LIF SPECTRA OF CYCLOHEXOXY RADICAL AND DIRECT KINETIC STUDIES OF ITS REACTION WITH O_2

LEI ZHANG, KATHERINE A. KITNEY, MELISSA A. FERENAC, WEI DENG and THEODORE S. DIBBLE, *Department of Chemistry, SUNY Environmental Science and Forestry, 1 Forestry Drive, Syracuse, NY 13210.*

Alkoxy radicals are important intermediates in the atmospheric degradation of volatile organic compounds (VOC) in the polluted air. Their chemistries in the atmosphere are of crucial importance for modeling smog chemistry. In this research, we measured the LIF spectra of cyclohexoxy at 226 K for the first time. A vibrational interval of about 690 cm^{-1} was observed to be the dominant progression, much higher than that dominating the spectra of the $\tilde{B}$ state of other alkoxy radicals. However, this is consistent with CIS/6-31G(d,p) calculations of the C-O stretch frequency for the axial conformer of cyclohexoxy radical. Based on these spectra, direct kinetic studies of the reaction of cyclohexoxy radicals with O_2 has been carried out for the first time using LIF to monitor the disappearance of cyclohexoxy radicals. The Arrhenius expression obtained for this reaction at 50 Torr is: $k_{O2} = (4.72 \pm 1.17) \times 10^{-12} \exp[(-13.8 \pm 0.6)$ kJ/mol/ RT] cm^3 $molecule^{-1}$ s^{-1} (225 - 301 K) Our room-temperature rate constant for the O_2 reaction with cyclohexoxy is not too different from Atkinson's recommended value, but both of our activation energy and A factor are larger than his recommendation. This leads to inconsistencies between the expected kinetics of the decomposition reaction and the Arrhenius parameters we obtain when we combine our k_{O2} results with the $k_{O2}/k_{decomposition}$ value obtained by Orlando's group.