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Technical Progress Report

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DISCLAIMER

I. Introduction

Chemists have a continuing interest in the factors which control rates and mechanisms of reaction. With the exception of reactions which have very early activated complexes, changes in relative energies of reactants and products will be reflected, at least in part, as a change in activation energy. Thus, a knowledge of the heat of reaction is essential to the study of most mechanistic problems. Even for reactions which have early activated complexes, energetic effects in the form of steric effects may strongly influence the course and/or stereochemistry of a reaction.

Thermochemical data are of value in many other contexts. Efforts to prepare organic compounds from alternate feed-stocks (such as coal) via catalytic methods would be facilitated by a knowledge of the energies of each of the compounds which might be formed. A knowledge of the thermodynamics of a reaction is essential in designing a plant for its utilization in preparing a compound on a large scale. Thermochemical data are essential in the calculation of the efficiency of various chemical methods for solar energy storage and conversion. I believe it is fair to say that thermochemical information lies at the heart of most chemical problems.

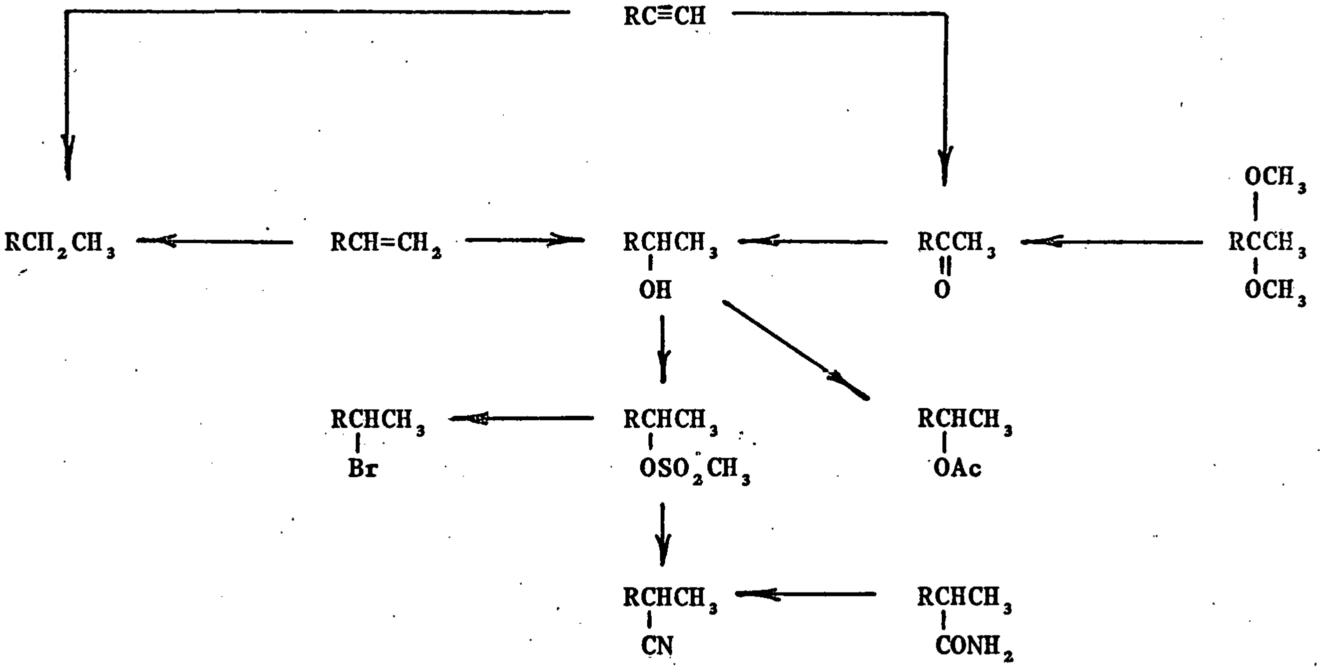
It is now possible to estimate the enthalpies of formation of many saturated hydrocarbons using molecular mechanics,[1] and experimental values, derived from enthalpies of combustion,[2] are available for many of them. However, data for the more interesting hydrocarbon derivative, such as alcohols, ketones and ester, are much less available. These data are needed if chemists are to make effective use of thermochemical information. Ideally, one would like to have a convenient method which would allow the reliable estimation of their thermochemical properties.

One of the simplest ways, of estimating the energies of compounds containing functional groups makes use of group replacement equivalents.[3] They give the change in energy on going from a parent saturated hydrocarbon to its functionalized derivative, and may take some structural factors into account. However, they have limited ability to take steric and conformational problems into account. Molecular mechanics provides a more powerful method for estimating both energy and conformation, and for including steric and polar effects. Both of these methods are empirical or semi-empirical and depend on the availability of data on key compounds in order to allow one to obtain the necessary parameters. Since there are surpisingly few data on enthalpies of formation of simple organic compounds, other than hydrocarbons, more data are required if these approximate methods are to become generally useful.

One way in which to obtain the needed data is via oxygen bomb calorimetry. Although this is essential for at least some of the compounds of interest, it does have serious disadvantages. First, it requires very high precision. The enthalpy of combustion of cyclohexane is 924.44±0.24 kcal/mol, the uncertainty interval is only 0.01% of the measured value. When this is converted into the more useful enthalpy of formation, it becomes 24.33±0.24 kcal/mol. Here the uncertainly is 1% of the value. Thus, exceptional precision in the measured quantity still results in only fair precision in the derived quantity.

A second problem is that systematic errors may frequently make the accuracy of the measurement significantly less satisfactory than the precision. In the case of the n-hexenes, we have been able to show that some of the reported enthalpies of formation are in error by more than 1 kcal/mole whereas the reported uncertainty intervals were on the order of 0.3 kcal/mole.[4] A third problem is the amount of material which is needed. Although micro bomb calorimeters have been designed,[5] they are satisfactory only for non-volatile solids, and some high boiling liquids. Even when they are applicable, they do not provide the possibility of analyzing the contents of the bomb after combustion in order to quantitatively determine the amount of carbon dioxide formed. In the case of a standard oxygen bomb calorimeter, a sample size of 0.3-0.5g is necessary, and a minimum of six runs should be made, especially since all are not likely to be successful. Thus, 2-3g of exceptionally pure material is needed if all goes well. This is frequently not practical.

