Table III. Models for Sum and Density of States Calculations

Molecule	n^a	Frequencies, cm^{-1}	E_z,[b] cm^{-1}	β^c	Moments of inertia, g $cm^2 \times 10^{40}$ [d]
$C_6H_5CH_2CH_2C_6H_5$	78	3000 (14), 1550 (12), 1200 (14), 1000 (13),[e] 800 (4), 700 (4), 600 (2), 500 (4), 400 (4), 300 (5), 200 (2)	51550	1.4172	145.3 (2), 150.6
$O_2NC_6H_4CH_2CH_2C_6H_5$	84	3000 (15), 1550 (13), 1200 (15), 1000 (13),[e] 800 (5), 700 (3), 600 (2), 500 (4), 400 (4), 300 (7), 200 (3)			145.3, 150.6, 208.2
$HN_2C_6H_4CH_2CH_2C_6H_5$	84	3000 (15), 1550 (13), 1200 (15), 1000 (13),[e] 800 (5), 700 (3), 600 (2), 500 (4), 400 (4), 300 (7), 200 (3)			145.3, 150.6, 147.9, 2.55

[a] Number of vibrational degrees of freedom. [b] Zero point energy. [c] β-Parameter[36] without internal rotations. [d] For each internal rotation included, one low-frequency ($\sim$300 cm^{-1}) vibrational mode is removed. [e] One of these frequencies is transformed into the reaction coordinate in the activated complex.

$$\Sigma \mathbf{P}^{\pm}(E - E_a) = \sum_{E_v^{\pm}=0}^{E^{\pm}} \mathbf{P}^{\pm}(E_v^{\pm})(8\pi^2/h^2)^{r^{\pm}/2} \times (E^{\pm} - E_v^{\pm})^{r^{\pm}/2} \prod_i I_i^{1/2} \Gamma(1/2)/\Gamma(1 + r^{\pm}/2); \quad r^{\pm} \neq 0$$

$$= \sum_{E_v^{\pm}=0}^{E^{\pm}} \mathbf{P}^{\pm}(E_v^{\pm}); \quad r^{\pm} = 0 \quad (13)$$

$$\rho^*(E) = \sum_{E_v=0}^{E} \mathbf{P}^*(E_v^*)\,(8\pi^2/h^2)^{r^*/2}(E^* - E_v^*)^{(r^*/2)-1} \times \prod_i I_i^{1/2} \Gamma(1/2)/\Gamma(r^*/2); \quad r^* \neq 0$$

$$= \left(\frac{\delta \sum_{E_v=0}^{E} \mathbf{P}^*(E_v)}{\delta E} \right)_{E_v = E}; \quad r^* = 0 \quad (14)$$

where $\Sigma \mathbf{P}(E_v)$ is the sum of vibrational eigen states, r is the number of active rotations, I_i is the ith moment of inertia, Γ is the gamma function, and the other terms are as defined for eq 2. Exact enumeration of states, with from three to five vibrational frequency groups, was employed to evaluate $\Sigma \mathbf{P}(E_v)$ and $\Sigma \mathbf{P}(E_v)(E - E_v)^{r/2}$ at low energies. The approximation formulas of Rabinovitch and coworkers[36] were employed for p-$NH_2C_6H_4CH_2CH_2C_6H_5$ at high energies. Vibrational frequencies for $YC_6H_4CH_2CH_2C_6H_5$ were constructed from those of toluene[56] and of amino and nitro groups. The frequencies in the active molecule ion were assumed to be equal to those in the corresponding neutral molecule; although there undoubtedly is some reduction in the number of vibrational states, the relative change should have only a small effect on $k(E)$. Some or all of the torsional vibrational frequencies were changed into internal rotations and the respective moments of inertia calculated from plausible bond distances and angles. One carbon–carbon stretching frequency was changed to be the reaction coordinate in the activated complex. The models for the calculations (including vibrational frequencies, moments of inertia, parameters for the approximation formulae[36]) are presented in Table III.

