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Thermodynamics of Hydrolysis of Aliphatic Ketals. An Entropy Component of Steric Effects
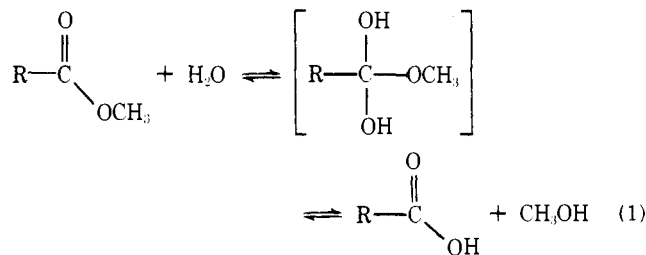
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Abstract: The enthalpies and free energies of the acid-catalyzed hydrolysis of a series of alkyl-substituted dimethyl ketals have been determined in a model study of steric effects. The measured enthalpy differences did not correlate with standard quantitative notions of the steric bulk of the substituents, although the overall free-energy changes fit the expected order. The entropy effect of the substituents is a dominant factor in determining the equilibrium composition for this reaction. Possible origins for these entropy effects are discussed.
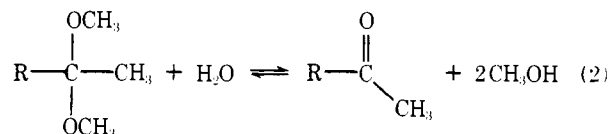
Introduction

Steric effects are widely recognized as one of the most important factors which may act to control the course of an organic reaction. Most of the quantitative information concerning steric effects of simple alkyl groups is derived from the extensive kinetic correlations obtained from studies of the acid-catalyzed hydrolysis of esters.[1] The reaction is believed to involve conversion of the trigonal ester reactant to a tetrahedral hydrated species which lies close to the activated complex on the reaction coordinate. Since the polar effects of the substituents are known to be minimal in this reaction, the differences in rate correspond to differences in steric interaction between the alkyl group and the trigonal center of the reactant vs. the tetrahedral center of the activated complex (eq 1).

Taft's E_s values are the logarithms of the relative rate ratios referred to methyl as the standard group, and are proportional to the free-energy changes attending substitution. Other steric substituent parameters have been developed which correct this basic scheme for additional effects on the relative rates (i.e., hyperconjugation),[2] but most of the approaches agree on the relative ordering of the steric effects of simple alkyl substituents.

$$R-\underset{OCH_3}{\overset{O}{\underset{\|}{C}}} + H_2O \rightleftharpoons \left[R-\underset{OH}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-OCH_3 \right] \rightleftharpoons R-\underset{OH}{\overset{O}{\underset{\|}{C}}} + CH_3OH \quad (1)$$

We wished to determine the enthalpy component of the steric interaction of an alkyl group with a trigonal vs. tetrahedral center and thus were led to examine the enthalpies of hydrolysis of substituted dimethyl ketals (eq 2). Here the

$$R-\underset{OCH_3}{\overset{OCH_3}{\underset{|}{\overset{|}{C}}}}-CH_3 + H_2O \rightleftharpoons R-\underset{CH_3}{\overset{O}{\underset{\|}{C}}} + 2CH_3OH \quad (2)$$

structures of the species taking part in the steric interactions are well defined, and the hydrolysis is considered to be a reasonable model for the activation process depicted in eq 1.

Table I

ketal	bp, °C	density 20 °C, g/mL
2,2-dimethoxypropane	82–83	0.845
2,2-dimethoxybutane	108–109	0.850
2,2-dimethoxy-3-methylbutane	126–127	0.683
2,2-dimethoxypentane	133–134	0.855
2,2-dimethoxy-4-methylpentane	146–148	0.853
2,2-dimethoxy-3,3-dimethylbutane	149–150	0.872
2,2-dimethoxy-3-methylpentane	67 (35 mmHg)	0.867
2,2-dimethoxy-4,4-dimethylpentane	74 (27 mmHg)	0.856