Our interest in learning more about the energies of organic compounds has led us to make use of reaction calorimetry. This has two advantages over oxygen bomb calorimetry. First, the quantity of interst is measured directly rather than being obtained as the small difference between two large numbers. Second, it can be carried out using considerably smaller quantities of material than is possible in bomb calorimetry. In order to obtain the data of interest, we have made a start at carrying out a series of transformations, all of which may be related to some saturated hydrocarbon. The concept may be illustrated by the following equations:



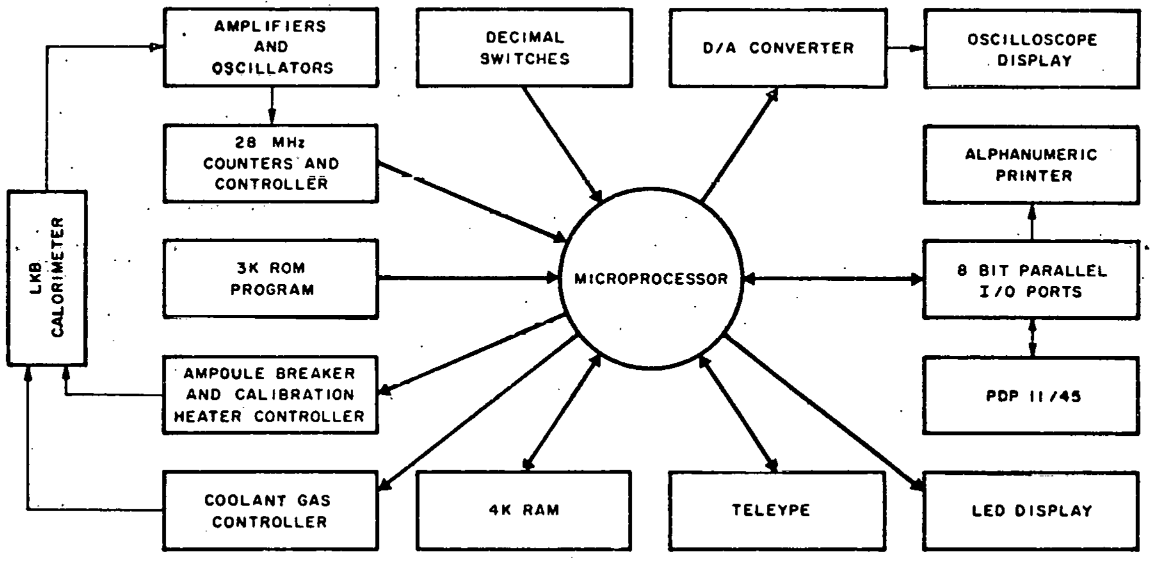
Enthalpies of hydrogenation of alkenes and alkynes have been measured,[6] and have been one of the important sources of information concerning structural effects on energies of these compounds. We have been able to effect hydration of alkenes[4] (cf. progress report) and we believe a similar approach will allow us to obtain the enthalpies of hydration of alkynes. We have investigated the reduction of carbonyl compounds to alcohols, and we are cautiously optimistic that this may be carried out in a fashion suitable for calorimetry. We have studied the enthalpies of hydrolysis of ketals,[7,8] acetals[9] and orthoesters (cf. progress report), and we also have studied the enthalpies of conversion of alcohols to esters with anhydrides. Thus, most of the reactions have been demonstrated to be suitable for reaction calorimetry. The other reactions have not as yet been studied, but we believe that it will be possible to obtain suitable conditions. It may be noted that some of the reactions are part of cycles. The completion of a cycle would provide a separate assessment of the accuracy of our results.

If calorimetric data are valuable, why have so few organic chemists chosen to obtain such data? One reason is that the methods available for carrying out the experiments have generally not been convenient, and required much operator attention during the course of the experiments. In order to remove this impediment to obtaining a relatively large amount of data with high precision, we have worked on developing automated reaction calorimetry systems (cf. progress report). It is now only necessary to set up the experiment - all subsequent operations (data collection, ampoule breaking, electrical calibration) are carried out automatically under computer control. In this way, the scientific personnel can spend most of their time in the preparation of compounds, their purification and analysis, as well as studying other reactions which may be prove to be satisfactory for calorimetric investigation. The progress report will present our results on the development of the calorimetric systems, and of their application to chemical problems.

II. Progress Report

A. Reaction Calorimetry Systems. One of the goals of our research program is to obtain a large amount of high quality calorimetric data. Manual methods of data collection appeared inadequate for this purpose, and thus, we were led to develop automatic computer controlled systems.

Our first automated calorimeter made use of a quartz thermometer as the temperature measuring element. This gives a 28 MHz signal which changes by 1000 Hz per degree C. By using a 10 sec. measuring period, we are able to resolve 0.1 millidegree. A pair of 28 MHz counters were constructed as interfaces for a microprocessor, and in order to minimize the normal quantization error usually associated with counters, a data synchronizer was included so that all of the pulses from the quartz thermometer were counted by one or the other of the pair of counters. A diagram of the calorimetric system is shown below, and it has been described in more detail.[7]



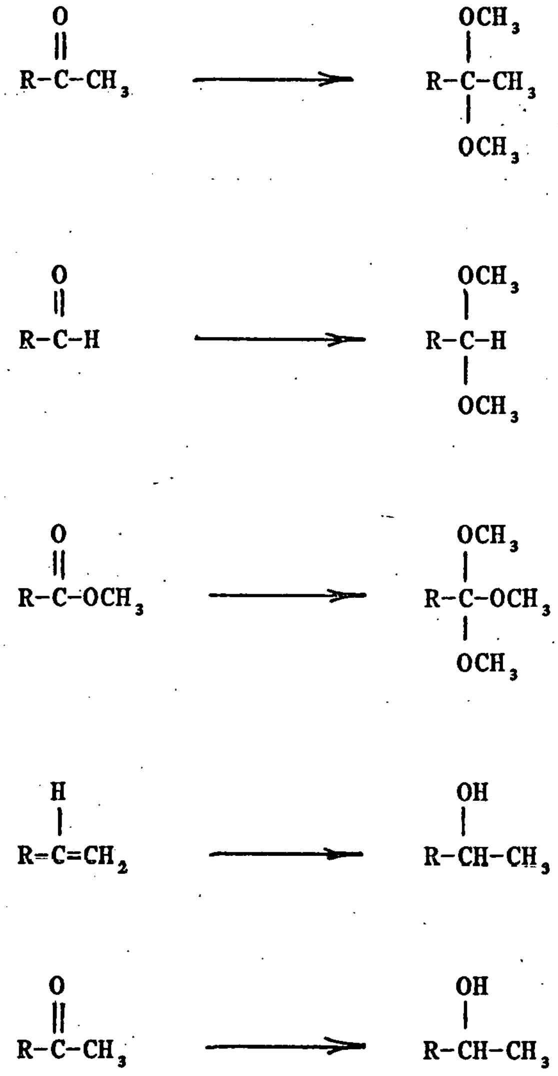
Block diagram of calorimeter-data collection system

