MASTER

Progress Report

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Progress Report

A. Automated Reaction Calorimeters: We have for many years been interested in obtaining calorimetric data. Some systems were studied using conventional manual data collection and processing techniques,[8-12] but the rate of progress was relatively low. Many of the systems which are of interest to us would require a relatively large number of calorimetric determinations, and high precision appeared to be essential. These considerations led us to develop automatic reaction calorimeters.

The first system used a HP quartz thermometer probe as the temperature sensing element, and a locally constructed preamplifier to convert the signal to standard TTL levels (0.8 - 4 v). The 28 MHz signal thus obtained varies by approximately 1000 Hz/°C and is highly reproducible. The data collection system made use of a microcomputer having an 8080 as the CPU. A pair of 28 MHz counters and a controller were constructed on prototype boards, and connected to the processor bus.

In order to minimize the normal ±1 quantization error associated with most counters, each of the 28 MHz counters was constructed as a pair of 32 bit counters. The input signal was steered to one or the other of the counters via a data synchronizer and a 0.1 Hz signal derived from a very stable 10 MHz HP quartz oscillator. In this way, the values appearing in the counters are correlated. The temperature resolution of the counters using a 10 sec counting period is 0.0001°. When a slow and steadily rising temperature ramp was examined, the rms error in fitting the data to a smooth curve was ±0.00005, or one-half the resolution. This is the expected result using correlated counters provided the inherent precision of the probe is better than the apparent error. When a 100 sec counting period was used, the resolution was $10\mu^{o}$ and the rms error was $6\mu^{o}$.[13] Besides minimizing the quantization error, counters of this type are particularly convenient for carrying out corrections to the observed temperature change since the sum of the counts over the reaction period is the integral of the temperature with respect to time.

A number of other interfaces were constructed for displaying the temperature on LED displays, reading BCD switches which could be set for the 0°C offset, displaying the temperature/time data on an oscilloscope, breaking the ampoule to start the reaction, cooling the reaction cell to the original temperature after the reaction run is completed, and initiating an electrical calibration. A diagram of the computer system is shown in Figure 1. This data collection and calorimeter control system has been used with an LKB precision calorimetric system and has given large amounts of very precise data. It was tested using the reaction of TRIS with 0.1N hydrochloric acid and gave $\Delta H_r = -7114 \pm 3$ cal/mole which may be compared with the commonly accepted value: -7115 ± 7 cal/mole.[14] The details of this calorimetric system have been published.[15]

One of the few disadvantages of the quartz thermometer probe is its large size (3/8"X1/2"). This makes it impractical for use in small cells. (The above system uses 100 ml reaction vessels.) With 25 ml or smaller cells, a thermistor would be the ideal temperature sensing element. One of the main problems with the use of a thermistor in an automated data collection system has been the difficulty in measuring its resistance with high precision

(±0.1 Ω for a 10,000 Ω thermistor). The development of high resolution digital voltmeters has solved this problem. We have used a Fluke model 8500 6 1/2 digit voltmeter as the measuring device. A constant current supply was constructed, and supplied 0.1 ma to a 10,000 Ω precision resistor in series with the measuring 10,000 Ω (25 °C) thermistor. A relay was used to switch the voltmeter to read the voltage across each of the resistors in turn.

The voltmeter operated under the control of a PDP 11/03 microcomputer. At the end of each 10 sec period, the latter would send a read command to the voltmeter, accept the voltage across the thermistor, switch the relay, send another read command, and then accept the voltage across the fixed resistor. The resistance of the thermistor could be derived from the ratio of the voltages.

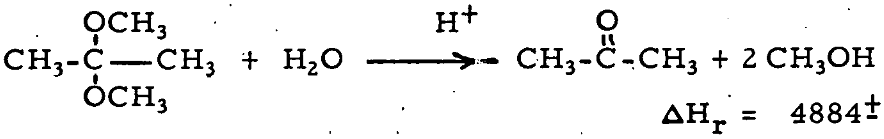
Interfaces were constructed for the microprocessor which allowed it to control the course of the reaction in the same fashion as for the first system. The rms error in fitting a steady temperature ramp was ±0.0007 °C, very close to that obtained using the quartz thermometer probe. This system will be described in a future publication.

The availability of these two systems has made it possible for the users to concentrate on the preparation of the compounds to be studied, devising analytical methods for determining purity and extent of reaction and carrying out other studies such as equilibrium constant measurements.

<u>B. Enthalpies of Hydration of Polyoxygenated Methanes:</u> The first system to be studied using the automated calorimeter was the hydrolysis of polyoxygenated methanes.[15] This reaction was chosen since there was some data

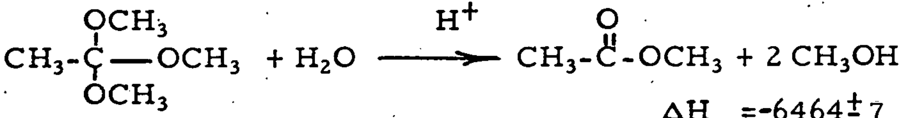
available with which our results could be compared, and since a number of planned studies involved similar reactions.

