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Kinetic and mechanism of the reaction between Cl and several mono-methyl branched alkanes

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ABSTRACT

Branched alkanes are ubiquitous in the troposphere and play an important role in the chemical processes. In this work, the rate constants and products for the reaction of Cl atoms with 3-methylhexane and 2-methylheptane were measured at room temperature (298 ± 0.2 K) and atmospheric pressure using a conventional relative rate method. The rate constants of 3-methylhexane and 2-methylheptane in units of $\text{cm}^3/(\text{mol}\cdot\text{sec})$ are $(3.09 \pm 0.31) \times 10^{-10}$ and $(3.67 \pm 0.40) \times 10^{-10}$, respectively. Furthermore, the corresponding atmospheric lifetime of the studied branched alkanes with Cl was 6.92–89.90 hours and 5.82–75.69 hours, respectively. The estimated atmospheric lifetimes indicated that the reaction with Cl atoms could be the most important atmospheric degradation pathway for 3-methylhexane and 2-methylheptane. Primary gas-phase products of the reactions were identified and quantified, and particle-phase products were also obtained. The atmosphere oxidation mechanism of Cl atoms with 3-methylhexane and 2-methylheptane is proposed. The SOA yields of 3-methylhexane and 2-methylheptane from the reaction of Cl atoms were determined to be $7.96\% \pm 0.89\%$ and $13.35\% \pm 1.50\%$ respectively. Overall, the results reveal that the primary loss process of branched alkanes is the reaction with Cl atoms, which impacts its degradation on a regional scale.

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Introduction

Non-methane hydrocarbons (NMHCs) in the atmosphere have been thoroughly studied on account of the use of NMHCs in emission source identification and their importance to atmospheric chemistry (Chauhan et al., 2013; Guo et al., 2017). Once released into the atmosphere, the degradation of NMHCs includes photolysis and gas-phase reactions with different oxidants. One of the important ways in which VOCs degrade in the atmosphere is their reaction with hydroxyl radicals. Meanwhile, the reaction with ozone or NO_3 is also important. However, the reaction rate constants of hydrocarbons with chlorine atoms are usually 1–2 orders of magnitude higher than those with hydroxyl radicals, especially for alkanes. Therefore, much of the concern has been focused on the Cl-initiated oxidation of VOCs (Spicer et al., 1998), not only in marine and coastal environments but also in urban and rural areas where more alkanes are oxidized by chlorine atoms rather than by hydroxyl radicals (Breton et al., 2018; Liu et al., 2017).

Branched alkanes, varied in structure, can be released by both biogenic and anthropogenic sources, such as plants, vehicular exhaust, industrial sources. 3-methylhexane and 2-methylheptane, two important branched alkanes, are widely measured around the world (Cai et al., 2010; Christensen et al., 1999; Duan et al., 2008; Jia et al., 2016; Li et al., 2017; Ma et al., 2019; Zou et al., 2015). For example, 3-methylhexane and 2-methylheptane are compositions of conventional gasoline and diesel fuels and have been measured in the tunnel field observations (Hwa et al., 2002; Zielinska et al., 1996) and petroleum refineries (Wei et al., 2014). In addition, emissions of 3-methylhexane have also been found in specific plants (Khalil and Rasmussen, 1992), biomass combustion (Zhang et al., 2013), and 3D printing (Gu et al., 2019). Emissions of 2-methylheptane are detected from crumb rubber modified asphalt (Yang et al., 2019) and the meat cooking process (Schauer et al., 1999). In urban areas, alkanes are also vital precursors to secondary organic aerosol (SOA) (Gentner et al., 2012), which could cause adverse health effects on residents. According to a comprehensive literature survey (Appendix A Table S1), the atmospheric concentrations of 3-methylhexane and 2-methylheptane have a variant range from 0.05–2.85 ppb and 0.08–1.49 ppb, respectively.

In consideration of a certain contribution of branched alkanes to the atmospheric NMHCs, a study is performed aiming at offering new experimental data on the gas-phase reactivity of branched alkanes. Here, the experimental kinetic rate constants of 3-methylhexane and 2-methylheptane reacted with Cl atom were obtained at 298 K and atmospheric pressure. The SOA yields in low- NO_x cases were measured. Combining the reaction rate constants, gas-phase products, particle-phase products, and SOA yield, we would have a further understanding of the atmospheric chemical behavior of 3-methylhexane and 2-methylheptane and enrich the available database for model simulation.

1. Experiment section

1.1. Environmental system

A detailed description of the photochemical reactor system applied in this study was provided in our previous papers (Shi et al., 2019a; Shi et al., 2019b; Wang et al., 2015). Here, we only show essential details briefly. The experiments were performed at atmospheric pressure and room temperature (298 ± 0.2 K). In this study, the purified air was produced by a pure air generator (Model 737, AADCO Instruments Inc., USA) to perform SOA yields derived from 3-methylhexane and 2-methylheptane. The RH of the reacting chamber remained at RH below 5% RH measured by a dew point meter (Optidew, Michelle Instruments Ltd. UK) during measurements. Lamps with a narrow peak at 365 nm were utilized to generate Cl atoms from Cl_2 gas (Huayuan Gas Chemical Co., Ltd. Beijing, China) during the experiments. A 300 L Teflon chamber was used to perform the kinetic experiments. A 1000 L Teflon chamber was used to perform the SOA yields experiments, and the particle-phase products were obtained with these experiments. The Teflon chamber was thoroughly flushed, baked, and passivated before each experiment to ensure that there were no detectable VOCs and inorganic gases, e.g., NO_x , O_3 , SO_2 , et al. Experiment details can be referred to previous studies (Wang et al., 2022).