Subsequently, we have further improved the design of the calorimetric system. Improved heating and timing circuits have been constructed, and the entire microcomputer has been rebuilt in order to improve reliability. The major change, which has not as yet been completed, is concerned with the frequency counters. The integrated circuits which carried the 28 MHz signal frequently failed after some months of use. The new design mixes the 28 MHz sensor signal with a crystal controlled 30 MHz signal to give an 2 MHz beat frequency. This is more easily counted, and should considerably decrease the maintenance which is required. The new system is one which could easily be duplicated by other investigators.

In operation, the sample is weighed into a 1 ml glass ampoule which is sealed and placed in the calorimetric vessel along with the reaction solvent. The calorimeter is placed in a constant temperature bath and is allowed to come to equilibrium. The computer begins the temperature measurement, and when it reaches 25.0000°, the ampoule is caused to break. After the data for the run has been collected, the vessel is automatically cooled to the original temperature, and an electrical calibration is carried out without the need for operator intervention. Finally, the data are transferred to a larger computer for processing.

The one disadvantage of this system is the relatively large size of the quartz sensor (3/8 x1/2). A second system was constructed using a thermistor as the temperature measuring element. Here, the thermistor was part of a Wheatstone bridge circuit. The resistors in the bridge and the gain of 1000 instrumental amplifier were contained in a shielded box which was thermostatted to ±0.1° in order to minimize noise and drift. The off-balance voltage from the bridge was measured using a 6 1/2 digit digital voltmeter, and transferred to the microprocessor. Except for the temperature measuring system, the other parts were a duplicate of that used in the first system. A more detailed description of this calorimeter will appear in a forthcoming paper.

B. Enthalpies of Hydrolysis of Ketals, Acetal, and Orthoesters. The application of molecular mechanics to carbonyl compounds, alcohols and ethers requires a detailed knowledge of steric interactions involving these groups.[10] Steric effects are frequently most easily studied by examining the interconversions of trigonal and tetrahedral carbons. Some examples of these reactions include:



$$R-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow R-\underset{OCH_3}{\overset{OCH_3}{C}}-CH_3$$

$$R-\overset{O}{\overset{\|}{C}}-H \longrightarrow R-\underset{OCH_3}{\overset{OCH_3}{C}}-H$$

$$R-\overset{O}{\overset{\|}{C}}-OCH_3 \longrightarrow R-\underset{OCH_3}{\overset{OCH_3}{C}}-OCH_3$$

$$R=\overset{H}{\overset{|}{C}}=CH_2 \longrightarrow R-\overset{OH}{\overset{|}{CH}}-CH_3$$

$$R-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow R-\overset{OH}{\overset{|}{CH}}-CH_3$$

Our initial investigation of these conversions made use of the first three reactions. In order to have data which might readily be compared with the extensive data on steric effects on rates of reaction, we examined the classical series of substituents in which R= CH_3, C_2H_5, $n-C_3H_7$, $i-C_3H_7$, $2-C_4H_9$, $i-C_4H_9$, $t-C_4H_9$ and neopentyl. The results are summarized in Table I, and were derived from measurements of enthalpies of reaction of the ketals, etc. with dilute acid in aqueous dioxane, along with measurements of the enthalpies of solution of the products.[7,8,9]

A plot of enthalpies of hydrolysis agains the Taft steric parameter (E_s)[11] did not show a linear relationship (Figure 1). Since the E_s values represent free energy difference rather than enthalpy changes, we also measured equilibrium constants for the first two reactions. Here, a linear relationship with E_s was found (Figure 2). The free energy changes for the smaller substituents were considerably larger than the enthalpy changes.

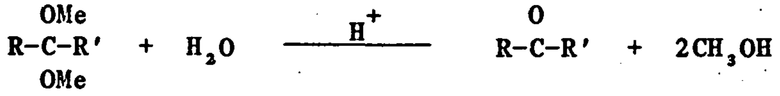
It is clear from these results that a large part of the steric effect arises from a change in entropy. One good possibility is that steric hindrance to solvation may be involved. This will receive further discussion in the proposal section.

In order to try to understand the changes in enthalpy in the three series, we have carried out a series of molecular mechanics calculations on the difference in energy between ketals and ketones. The main conclusion of this study was that many of the compounds had a number of conformations of approximately equal energy. Thus, it was not possible to make use of these data to adjust the parameters used in the calculations. They will, however, prove valuable in testing parameters derived from other studies.

<u>C. Hydrolysis of Norbornyl Ketals.</u> The results of the above study made it clear that we needed data for a series of compounds which had fixed conformations, and would allow a wide range of steric interactions. If a set of molecular mechanics parameters could be obtained which would reproduce these experimental data, they could then be tested with the open chain compounds.

TABLE 1

Enthalpies of Hydrolysis of Orthoesters, Ketals and Acetals, 25°C



$$\underset{\text{OMe}}{\overset{\text{OMe}}{\text{R-C-R}'}} + H_2O \xrightarrow{H^+} \overset{\text{O}}{\text{R-C-R}'} + 2CH_3OH$$

R	Orthoesters $R'=OCH_3$		Ketals $R'=CH_3$		Acetals $R'=H$		E_s
	ΔH	ΔΔH	ΔH	ΔΔH	ΔH	ΔΔH	ΔΔG
Me	-6463 ± 7	0	4884 ± 7	0	8622 ± 15	0	0.00
Et	-6280 ± 17	183	4620 ± 8	-264	8499 ± 17	-123	-0.20
n-Pr	-6315 ± 14	148	4666 ± 14	-218	8732 ± 23	110	-0.36
n-Bu	-6147 ± 8	316					-0.39
i-Pr	-7836 ± 14	-1373	4858 ± 9	-2	8698 ± 16	76	-0.47
2-Bu	-8197 ± 13	-1734	4762 ± 11	-122	8134 ± 33	-488	-1.13
i-Bu	-7367 ± 15	-904	3284 ± 13	-1600	8342 ± 23	-280	-0.93
t-Bu			819 ± 13	-4065	7925 ± 19	-697	-1.54
neopent			1642 ± 21	-3242	7968 ± 35	-654	-1.74

a. all enthalpies are in cal/mole
b. Uncertainties are given as two times the standard deviation from the mean (2s)
c. standard state is the pure liquid phase