The reactions examined were:



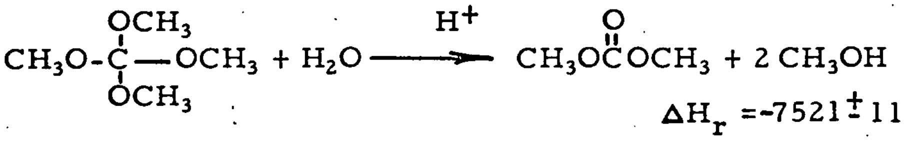
$$\mathrm{CH_3\text{-}\underset{OCH_3}{\overset{OCH_3}{C}}\text{—}CH_3 + H_2O \xrightarrow{H^+} CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + 2\,CH_3OH}$$

$\Delta H_r = 4884 \pm 7$ kcal/mole



$$\mathrm{CH_3\text{-}\underset{OCH_3}{\overset{OCH_3}{C}}\text{—}OCH_3 + H_2O \xrightarrow{H^+} CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_3 + 2\,CH_3OH}$$

$\Delta H_r = -6464 \pm 7$ kcal/mole



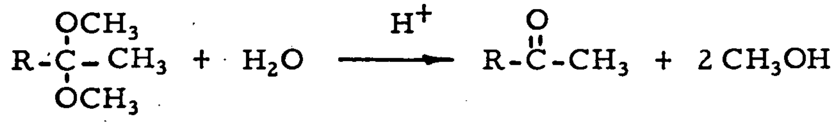
$$\mathrm{CH_3O\text{-}\underset{OCH_3}{\overset{OCH_3}{C}}\text{—}OCH_3 + H_2O \xrightarrow{H^+} CH_3O\overset{O}{\overset{\|}{C}}OCH_3 + 2\,CH_3OH}$$

$\Delta H_r = -7521 \pm 11$ kcal/mole

It can be seen that high precision was achieved. Using the known enthalpies of formation of the products, the enthalpies of formation of the reactants could be calculated.

There has been much discussion of "double bond-no bond" resonance in polyfluorinated compounds.[16] This is based on the non-linear change in enthalpy of formation as successive hydrogens of methane are replaced by fluorine. A similar examination of the data for methoxy substitution showed a corresponding trend. However, "double bond-no bond" resonance should be less important in this case. The above data allowed us to examine the enthalpy changes for the replacement of methyl groups in neopentane with methoxy. Here, constant increments were found. The replacement of methyl groups in neopentane by fluorine also was examined, and again constant increments were found. Thus, if "double bond-no bond" resonance is important, it must be important for methyl and methoxy groups as well as fluorine. The more likely possibility is that the unequal increments found in replacing hydrogens of methane with methyl, methoxy or fluorine is a general affect of replacing hydrogens with a second row element having different types of orbitals available.

C. Enthalpies of Hydrolysis of Ketals. One of the conveniently examined examples of the conversion of a tetrahedral carbon to trigonal is found in the hydrolysis of ketals:



$$R-\overset{OCH_3}{\underset{OCH_3}{C}}-CH_3 + H_2O \xrightarrow{H^+} R-\overset{O}{\overset{\|}{C}}-CH_3 + 2\,CH_3OH$$

As the size of the R group is increased, its interaction with the groups in the ketal will be greater than that in the ketone, thus destabilizing the former with respect to the latter. This was examined by determining the enthalpies of reaction for a series of ketals in which R was varied from methyl to neopentyl. The data are summarized in Table I. They have been corrected for the enthalpies of solution of the products and correspond to all compounds in the pure liquid state.

Table I

Enthalpies of Hydrolysis of Ketals

R	n[a]	ΔH_r (kcal/mole)	$\Delta\Delta H$
CH_3	7	4884 ± 7	0
C_2H_5	8	4620 ± 8	-264
n-C_3H_7	5	4666 ± 14	-218
i-C_3H_7	4	4858 ± 9	- 26
2-C_4H_9	6	4762 ± 11	-122
i-C_4H_9	6	3284 ± 13	-1600
t-C_4H_9	6	819 ± 13	-4065
neo-C_5H_{11}	4	1642 ± 21	-3242

a. Number of runs.

A surprising result was that the enthalpies of reaction when R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7 and 2-C_4H_9 were essentially constant whereas they are assigned quite different steric constants.[17] In order to further examine the system, equilibrium constants were measured for the cases where R = CH_3, C_2H_5, n-C_3H_7 and i-C_3H_7. With larger alkyl groups, the equilibrium constants were too large for accurate measurement. The enthalpies of reaction in the solvent used (methanol) also were obtained from the above values by including the enthalpies of solution in methanol. The data are presented in Table II.

