Theoretical and experimental investigation of gas-phase reaction mechanism for ozonolysis of limonene

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Abstract

Total emissions of volatile organic compounds (VOCs) from vegetation have been estimated to be about 1150 Tg carbon per year. More than half (54%) of the emissions are related to isoprene and monoterpenes (11%), such as α- and β-pinene and limonene. It is important to note that on a global scale natural emissions far exceed anthropogenic ones. Being produced by more than 300 species, limonene or 4-isopropenyl-1-methyl-cyclohexene is the most abundant monoterpenes, which have both endocyclic and exocyclic double bonds. Numerous atmospheric and indoor studies have indicated the existence of several gas-phase limonene oxidation products including, e.g. limononaldehyde (3-isopropenyl-6-oxo-heptanal, IPOH), keto-limononaldehyde, limononic acid, keto-limononic acid, limona ketone (4-acetyl-1-methyl-cyclohexene, AMCH), formaldehyde, glyoxal, limonene oxides, acrolein, and various carbonyl compounds. The reaction of the O3 addition to double bond of limonene in the gas phase has been investigated using ab initio methods. Two different orientations of C–C double bonds have been considered and two corresponding van der Waals complexes (Cp11 and Cp12) have been found for endo and exo-double bonds. The primary ozonide (PO) formation by the initial reaction of cycloaddition of O3 to the double bonds of limonene subsequently undergoes unimolecular decomposition to yield a chemical activated biradical, know as the carbonyl oxide or Criegee intermediates (CI) and aldehyde. Four Transition States (TS21, TS22, TS23, TS24) associated with the formation of CI have been identified (Figure 1).

All the theoretical computations have been carried out on the SGI Altix 4700 super computer using Gaussian 03 Unix edition suite of programs. Based on the theoretical investigation, a small smog chamber (1.5 m³) experiment was carried out with PTR-MS (Proton Transfer Reaction Mass Spectrum) and EEPS (Engine Exhaust Particle Sizer) 3090 instrument. Wall effect of the smog chamber experiment was characterized with O3 attenuation in the rate of 1.83×10⁻⁶ cm³ molecule⁻¹ s⁻¹. The experimental results show that a series of secondary organic products were detected with high concentration, for example ketene, formaldehyde and acetic acid. Characteristics of nine kinds of gaseous organic compounds were identified according to the evaluation of theoretic method and paper reported. An important oxidation product named ketene was found with the analysis of PTR spectrum and the mechanism of formation was also clarified using quantum chemistry computational method.

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The present study focused on comparison of different reaction pathways and determination energetically favorable bonds needed for the further elaboration of the oxidation mechanisms and assessment of the products identified in experiments. Moreover, the study is more important to understand the O3-limonene reaction system even the Alkene-O3 reaction mechanism.

Figure 1 O3-limonene reaction Coordinates

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