

FTIR DETECTION OF THE TERT-BUTYL HYDROPEROXIDE DIMER

CASPER VINDAHL JENSEN, HENRIK G. KJAERGAARD, *Department of Chemistry, University of Copenhagen, Copenhagen, Denmark.*

We have detected the *tert*-butyl hydroperoxide dimer (*t*-BuOOH)₂ in gas phase at room temperature using conventional FTIR techniques. The dimer is identified by an asymmetric absorbance band assigned to the hydrogen-bound OH_b-stretch. The gas-phase dimer assignment is supported by Ar matrix isolation FTIR experiments at 12 K. The dimer OH_b-stretching band is located at $\sim 3452\text{ cm}^{-1}$ redshifted by $\sim 145\text{ cm}^{-1}$ from the monomer OH-stretching band. Theoretically, we find the lowest energy structure of (*t*-BuOOH)₂ to be a doubly hydrogen bound 6-membered ring. The ring strain in this structure leads to non-optimal H-bond angles and a smaller than expected redshift. We calculate the transition frequency and oscillator strength of the OH_b-stretching transition with a 1D local mode model and DFT electronic structure methods. The constant of dimer formation *K* is estimated from the experimental integrated absorbance and the theoretically calculated oscillator strength of the OH_b-stretching band. The unitless *K* is estimated to be ~ 0.41 for (*t*-BuOOH)₂.

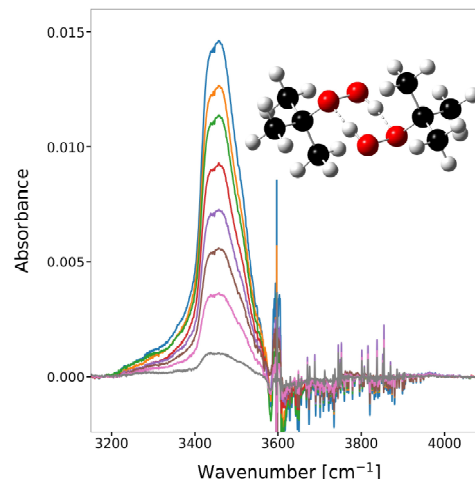


Figure 1: (*t*-BuOOH)₂ spectra at increased pressure.