Experimental Section

Materials. All samples of the dimethyl ketals were prepared from the corresponding commerically available ketones by reaction at 60 °C with 1.1 equiv of trimethyl orthoformate in an excess of acidified methanol for 4–8 h. The resulting reaction mixtures were washed with 10% sodium hydroxide, dried with potassium carbonate, and distilled. Each ketal was repeatedly fractionally distilled in a nitrogen atmosphere from metallic sodium until all spurious proton bands in the high-resolution NMR spectrum and/or peaks corresponding to carbonyl and hydroxyl stretching in the IR spectrum had completely disappeared. The lower limit of sensitivity of these assay techniques is about 0.1%, and 100% purity was considered to have been achieved in each case. The physical properties of the ketals prepared are presented in Table I. The ketones used for the heats of solution and equilibrium measurements were purified and fractionally distilled according to the procedures of Perrin.[3] Methanol (Fisher) was purified by distillation under nitrogen from a mixture of methyl benzoate and sodium methoxide.[4] Gas chromatograms of the methanol and each of the ketones showed no impurities, reliable to <0.1%. The calorimetry reaction solvent was prepared by mixing the appropriate amounts of 1,4-dioxane (Baker analyzed, distilled from benzophenone ketyl), distilled water, and standard 0.1 M perchloric acid to give a 35% by volume water–65% dioxane solution which was approximately 0.001 M in perchloric acid.

Calorimetric Measurements. The enthalpies of reaction were determined using an automated reaction calorimetry system developed in this laboratory.[5] It uses a quartz probe as the temperature sensing element, and data is collected directly via a minicomputer. In addition to measuring temperature, the system is capable of automatically performing all the necessary experimental functions for a complete isoperibolic enthalpy measurement. The operator need only introduce the reagents into the calorimeter and set the operating parameters by a dialogue with the computer. In approximately 2 h the experiment is complete, and the resulting enthalpy of reaction is output onto the teletype. The accuracy and precision of this system were determined by measurement of the exothermic enthalpy of reaction of tris(hydroxymethyl)aminomethane (Tris) with 0.1 N hydrochloric acid at 25 °C. The average of ten measurements was −7114 ± 3 cal/mol, in excellent agreement with the NBS value[6,7] of −7115 ± 7 cal/mol. The reaction of Tris with 0.05 N NaOH at 25 °C (+4104 cal/mol) has been shown to be a suitable standard endothermic reaction,[6] and we were able to obtain satisfactory results in this case also (4098 ± 3 cal/mol).

A typical run proceeds as follows. An approximately 0.5 g sample of the purified and assayed ketal is flame sealed into a thin-walled glass ampule. The reaction solvent (100 mL) is pipetted into the reaction

vessel, assembled with the ampule into the cannister, and placed in a constant-temperature bath at 25.3000 ± 0.0005 °C. After thermal equilibration, the steadily rising temperature of the stirred calorimeter is monitored by the minicomputer, and at exactly 25.000 °C the ampule is broken into the reaction solvent. After an additional 30 min of data collection, cooled carbon dioxide is allowed to flow into the cannister until the temperature is back below 25 °C. Data collection is repeated as above with the calibration heater turning on at 25.000 °C for a preset interval. At the end of the experiment, the stored data for both the chemical reaction run and its corresponding electrical calibration are sent to a larger computer where the necessary corrections and calculations are performed.[5] The final value of the enthalpy of reaction is then output. Table II gives a sample data set for the endothermic heat of reaction of 3-methyl-2-butanone dimethyl ketal.

Equilibrium Measurements. Equilibrium mixtures of ketone and ketal in wet acidic methanol were assayed with an HA-100 NMR spectrometer. The instrument was coupled with a minicomputer, allowing automatic collection and optimization of the continuous wave proton spectrum. Data sets collected and stored in this fashion were analyzed by Simpson's rule integration of the appropriate proton signals with correction for base line and noise. The accuracy of this technique was determined by reproducing known internal peak ratios for several compounds. The calculated ratios deviated by less than 1% from the theoretical ratio. Concentration ratios for standard mixtures could also be reproduced within 1% of the true value.

Since the ketone is greatly favored in all equilibria we studied, the effective concentration of water in the mixtures had to be kept as low as possible so that the final concentration of ketal could be determined. Mixtures were prepared by weighing absolutely dry methanol, ketone (or ketal), and water into a volumetric flask and adding a drop of anhydrous methanesulfonic acid just prior to assay. Samples were pipetted into an NMR tube and the spectrum was collected at 25 °C as described. In the case of the acetone/acetone ketal mixture, a known quantity of hexamethylethane was added as an internal reference for determining the concentration of ketal because it possesses a convenient nearby proton band. In all other cases, appropriate peaks from the ketal and ketone could be selected for the quantitative analysis. Equilibrium composition attained from both directions was assayed in all cases, and at least four runs were made for each sample. A sample data set from the analysis of an equilibrium mixture of 2-butanone (1) and 2,2-dimethoxybutane (2) is given in Table III.