1.2. Experimental methodology

A relative rate method with ethylbenzene and n-heptane as reference compounds was applied further to investigate the kinetic experiments of chlorine with selected alkanes. It is assumed that reaction with chlorine is the only fate of the reactant and the reference compounds.

$$\ln \left\{ \frac{[\text{Alkane}]_0}{[\text{Alkane}]_t} \right\} = \frac{k_a}{k_r} \ln \left\{ \frac{[\text{Reference}]_0}{[\text{Reference}]_t} \right\} \quad (1)$$

where, $[\text{Alkane}]_0$ and $[\text{Alkane}]_t$ stand for the concentrations of the investigated alkanes at times t_0 and t , respectively; and $[\text{Reference}]_0$ and $[\text{Reference}]_t$ are the concentrations of the reference compounds at times t_0 and t , respectively. k_a and k_r are the rate coefficients for the reactions of the chosen branched alkanes being studied and the reference compounds with Cl atoms. The uncertainties are the 2σ statistical error acquired from the linear least-squares method and the error associated with the reference rate coefficients.

1.3. Experimental apparatus

Thermal desorption gas chromatography with a flame ionization detector was employed to measure the mixing ratios of reactants in the chamber and determine the rate coefficients of Cl atoms with selected alkanes. A proton transfer reaction-quadrupole mass spectrometer (PTR-QMS 500, Ionicon, Austria) was used to identify and quantify the main primary products during the reaction process. The possible oxidation products were identified according to the specific structures of re-

actants and reasonable oxidation mechanisms. PTR-QMS has excellent performance for distinguishing the aldehydes and ketones in the products, which are in the same mass (Shi et al., 2019a). The initial concentrations of the alkanes and chlorine were in the range of 299–377 ppbV and 190–210 ppbV, respectively.

In addition, the products of carbonyl compounds were also identified and quantified using high-performance liquid chromatography-atmospheric pressure chemical ionization-mass spectrometry (Shimadzu LC-20AD, Shimadzu, Japan). An electrospray ionization Fourier transform ion cyclotron resonance mass spectrometer (ESI-FTICR-MS; Solarix, Bruker, Germany) with positive-ion mode was used to analyze the chemical compositions of SOA in the particles. The detail of the pretreatment method can be seen in the previous study (Wang et al., 2022).

The SOA yield was measured using a scanning mobility particle sizer (SMPS), which consisted of an electrostatic classifier (Model 3080, TSI, USA), differential mobility analyzer (Model 3081, TSI, USA), and condensation particle counter (Model 3776, TSI, USA). Centrifugal Particle Mass Analyzer (CPMA Mk1, Cambustion, UK) was used to measure the density of SOA. Measurement uncertainty of 5% is primarily associated with the uncertainty in calculating the density. In this section, a 1000L reaction chamber was utilized to minimize the wall loss.

The lifetimes (τ) were deduced by using the following calculating formula:

$$\tau = \frac{1}{k_a[X]} \quad (2)$$

where, k_a is the reaction rate constant for the reaction of the branched alkanes with the oxidant and $[X]$ stands for the atmospheric concentration of the oxidants. In calculating the lifetimes for the reaction of the branched alkanes with Cl atom, the rate coefficients obtained in this study were used.

1.4. Chemicals

All chemicals were used as received from the suppliers without further purification in this work: 3-methylhexane (TCI, > 95.0%), 2-methylheptane (Acros, 99%), n-heptane (TCI, 99%), ethylbenzene (Alfa, 99%), n-octanol (TCI, > 99.0%), 2-heptanol (TCI, > 98%), 3-methyl-1-pentanol (TCI, > 99.0%), octanal (TCI, > 98.0%), 2-methylbutyraldehyde (TCI, > 95.0%), 2-heptanone (TCI, 99%), 3-methylbutyraldehyde (TCI, 98%), 2-butanone (Acros, > 99%), 2-pentanone (TCI, > 99%), 3-hexanone (TCI, > 98.0%).