Acknowledgment. Valuable assistance was provided by Maurice M. Bursey and G. E. Van Lear in the preparation of compounds and other important initial phases of this research, by J. Hribar in obtaining the temperature-effect metastable ion data, and by Paul Bente in performing the calculations. We are deeply indebted to R. B. Fairweather, M. L. Gross, I. Howe, D. J. McAdoo, B. S. Rabinovitch, H. M. Rosenstock, J. C. Tou, and A. L. Wahrhaftig for valuable discussions. Generous financial support was provided by the Public Health Service (National Institutes of Health Grant No. GM16609).

(56) K. S. Pitzer and D. W. Scott, *J. Amer. Chem. Soc.*, 65, 803 (1943).

Kinetic and Thermodynamic Studies of Acetals and Ketals in the Naphthalene Series[1]

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Contribution from the Evans Chemistry Laboratory of the Ohio State University, Columbus, Ohio 43210. *Received May 2, 1970*

Abstract: The rates of acid-catalyzed hydrolysis of a number of acetals and ketals formed from 1- and 2-naphthaldehyde and 1- and 2-naphthyl methyl ketones with 2,2-disubstituted 1,3-propanediols have been measured at at 34.3°. The equilibrium constants for the acetals and some ketals were also determined at 34.3°. From the results it appears likely that the rate-determining step for hydrolysis of the acetals may occur at the cleavage into two moiety step rather than in the ring-opening step.

Ethylene glycol has been the reagent of choice whenever conversion of a ketone to a cyclic ketal was desired. In general, ketones react rapidly with ethylene glycol and the resulting ketals (1,3-dioxolanes) are reasonably stable toward hydrolysis. The use of 1,3-propanediol is less desirable not only because the rate of

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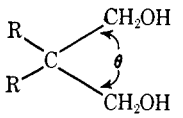
formation of the cyclic ketals (1,3-dioxanes) is considerably slower than when ethylene glycol is used but also because the 1,3-dioxanes hydrolyze more rapidly than do the corresponding 1,3-dioxolanes.

We have been interested in discovering what effect gem substitution in 1,3-propanediols has on the rate of hydrolysis of the corresponding acetals and ketals and on the equilibrium constants for the reactions with representative aldehydes and ketones.

Previous studies from this laboratory on the *gem-dialkyl effect*[2] have been concerned with kinetic and equilibrium studies of ketal formation and hydrolysis involving derivatives of monocyclic ketones[3] and 3,17-androstanedione.[4] The glycols involved were ethylene glycol, 1,3-propanediol, and 2,2-dialkyl-1,3-propanediols. In general, the larger the *gem*-alkyl groups in the 1,3-propanediols the more rapid the rate of formation of cyclic ketal (qualitative observation) and the slower the rate of hydrolysis of the cyclic ketal (rate measurements). These results are probably due mainly to the steric effects of the *gem*-dialkyl groups on the bond angle θ.



In order to obtain more data on the effect of the bond angle θ and the steric effects, we have undertaken a study of the rates of hydrolysis of cyclic acetals of 1- and 2-naphthaldehyde and cyclic ketals of 1- and 2- naphthyl methyl ketone involving 1,1-(bishydroxymethyl)cycloalkanes of formula $(CH_2)_nC(CH_2OH)_2$ where n = 2, 3, 4, and 5. In addition the equilibrium constants for these reactions were to be determined. The 1,1-(bishydroxymethyl)cycloalkanes were chosen because these diols offer the best choice of 1,3-diols in which the bond angle, θ, in question can be varied while keeping the other steric effects of substituents in the 2 position nearly constant.[5] The naphthalene compounds were chosen in order to have comparative studies on aldehydes and methyl ketones in which an ortho effect could be evaluated while keeping the polar effects relatively constant in the carbonyl component. For reasons pointed out in the Discussion, not all of the possible ketal measurements were made.

Experimental Section

The 1,1-(bishydroxymethyl)cycloalkanes were prepared by lithium aluminum hydride reduction of the corresponding diethyl cycloalkyl-1,1-dicarboxylates. The properties agreed well with literature values[6] and the purities were checked by glpc.

