

3P012

低分子量アルケン類と塩素原子の反応の圧力依存性

(¹名大院理・STE 研, ²フォード自動車)

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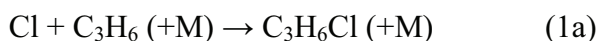
Pressure Dependent Rate Coefficients for the Reactions of Chlorine Atoms with Light Alkenes

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The reactions of chlorine atoms with hydrocarbons are of considerable interest with respect to understanding the chemistry of the lower atmosphere. Given the higher ozone-forming potential of alkenes compared to alkanes understanding their oxidation paths in marine and coastal areas is particularly important.

The title reactions are of special kinetic and mechanistic interest, since they proceed via multiple reaction channels. For example the reaction of chlorine atom with propene (C₃H₆) at room temperature gives two sets of products:



The reaction proceeds by chlorine atom addition to the double bond to form an excited adduct, and also by abstraction of a hydrogen atom through two different mechanisms: direct abstraction, and addition-elimination. Decomposition of the excited adduct competes with stabilization at low pressures. A precise understanding of these reaction channels requires further information on the kinetics and mechanism of the reactions of chlorine atom with smaller unsaturated hydrocarbons at low pressures.

We have conducted absolute rate studies of the reactions of chlorine atoms with propene (C₃H₆), ethene (C₂H₄), and acetylene (C₂H₂). Rate coefficients were measured over the range 2-20 Torr in N₂ at 295 ± 2 K using a pulsed laser photolysis / laser-induced fluorescence (PLP-LIF) technique. Molecular chlorine diluted in N₂ gas was photolysed at 351 nm to produce chlorine atoms in the presence of C₃H₆, C₂H₄, or C₂H₂. Cl(²P_{3/2}) atoms were detected by PLP-LIF at 134.72 nm corresponding to the 3p⁵2P_{3/2} - 3p⁴4s²P_{3/2} transition. By monitoring the temporal decay profiles of Cl(²P_{3/2}) atoms, the absolute rate coefficients for the reactions of Cl(²P_{3/2}) atoms with C₃H₆ (1), C₂H₄ (2), and C₂H₂ (3) were determined.

In this presentation, we will report the results from our PLP-LIF experimental study of the title reactions and compare these with the literature data. These data improve our understanding of the mechanisms of reactions of chlorine atoms with unsaturated hydrocarbon, and facilitate improved assessments of the atmospheric chemistry of C₃H₆, C₂H₄, or C₂H₂ in marine and coastal environments.