2. Results and discussions

2.1. Rate constant measurement

Ethylbenzene and n-heptane were selected as reference compounds. The rate constants of n-heptane and ethylbenzene with chlorine atoms are $(3.65 \pm 0.6) \times 10^{-10} \text{ cm}^3/(\text{mol}\cdot\text{sec})$ (Hooshiyar and Niki, 1995) and $(1.15 \pm 0.04) \times 10^{-10}$

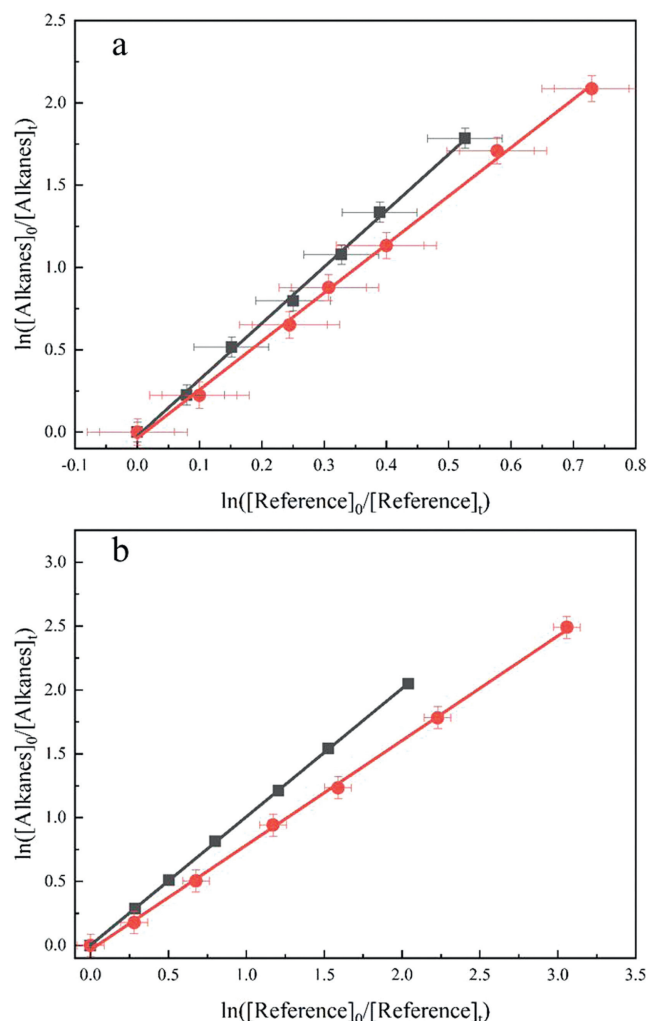


Fig. 1 – Relative rate plots for the reaction of Cl atoms with 3-methylhexane (red circles) and 2-methylheptane (black squares), using (a) ethylbenzene and (b) n-heptane as the reference compound.

$\text{cm}^3/(\text{mol}\cdot\text{sec})$ (Anderson et al., 2007), respectively. Relative rate constants for the reaction of Cl atoms with 3-methylhexane (red circles) and 2-methylheptane (black squares) are shown in Fig. 1 and Table 1. Errors on both abscissa and ordinate scales were taken into account (Brauers and Finlayson-Pitts, 1997). As shown in Fig. 1, the obtained rate constants (in units of $10^{-10} \text{ cm}^3/(\text{mol}\cdot\text{sec})$) of 3-methylhexane and 2-methylheptane are 3.09 ± 0.31 and 3.67 ± 0.40 , respectively. The rate constants using different reference compounds are in good agreement. According to the calculation method of collision limit from Wang et al. (2022), the calculated collision limits of 3-methylhexane and 2-methylheptane are $2.22 \times 10^{-9} \text{ cm}^3/(\text{mol}\cdot\text{sec})$ and $2.46 \times 10^{-9} \text{ cm}^3/(\text{mol}\cdot\text{sec})$, respectively. In this study, we measured the rate constant and its value is $(3.09 \pm 0.31) \times 10^{-10} \text{ cm}^3/(\text{mol}\cdot\text{sec})$ and $(3.67 \pm 0.40) \times 10^{-10} \text{ cm}^3/(\text{mol}\cdot\text{sec})$. Thus, the calculated collision limit is about one order of magnitude higher than the measured rate constants (Wang et al.,

Table 1 – Summary of rate constants for the reaction of selected alkanes with Cl atoms.

Reaction	Reference	$k_a 10^{-10} \text{ cm}^3/(\text{mol}\cdot\text{sec})^a$	$k_a 10^{-10} \text{ cm}^3/(\text{mol}\cdot\text{sec})$
3-Methylhexane	n-heptane	2.93±0.48	3.09±0.31
	n-heptane	3.11±0.51	
	ethylbenzene	3.08±0.13	
	ethylbenzene	3.27±0.13	
2-Methylheptane	n-heptane	3.67±0.60	3.67±0.40
	n-heptane	3.69±0.61	
	ethylbenzene	3.83±0.15	
	ethylbenzene	3.50±0.22	

^a The errors combined the precision of our measured values with the quoted uncertainties in the rate constant of references.

Table 2 – Estimated atmospheric lifetimes of the test alkanes.

Compounds	k_{Cl}^a $10^{-10} \text{ cm}^3/(\text{mol}\cdot\text{sec})$	τ_{Cl}^b hour	k_{OH}^c $10^{-12} \text{ cm}^3/(\text{mol}\cdot\text{sec})$	τ_{OH}^d day
3-Methylhexane	3.09±0.31	6.92-89.90	6.69±0.10	3.17
2-Methylheptane	3.67±0.40	5.82-75.69	9.10±0.30	1.27

^a This work.