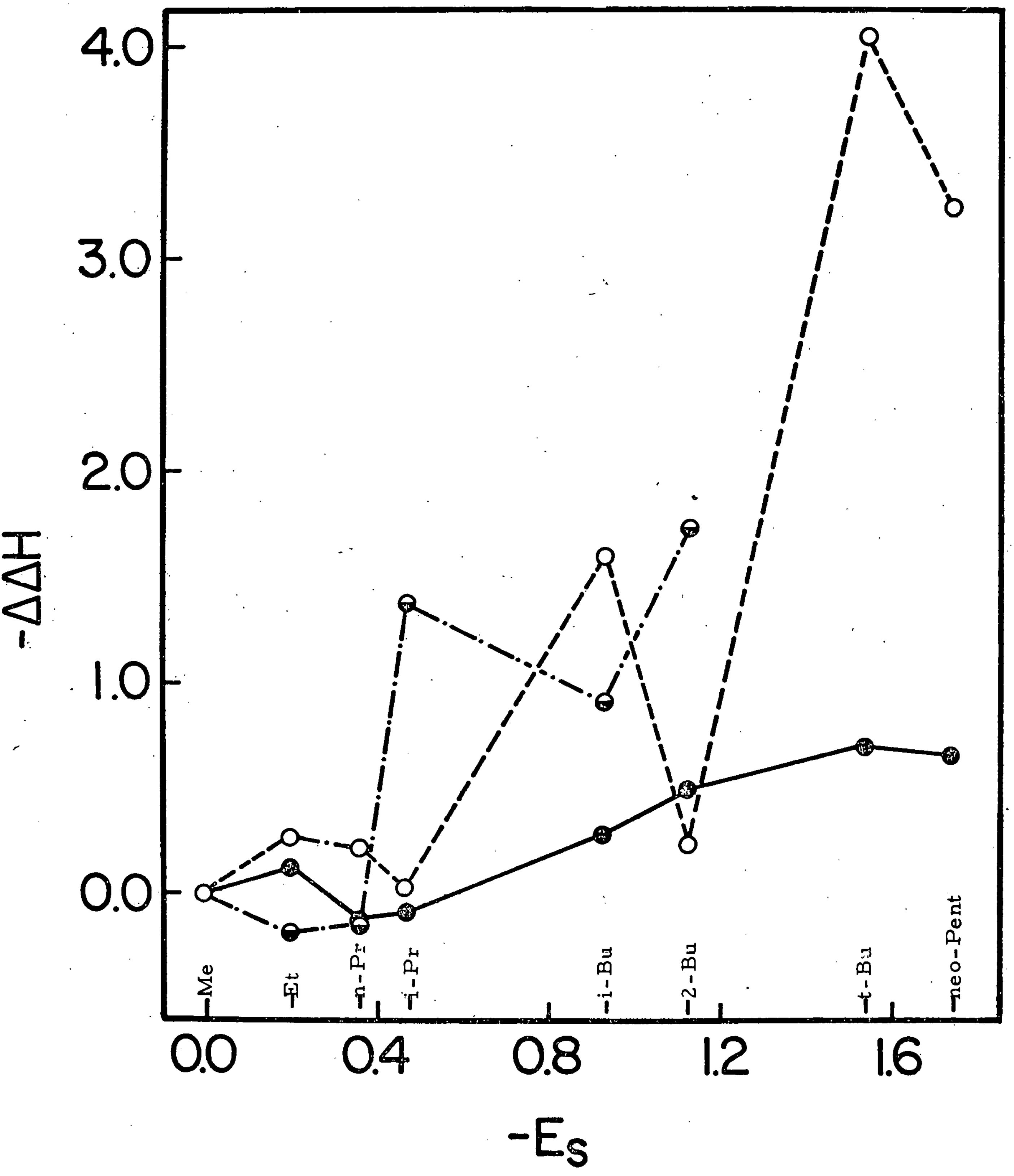


Figure 1. Relationship between enthalpies of hydrolysis of acetals (closed circles), ketals (open circles) and orthoesters (half circles) and the steric parameter E_s.

