



# Reaction kinetics of Cl atoms with limonene: An experimental and theoretical study



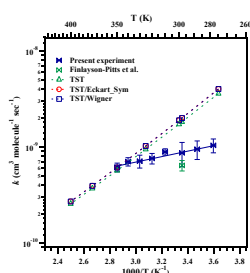
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## HIGHLIGHTS

- First kinetic study of the reaction of Cl atoms with limonene as a function of temperature.
- Additions and abstraction kinetics of limonene by Cl atom were discussed.
- Atmospheric lifetime of limonene was computed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Rate coefficients for the reaction of Cl atoms with limonene ( $C_{10}H_{16}$ ) were measured between 278–350 K and 800 Torr of  $N_2$ , using the relative rate technique, with 1,3-butadiene ( $C_4H_6$ ), n-nonane ( $C_9H_{20}$ ), and 1-pentene ( $C_5H_{10}$ ) as reference compounds. Cl atoms were generated by UV photolysis of oxalyl chloride ( $(COCl)_2$ ) at 254 nm. A gas chromatograph equipped with a flame ionization detector (GC-FID) was used for quantitative analysis of the organics. The rate coefficient for the reaction of Cl atoms with limonene at 298 K was measured to be  $(8.65 \pm 2.44) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The rate coefficient is an average value of the measurements, with two standard deviations as the quoted error, including uncertainties in the reference rate coefficients. The kinetic data obtained over the temperature range of 278–350 K were used to derive the following Arrhenius expression:  $k(T) = (9.75 \pm 4.1) \times 10^{-11} \exp[(655 \pm 133)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Theoretical kinetic calculations were also performed for the title reaction using conventional transition state theory (CTST) in combination with G3(MP2) theory between 275 and 400 K. The kinetic data obtained over the temperature range of 275–400 K were used to derive an Arrhenius expression:  $k(T) = (7.92 \pm 0.82) \times 10^{-13} \exp[(2310 \pm 34)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The addition channels contributes maximum to the total reaction and H-abstraction channels can be neglected in the range of studied pressures. The Atmospheric lifetime ( $\tau$ ) of limonene due to its reaction with Cl atoms was estimated and concluded that the reaction with chlorine atoms can be an effective tropospheric loss pathway in the marine boundary layer and in coastal urban areas.

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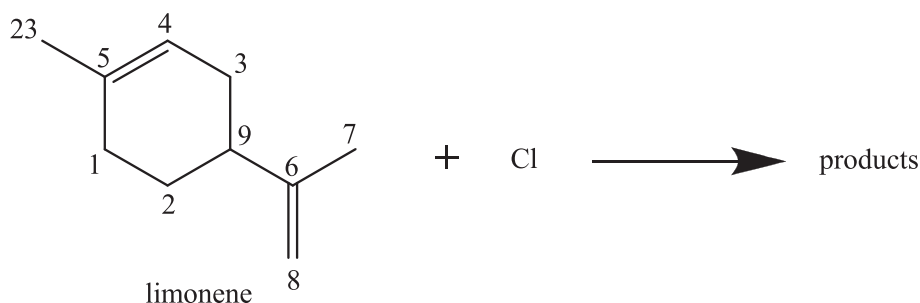
## 1. Introduction

Biogenic volatile organic compounds (BVOCs), those are released into the troposphere react mainly with hydroxyl radical (OH) which is major tropospheric oxidant. Chlorine atoms (Cl) are also known to contribute significantly in the oxidative capacity of the troposphere particularly in the early morning (Thornton et al.,

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2010). Cl atoms react rapidly with BVOCs approximately about 10–100 times faster than corresponding OH radical reactions. Cl atoms can react with BVOCs by two competitive processes. First one is Cl atom addition to the carbon–carbon double bond to form chloroalkyl radicals and the second one is abstraction of a hydrogen atom to form an alkyl radical and HCl. Abstraction reaction is an endothermic process with estimated activation energy of (3–7) kcal mol<sup>-1</sup> (Stevens and Spicer, 1977; Lee and Rowland, 1977; Parmar and Benson, 1988; Dobis and Benson, 1991; Kaiser and Wallington, 1996; Pilgrim and Taatjes, 1997), whereas, addition reaction is an exothermic process and proceeds through a little or