^b $[Cl]=1.0 \times 10^4$ – $1.3 \times 10^5 \text{ mol/cm}^3$ (Hossaini et al., 2016; Spicer et al., 1998).

^c The rate constants of 3-methylhexane and 2-methylheptane with OH atom are $(6.69 \pm 0.10) \times 10^{-12} \text{ cm}^3/(\text{mol}\cdot\text{sec})$ (Sprenghether et al., 2009) and $(9.10 \pm 0.30) \times 10^{-12} \text{ cm}^3/(\text{mol}\cdot\text{sec})$ (Shaw et al., 2020), respectively.

^d $[OH]=1 \times 10^6 \text{ mol/cm}^3$ (Prinn et al., 1995).

2022). For the reaction of 2-methylheptane with Cl atoms, the rate constant was measured to be $(4.26 \pm 0.77) \times 10^{-10} \text{ cm}^3/(\text{mol}\cdot\text{sec})$ at 295 K (Shaw et al., 2020), slightly higher than the result in this work. The difference may be on account of the temperature effects and the use of the different experimental methods. For the reaction of 3-methylhexane with Cl atoms, the master chemical mechanism (MCM) provides an estimated value of $3.12 \times 10^{-10} \text{ cm}^3/(\text{mol}\cdot\text{sec})$, which corresponds to our work perfectly. The overall rate constants estimated based on the structure-activity relationship (SAR) for 3-methylhexane and 2-methylheptane are $2.85 \times 10^{-10} \text{ cm}^3/(\text{mol}\cdot\text{sec})$ and $3.49 \times 10^{-10} \text{ cm}^3/(\text{mol}\cdot\text{sec})$, respectively (Aschmann and Atkinson, 1995), which are similar with the experimental results.

The rate constants and estimated lifetimes of selected branched alkanes are present in Table 2. The rate constants of 3-methylhexane and 2-methylheptane with OH radicals are $(6.69 \pm 0.10) \times 10^{-12} \text{ cm}^3/(\text{mol}\cdot\text{sec})$ (Sprenghether et al., 2009) and $(9.10 \pm 0.30) \times 10^{-12} \text{ cm}^3/(\text{mol}\cdot\text{sec})$ (Shaw et al., 2020), respectively. The concentration of OH radicals is about $1 \times 10^6 \text{ mol/cm}^3$ (Prinn et al., 1995). The corresponding tropospheric lifetimes concerning reaction with OH radicals are about 3.17 days and 1.27 days for 3-methylhexane and 2-methylheptane,

Table 3 – Rate constants for the reaction of branched alkanes with Cl atoms and OH radicals.

Alkanes	k_{Cl}^c $10^{-10} \text{ cm}^3/(\text{mol}\cdot\text{sec})$	k_{OH} $10^{-12} \text{ cm}^3/(\text{mol}\cdot\text{sec})$
2-Methylpropane	1.3 ^a	2.12 ^b
2-Methylbutane	1.94 ^a	3.6 ^b
2-Methylpentane	2.58 ^a	5.2 ^b
2-Methylhexane	3.12 ^a	6.69 ^c
3-Methylhexane	3.09	6.69 ^c
2-Methylheptane	3.67	9.10 ^d

^a Ref. (Hooshiyar and Niki, 1995).

^b Ref. (Atkinson, 2003).

^c Ref. (Sprenghether et al., 2009).

^d Ref. (Shaw et al., 2020).

respectively. Wingenter et al. (1996) stimulated and estimated the atmospheric concentration of Cl atoms to be $\sim 1.0 \times 10^4 \text{ mol/cm}^3$ (Wingenter et al., 1996). Also, Spicer et al. (1998) measured the atmospheric concentration of Cl atoms in coastal regions or severely polluted areas. They found the concentration of Cl atoms is up to $1.3 \times 10^5 \text{ mol/cm}^3$ (Spicer et al., 1998). Thus, the atmospheric concentration of Cl atoms has a variant range from 1.0×10^4 to $1.3 \times 10^5 \text{ mol/cm}^3$, which corresponds to atmospheric lifetimes of 3-methylhexane and 2-methylheptane reacting with Cl atoms of 6.92–89.90 hours and 5.82–75.69 hours, respectively. The degradation via reaction with Cl atoms may be more vital. The magnitude concerning the rate constant with NO_3 would be about $10^{-16} \text{ cm}^3/(\text{mol}\cdot\text{sec})$ (Atkinson, 1991). Given the NO_3 concentration of $5 \times 10^8 \text{ mol/cm}^3$ (Atkinson, 1991), the corresponding tropospheric lifetimes concerning reaction with NO_3 radicals is about a few months. The role of Cl atoms in degradation of branched alkanes is comparable to or even exceeds that of OH.

