

DOE/ER/13460--1

Technical Progress Report

Energies of Organic Compounds

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DE-FG02-86ER13460

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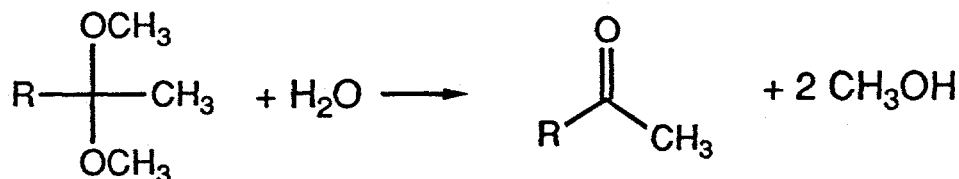
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1. Hydrolysis of Ketals. Our study of the enthalpies of hydrolysis of ketals and related compounds has now come full circle. We began with the experimental observation that α -substitution in R:



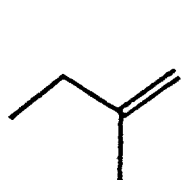
(i.e. replacing n-propyl by isopropyl) had no significant effect on the enthalpy of reaction,¹ whereas with the closely related orthoesters,² there was a large effect as would be expected from considerations of steric interactions. In order to gain an understanding ^{of} the anomalous α -substitution effect with ketals, we carried out a number of theoretical calculations.

We were able to show that the preferred conformation of aldehydes and n-alkyl ketones resulted from a dipole-induced dipole interaction between the carbonyl dipole and the C-C bond of the substituent.³ We then went on to examine α -substituted compounds, and found that α -substitution with ketones led to a destabilizing gauche interaction.⁴ As a result, these ketones are destabilized by ~ 1 kcal/mol. It is this destabilization of the ketones which leads to the anomaly described above. This important interaction had not been previously recognized.

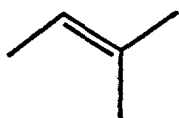
David Goldsmith (Emory University) had studied some methyl substituted decalones, and found that the commonly used MM2 molecular mechanics program predicted a cis/trans isomer ratio which was the opposite of that observed experimentally. Clark Still (Columbia) used our calculated barriers to reparameterize MM2 torsional interactions. With these new parameters, the correct cis/trans ratio was calculated. This has proven to be a very satisfactory interaction between experiment and theory - and back to experiment.

2. Hydrolysis of 2,2-Dimethoxynorbornanes. Our study of the hydrolysis of 9 methyl substituted derivatives has been prepared for publication and will shortly be submitted to J. Org. Chem.

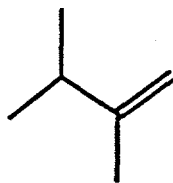
3. Hydration of Alkenes. There is considerable interest in substituent effects on alkenes. In a continuation of our study of the enthalpies of hydration of alkenes,⁵⁻⁷ we have examined the following compounds:



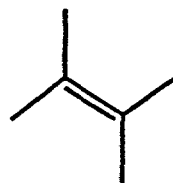
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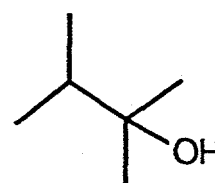
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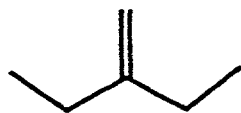
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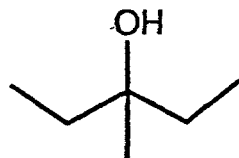
-8369+23



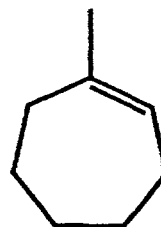
-21063+46



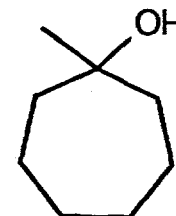
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-21030+16



-7563+23



-20389+59

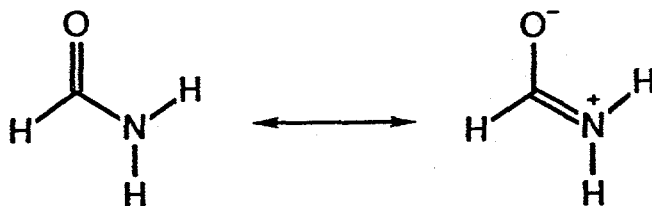
The energies shown are for reaction with trifluoroacetic acid containing 0.25 M trifluoroacetic anhydride. The compounds in the first line provide precise values for the difference in enthalpies of formation between isomeric alkenes which differ in the degree of substitution at the double bond. The data are considerably more precise than those obtained via enthalpies of combustion or enthalpies of hydrogenation. These energy differences have been of interest to chemists for many years.

