Laboratory study on the atmospheric reaction of cyclohexanone

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Ketones are an important class of oxygenated volatile organic compounds (VOCs) used as solvents and formed during the atmospheric oxidation of organic compounds. Some of them are directly emitted from vegetation and biomass burning. In general, they have harmful effects on the human health. For example, cyclohexanone studied in this work, in high vapor concentrations may cause drowsiness and eyes irritation or respiratory tract and prolonged or repeated skin contact may cause drying, cracking, or irritation. Quantification of their atmospheric impact requires knowledge of their origin and their removal processes. The atmospheric degradation of ketones is initiated by their photodissociation and chemical reactions with oxidants such as OH radicals, Cl atoms. The reaction with Cl atoms have been postulated to be an additional and significant removal process of VOCs in marine troposphere, where the concentration of Cl precursor species from the reactions of NaCl in sea salt particles has been reported to be high, and it may significantly contribute to the formation of ozone and other components of the photochemical smog in these areas. Photodissociation rates of ketones in the atmosphere depend on their absorption cross sections, their primary quantum yields and actinic flux. We therefore performed laboratory experiments to investigate the Cl-initiated oxidation processes of cyclohexanone by using a technique of pulsed laser photolysis / vacuum ultraviolet laser induced fluorescence spectroscopy (PLP-LIF). A small amount of Cl_2 in an excess amount of cyclohexanone diluted in Ar gas was photolysed at 351 nm to produce chlorine atoms, and the Cl($^2P_{3/2}$) atoms was detected by PLP-LIF at 134.72 nm ($3p^5\ ^2P_{3/2}$-$3p^4 4s\ ^2P_{3/2}$ transition). By monitoring the temporal decay of the relative concentrations of chlorine atoms, the absolute rate coefficients for the reactions of Cl($^2P_{3/2}$) atoms with cyclohexanone in 6 Torr of Ar diluents at 295 K have been determined. The rate coefficient is determined to be (1.94+-0.04)x10^{-10}cm^3 molecule^{-1} s^{-1}. In the present study, we also reported the absorption cross sections of cyclohexanone over the wavelength range 225-350 nm. The UV spectrum is Gaussian in shape centered at 289 nm with a maximum UV cross section of (3.8+-0.4)x10^{-20}cm^2 molecule^{-1}. The obtained data were used to estimate the photolysis lifetime of cyclohexanone and compared to that with respect to the reaction with Cl atoms.