The rate constants of branched alkanes with Cl atoms and OH radicals increase monotonically with the increase of the chain length (Table 3). As the chain length increases, more hydrogens are available to be abstracted, and the rate constant increases (Ullerstam et al., 2001). There are specific trends in the reaction activity of C-H bonds, especially for alkanes with various numbers of $-\text{CH}_3$, $-\text{CH}_2-$, and $>\text{CH}-$, as C-H bonds in different positions possess different dissociation energies. Compared with the reactivity of branched alkanes with OH radicals, Cl atoms are more reactive. This behavior could account for the different sizes and electronic properties of each oxidant, which make the Cl atoms more reactive but also less selective (Thévenet et al., 2000; Ullerstam et al., 2001). The effect of chemical structure on Cl reaction rate coefficients is less significant than OH reaction rate constants. Because the H-abstraction activities of OH radicals and Cl atoms on $-\text{CH}_3$, $-\text{CH}_2-$, and $>\text{CH}-$ are different in both SAR rules and the master chemical mechanisms (MCM v3.3.1: <http://mcm.leeds.ac.uk/MCMv33.1/home.htm>). The difference in the relative activity of OH radicals is larger than the difference in the relative activity of Cl atoms in terms of both SAR rules and MCM (Wang et al., 2022). Thus, compared to the effect of chemical structure on the OH reaction rate coefficient, chemical structure affects Cl reaction rate coefficients insignificantly.

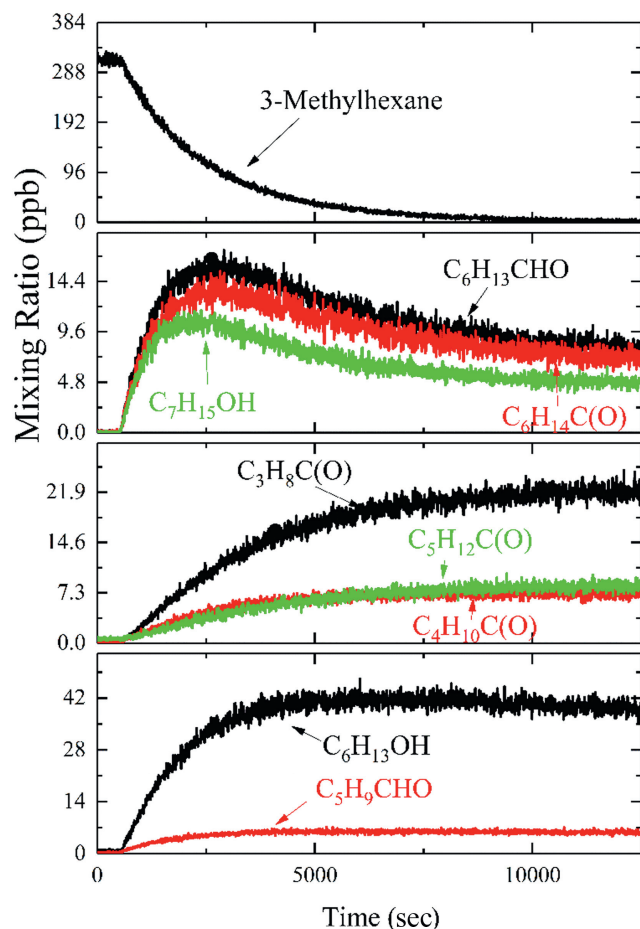


Fig. 2 – The gas-phase products for the reactions of 3-methylhexane with Cl atoms.

2.2. Products of the reactions

The gas-phase products of 3-methylhexane with Cl atoms were measured via PTR-QMS (Fig. 2). The mixing ratios of products represented the total concentrations of all the isomers with the same functional group. As the reaction proceeded, the mixing ratio of 3-methylhexane gradually decreased. In addition, some first-generation organic species, e.g., $C_7H_{16}O$, were generated and consumed simultaneously. In the initial stage, the generation rate was higher than the consumption rate. The contrary was the case after the concentration reached the peak stage. Finally, the concentrations kept constant after the total consumption of oxidants. On the other hand, C_4H_8O , the second generation product, was generated continuously during the whole period. The detected products of the 3-methylhexane reacting with Cl atoms and the yields are listed in Table 4.

Fig. 3 shows the temporal trends of 2-methylheptane and products oxidized by Cl atoms. During the reaction period, the concentration of the products ($C_6H_{13}OH$, $C_8H_{17}OH$, and $C_2H_6C(O)$) is relatively high. As the primary product, the concentration of acetone increases steadily, which means that acetone is likely produced directly from the reactant and belongs to the first-generation products. The detected products

Table 4 – Main products of the 3-methylhexane reacting with Cl atoms and their yields.

Products ^a	Mass ^b	Yields (%) ^c	Yields (%) ^d
HCHO	30		4.62±0.46
CH ₃ CHO	44		3.82±0.38
C ₂ H ₆ C(O)	58		0.44±0.04
C ₂ H ₅ CHO	58		1.38±0.14
C ₆ H ₁₃ OH	102	16.07 ± 0.58	
C ₆ H ₁₃ CHO	114	8.73 ± 0.39	
C ₆ H ₁₄ C(O)	114	6.86 ± 0.42	
C ₇ H ₁₅ OH	116	5.80 ± 0.35	
C ₃ H ₈ C(O)	72	3.50 ± 0.13	1.24±0.12
C ₄ H ₉ CHO	86	1.80 ± 0.11	
C ₄ H ₁₀ C(O)	86	1.75 ± 0.10	
C ₅ H ₁₂ C(O)	100	1.48 ± 0.17	

^a The product represents all of the isomers with the similar structure.