The enthalpies of reaction of an alkene and of its corresponding alcohol may be used to determine the enthalpy of hydration. If ΔH_f of the alkene is known, the data lead to ΔH_f of the alcohol. The tertiary alcohols are of particular interest to us because there are few data for their enthalpies of formation, and because

these are the alcohols which are most likely to show significant steric interactions.

4. Barrier to Rotation about C-O Bonds in Esters and Acids. Our study of the barrier to rotation about the C-C bonds adjacent to carbonyl groups^{3,4} led to our interest in the barrier on the other side of the carbonyl (i.e. the C-O bond) in esters and acids. We have calculated the barrier for formic acid, methyl formate, acetic acid and methyl acetate. Whereas the 6-31G* basis set generally gives good predictions of the C-C barriers, it was necessary to include diffuse functions and electron correlation in order to reproduce the experimental data for the C-O bonds.

In order to gain an understanding of the E/Z energy differences, we carried out an extended study of structural effects on carbonyl groups, and of the barrier to rotation in formamide. Whereas the barrier in the amide is normally attributed to amide resonance:

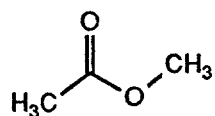


which would be lost on rotation, the computational results did not support this idea. The C=O bond length as well as the electron population at oxygen was hardly affected by rotation about the C-N bond. On the other hand, the C-N bond length as well as the C and N electron populations changed markedly. Thus, the barrier is concerned just with the interaction between C and N. A similar situation was found with the esters.

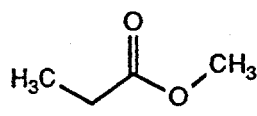
5. Hydrolysis of Lactones. Our theoretical study of esters showed that with methyl acetate, the Z conformer was 8.5 kcal/mol more stable than E. This suggested that lactones with 8 or less atoms in the ring, which must adopt the E conformation,

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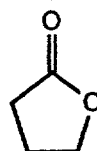
should be destabilized with respect to open chain esters which always take the Z arrangement. We have begun to examine this experimentally by measuring the enthalpies of hydrolysis of esters. Our experimental enthalpies of reaction with sodium hydroxide in aqueous ethanol are as follows:



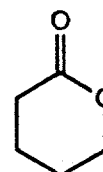
-10361+24



-9847+48



-12330+12



-14032+17

6. Reduction of Ketones. We have designed a new completely sealed calorimetric vessel which has an integral stirrer. The stirrer is a specially designed magnetic stir bar which can be operated via an external magnet. This has been successful in reproducing the literature values for the heats of reduction of acetone and of cyclopentanone via measurement of their heats of reaction with a complex metal hydride, and of the reaction of the corresponding alcohol with the reagent. The continuation of this study is described in the proposal section.

7. Non-bonded Interactions. Our interest is in developing better ways in which to predict the properties of organic compounds via procedures such as molecular mechanics. One of the least understood of the intramolecular potentials which are used in these procedures are those for non-bonded interactions. They are, of course, responsible for steric interactions. We have carefully examined the available theoretical data for hydrogen-hydrogen interactions, and have developed an expression which fits the data quite well, and incorporates the anisotropic nature of the interaction. This study has been prepared for publication.

8. Enthalpies of Vaporization. The enthalpies of vaporization of 2 ketones and 9 ketals have been measured, along with several other compounds. These data show that the assumption that liquid phase and gas phase energy differences would be

related in a simple linear fashion is only a rough approximation. We are in the process of measuring the enthalpies of vaporization of other classes of compounds. All of the available data on heats of vaporization have been collected, and have been fit fairly well via a group equivalent scheme.

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