Results and Discussion

The ketal hydrolysis reaction is very rapid under our conditions, and half-lives on the order of 30 s were calculated from computer simulations of the time/temperature curves. All reactions were essentially quantitative and totally free of side products as determined by 100-MHz proton spectra of each of the final reaction mixtures. The observed enthalpies refer to liquid ketal reacting with water in solution to form ketone and methanol in solution, and these data are shown in column 1 of Table IV. These values represent a summation of heat effects due to the chemical transformation plus heat effects due to any species entering or leaving the reaction medium. To derive the corresponding enthalpy of reaction with all components in the pure liquid phase, the heats of solution of the ketones, methanol, and water must be determined. The results of our measurements of these quantities are shown in column 2. The observed enthalpies are combined with the heats of

Table II. Reaction of 3-Methyl-2-butanone Dimethyl Ketal with 65% (v/v) Aqueous Dioxane, 0.001 N in HClO$_4$, 25 °C

run no.	E_{calib},[a] cal °C^{-1}	ΔT_{cor},[b] °C	cal	sample[c] wt, g	mol × 10^3	ΔH_{obsd}, cal mol^{-1}
1	74.398	−0.246 98	18.375	0.436 76	3.303	5561.
2	74.649	−0.260 24	19.427	0.462 92	3.502	5548.
3	74.535	−0.203 91	15.198	0.362 82	2.744	5544.
4	74.406	−0.192 91	14.354	0.341 37	2.582	5559.
					mean value	5553. ± 8.[d]

[a] Electrical calibrations are automatically performed for every chemical reaction run. [b] Corrected for heat effects due to stirring and thermal leakage (ref 5). [c] Corrected to in vacuo. [d] Uncertainty given is $2\bar{s}$.

Table III. Equilibration of 2-Butanone (**1**) and 2-Butanone Dimethyl Ketal (**2**) at 25 °C

| | initial concn, mol fraction | | | | | |
1	2	CH_3OH	H_2O	area 1[a]	area 2[a]	$K_{hydrolysis}$[b]
0	0.029 01	0.9279	0.043 03	270 449	31 248	488.2
0	0.029 01	0.9279	0.043 03	207 739	30 167	372.6
0	0.029 01	0.9279	0.043 03	208 507	29 063	391.3
0	0.029 01	0.9279	0.043 03	215 460	32 526	355.7
0	0.029 01	0.9279	0.043 03	163 395	25 468	342.3
0.047 31	0	0.9527	0	241 024	58 537	388.7
0.047 31	0	9.9527	0	181 462	43 116	404.7
0.047 31	0	0.9527	0	165 521	44 112	327.9
					mean value 383.9 ± 35.0[c]	

[a] Arbitrary units. Obtained from digital integration of methyl singlets for ketone and ketal at δ 2.1 and 1.3 (Me_4Si), respectively. [b] The equilibrium concentrations and $K_{hydrolysis}$ were determined using the equations $N^e_1 = [A_1/(A_1 + A_2)]N^0_2$, $N^e_2 = N^0_2 - N^e_1$, $N^2_{CH_3OH} = N^0_{CH_3OH} + 2N^e_1$, $N^e_{H_2O} = N^0_{H_2O} - N^e_1$, and $K_{hydrolysis} = [N^e_1(N^e_{CH_3OH})^2]/(N^e_2 N^e_{H_2O})$, where N^e_R = equilibrium mole fraction of species R, N^0_R = initial mole fraction of species R, and A_R = area of proton signal corresponding to species R. [c] Uncertainty given is 2s.

Table IV. Enthalpies of Hydrolysis of Ketals, 25.0 °C

R	ΔH_{obsd},[a] cal/mol	ΔH_{soln},[b] cal/mol	ΔH_r(liquid phase),[c] cal/mol	E_s
methyl	4963 ± 6	55 ± 3	4884 ± 7	0.00
ethyl	4991 ± 8	344 ± 1	4620 ± 8	−0.07
n-propyl	5450 ± 11	757 ± 8	4666 ± 14	−0.36
isobutyl	4428 ± 12	1117 ± 6	3284 ± 13	−0.93
neopentyl	3068 ± 19	1400 ± 7	1642 ± 21	−1.74
isopropyl	5553 ± 8	669 ± 3	4858 ± 9	−0.47
2-butyl	5802 ± 11	1014 ± 3	4762 ± 11	−1.13
tert-butyl	1876 ± 12	1031 ± 2	819 ± 13	−1.54