^b The mass of products identified via PTR-QMS.

^c The yield is the slope of the increase of product plotted the loss of 3-methylhexane.

^d The products identified by using HPLC-MS.

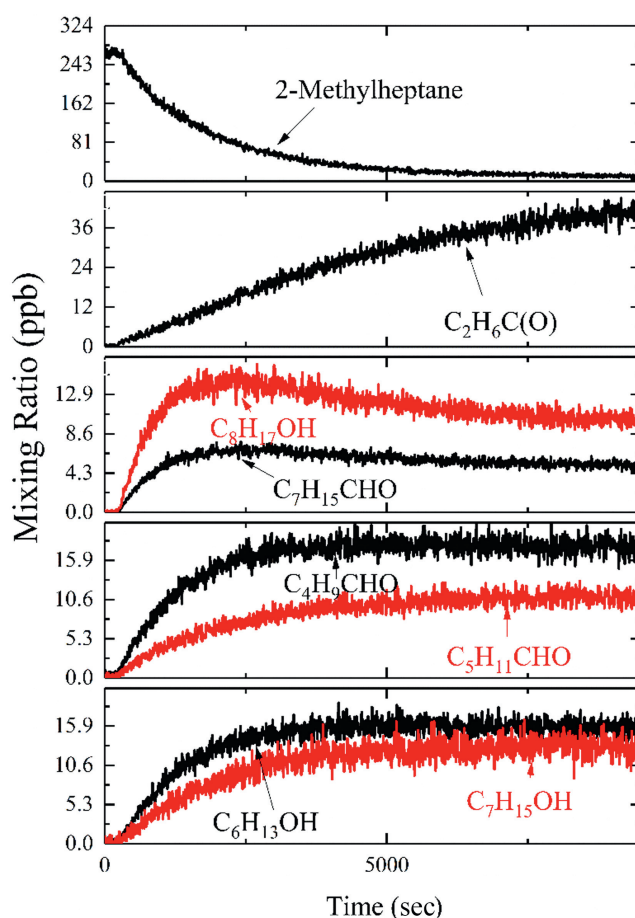


Fig. 3 – The gas-phase products for the reactions of 2-methylheptane with Cl atoms.

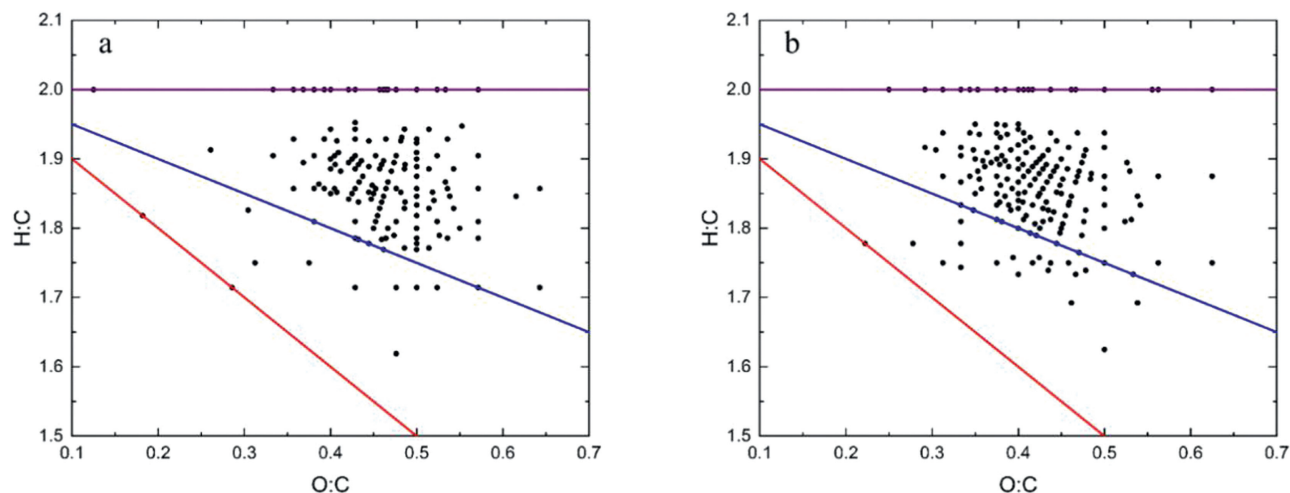


Fig. 4 – Van Krevelen diagram of SOA from Cl-initiated (a) 3-methylhexane and (b) 2-methylheptane oxidation.

Table 5 – Main products of the 2-methylheptane reacting with Cl atoms and the yields.