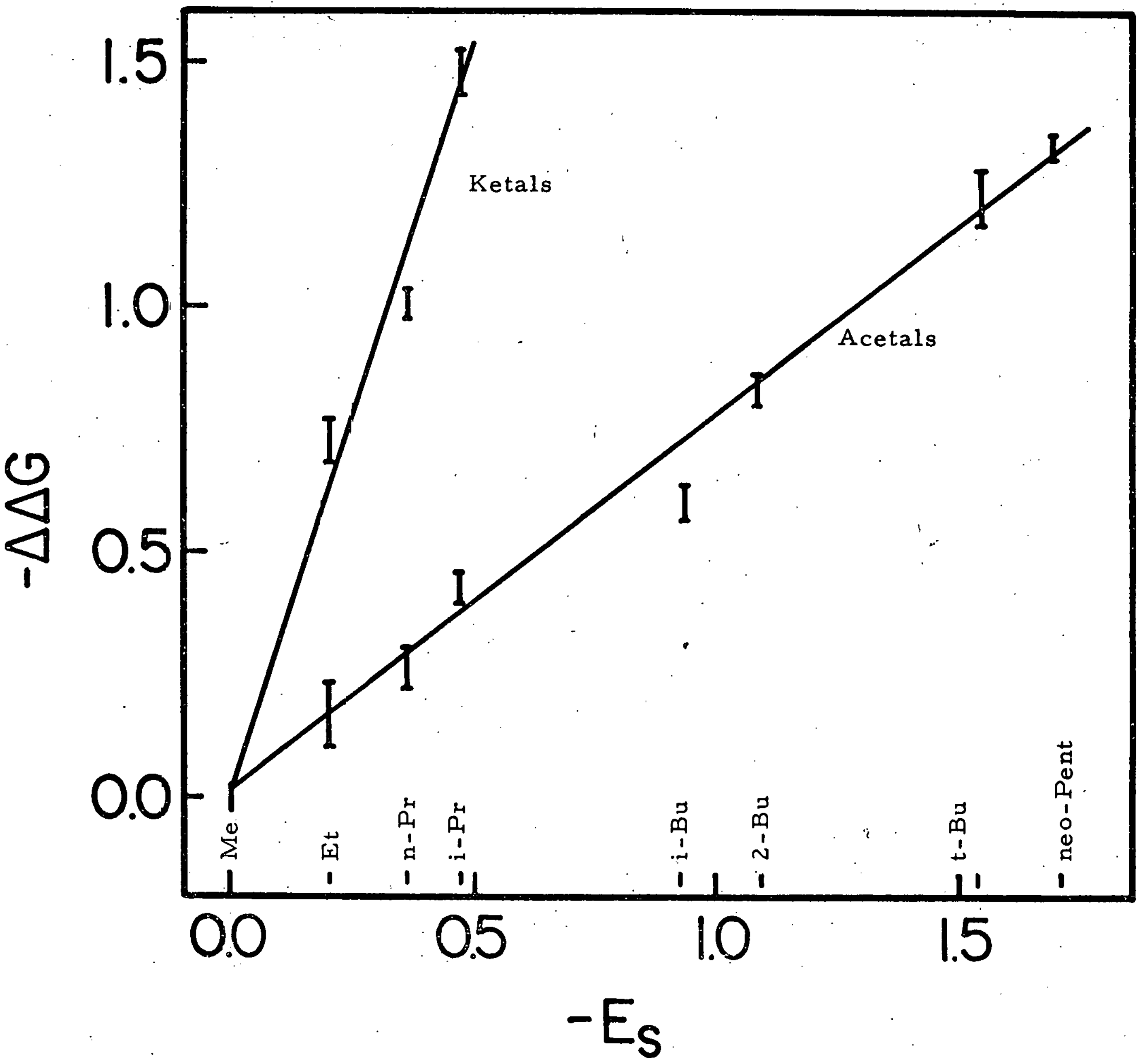
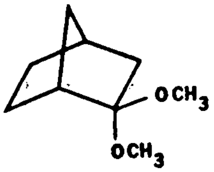
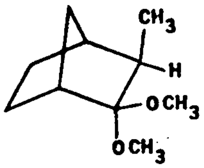
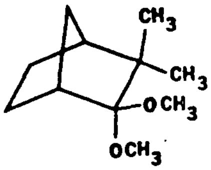


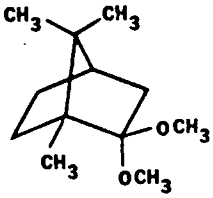
Figure 2. Relationship between the free energies of hydrolysis of ketals and hemiacetals and the steric parameter E_s.

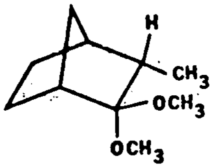
We have chosen to examine a series of norbornyl ketals:

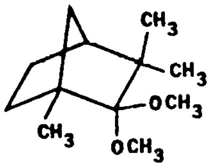


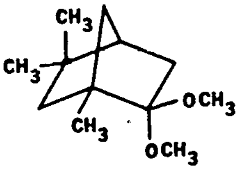


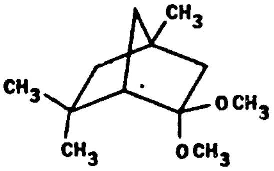












We have prepared the first four ketals, and we believe we now have methods available for the preparation of the ketones corresponding to the remaining ketals. In the case of severely hindered ketones, such as camphor, the conversion to the ketal using methyl orthoformate does not proceed to completion. In these cases, it was possible to remove the ketone from the mixture using a measured amount of diisobutylaluminum hydride. In this way, pure samples of the ketals could be obtained, as indicated by the lack of carbonyl absorption in the infrared. Preliminary values of the enthalpies of hydrolysis have been obtained, and are recorded in Table II.

Table II

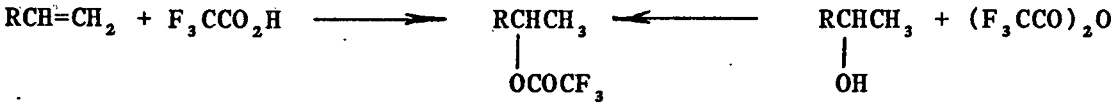
<u>Enthalpies of Hydrolysis of Norbornyl Ketals</u>

Compound	ΔH_{hydrol}
Norbornyl	6088
exo-3-Methylnorbornyl	5114
3,3-Dimethylnorbornyl	2661
1,7,7-Trimethylnorbornyl	1595

The range of enthalpies of hydrolysis is large in this case, making it an ideal system for the present purpose. The continuation of this study will be described in the proposal section.

D. Enthalpies of Hydration of Alkenes. The enthalpies of hydrogenation of alkenes has proven very valuable in the study of unsaturated compounds.[12] Enthalpies of hydration have the potential of giving even more information since the product has a functional group. The conversion of an alkene to an alcohol also is another example of a trigonal carbon to tetrahedral carbon conversion.

The direct acid catalyzed hydration of alkenes is not practical since it proceeds too slowly. However, we have found that the acid catalyzed reaction with trifluoroacetic acid leads to a rapid conversion to a trifluoroacetate.[13] We add trifluoroacetic anhydride to the trifluoroacetic acid reaction solvent so that we can obtain the same product trifluoroacetates by the reaction of the corresponding alcohols with the solvent.



$$RCH{=}CH_2 + F_3CCO_2H \longrightarrow \underset{\displaystyle OCOCF_3}{\underset{|}{RCHCH_3}} \longleftarrow \underset{\displaystyle OH}{\underset{|}{RCHCH_3}} + (F_3CCO)_2O$$

The combination of the two heats of reaction with the heat of reaction of water with the solvent gives the enthalpy of hydration.

In our first study, we examined the enthalpies of hydration of the five n-hexenes. They were chosen since the enthalpies of formation had been determined via bomb calorimetry,[14] and we anticipated that a combination of enthalpies of hydration and enthalpies of formation (in the least squares sense) would lead to improved values of the latter quantities.