Formation of Acetals. In a typical case a solution of 13.0 g (0.10 mol) of 1,1-(bishydroxymethyl)cyclopentane, 15.8 g (0.11 mol) of 1-naphthaldehyde, 2 ml of concentrated hydrochloric acid, and 150 ml of benzene was refluxed into a short column fitted with a small phase-separating head to remove water as formed until a volume of 50 ml was reached. When *p*-toluenesulfonic or sulfuric acids were used the reaction mixture became dark and purification of the product was more difficult. The solution was cooled and treated with anhydrous potassium carbonate. After filtration, the solvent was distilled until a volume of about 20 ml was reached. Addition of an equal volume of Skellysolve B (petroleum ether, bp 65–70°) yielded 22.8 g (86%) of 8-(1-naphthyl)-7,9-dioxaspiro-[5,4]decane (5-1-A),[7] mp 78–82°. Recrystallization from the same solvents afforded pure 5-1-A, mp 88–89°, with little loss. Obviously, the lower melting product was a polymorphic form. There was evidence of polymorphic forms in several of the acetals as judged by their behavior on melting.

The yields of acetals listed in Table I are based on the diol used except for the acetals formed by reaction of 1,3-propanediol and 2,2-dimethyl-1,3-propanediol with 2-naphthaldehyde. The samples

Table I. Spirocyclic Acetals

Name	Notation[a]	Yield, %[b]	Mp, °C[c]	Bp, °C (2 mm)[d]
6-(1-Naphthyl)-5,7-dioxaspiro[5,2]octane	3-1-A*	44	90–92	165–175
7-(1-Naphthyl)-6,8-dioxaspiro[5,3]nonane	4-1-A*	80	110–112	170–180
8-(1-Naphthyl)-7,9-dioxaspiro[5,4]decane	5-1-A*	86	88–89	*e*
3-(1-Naphthyl)-2,4-dioxaspiro[5,5]undecane	6-1-A*	91	116–119	*e*
6-(2-Naphthyl)-5,7-dioxaspiro[5,2]octane	3-2-A*	57	90–92	170–180
7-(2-Naphthyl)-6,8-dioxaspiro[5,3]nonane	4-2-A*	67	89–90	150–160
8-(2-Naphthyl)-7,9-dioxaspiro[5,4]decane	5-2-A*	95	119–120	*e*
3-(2-Naphthyl)-2,4-dioxaspiro[5,5]undecane	6-2-A*	14[f]	89–91	*e*
2-(2-Naphthyl)-1,3-dioxane	0-2-A*	88	75–77	*e*
5,5-Dimethyl-2-(2-naphthyl)-1,3-dioxane	DM-2-A*	92	96–97.5	*e*

[a] Carbon and hydrogen analyses, agreeing within ±0.3% of the calculated values, have been provided to the Editor for all of the new compounds indicated by an asterisk in Tables I and II. [b] Yield based on the amount of compound in the crude product as estimated by glpc analysis. [c] Melting point of compound purified by recrystallization from Skellysolve B (petroleum ether, bp 65–70°). The behavior on melting of several of these acetals indicated that polymorphic forms were at hand. Only the higher melting polymorph is reported. All analytical samples were sublimed. [d] The boiling point listed is the range obtained by rapid distillation from a Claisen flask. [e] No distillation was carried out as crystallization was effective. [f] This low yield was caused by decomposition on attempted distillation. An 85% yield was obtained from an acetalization at room temperature for 2.6 days involing 6.3 g of 2-naphthaldehyde, 6.8 g of 1,1-(bishydroxymethyl)cyclohexane, and 100 ml of dry dioxane containing about 1 g of HCl gas. The product was isolated by crystallization from Skellysolve B.

(2) (a) For a discussion see G. S. Hammond in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956; (b) the Ph.D. Thesis of R. E. Dickson, Ohio State University, 1968, contains more recent examples.