Table II

Equilibrium Constants and Free Energies of Hydrolysis

R	K	ΔG (kcal/mole)	ΔH kcal/mole	ΔS (eu)
CH_3	113.6 ± 3.6	-2803 ± 19	5488 ± 10	27.81 ± 0.07
C_2H_5	383.9 ± 35	-3521 ± 51	5189 ± 13	29.21 ± 0.18
n-C_3H_7	606.0 ± 18	-3795 ± 17	5136 ± 18	29.95 ± 0.08
i-C_3H_7	1344 ± 155	-4260 ± 67	5331 ± 13	32.17 ± 0.23

Whereas the enthalpies of reaction are essentially constant, the free energies vary considerably. Thus, the equilibrium constant changes in this solvent result almost entirely from entropy changes.[18]

D. Enthalpies of Hydrolysis of Acetals: We wished to examine cases in which the effects of the alkyl groups might be minimized or amplified. If the methyl group in the ketal is replaced by hydrogen giving an acetal, the steric interaction of the R group should be decreased. On the other hand, if the methyl is replaced by methoxy giving an orthoester, one might expect the steric interaction to be increased.

Acetal hydrolysis was examined for a variety of R groups giving the data in Table III. It can be seen that the range of ΔH_r values is significantly less than that found for the ketals.

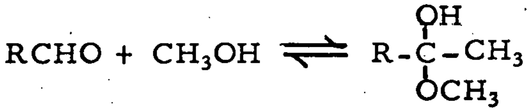
Table III

Enthalpies of Hydrolysis of Acetals

R	n	ΔH_r (kcal/mole)	$\Delta\Delta H$
CH_3	5	8622 ± 15	0
C_2H_5	4	8499 ± 17	-123
n-C_3H_7	4	8732 ± 23	110
i-C_3H_7	5	8698 ± 16	76
2-C_4H_9	6	8134 ± 33	-488
i-C_4H_9	5	8342 ± 23	-280
t-C_4H_9	4	7925 ± 19	-697
neo-C_5H_{11}	3	7968 ± 35	-654

The small alkyl groups, CH_3, C_2H_5, n-C_3H_7 and i-C_3H_7 all lead to similar ΔH_r values. Larger alkyl groups lead to somewhat larger changes in ΔH_r. It is interesting that 2-butyl, which gave only a small effect in ketal hydrolysis, gives a relatively large enthalpy change in acetal hydrolysis.

The results for the ketals and acetals are compared with the Taft steric parameters $(E_S)^{17}$ in Figure 2. A linear correlation is not found in either case, but the acetals at least give a relatively smooth curve. In order to see if entropy effects are important in this case, the equilibrium constants for hemiacetal formation were measured:



$$RCHO + CH_3OH \rightleftharpoons R\text{-}\underset{\displaystyle OCH_3}{\overset{\displaystyle OH}{C}}\text{-}CH_3$$

It was not possible to measure the equilibrium constant for acetal formation because of the complex equilibrium between hydrate, hemiacetal and acetal which is formed when acid is added to the above reaction mixture. The effect