We were surprized to find large discrepencies between our energy differences and those obtained from the enthalpies of formation. After much checking of the data, and demonstration of reproducibility between samples of alkenes obtained from different sources, and between different batches of reaction solvent, as well as independence of alkene or mineral acid concentration, we became convinced that our values are correct. Recently, we have carried out a similar study for the n-heptenes, and here we have obtained excellent agreement with the enthalpies of formation derived from bomb calorimetry.[15] We are now quite confident that our results (Table III and Figure 3) are correct. The data represent the most precise determinations thus far available for the differences in enthalpy between cis and trans isomers, and provide enthalpies of formation for all of the n-hexanols and n-heptanols. We have begun an investigation of some alkenes which are of more general chemical interest. This will be described in the proposal section.

E. Enthalpies of Formation of Small Ring Hydrocarbons. We have had a long-standing interest in the energies of small ring hydrocarbons, and the relationship between structure, energy and reactivity. Some time ago, we determined the enthalpies of combustion of cyclopropene,[16] cyclobutene, bicyclo[1.1.0]butane, methylenecyclopropane and 1-methylcyclopropene[17] via flame calorimetry. Our more recent studies are outlined below.

In connection with other studies, we wished to know the difference in energy between cis- and trans- substituted cyclopropanes. We determined the enthalpies of combustion of cis and trans-1,2-diethylcyclopropane.[18] Although the precision of the measurements was good, the small difference in energy had a relatively large uncertainty. In order to obtain a better value for the difference, we examined the enthalpy of reaction with trifluoroacetic acid. Both gave essentially the same products, and it was possible to correct for the small difference. This gave an energy difference of 1.5±0.1 kcal/mol.

A comparison of the energies of substituted cyclopropanes with substituted

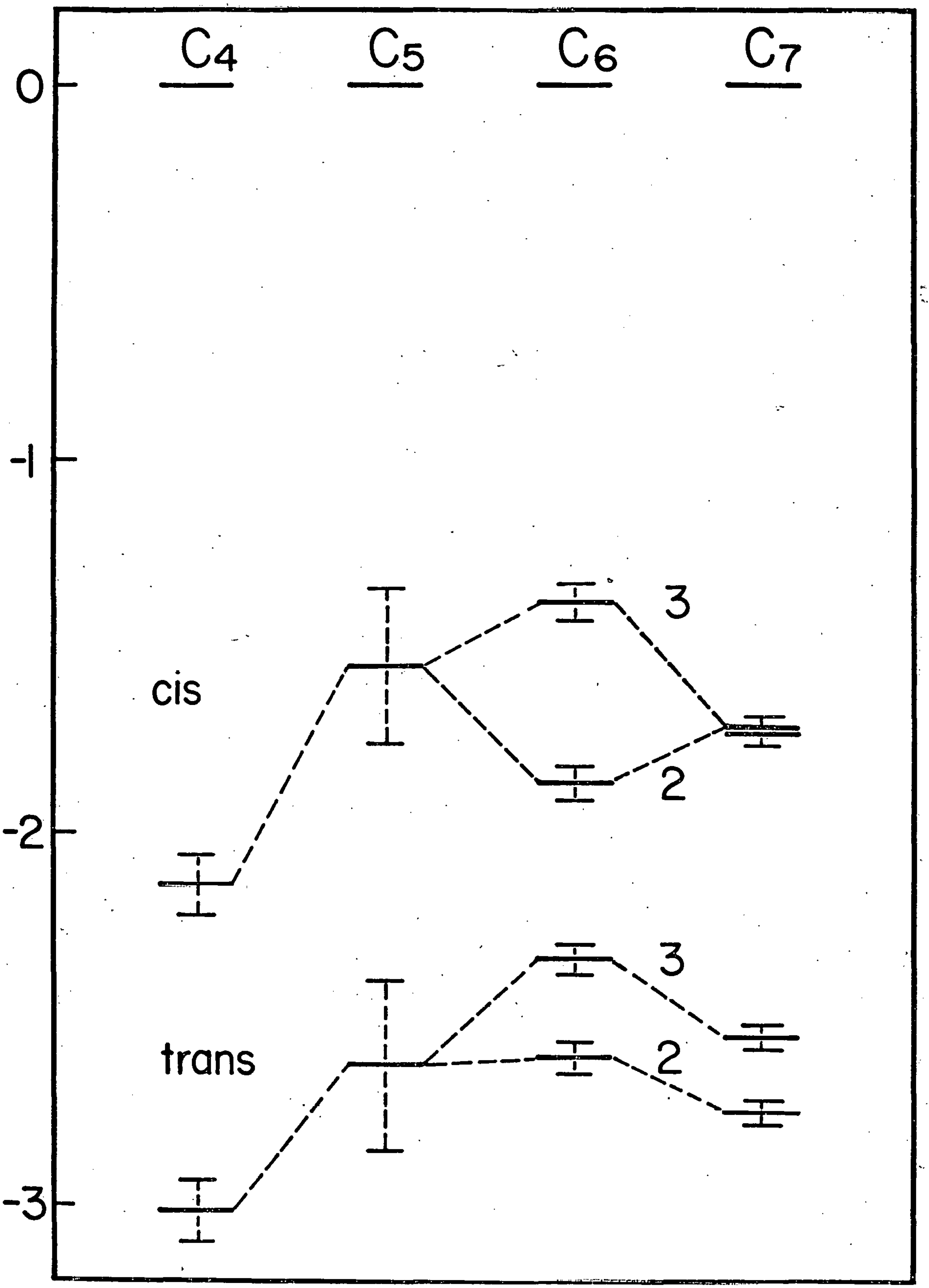


Figure 3. Changes in enthalpy of formation of alkenes with changes in position of the double bond. The 1-alkenes were taken as the reference. The C_6 and C_7 data arise from our measurements.

alkenes is shown in Figure 4. It can be seen that the effects of alkyl substitution are essentially the same in the two series, and is quite different from that found with their saturated analogs.

We have also examined the enthalpy of combustion of cis and trans-bicyclo[6.1.0]nonanes.[17] Here, we wished to compare them with cis and trans-cyclooctene for which the difference in energy is known to be 11.4 kcal/mol.[19] We found that they had essentially the same energy, within experimental error. It was possible to rationalize the results in the context of molecular mechanics calculation for there are conformations of cyclooctane[20] which may accommodate either cis or trans-fusion of a cyclopropane ring (Figure 5).