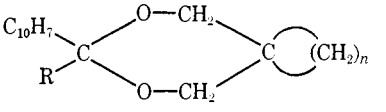
(3) M. S. Newman and R. J. Harper, Jr., *J. Amer. Chem. Soc.*, **80**, 6350 (1958).

(4) S. W. Smith and M. S. Newman, *ibid.*, **90**, 1249, 1253 (1968);

(5) See P. von R. Schleyer, *ibid.*, **83**, 1368 (1961), for a discussion of the Thorpe–Ingold hypothesis of valency deviation in these dimethanols as well as numerous references to the *gem*-dialkyl effect.

(6) See ref 2b for details.

(7) The nomenclature and notation for the acetals and ketals of general formula are the following. The number of atoms in the spirane



structure is used to determine the basic hydrocarbon name (*e.g.*, spirodecane, etc.). The numbering starts at the atom adjacent to the spirane carbon in the smaller ring and progresses so as to include the spirane carbon. If the two rings contain equal numbers of atoms the oxygenated ring takes preference. The numbers of atoms in the two spiro rings (not including the spiro carbon) are indicated by the numbers in brackets, the larger number first. The notation used in this paper to designate the acetals and ketals has the first number represent the number of carbons in the all-carbon ring, including the spirane carbon, the second number represents the 1 or 2 position of the naphthalene ring, and the letters, A and K, refer to acetal and ketal. Thus, the compound formed from 1-naphthaldehyde and 1,1-(bishydroxymethyl)-cyclopentane is named 8-(1-naphthyl)-7,9-dioxaspiro[5,4]decane. The notation is 5-1-A.

Table II. Spirocyclic Ketals

Name[a]	Notation[a]	Yield, %[b]	Mp, °C[c]	Bp, °C[d]
6-Methyl-6-(1-naphthyl)-5,7-dioxaspiro[5,2]octane	3-1-K*	11[e]	53–56	150–170 (2.5 mm)
7-Methyl-7-(1-naphthyl)-6,8-dioxaspiro[5,3]nonane	4-1-K*	50	82.0–83.5	160–190 (5 mm)
3-Methyl-3-(1-naphthyl)-2,4-dioxaspiro[(5,5]undecane	6-1-K*	83	83–86	*f*
7-Methyl-7-(2-naphthyl)-6,8-dioxaspiro[5,3]nonane	4-2-K*	65	128–130	*f*
8-Methyl-8-(2-naphthyl)-7,9-dioxaspiro[5,4]decane	5-2-K*	79	99–101	*f*
3-Methyl-3-(2-naphthyl)-2,4-dioxaspiro[5,5]undecane	6-2-K*	72	107–109	*f*

[a] See ref 7; carbon and hydrogen analyses, agreeing within ±0.3% of the calculated values, have been provided to the Editor for all of the new compounds indicated by an asterisk in Tables I and II. [b] Yield based on the amount of compound in the crude product as estimated by glpc analysis. [c] Melting point of compound purified by recrystallization from Skellysolve B. The behavior on melting of several ketals indicated that polymorphic forms were at hand. Only the higher melting polymorph is reported. [d] The boiling point listed is the range obtained on rapid distillation from a Claisen flask. [e] The final purification was affected by preparative glpc using a 10-ft 20% FFAP, a polyglycol polymer, on Chromosorb W at 180°. [f] Purified only by recrystallization from Skellysolve B.

used for the rate and equilibrium measurements were further purified by vacuum distillation and/or recrystallization until homogeneous as determined by glpc on 3- or 5-ft columns packed with 2% XE-60 (a cyanosilicone polymer) on Diatoport-S (a Hewlett-Packard support especially treated to reduce tailing). The yields of acetals prepared from 1,1-(bishydroxymethyl)cyclopropane were generally poor because of acid sensitivity of the diol.