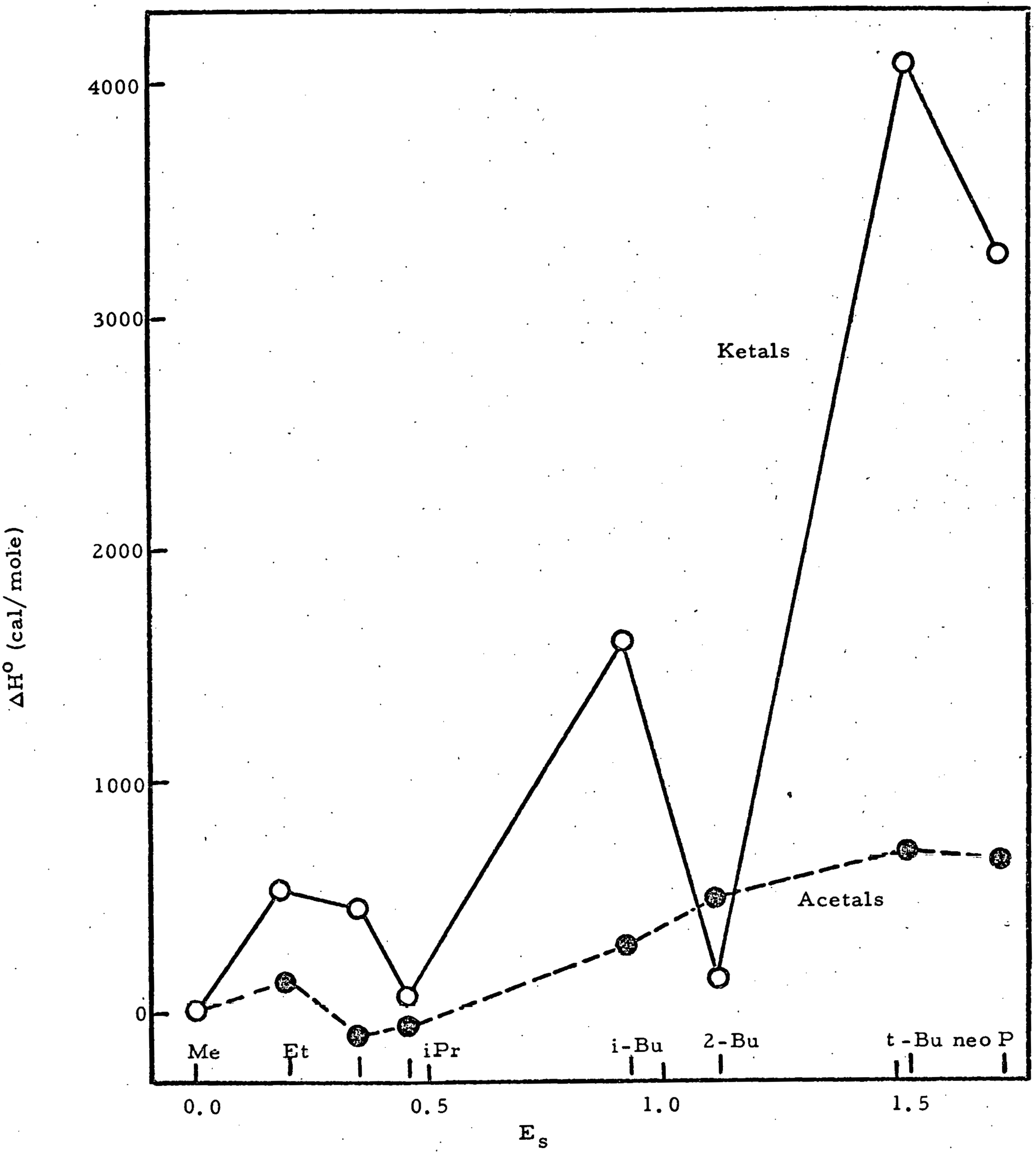


Figure 2. Relation between ΔH° for ketal and acetal hydrolysis and the steric parameter, E_s.

of R on the hemiacetal equilibria should be closely related to its effect on acetal equilibria since the structural changes are very similar for the two cases. The data are shown in Table IV.

Table IV

Equilibrium Constants for Hemiacetal Formation

R	K	n[a]	ΔG° (kcal/mole)
Me	18.85±0.91	7	-1739±29
Et	14.09±1.45	5	-1567±61
n-Pr	12.01±0.60	8	-1473±30
i-Pr	9.177±0.232	4	-1313±15
i-Bu	6.868±0.199	9	-1142±17
2-Bu	4.659±0.177	3	-911.6±23
t-Bu	2.387±0.196	4	-515.4±49
neo-Pent	2.015±0.035	7	-415.1±10

a. Number of runs.

It can be seen that there is a steady decrease in the equilibrium constant as the size of the alkyl group is increased. The ΔG° values agree well with the Taft steric parameters (Figure 3). Thus, here also, entropy plays an important role in determining the magnitude of the equilibrium steric effect.

A manuscript dealing with these results, as well as a molecular mechanics calculations for these compounds, is in preparation.

E. Enthalpies of Hydrolysis of Orthoesters: As mentioned above, it might be expected that the replacement of the methyl group in the ketals by a methoxy group would lead to an increase in steric interactions. It was also possible that it would lead to a different ordering of steric interactions since the anomeric effect[19] would apply here also and restrict the number of conformations

