M.Sc. THESIS ABSTRACT

TITLE: Computational Study of Conformational Behavior and Analyses of Vibrational Spectra of Some Ketenes.

FIELD: Physical Chemistry.

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The structural stability of a chosen set of important ketenes was investigated using ab initio calculations. The 6-311++G** extended basis set at the DFT-B3LYP level was employed in most of the work. Full energy optimization was performed at the ground states as well as the transition states for the systems under the study. It was found that when the conjugation effect in formyl ketene, fluorocarbonyl ketene, chlorocarbonyl ketene and vinyl ketene is dominant, theses systems exist as a mixture of *cis* and *trans* conformations. Moreover, they were of a relatively high-calculated rotational barrier as compared to the corresponding isocyanates. In the case of non-conjugated ketenic systems, such as trifluoromethyl ketene and chloromethyl ketene, the barrier to interconversion was calculated to be considerably lower and the *gauche* form was expected to appear as a stable form. In such systems, the steric effect, the intramolecular electrostatic attraction and the molecular orbital destabilization may play competitive roles in controlling the conformational behavior. The *cis* form was calculated to be the most stable conformation in tri- and difluoromethyl ketene with the *gauche* conformation being the less stable form in only the difluoro derivative. While in halomethyl ketene only the *gauche* form was the stable form. Additionally, complete normal coordinate analyses were performed to derive the potential energy

distributions (PED) for each stable conformation in the molecular systems. The calculated vibrational spectra for each system were plotted and reliable assignments of the vibrational wavenumbers were made based on the vibrational frequencies, calculated PED values, Raman activities, IR intensities, depolarization ratios as well as the observed frequencies of similar molecules.