Compound 6-2-A, 3-(2-naphthyl)-2,4-dioxaspiro[5,5]undecane, was also prepared by allowing a solution of 6.3 g of 2-naphthaldehyde and 6.8 g of 1,1-(bishydroxymethyl)cyclohexane in 100 ml of dioxane containing about 1 g of HCl gas to stand at room temperature for 63 hr. After adding 1 g of K_2CO_3 the dioxane was removed on a rotary evaporator under reduced pressure. The residue was taken up in benzene and most of the unreacted diol crystallized. Addition of Skellysolve B to the filtrate resulted in crystallization of 6-2-A in 85% yield based on aldehyde.

Formation of Ketals. The ketals listed in Table II were prepared as described above for acetals except that *p*-toluenesulfonic acid was used as catalyst. Only low yields of 3-1-K and no pure 3-2-K were obtained in this way. In addition ketals 4-2-K and 6-2-K were prepared as follows. About 4 g of Dowex W-X4, an acidic ion exchange resin, was dried for 2 hr at 78° in a drying pistol. The dried resin was suspended in 50 ml of benzene containing 1.52 g of 2-naphthylacetylene, 2.46 g of 1,1-(bishydroxymethyl)cyclohexane, and 0.5 g of mercuric sulfate. After 3 hr at reflux the mixture was filtered through a cone of anhydrous potassium carbonate. After removal of solvent, vacuum distillation yielded a product which was taken up in Skellysolve B whereupon the diol present crystallized rapidly and was removed. Recrystallization of the crude 6-2-K afforded pure material, mp 107–109°, in 65% yield. Ketal 4-2-K was obtained in 60% yield in this way but all attempts to prepare 3-2-K by this route or the homogeneous route failed.

2-Naphthylacetylene, mp 38–40°, was prepared in 58% yield by dehydrochlorination with sodium amide in liquid ammonia of the product formed by treatment of 2-naphthyl methyl ketone with phosphorus pentachloride in benzene at reflux.[8]

Measurement of Rates of Hydrolysis of Acetals and Ketals. A solution of acetal or ketal in 15–20 ml of dry degassed dioxane in a 25-ml volumetric flask was placed in a constant temperature bath held at 34.3 ± 0.1°. After standing overnight, 5 ml of standard aqueous hydrochloric acid was added together with sufficient dioxane to bring the volume to 25.0 ml. Both the dioxane and hydrochloric acid were at 34.3° when added (zero time). At time intervals 1.0-ml aliquots were withdrawn and added to dioxane containing a known concentration of 2-methoxy-6-bromonaphthalene and 0.01–0.03 ml of triethylamine. The concentration of aldehyde or ketone was determined to ±3–4% by glpc on an F and M Model 609 flame ionization gas chromatograph with programmed temperature. From 5 to 10 injections for each aliquot were made and averaged. For acetals a 3- or 5-ft 2% XE-60 (a cyanosilicone polymer) on Diatoport-S column was used. For ketals a 5-ft FFAP (a polyglycol polymer) on Chromosorb W column was used. Standard solutions of known concentration were checked frequently to determine the instrument response. Measurements were made until the reactions were 60–85% complete.

The rate constants were obtained from the slope of a plot of the equation for a first-order reaction (eq I)

$$\log [A] = (-k/2.3)t + \log [A_0] \qquad \text{(I)}$$

where $[A]$ = acetal or ketal concentration at time t and $[A_0]$ = acetal or ketal concentration at t_0.

Since the concentration of aldehyde (or ketone) was measured the concentration of acetal $[A]$ (or ketal) was calculated by subtracting the aldehyde (ketone) concentration from $[A_0]$ For convenience in calculating the rate, a constant, 3, was added to each side of eq I and $3 + \log [A]$ plotted against time (minutes). The slope of the line was determined by the best fit. The second-order rate constant was determined by dividing the observed rate constant by the acid concentration. A typical result is shown in Table III and the rate data are summarized in Table IV.