Products ^a	Mass ^b	Yields (%) ^c	Yields (%) ^d
HCHO	30		1.92±0.19
CH ₃ CHO	44		1.49±0.15
C ₂ H ₅ CHO	58		1.05±0.11
C ₃ H ₇ CHO	72		0.31±0.03
C ₆ H ₁₃ OH	102	7.33 ± 0.29	
C ₈ H ₁₇ OH	130	7.28 ± 0.39	
C ₂ H ₆ C(O)	58	5.79 ± 0.29	5.20± 0.52
C ₄ H ₉ CHO	86	3.90 ± 0.19	
C ₇ H ₁₅ CHO	128	3.65 ± 0.17	
C ₅ H ₁₁ CHO	100	3.19 ± 0.17	
C ₇ H ₁₅ OH	116	1.69 ± 0.09	

^a The product represents all of the isomers with the similar structure.

^b The mass of products identified by using PTR-QMS.

^c The yield is the slope of the increase of product plotted the loss of 2-methylheptane.

^d The products identified by using HPLC-MS.

of the 2-methylheptane reacting with Cl atoms and the yields are listed in Table 5.

Hundreds of particle-phase products were identified according to the mass spectra. The molecular formulas are displayed in Appendix A Table S2 and Appendix A Table S3. The signal of monomers was weak among the products in the mass spectra. The results showed that dimers, trimers, tetramers, and pentamers were formed, and hexamers could be detected via Cl-initiated 3-methylhexane oxidation. Fig. 4 shows the Van Krevelen diagram. A slope of 0 (purple line) represents the addition of a hydroxy or peroxy group. A slope of -1 (blue line) represents the formation of a carboxylic acid group or the addition of a hydroxy group and a carbonyl group individually. A slope of -2 (red line) represents the addition of a carbonyl group.

2.3. Reaction mechanism

Degradation mechanisms for the selected branched alkanes with the Cl atoms were proposed (Scheme 1 and Scheme 2), considering the detected products and the yields obtained in the gas phase. Hydrogen abstraction from the reactant is the primary channel for the reactions of chlorine atoms with saturated VOCs. Followed by the addition of oxygen, RO₂· is formed. The self- or cross-reactions of RO₂· form the alkoxy groups. In addition to the formation of aldehydes, RO· + O₂ reaction and RO· decomposition also generate a variety of ketones during the reaction process (Atkinson and Arey, 2003). Alcohols, generated from the self-reaction of RO₂·, can also contribute to the gas products (Orlando and Tyndall, 2012).

For both 3-methylhexane and 2-methylheptane, primary reaction pathways are presented in Schemes 1 and 2. The mechanisms of these two reactions were similar, and the main difference between the two reactions was that the products of 3-methylhexane were more varied because the structure was more complicated than 2-methylheptane. Branch ratios are marked on the graph, estimated based on the SAR (Aschmann and Atkinson, 1995). In addition, we inferred that the main formation pathway of ketones was through hydrogen abstraction from the branched-chain site.

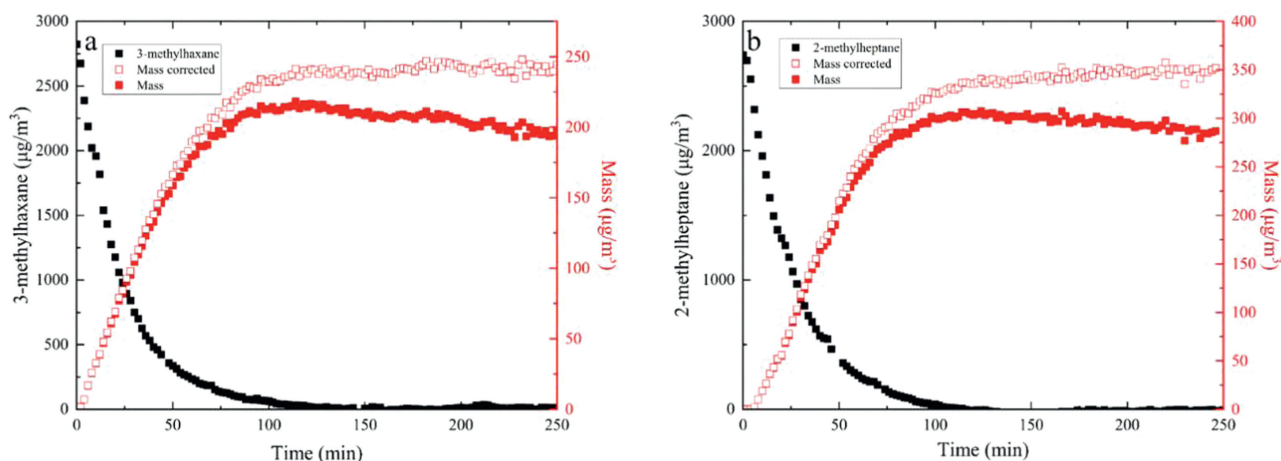
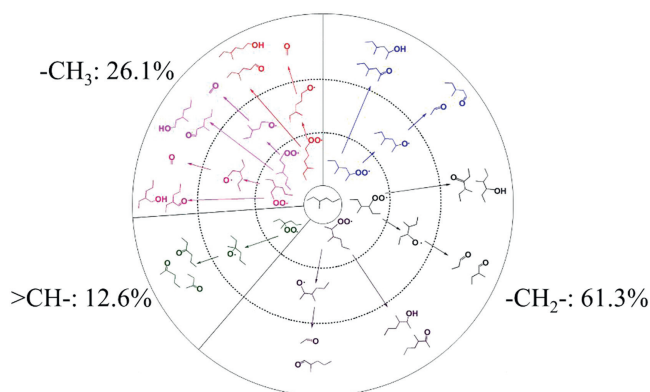
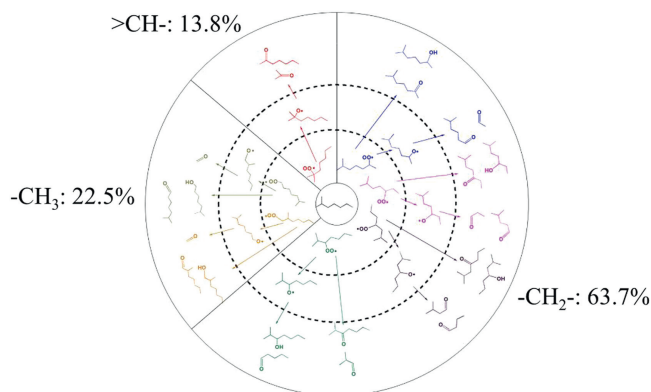
2.4. SOA density and yield

