

Experimental and Computational Study of the Thermochemistry of Fluoro- and Chloro-Phenols

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Halogenated phenols are widely used in industry as intermediates in the production of polymers, surfactants, stabilizers, and other materials. Despite the practical importance of halophenols, relevant thermochemical information at the reference temperature $T = 298.15$ K is very restricted. Halophenols also demonstrate an interesting pattern for the study of intra- and intermolecular hydrogen bonding. Although ortho-halogenated benzenes are probably the most commonly cited examples of intramolecular Hydrogen bonding, there is still not enough thermodynamic data available to enable the formulation of a general rule regarding the quantitative values for its strength. The aim of this study has been to obtain insight into the energetics of the substituent interactions on the benzene ring, as well as the intramolecular H bonds in ortho-fluoro- and ortho-chloro-phenols. As a rule, the strength of the H bond has been quantified from experimental (stretching frequency shifts and torsional frequency shifts) as well as ab initio methods. Unfortunately, the ab initio computed strength of H bond for 2-fluoro- or 2-chloro-phenol is about two times the spectroscopically determined value for each compound! However, such comparisons can be misleading, since spectroscopic results also may be affected by geometric as well as by some other factors. In order to reconcile the experimental and theoretical results available in literature, thermochemical measurements have been performed. We have performed thermochemical measurements (combustion calorimetry and vapor pressure measurements) on isomeric mono-fluoro-phenols. Sublimation and vaporization enthalpies of a number of di-chloro-benzenes, mono-, di-, tri-, and penta-chloro-phenols have been measured using the transpiration method. The interactions between substituents on the benzene ring and the strengths of intramolecular hydrogen bonding in halophenols have been derived and discussed in terms of the difference between the experimental gaseous enthalpy of formation and the sum of the group-additivity increments.

In addition, the high-level ab initio calculations of the halogenated benzenes and phenols have been performed using the GAUSSIAN-03 program package. Absolute electronic energy values of the molecules have been obtained at the G3(MP2) level of theory. Calculated gaseous enthalpies of formation data are found to be in acceptable agreement with the data obtained from the thermochemical measurements.

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