Table III. Hydrolysis of 5-1-A in 4:1 Dioxane–Water at 34.3 ± 0.1°

Run 2[a]		Run 3[a]	
Time, min	[Acetal] × 10^3, mmol/ml[b]	Time, min	[Acetal] × 10^3, mmol/ml[b]
0	23.6	0	26.2
9	22.9	10	25.4
21	22.0	43	23.0
48	20.8	71	21.0
81	18.7	126	18.0
128	16.7	193	14.1
168	14.0	251	12.2
226	12.1	311	10.3
296	10.3	396	9.4
348	8.8		
416	7.6		
k = 0.140 l. mol^{-1} min^{-1}		k = 0.148 l. mol^{-1} min^{-1}	

[a] Acid concentration 0.02 *N* HCl. [b] Each number reported represents the average of from five to ten injections.

Measurement of Equilibrium Constants. The solutions for the equilibrium experiments were made up in dry degassed dioxane in a 5-ml double-sealed volumetric flask the air space of which was filled with nitrogen. The stoppered flask was then placed in a brown bottle suspended in a constant temperature bath held at 34.3 ± 0.1°. After standing for 1–3 days an aliquot was withdrawn and added to a known concentration of 2-methoxy-6-bromonaphthalene in dioxane containing 0.03–0.05 ml of triethylamine. The concentration of diol, aldehyde, and acetal were determined by glpc and the concentration of water was calculated from starting concentrations and extent of reaction as determined from the other three components. Two determinations of K_{equil} were made,

(8) I. Iwai and Y. Yura, *Takamine Kenkyusho Nempo*, **10**, 30 (1958); *Chem. Abstr.*, **55**, 4400*f* (1958)), report a mp of 39–40°.

Table IV. Relative Rates of Hydrolysis of Acetals and Ketals[a]

Compd	k	Rel rate	Compd	k	Rel rate	$\Delta\theta$[b]
3-1-A	4.2 ± 0.4	47	3-2-A	4.3[c]	63	5.2
4-1-A	0.28 ± 0.03	3.1	4-2-A	0.224 ± 0.004	3.3	1.1
5-1-A	0.114[c]	1.6	5-2-A	0.143 ± 0.003	2.1	0.2[d]
6-1-A	0.090 ± 0.003	1.0	6-2-A	0.068 ± 0.003	1.0	−0.1[d]
			0-2-A[e]	1.6[f]	24[g]	2.7
			DM-2-A[h]	0.11[c]	1.6[g]	0.2[d]
3-1-K	3.6[i]	103				
4-1-K	0.32[c]	9.1	4-2-K	1.8 ± 0.1	3.7	
6-1-K	0.035[c]	1.0[j]	6-2-K	0.49[c]	1.0[j]	

[a] All second-order rate constants (expressed in l. mol^{-1} min^{-1}) from which relative rates were calculated were the average of 3 runs unless otherwise noted. [b] $\Delta\theta$, a change in the bond angle formed by the three carbons in the 1,3-diols used relative to 109.5°, was calculated by Schleyer (P. von R. Schleyer, *J. Amer. Chem. Soc.*, **83**, 1368 (1961)) by assuming that a 4-cm^{-1} change in the intramolecular OH stretching frequency of a 1,3-diol results from a 1° change in θ. [c] Average of 2 runs. [d] Little significance should be attached to very small angle changes. [e] The cyclic acetal from 2-naphthaldehyde and 1,3-propanediol. [f] One run. [g] Relative to 6-2-A. [h] The cyclic acetal from 2-naphthaldehyde and 2,2-dimethyl-1,3-propanediol. [i] One run, approximate. [j] The relative rates of 6-1-K and 6-2-K are as 1.0 to 14.

the second after allowing 1 or 2 days to elapse after the withdrawal of the first aliquot. It was assumed that equilibrium was reached when K was constant for two successive aliquots. A typical experiment is summarized in Table V and the equilibrium constants,

Table V. Determination of the Equilibrium Constant for 6-1-A[a]

