

CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

Enthalpy of Formation of Acyclic Saturated Ketones*

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Abstract—The dependences of $\Delta_f H$ on the size of molecule, position of carbonyl group, and branching of molecule are investigated at the PM5 level of theory. The major part of $\Delta_f H$ is determined with the size of molecule, whereas fine structure of $\Delta_f H$ is determined with the branching of molecule and position of carbonyl group.

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INTRODUCTION

Enthalpy of formation ($\Delta_f H$) is an important physico-chemical property of substances, from which one can calculate enthalpies of reactions before performing experiments. Like many other properties, enthalpy of formation is dependent on molecular structure. This is illustrated with Fig. 1, where a plot of $\Delta_f H$ versus the number of carbon atoms n of 2-ketones is presented. The dependence of $\Delta_f H$ on the size of molecule is obviously linear, where only the value for 2-octanone deviates from linearity (the correlation coefficient for this straight line where 2-octanone is excluded from consideration is equal to -0.99997).

It is well-known that boiling points of ketones are influenced by the position of carbonyl group within a molecule. One can suppose that enthalpy of formation of ketones also depends on the position of carbonyl group, and perhaps on some other structural details. To examine the dependence of enthalpy of formation of ketones on molecular structure it is necessary to calculate the values for those ketones for which the experimental enthalpies are not available.

In the past decade, accurate prediction of the enthalpies of formation of gas-phase molecules has been achieved via high level quantum chemistry methods. For more information on the applications of quantum chemical calculations to thermochemical quantities a reader is referred to the review [1] and the references given therein. As for ketones, the G2 *ab initio* approach was applied to calculate enthalpies of formation of cyclopropanone, cyclopropanone, and acetone [2]. Similar methodologies have not been employed in calculation of $\Delta_f H$ values of larger ketones.

To examine the dependence of $\Delta_f H$ of ketones on molecular structure, molecules of interest are much larger than those that can be studied by means of G2 and G3 theories. Thus, computational methods that are less CPU demanding are necessary. Bond and

group additivity approaches based on an empirical experimental data set have been widely used in estimating enthalpies of formation. A combined HF/6-31*—empirical scheme for calculating enthalpies of formation of carbonyl compounds was developed [3]. In addition, molecular mechanics MM3 and MM4 calculations of the enthalpies of formation for about 50 open chain, ring, and fused ring carbonyl compounds were performed [4]. The MM4 calculated enthalpies of formation showed improvement over those of MM3.

In some cases, the disagreement between the experimental and calculated values (using either the bond and group equivalent scheme or molecular mechanics methods) was observed [3, 4]. It was concluded that the experimental enthalpies of formation of some carbonyl compounds (e.g. cycloheptanone and norbornanones) were seriously in error.

There is an ever growing demand for semiempirical methods, especially for investigations of larger molecular systems, where *ab initio* and density functional

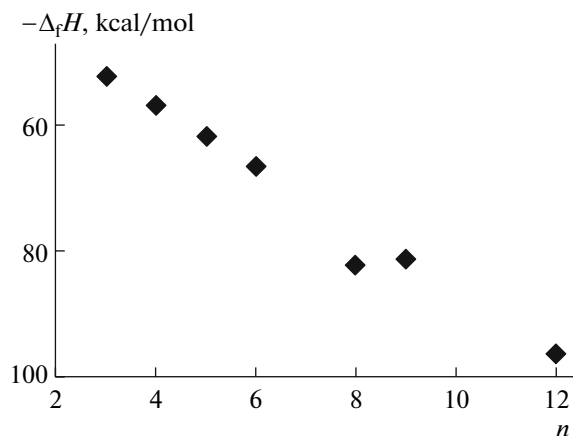


Fig. 1. Experimental enthalpy of formation of 2-ketones versus number of carbon atoms.

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