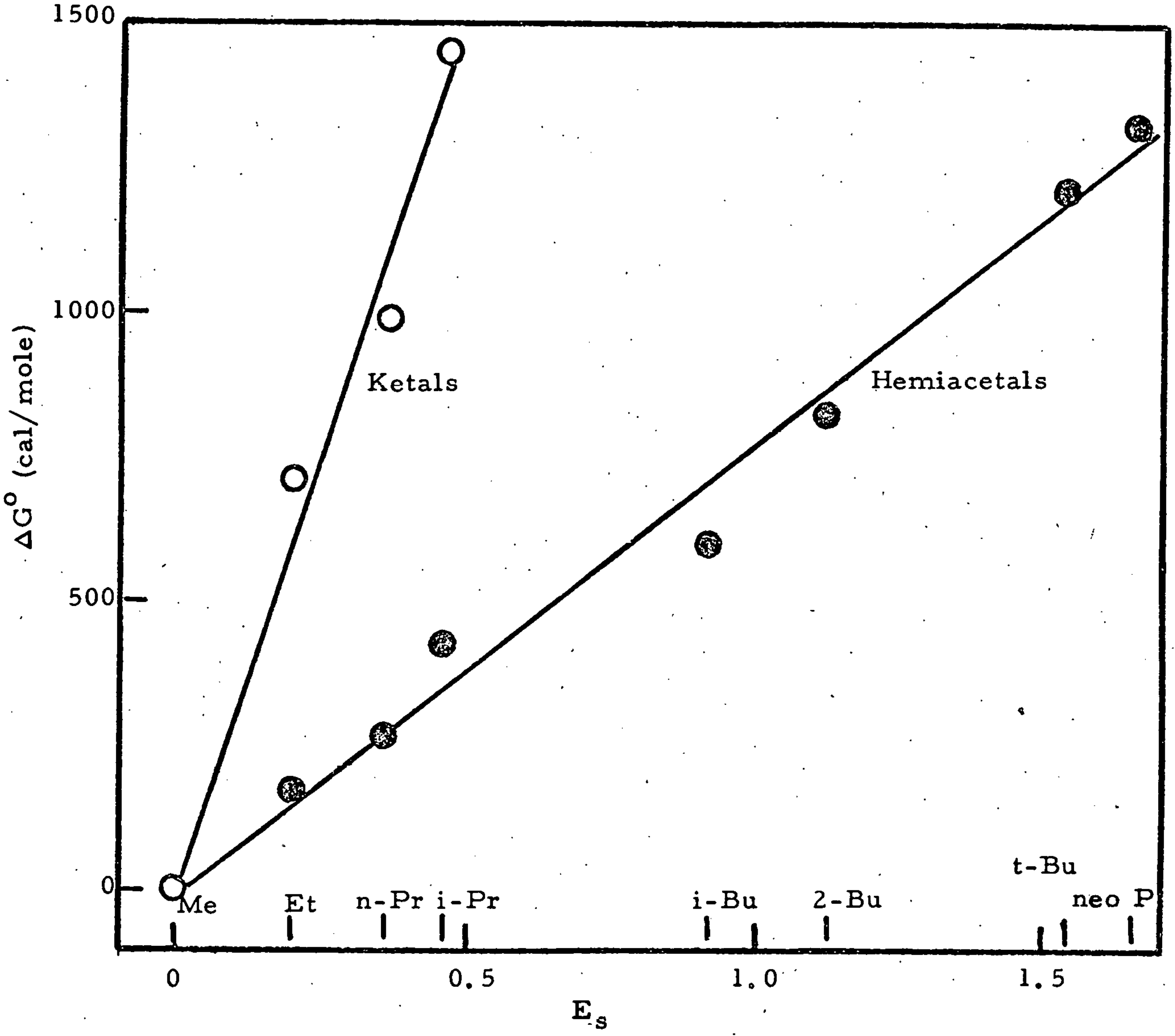


Figure 3. Relation between ΔG^{o} for ketal and acetal hydrolysis and the steric parameter, E_s.

available for the methoxy groups. The orthoester hydrolysis could be examined in the same fashion as the ketal hydrolysis and gave the data in Table V.

Table V

Enthalpies of Hydrolysis of Orthoesters

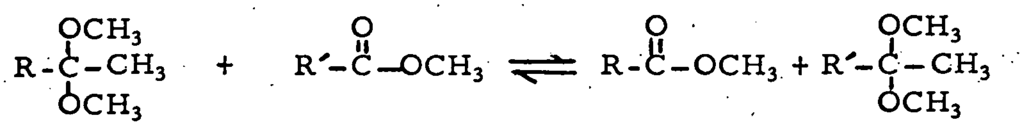
R	ΔH_r (kcal/mole)	$\Delta\Delta H$
CH_3	-6463±7	0
C_2H_5	-6280±17	183
$n\text{-}C_3H_7$	-6315±14	148
$n\text{-}C_4H_9$	-6147±8	316
$i\text{-}C_3H_7$	-7836±14	-1373
$i\text{-}C_4H_9$	-7367±15	-904
$2\text{-}C_4H_9$	-8197±13	-1734

Here, the straight chain alkyl groups gave positive values of $\Delta\Delta H$ as compared to methyl, indicating a small negative steric effect. However, when branched chain cases were examined, both α- and β- branching led to a large change in ΔH_r. It would be of interest to have data for R= t-butyl and neopentyl. These compounds have not been reported in the literature and our attempts to prepare them have not as yet proven to be successful.

Again, we wish to be able to compare enthalpies and free energies of reaction. The equilibrium constant for the reaction

$$R\text{-}\overset{O}{\overset{\|}{C}}OCH_3 + 2\,CH_3OH \rightleftharpoons R\text{-}\underset{OCH_3}{\overset{OCH_3}{C}}-CH_3 + H_2O$$

cannot be measured directly since it lies essentially entirely to the right. However, preliminary experiments indicate that the following equilibrium is established rapidly in the presence of an acid catalyst, and that concentrations can be measured by nmr spectroscopy:

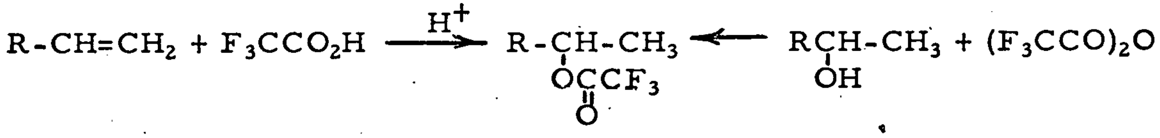


$$R\text{-}\overset{OCH_3}{\underset{OCH_3}{C}}\text{-}CH_3 + R'\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_3 \rightleftharpoons R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_3 + R'\text{-}\overset{OCH_3}{\underset{OCH_3}{C}}\text{-}CH_3$$

This will allow the free energy changes caused by the alkyl groups to be determined.

<u>F. Enthalpies of Hydration of Alkenes:</u> It was clear that a method for measuring the enthalpies of hydration would be useful for determining the difference in enthalpy between double bond isomers and for determining the enthalpy of formation of alcohols. It would represent one of the important steps in the series of reactions which could be used to interconvert functional groups.