[a] Enthalpy of conversion of liquid ketal to ketone in 65% dioxane solution. [b] Enthalpy of solution of ketone in 65% dioxane solution. $\Delta H_{soln}(CH_3OH) = -98.04 \pm 0.22$ cal/mol, $\Delta H_{soln}(H_2O) = -222.26 \pm 0.36$ cal/mol. [c] Enthalpy of reaction with all components in the pure liquid phase. [d] Uncertainties are twice the standard deviation of the mean.

solution according to eq 3, yielding the liquid-phase enthalpies listed in Table IV, column 3. For reference, Taft's steric substituent parameters $(E_s)^1$ for each alkyl group are shown in column 4.

$$\Delta H_r \text{ (pure liquid)} = \Delta H_{obsd} + \Delta H_{soln}(H_2O)$$
$$- 2\Delta H_{soln}(CH_3OH) - \Delta H_{soln}(\text{hydrolysis product}) \quad (3)$$

If one examines the series in which branching occurs at the β position, the changes in ΔH_r are in the expected order. That is, the ketals bearing larger alkyl substituents have less endothermic enthalpies for conversion to the less strained ketones. However, the effects of α substitution are not in accord with this qualitative scheme. The ketal from isopropyl methyl ketone gives about the same ΔH_r as that from acetone, whereas a smaller value would be expected. Similarly, the ketal from 2-butyl methyl ketone gives a considerably larger ΔH_r than that from isobutyl methyl ketone.

The enthalpies of reaction and the E_s values are not directly comparable since they differ by an entropy contribution. The importance of entropy terms as well as enthalpy changes in determining the total steric effect on free-energy differences has been recognized,[8] but rigorous separation of these components has been hindered by the lack of precise thermochemical data. In order to achieve a successful decompositon of the steric effects in our hydrolysis system, the free-energy differences had to be determined with a precision comparable to that of the enthalpy measurements. The equilibrium constants for the reaction described in eq 2 could be determined in methanol solution for the ketones where R = CH_3, C_2H_5, *n*-C_3H_7, and *i*-C_3H_7:

$$K = \frac{[\text{ketone}][\text{MeOH}]^2}{[\text{ketal}][H_2O]} \quad (4)$$

A considerable difference in the equilibrium constants was

Table V. Equilibrium Constants and Free Energies of Hydrolysis, 25.0 °C

R	K[a]	ΔG, cal/mol	ΔH,[b] cal/mol	ΔS, eu
methyl	113.6 ± 3.6	−2803 ± 19	5488 ± 10	27.81 ± 0.07
ethyl	383.9 ± 35	−3521 ± 51	5189 ± 13	29.21 ± 0.81
n-propyl	606.0 ± 18	−3795 ± 17	5136 ± 18	29.95 ± 0.08
isopropyl	1344 ± 155	−4260 ± 67	5331 ± 13	32.17 ± 0.23

[a] The solvent was 98% methanol–2% water (v/v). [b] Based on ΔH_r for the pure liquid phase and corrected for the enthalpies of solution in 98% methanol containing 0.005 N sodium hydroxide. [c] Uncertainties given are twice the standard deviation of the mean.
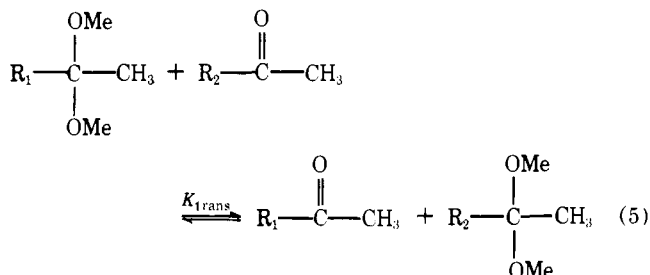
found as indicated in Table V, column 1. The corresponding differences in the ΔG values are in much better accord with the E_s values than are the enthalpies of hydrolysis.

Measurement of the heats of solution of all the reaction components of eq 2 in 98% methanol along with the data in Table IV permit a calculation of the enthalpies of hydrolysis in the same solution as that in which the equilibrium measurement were made. The resulting values are given in Table V, column 3. Entropies of hydrolysis in methanol solution may be calculated from the free energies and enthalpies, and these data are shown in column 4.

