Final Report for DOE Grant

The objective of these investigations was to gain information on the energies of organic compounds and on the factors that control energies. The work involved calorimetric measurements of energy changes and theoretical studies of intramolecular interactions and molecular energies.

a. Ketal and Acetal Hydrolysis:

A computer controlled reaction calorimeter was developed which allowed precise determinations of enthalpies of reaction.\(^1\) It made use of a quartz thermometer as the temperature sensing element allowing temperature changes to be measured to ±0.0001°. The entire calorimetric process was controlled by the computer including an electrical calibration, and the final result was the enthalpy of reaction. The precision and accuracy were checked by the use of the standard reaction of TRIS with 0.1N HCl.

The enthalpies of hydrolysis of a series of acetals\(^2\) and ketals\(^3\) was examined, and led to the observation of an important steric interaction resulting from the conversion of a tetrahedral carbon to trigonal. Since the heats of formation of the carbonyl compounds were known, the data provided the heats of formation of the acetals and ketals.

In a continuation of this study, the enthalpies of hydrolysis of a series of orthoesters also were studied.\(^12\) Here, the product is the normal ester, and allowed the examination of the energetic effects of groups on the tetrahedral to trigonal conversion with different groups attached to the central carbon.

The hydrolysis of norbornyl ketals also was examined in order to gain information on the effect of methyl groups at different positions on this rigid ring system on the energetics of the tetrahedral to trigonal conversion.\(^19\)
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b. Enthalpies of hydration of alkenes.

Enthalpies of formation of many common alcohols have not been determined experimentally. Also, the enthalpies of formation of some common alkenes were not as well determined as one might like. We have developed a system in which the heats of hydration of alkenes may be measured.\textsuperscript{4,9} In examining a series of alkenes that give the same product alcohols, it was possible to determine the relative enthalpies of formation with high precision, and this allowed the enthalpies of formation of the alkenes to be better determined. In some cases, it was found that the literature values were in error by over 1 kcal/mol. The enthalpy of formation of alcohols were then obtained from the improved energies of the alkenes and the heats of hydration.

The method also was applied to a series of cycloalkenes in order to obtain better information on the difference in energy between exocyclic and endocyclic double bonds.\textsuperscript{11}

c. Enthalpies of reduction of carbonyl compounds.

Aldehydes, ketones and alcohols are among the most important of organic compounds, and it appeared that a method of interrelating their energies might prove useful. We have developed a reaction that allows precise determination of heats of reduction of the carbonyl compounds - reduction with triethylborohydride in diglyme solution.\textsuperscript{21} The data provided new heats of formation for some carbonyl compounds and alcohols. The additional information gained in this study allowed us to make a careful examination of the difference between a methyl group and a hydroxy group as the substituent on primary, secondary and tertiary carbons.

It also proved possible to carry out reductions of esters to two molecules of alcohols, and this provided a useful alternative to the use of hydrolysis reactions in studying energies of alcohols. It was applied to a series of lactones, and allowed the determination of the effect of ring size on the strain energies of lactones.\textsuperscript{22}
d. Rotational barriers.

One of the important intramolecular effects is that which leads to barriers to rotation about single bonds. We have examined a number of these cases theoretically via ab initio molecular orbital calculations. The rotational barriers in carbonyl compounds was found to result in part from an attractive interaction between an alkyl group and the carbonyl group.\textsuperscript{10} The difference between an \textit{n}-propyl group and an isopropyl group attached to a ketone carbonyl was studied, and was found to arise from a reduction in the number of low energy conformers.\textsuperscript{13}

The rotational barrier in 1,2-dihaloethanes was examined, with special attention to the preference for a gauche arrangement with 1,2-difluoroethane.\textsuperscript{14} This was shown to result from the formation of bent bonds which weakens the C-C bond in the trans forms, but does not affect the gauche form to a significant extent.\textsuperscript{20}

The rotational barrier in 2-haloethanols was examined, and it was found that the gauche form was stabilized by a hydrogen-bond like interaction between the alcohol proton and the halogen.\textsuperscript{17}

The rotational barrier in esters and amides was studied and led to a revised interpretation of resonance interactions in these systems.\textsuperscript{15}

e. Other studies:

Procedures for converting ab initio calculated energies into heats of formation were studied, and were found to give an average deviation with respect to the observed values of about $\pm 1$ kcal/mol using the HF/6-31G* model.\textsuperscript{8} Non-bonded interaction that are important in molecular modeling were studied.\textsuperscript{16} The relationship between bond bending and hybridization also was studied.\textsuperscript{18}
Publications derived from DOE Grants


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