It was not practical to obtain enough trans-bicyclo[5.1.0]octane to permit an enthalpy of combustion determination, and the cis and trans isomers give quite different products making it impractical to determine their energy difference via measurement of the enthalpy of reaction with trifluoroacetic acid. Thus, we were led to try to calculate the energy difference for this case, as well as for the still unknown trans-bicyclo[4.1.0]heptane, via molecular mechanics. The results are shown in Table IV, and provide an important key to estimating reactivity and difficulty of preparation.

The strain energies of the tricyclic 'propellanes' also was of interest to us. In the case of the [3.2.1]propellane and 1,3-dehydroadamantane, we were able to measure the enthalpy of reaction with acetic acid to cleave the central C-C bond.[21] A comparison with the enthalpy of cleavage of simple C-C bonds (calculated from available thermochemical data) gave the strain energy release on cleaving the bond. Knowing the strain energies of the products, we were able to obtain strain energies for the propellanes. The value thus obtained for the [3.2.1]propellane agreed with that estimated from our earlier determination of the enthalpy of combustion of the 8-oxa-[3.2.1]propellane.[22]

Table III

Molecular Mechanics Calculations[a]

Compound	ΔH_f(calc)	ΔH_f(obs)	SE[b]
cis-Bicyclo[4.1.0]heptane (5)	1.3	0.4	27.2
trans-Bicyclo[4.1.0]heptane (6)	27.3		54.1(calc)
cis-Bicyclo[5.1.0]octane (7)	-3.0	-4.0	27.8
trans-Bicyclo[5.1.0]octane (8)	8.1		39.9(calc)
cis-Bicyclo[6.1.0]nonane (3)	-5.8	-5.0	31.7
trans-Bicyclo[6.1.0]nonane (4)	-3.1	-4.5	32.2
cis-1,2-Diethylcyclopropane (1)	-11.3	-10.3	26.9
trans-1,2-Diethylcyclopropane (2)	-12.3	-11.8	25.4

a. All values are given in kcal/mol.

b. Based on experimental values except when marked calc.

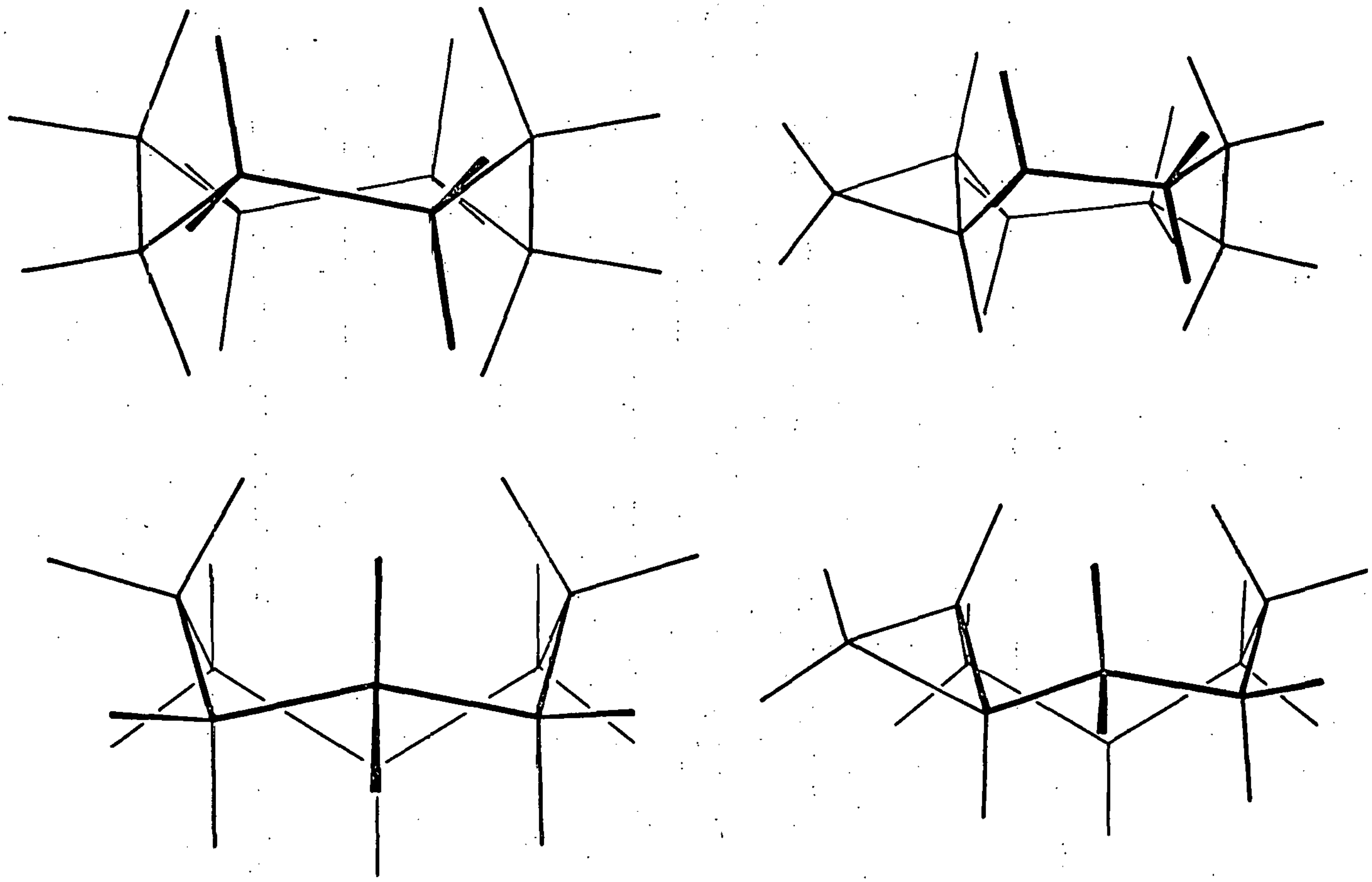
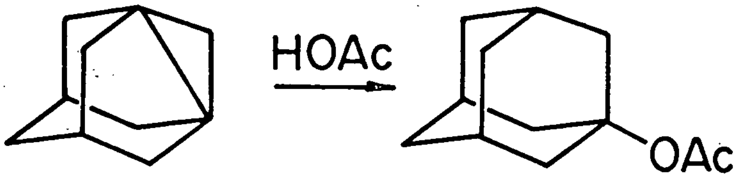
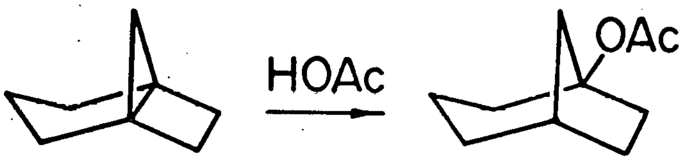


Figure 5. Conformations of cyclooctane (left) and corresponding conformations of bicyclo[6.1.0]nonane (right).