We have found that alkenes quickly react with trifluoroacetic acid in the presence of trifluoromethanesulfonic acid to give trifluoroacetic esters. It was convenient to add 4 % trifluoroacetic anhydride, for then the reaction of the corresponding alcohols with the solvent would give the same esters:



$$R\text{-}CH{=}CH_2 + F_3CCO_2H \xrightarrow{H^+} R\text{-}\underset{OCCF_3}{\underset{|}{C}H}\text{-}CH_3 \longleftarrow R\underset{OH}{\underset{|}{C}H}\text{-}CH_3 + (F_3CCO)_2O$$

The n-hexenes were first examined since all 5 compounds were available in pure form, and since the enthalpies of formation had been determined by oxygen bomb calorimetry.[20] Thus, we would have data with which our results could be compared. The results are given in Table VI.

Table IV

Enthalpies of Trifluoroacetolysis of Alkenes

Alkene	n	ΔH_r (kcal/mole)	$\Delta\Delta H$
1-Hexene	5	$-11,996 \pm 25$	0
cis-2-Hexene	5	$-10,167 \pm 36$	1829
trans-2-Hexene	4	$-9,602 \pm 19$	2394
cis-3-Hexene	5	$-10,661 \pm 23$	1335
trans-3-Hexene	4	$-9,621 \pm 30$	2375

It can be seen that high precision again was achieved. In order to be sure that there was no complication due to dimerization or other reactions which might occur to a small extent, the reaction enthalpy was determined for a five-fold range of acid concentrations and a two-fold range of alkene concentrations. The observed values were unchanged over this range of concentrations.

The reaction of the alkenes with trifluoroacetic acid led to the formation of a mixture of 2- and 3-hexyl trifluoroacetates as a result of hydride shifts. It was possible to measure the equilibrium constant for the acid catalyzed interconversion of the esters over the range 40-150°C. The change in equilibrium constant with temperature led to $\Delta\Delta H = 172 \pm 21$ cal/mole and $\Delta\Delta S = 0.46$ eu. The ratio of esters formed from each of the alkenes was determined, and the ΔH_r values were corrected to the formation of the equilibrium mixture of the two esters. In all cases, this correction was very small.

We were disturbed to find that our $\Delta\Delta H$ values did not agree with those derived from the enthalpies of combustion.[20] The reported enthalpies of

