheric chemistry is significant, altering our thinking about the oxidising capacity of the Earth's atmosphere and the rate of formation of SOA. Currently, the steady state estimation of sCl and its impact on the troposphere is a complex task because of the underlying uncertainties of the unimolecular and bimolecular rate coefficients of larger and more complicated sCl especially biologically important species (e.g. isoprene and terpenes) derived sCl. Future research should be focused on the direct measurement of the unimolecular and bimolecular rate co-efficient of the loss processes of sCl with longer alkyl chain in order to predict the global burden of sCl and also on the experimental determination of sCl which will be beneficial to validate the model results.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank NERC (grant code-NE/K004905/1) and Bristol ChemLabS under whose auspices various aspects of this work was funded. The participation of CAT and RLC is supported by the Office of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, United States Department of Energy. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. All flight and field measurement datasets used in this paper are properly cited and referred to in the reference list.

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