no activation barrier (Stevens and Spicer, 1977). Therefore, at lower temperatures (<500 K), addition reaction is dominated over abstraction reaction, and at higher temperatures the abstraction reaction is more important than addition reaction. Although the global average concentration of Cl atoms is only about 10<sup>3</sup> atoms cm<sup>-3</sup> (Singh et al., 1996; Wingenter et al., 1999), which is three orders of magnitude lower than the global average OH concentration i.e., 10<sup>6</sup> radicals cm<sup>-3</sup> (Prinn et al., 1995), it is significantly higher in the marine boundary layer (MBL), coastal regions, reaching a peak concentration of about 10<sup>5</sup> atoms cm<sup>-3</sup> (Spicer et al., 1998). The main source of chlorine atoms is the photolysis of chlorine containing compounds generated in the sea-salt aerosols (Spicer et al., 1998; George et al., 2010). Recently, nitryl chloride (ClNO<sub>2</sub>) was observed to be a gaseous photolytic Cl atom precursor (Ravishankara, 2009; Thornton et al., 2010; Glasow, 2010), which is formed in the night-time reaction of N<sub>2</sub>O<sub>5</sub> with chloride-containing aerosol (Osthoff et al., 2008). The interaction of biogenic compounds with chlorine atoms can occur when sea breezes carry marine air masses inland and some biogenic compounds such as isoprene are expected to be emitted by the oceans as well (Bonsang et al., 1992; Moore et al., 1994; Milne et al., 1995; McKay et al., 1996; Ratte et al., 1998). These organics also can react with OH radicals during the day time, NO<sub>3</sub> at night time, and O<sub>3</sub> during both day and night times.

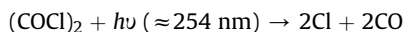
Limonene [4-isopropenyl-1-methyl-cyclohexene] is a naturally occurring monocyclic monoterpene emitted from vegetation. The purpose of this work is to study the kinetics of chlorine atoms with limonene as a function of temperature and pressure. This work provides the first kinetic data for the reaction of limonene with chlorine atoms as a function of temperature. To the best of our knowledge, only one investigation on Cl atom reaction with limonene is available in the literature (Finlayson-Pitts et al., 1999) at room temperature. Finlayson-Pitts et al. (1999) carried out the reaction at 298 K and 1 atm pressure using relative rate technique. The reported rate coefficient (in the units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) is:  $k(\text{limonene} + \text{Cl}) = (6.4 \pm 0.8) \times 10^{-10}$ . Temperature dependent rate coefficients for this reaction are not available in the literature till to date, to the best of our knowledge. In addition, theoretical calculations of the potential energy surfaces for this reaction at

various levels of theory are also presented to provide some additional insights into the energetics. The rate coefficients are also computed using conventional transition-state theory (CTST) in combination with Wigner's and Eckart's symmetrical tunneling methods in the temperature range of 275–400 K. The computed temperature dependent rate coefficients are compared with the experimentally measured rate coefficients and the available literature value at room temperature. The data obtained in this work were used to estimate the effective lifetime of limonene in the troposphere.

## 2. Experimental and computational methods

### 2.1. Room temperature study

Reactions were carried out in a quartz reaction chamber of ~1750 cm<sup>3</sup> volume at 298 K and ~800 Torr of N<sub>2</sub>/Air. The details of the experimental set-up are given elsewhere (Dash and Rajakumar, 2013; Dash et al., 2013) and only a brief description is given here. Cl atoms were generated by photolysis of oxalyl chloride ((COCl)<sub>2</sub>) at 254 nm, using two UV lamps (SANKYO DENKI G8T5, 8 W).



The reaction mixtures, consisting of limonene, 1,3-butadiene as a reference compound, oxalyl chloride, and nitrogen were prepared in the reaction chamber, using a vacuum manifold system. The prepared reaction mixtures were kept for 30–45 min for equilibration before photolysis, which was confirmed by repeatability of the gas chromatogram. The mixtures were photolyzed for a period of 30 s, in steps of 10 s, and after each photolysis step the decrease in the concentration of the limonene and the 1,3-butadiene were determined, using gas chromatograph (Agilent Technologies 6890N), with a flame ionization detector (FID). A sample of 300 μL was transferred from the reaction chamber (~2 L volume) to GC, using a gas-tight syringe in each GC analysis and which is negligible compared to the total volume of the reaction chamber. Therefore, the change in volume and concentration due to sampling in order to analyze the reaction mixture with GC/FID is negligible. The GC column used in this experiment was a capillary column (HP-5, 30 m × 0.320 mm × 0.25 μm, 19091J-413) run at 75 °C constant oven temperature. The column was operated at GC inlet temperature of 160 °C and detector temperature of 170 °C.

### 2.2. Temperature dependence study

The experiments were carried out in a double-walled Pyrex reaction chamber of ~1250 cm<sup>3</sup> volume closed at both ends by UV fused silica broadband precision windows (50.8 mm diameter, THORSLABS). The temperature in the reaction cell was maintained

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