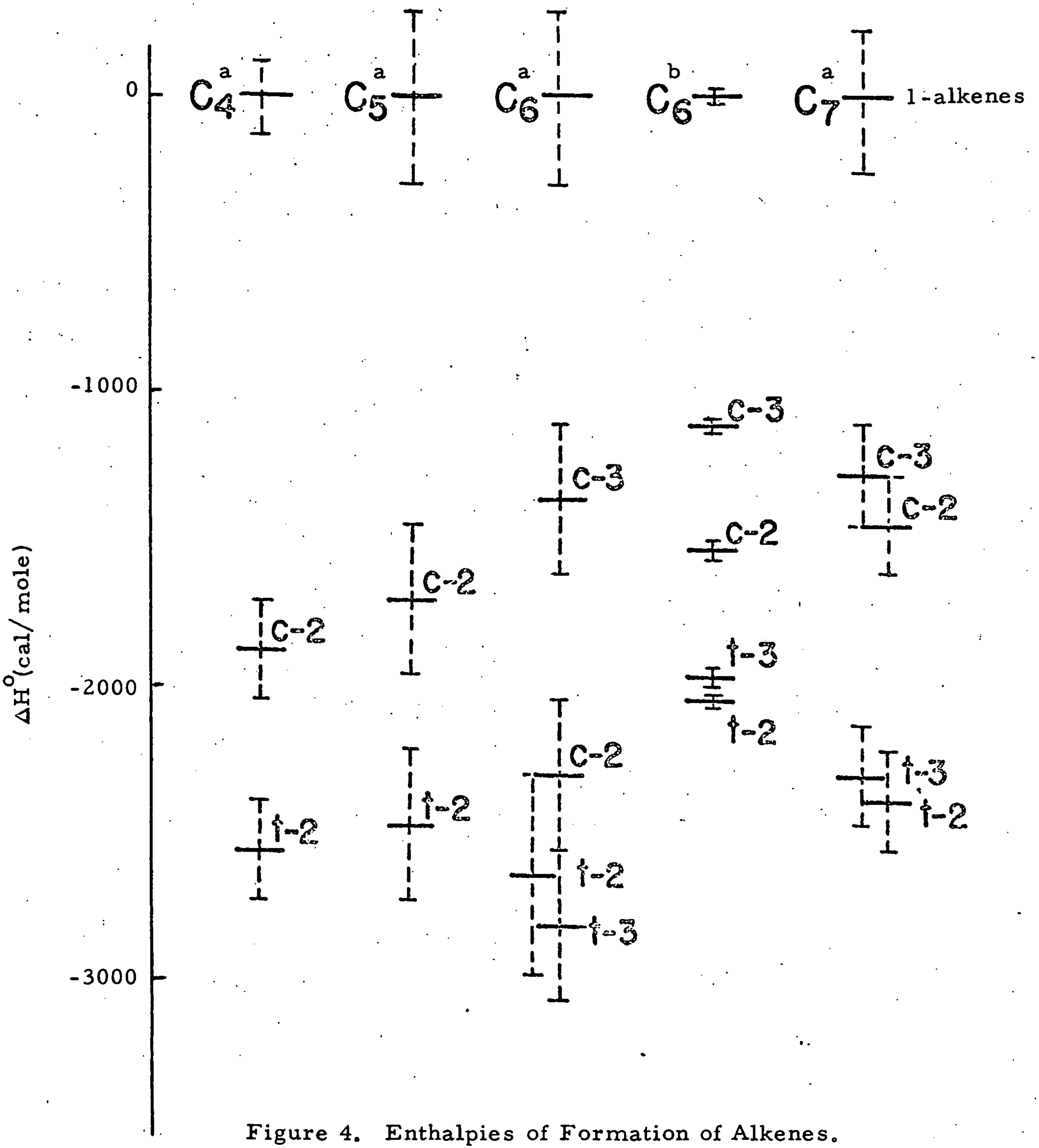


Figure 4. Enthalpies of Formation of Alkenes.

a. Literature values.
b. Our data.

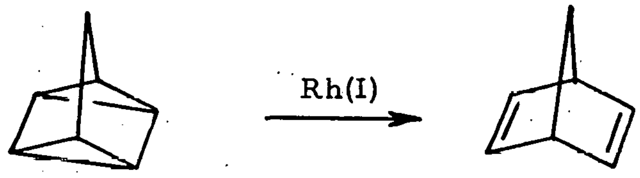
formation of the 1-n-alkenes change linearly with the number of carbons. Assuming that these values are correct, we plotted the reported differences with respect to the 1-n-alkenes for the C_4, C_5, C_6 and C_7 alkenes (Figure 4). It can be seen that the reported values for the cis-2-hexene must be in error, and some of the other data for the hexenes probably are incorrect.[21]

A preliminary examination of the n-heptenes has given ΔΔH values in good agreement with those reported for these compounds.[22] Thus we have confidence that our values are correct.

We are in the process of measuring the enthalpies of reaction of water, 2-hexanol and 3-hexanol with the trifluoroacetic acid/trifluoroacetic anhydride mixture. We are confident that we shall be able to obtain enthalpies of reaction with a precision comparable to that found for the reaction of the alkenes.

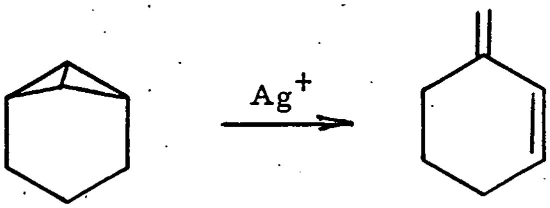
G. Enthalpies of Acetolysis and Combustion of Cyclopropane Derivatives:

Cyclopropanes are among the most common of those compounds which are strongly destabilized by bond angle deformation. In earlier investigations, we determined the enthalpies of combustion of cyclopropene,[8] methylenecyclopropene,[9] 1-methylcyclopropene,[9] and bicyclobutane[9] and also determined the enthalpies of the metal catalyzed isomerizations of nortricyclene (1) to norbornadiene and of tricyclo[4.1.0.0^{2,7}]heptane (2) to 3-methylenecyclohexane.[11]



1

ΔH_r = -26.16 ± 0.24 kcal/mole

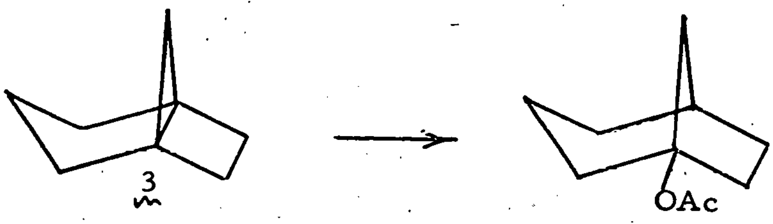


2

ΔH_r = -29.99 ± 0.08 kcal/mole

Since information of this type is of interest both for practical applications and for theoretical reasons, we have continued the study of cyclopropane derivatives. Among the more unique of these compounds are the [3.2.1]-propellane (3) and 1,3-dehydroadamantane (4). In these compounds, the normal tetrahedral arrangement about the bridgehead carbons has been "inverted" (i.e. all of the bonds to the bridgehead atoms lie on one side of a plane). Both react rapidly with acetic acid to cleave the central bond, and the enthalpies of these reactions were determined.