It can be seen that essentially all the difference between these substituents may be ascribed to an entropy effect. The entropy differences produce a range of over 1300 cal in the free energy, whereas the enthalpy changes account for only up to a fourth of this amount. Since an increase in the number of carbons leads to an increase in the entropy, and the entropy difference between the ketals and corresponding ketones appears to be increasing in the homologous series represented in Table V, one may say that the entropy of the ketones increases

more rapidly than the entropy of the ketals. The results also indicate that branching accentuates this trend.

The exact origin of these substantial entropy differences is probably manyfold, though two important features of our system stand out. Since these effects have been characterized in a hydrogen-bonding solvent, differential solvation of the ketones and ketals could have an important contribution. Differences in electrostriction of solvent have been shown to be the key element in determining entropy effects in a variety of reactions involving polar and ionic species.[9] One way to minimize the effects of solvation would be to measure the relative free energies of hydrolysis via an acid-catalyzed transketalization reaction (eq 5). That is, knowledge of the

$$
\begin{array}{c}
\text{OMe} \qquad\qquad\quad \text{O} \\
| \qquad\qquad\qquad\; || \\
R_1\text{---}C\text{---}CH_3 \;+\; R_2\text{---}C\text{---}CH_3 \\
| \\
\text{OMe}
\end{array}
$$

$$
\xrightleftharpoons{K_{\text{trans}}} \;
\begin{array}{c}
\text{O} \qquad\qquad\qquad \text{OMe} \\
|| \qquad\qquad\qquad\; | \\
R_1\text{---}C\text{---}CH_3 \;+\; R_2\text{---}C\text{---}CH_3 \\
\qquad\qquad\qquad\qquad | \\
\qquad\qquad\qquad\; \text{OMe}
\end{array}
\qquad (5)
$$

hydrolysis equilibrium constant for either ketal in eq 5 when combined with K_{trans} would allow calculation of the other. Comparison of these values with those obtained directly in methanol solution might give a clue as to the relative magnitudes of solvation effects on the free-energy differences. Experiments of this type are currently underway.

The internal contributions to the entropy differences are most likely a function of internal rotational characteristics. A useful decomposition of these effects can be derived from empirical force field calculations, provided that a reasonable balance of internal forces is achieved.[10] We are currently engaged in attempts to generate a reliable force field for the ketones and ketals, and we shall report our results from this work at a later time.

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Linear and Circular Dichroism Studies of $\pi \rightarrow \pi^*$ Transitions in Steroidal Dienes and α,β-Unsaturated Ketones[1a]

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Abstract: The diene and α,β-unsaturated keto chromophore in different conformations and orientations in a number of steroids were studied by circular dichroism (CD) in solution and linear dichroism (LD) in a stretched polyethylene matrix. The geometries of the chromophores were obtained from force-field calculations, and the energies, transition moments, and oscillator strengths for the $\pi \rightarrow \pi^*$ transitions were calculated by the VESCF-CI method including all singly and doubly excited configurations. CD, supported by LD, confirms the presence of an additional transition around 200 nm (6 eV), not observed in the UV spectra of dienes and α,β-unsaturated ketones. An analysis of the spectra shows, in agreement with the calculations, that the first two $\pi \rightarrow \pi^*$ transitions occur close to each other in the region 200–260 nm. The importance of taking doubly excited configurations into account is demonstrated by the fact that the second transition is otherwise obtained at very high energy. The experimental and calculated transition moments were in reasonable agreement, and a rule for the transition moment direction of the first absorption band was provided by the line between the end atoms of the diene or enone moieties, even for twisted chromophores. The circular dichroism is discussed with respect to chromophore dihedral angle. Unexpectedly large rotational strengths shown by the planar conformations of the chromophore indicate a very strong influence from substituents.

Introduction

Simple conjugated olefinic systems have been the subject of extensive theoretical and spectroscopic (UV, PE) studies over the past decade, with the aim of establishing energy levels and electronic transitions.[2] In cases where the conjugated system is part of a chiral framework, circular dichroism (CD) provides a particularly powerful method. Much attention has been paid to long-wavelength Cotton effects in dienes and α,β-unsaturated ketones,[3-5] but there has been little discussion of the short-wavelength transitions ($\pi \rightarrow \pi^*$), although they can be easily seen in the circular dichroism (CD) spectrum, as will be shown below.

The present study is concerned with a firmer characteriza-