ABSTRACT

EFFECTS OF ELECTRONEGATIVITY ON
MOLECULAR CHARGE DISTRIBUTION
AND
THE ENTHALPY OF FORMATION
OF BRANCHED AND CYCLIC ALKANES

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An expression for the electronegativity of multi-bonded atoms is formulated by incorporating the energy changes due to the electron occupation of their valence orbitals which is primarily based on Ruedenberg's[*] definition of the valence state atom-in-a-molecule. On applying Sanderson's[†] electronegativity equalization principle, consistent partial charges for sixty four (64) polyatomic molecules are determined. The partial charges obtained correlate with point charges derived from molecular electrostatic potential (MEP) methods. They are used to determine the electric dipole moment of molecules spanning seven homologous series and the electrostatic energy component of the enthalpy of formation for alkanes.

The electric dipole moment of thirty seven (37) molecules is calculated. The agreement between the calculated and experimental values give % deviations of less than 25% with the best agreement for the alkyne, alcohol, carbonyl and nitrile molecules. The electrostatic energy from the derived partial charges is calculated and used to determine the enthalpy of formation for thirty two (32) acyclic and cyclic alkane molecules. Replacing the empirical group energy parameters of Allinger[‡], an electrostatic energy component is included to account for the increased stability brought about by branching (branching effect) and decreased stability due to ring formation (cyclization effect). By taking into account the effect of hybridization, the enthalpy of formation is determined. The standard deviation of the calculated enthalpy of formation from the experimental values is 4.07 kcal mol^{-1} with optimized C-C and C-H hybridizations which gives calculated bond energies of -91.29 and -103.59 kcal mol^{-1} respectively. For the sp^3 hybridization, the standard deviation is 4.13 kcal mol^{-1} with calculated bond energies of -91.27 and -103.32 kcal mol^{-1} for the respective C-C and C-H bonds. However, the calculated enthalpy of formation with the optimized hybridizations give better agreement to the experimental data and therefore better models the branching and cyclization effects.

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