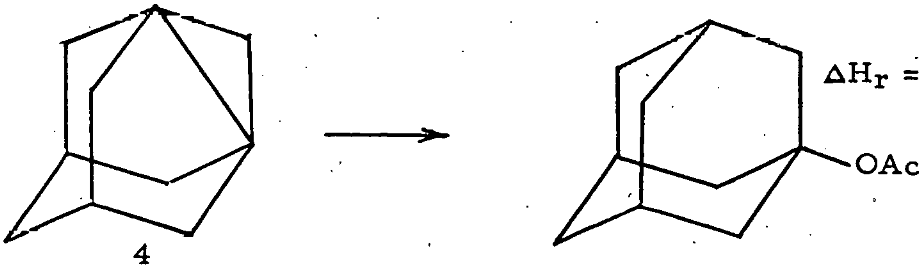
HOAc +



3

ΔH_r = -41.18 ± 0.24 kcal/mole

HOAc +

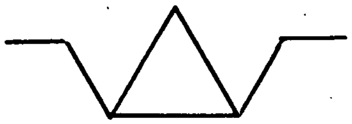


4

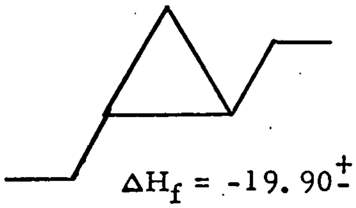
ΔH_r = -43.49 ± 0.08 kcal/mole

The enthalpy of cleavage of a normal C-C bond by acetic acid may be calculated to be 14 kcal/mole. Thus, the strain relief in the reaction of 3 was 55 kcal/mole whereas that for 4 was 57 kcal/mole. The strain energies of the compounds may be obtained from these data. The results of this investigation have been published.[23]

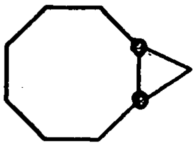
We also have been interested in the steric interaction between two cis-substituents on a cyclopropane ring. In the case of double bonds, the cis-substituted compounds are normally 1.0 kcal/mole less stable than the corresponding trans-isomer.[24] However, when the double bond is contained in a ring, the order may be changed because of geometrical restraints. Thus, trans-cyclooctene is 10 kcal/mole less stable than cis-cyclooctene.[25] In order to obtain information concerning the corresponding cyclopropanes, we have determined the enthalpies of combustion of cis- and trans-diethylcyclopropanes and of cis- and trans-bicyclo[6.1.0]nonanes. The enthalpies of formation are as follows:



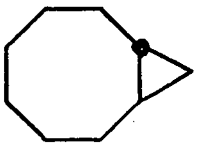
$\Delta H_f = -19.09 \pm 0.31$



$\Delta H_f = -19.90 \pm 0.37$



$\Delta H_f = -16.73 \pm 0.23$



$\Delta H_f = -16.23 \pm 0.23$

It can be seen that the difference in enthalpy of formation between the two bicyclo[6.1.0]nonanes is quite small (0.50 ± 0.33 kcal/mole) in contrast to the much larger difference found with the cyclooctenes. This results in part from the smaller trans-dihedral angle in cyclopropane (120°) as compared to an alkene (180°). The difference in energy could be reproduced by molecular mechanics calculations which allow a more detailed analysis of the energies.

The difference in energy between cis- and trans-diethylcyclopropanes is 0.81 ± 0.48 kcal/mole. We should like to obtain a more precise value for the difference in energy. It appears that the two cyclopropanes will react with trifluoroacetic acid (trifluoromethanesulfonic acid catalyst) to give the same products. We plan to measure the enthalpies of trifluoroacetolysis which should provide the needed information. The data also allows a calculation of the stabilization of a cyclopropane ring by alkyl substitution.

H. Molecular Mechanics Calculations: Before attempting to study ketones and ketals via molecular mechanics, it was necessary to develop suitable potential functions for rotation about C-C bonds involving carbonyl groups or ketal groups. The ketones have an alkyl group eclipsed with the carbonyl in the lowest energy conformer,[26] and in the ketals, the anomeric effect[19] must be included. In each case, it was necessary to include other non-bonded interactions when studying the torsional potential.[27] We have been able to obtain suitable torsional functions which allow the observed energy differences to be reproduced.

The ketals and ketones were then examined, using approximate non-bonded potential functions at oxygen. It was found that many of the compounds were predicted to exist in several conformations, all with approximately equal free energies.

The plan was to adjust the potential functions at oxygen so as to fit the experimental data. The large number of conformers made this impractical.

Thus, as indicated in the proposal section, we now plan to examine another group of ketals which have fixed geometry at the α-position to the carbonyl This will greatly simplify the analysis via molecular mechanics. Then, when appropriate parameters have been obtained, they can be tested with the data for the open chain ketones and ketals. If the data for both types of compounds may be reproduced, one may have confidence in the parameters.

I. Charge Distribution in Organic Compounds: One of the terms which should be included in a classical modeling of intramolecular potentials is the Coulombic interactions between atomic charges. This is frequently neglected because little is known about charge distributions in organic compounds. Although this is probably satisfactory for hydrocarbons, it should not be correct for heteroatom substituted compounds. The carbonyl group is known to have a significant dipole moment, and the C-O bond in ketals should also have a significant dipole resulting from the difference in electronegativity between carbon and oxygen.

We have studied substituent effects via ab initio molecular orbital calculations. The wave functions were first tested via comparison of calculated dipole moment/ coordinate derivatives with experimental infrared intensities.[28] Having satisfactory wave functions, we studied the partitioning of the calculated electron densities among the atoms in a series of methyl derivatives. It was found that the effects could be separated into σ and π-contributions. A detailed analysis was made. The results of these investigations have been published.[29]

We also have studied different methods for partitioning electron density.

The most satisfactory appears to be that of Bader[30] which makes use of zero-flux surfaces to separate regions that may be assigned to different atoms. The basis set dependence of this separation was examined. The results of this investigation have been accepted for publication.[31]

Publications Derived from Current Grant

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.

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