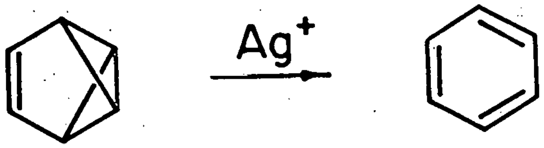


$\Delta H = -43.5$ kcal/mole

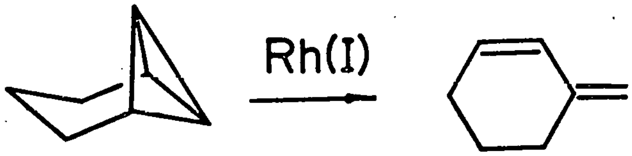


$\Delta H_r = -41.2$ kcal/mole

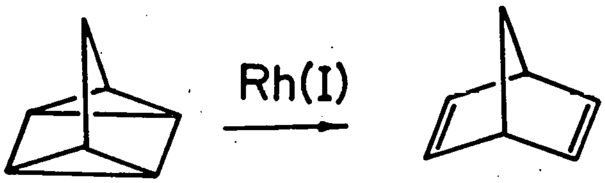
The enthalpies of the metal catalyzed rearrangements of benzvalene,[23] tricyclo[4.2.1.0^{2,4}]heptane and of quadricyclane[24] were determined giving the results shown below:



$\Delta H_r = -67.5$ kcal/mole



$\Delta H_r = -30.0$ kcal/mole



$\Delta H_r = -26.1$ kcal/mole

Knowing the difference in energy between benzvalene and benzene, along with the activation energy for the thermal rearrangement of benzvalene to benzene, one may calculate that the activated complex for the thermal rearrangment has an energy greater than that of the benzene triplet. Since the triplet was not formed, even though the energy was sufficient, one may conclude that the reaction proceeds via an allowed pathway.[23] The energies of rearrangement of the other two compounds provide information on their strain energies. This is of some interest since the norbornadiene-quadricyclane pair is one which has been suggested as a possible solar energy storage system.

F. Charge Distribution in Hydrocarbons. The successful application of molecular mechanics requires that one have satisfactory models for all of the intramolecular interactions. One which is potentially important, but which has received little study, is the Coulombic interactions between the small partial charges associated with the atoms in a molecule.[25] The study of these interactions requires a knowledge of charge distributions in molecules. However, this has not received adequate study, and it is only recently that good evidence concerning the sign of the C-H bond dipole has been obtained.

We have approached this problem using a combination of studies of intensities of infrared bands, and theoretical calculations.[26] [28] The intensity of the infrared bands depends on the rate of change of the dipole moment with changes in nuclear coordinates for the motion corresponding to the given band. The interpretation of the dipole moment derivatives has been difficult. In ethylene, for example, one deduces one sign of the bond dipole from the stretching bands ($\overset{+}{C}\overset{-}{H}$) and the opposite from the bending bands ($\overset{-}{C}\overset{+}{H}$). We have now been able to show that, contrary to common belief, the stretching modes give the correct bond moment, and the bending modes are complicated by incomplete orbital following and the formation of bent bonds.

We have calculated charge distributions from high quality ab initio wave functions for a series of methyl and ethyl derivatives. In our earlier work on the methyl derivatives,[29] we were only able to obtain the change in charge distribution resulting from the introduction of substituents. However, more recently, we have been able to obtain absolute electron populations. Here, we make use of the quantum topology concepts developed by Bader and his co-workers.[30] We have examined the basis set dependence of the the Bader criterion for partitioning electron population among atoms,[31] This has been applied to a large set of substituted methanes and ethanes, and has provided information on how substituents interact with alkyl groups, and how electron populations are affected by these substitutents.

Cumulative Publication List

1. 'Infrared Intensities. The Methyl Halides. Effect of Substituents on Charge Distributions.' K. B. Wiberg, J. Am. Chem. Soc., 101, 1718-1722 (1979).

2. 'Sigma and Pi Components of Substituent Effects in Saturated Systems. Monosubstituted Methanes.' K. B. Wiberg, J. Am. Chem. Soc., 101, 2204-2205 (1979).

3 'Thermodynamics of Hydrolysis of Aliphatic Ketals. An Entropy Component of Steric Effects.' K. B. Wiberg and R. R. Squires, J. Am Chem. Soc. 101, 5512-5515 (1979).

4. 'A Microprocessor-controlled System for Precise Measurement of Temperature Changes. Determination of the Enthalpies of Hydrolysis of Some Polyoxygenated Hydrocarbons.' K. B. Wiberg and R. R. Squires J. Chem. Thermodynamics 1979, 11, 773-786.

5. 'Enthalpies of Acetolysis of Tricyclo[3.2.1.$0^{1,5}$]octane [3.2.1]-Propellane) and 1,3-Dehydroadamantane.' K. B. Wiberg, H. A. Connon and W. E. Pratt, J. Am. Chem. Soc. 101, 6970-6972 (1979).

6. 'Effect of Substituents on the Electron Densities in Methane. σ and π Interactions in Saturated Systems.' K. B. Wiberg, J. Am. Chem. Soc. 102, 1229-1237 (1980).

7. 'The Electrical Nature of C-H Bonds and its Relationship to Infrared Intensities.' K. B. Wiberg and John J. Wendoloski, J. Comput. Chem. 2, 53-57 (1981).

8. 'Thermochemical Studies of Carbonyl Reactions. II. Steric Effects in Acetal and Ketal Hydrolyses.' K. B. Wiberg and R. R. Squires, J. Am. Chem. Soc. 103, 4473-4478 (1981).

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11. 'Enthalpies of Formation of cis and trans-Diethylcyclopropanes and cis and trans-Bicyclo[6.1.0]nonanes; Stabilization of Cyclopropane Rings by Alkyl Groups.' K. B. Wiberg, E. C. Lupton, Jr., D. J. Wasserman, A. de Meijere and S. Kass, J. Am. Chem. Soc. 104, 0000-0000 (1982).

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