Density is also an important parameter of SOA. The SOA densities derived from 3-methylhexane and 2-methylheptane were 1.08 ± 0.05 g/cm³ and 1.14 ± 0.06 g/cm³, respectively. Wang et al. (2022) reported a density of 1.02 g/cm³ for the Cl-initiated n-alkylcyclohexanes SOA generated under low-NO_x conditions. The difference may be due to different precursors and concentrations used in experiments.

The SOA yields were $7.96\% \pm 0.89\%$ and $13.35\% \pm 1.50\%$ for 3-methylhexane and 2-methylheptane, respectively (Table 6). The uncertainties of SOA yields were combined with the uncertainties of SMPS (10%) and PTR-QMS (5%). Time profiles

Table 6 – Summary of aerosol yields obtained from the oxidation of alkanes.

Reaction	M_0 ($\mu\text{g}/\text{m}^3$)	ΔHC ($\mu\text{g}/\text{m}^3$)	Y (%)	Final Y (%)
2-Methylheptane	234.98	2822.80	8.32 ± 0.93	7.96 ± 0.89
	226.01	2973.99	7.60 ± 0.85	
3-Methylhexane	351.99	2738.89	12.85 ± 1.44	13.35 ± 1.50
	389.62	2813.93	13.85 ± 1.55	

**Fig. 5 – Reaction profiles of SOA formation initiated by Cl atoms with (a) 3-methylhexane and (b) 2-methylheptane.****Scheme 1 – Proposed reaction mechanism of 3-methylhexane with Cl atoms.****Scheme 2 – Proposed reaction mechanism of 2-methylheptane with Cl atoms.**

of SOA formation for 3-methylhexane and 2-methylheptane with Cl atoms are shown in Fig. 5. Experimental measurements on 2-methylheptane reacting with Cl atoms were performed under high NO_x conditions (Appendix A Fig. S4). It is found the SOA yield derived from 2-methylheptane is $14.70\% \pm 1.81\%$ lower than the SOA yields ($16\% - 18\%$) of n-octane initiated by Cl atoms under high NO_x conditions (Wang and Hildebrandt Ruiz, 2018). Thus, branched alkanes from Cl-initiated oxidation might produce less SOA than linear n-alkanes. Also, previous studies reported that both linear n-alkanes and branched cycloalkanes might produce more SOA than branched alkanes from Cl-initiated oxidation (Jahn et al.,

2021). More alkoxy radical intermediates are produced with branching degree increasing. The decomposition of alkoxy radical intermediates can produce two molecules of higher volatility than the parent molecule, thereby decreasing SOA formation. The different carbon chain lengths and structure of precursors may influence the SOA yields. Chlorine-initiated oxidation of alkanes has been shown to rapidly form SOA at higher yields than OH-alkane reactions (Dhulipala et al., 2019; Jahn et al., 2021; Wang and Ruiz, 2017). For the selected mono-methyl branched alkanes in this work, there are no SOA yields initiated by OH radicals for comparison to the best of our knowledge, which needs further investigation in the future.

3. Atmospheric implications

Branched alkanes are emitted into the environment from both anthropogenic and biogenic sources. In this work, the rate coefficients for the Cl atom-initiated oxidation of 3-methylhexane and 2-methylheptane were determined. The atmospheric lifetimes of the branched alkanes studied in this work were also evaluated, which were roughly equal to 6.92–89.90 hours and 5.82–75.69 hours for 3-methylhexane and 2-methylheptane respectively. The main gas-phase and particle-phase products formed were identified, which deepened the understanding of oxidation mechanisms. The SOA could also be generated from the reaction of Cl atoms and branched alkanes. Combined with the high concentration of alkanes in the atmosphere, those results suggest that the branched alkanes could rapidly decompose in the troposphere and affect the regional environment.

Declaration of Competing Interest

All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version. This manuscript has not been submitted to, nor is under review at, another journal or other publishing venue. The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript.

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Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2022.08.010.

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