Diol/std	Aldehyde/std	Acetal/std
0.29[b]	0.49[b]	1.80[b]
0.37[c]	1.12[c]	1.29[c]

$$[\text{Diol}]_{\text{equil}} = \frac{0.29 \times 0.204 \times 5}{0.37} = 0.80$$

$$[\text{Aldehyde}]_{\text{equil}} = \frac{0.49 \times 0.204 \times 5}{1.12} = 0.45$$

$$[\text{6-1-A}]_{\text{equil}} = \frac{1.80 \times 0.204 \times 5}{1.29} = 1.41$$

$$K_{\text{equil}} = \frac{[\text{6-1-A}][\text{water}]}{[\text{aldehyde}][\text{diol}]} = \frac{(1.41)(16.7 - 0.45)}{(0.45)(0.80)} = 63.6$$

[a] The starting mixture (5 ml in all) contained 0.536 g (1.90 mmol) of 6-1-A, 0.40 mmol of diol, 16.7 mmol of water, 0.3 ml of 0.1 N HCl, and was made 0.204 M in 2-methoxy-6-bromonaphthalene which was added just before injection (glpc analysis). [b] These values represent the ratio of the areas under the peaks for the glpc analysis of the equilibrium component relative to the standard 2-methoxy-6-bromonaphthalene. [c] Instrument response was frequently checked by the response from a known concentration of components and internal standard.

each of which represents the average of from 4 to 6 runs, are reported in Table VI. As we were unable to obtain an analytically pure sample of 3-1-K, the approximate value was obtained by measurement of a preliminary run on impure 3-1-K. As the impurity was mainly methyl 1-naphthyl ketone the result is probably of the correct order of magnitude.

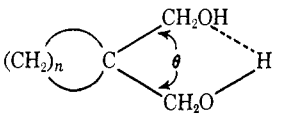
Table VI. Summary of Equilibrium Data[a]

Compd	K_{equil}	k_f[b]	Comp	k_{equil}	k_f
3-1-A	0.94 ± 0.09	4.0	3-2-A	1.27 ± 0.05	5.5
4-1-A	11.0 ± 0.6	3.1	4-2-A	9.6 ± 0.8	2.1
5-1-A	26.2 ± 1.4	3.6	5-2-A	26.6 ± 1.4	3.7
6-1-A	61 ± 3	5.5	6-2-A	66 ± 3	4.5
3-1-K	0.002[c]				
4-1-K	0.021 ± 0.002		4-2-K	0.023 ± 0.002	
6-1-K	0.24[d]		6-2-K[e]	0.20 ± 0.01	

[a] The K_{equil} are the average of from 4 to 6 runs unless otherwise noted. [b] $K_f = K_{\text{equil}}k_h$. [c] Results of one run. [d] Average of two runs, 0.21 and 0.26. [e] Average of 3 runs.

Discussion of Results

Acetals. The effect of structure of the diol moiety on the rate of hydrolysis of the acetals is essentially the same in the 1- and 2-naphthyl series. In each the rate is greatest for the acetals yielding 1,1-(bishydroxymethyl)cyclopropane and least for the acetals yielding 1,1-(bishydroxymethyl)cyclohexane. The rates of hydrolysis roughly parallel the change in bond angle (θ)[9] for 1,3-propanediols, the greater θ the greater the rate of hydrolysis (see Table IV).



The finding that the cyclic acetals of 2-naphthaldehyde with 1,3-propanediol and 2,2-dimethyl-1,3-propanediol, 0-2-A and DM-2-A, respectively, hydrolyze at rates that fit the bond angle correlation, supports the assumption that the only important steric factor in the series herein covered is the strain in the cycloalkane ring which causes the changes in θ.

According to the generally accepted mechansim for acid-catalyzed acetal hydrolysis the slow step involves cleavage of a protonated ether bond to yield a hydroxy carbonium ion and an alcohol molecule.[10] If a cyclic acetal is involved, as in the present cases, the slow step should involve opening of the ring as shown below in eq 2.

Evidence that hydrolysis of cyclic acetals proceeds by a similar mechanism lies in the maintenance of configuration in hydrolysis of acetals of optically active glycols.[11]

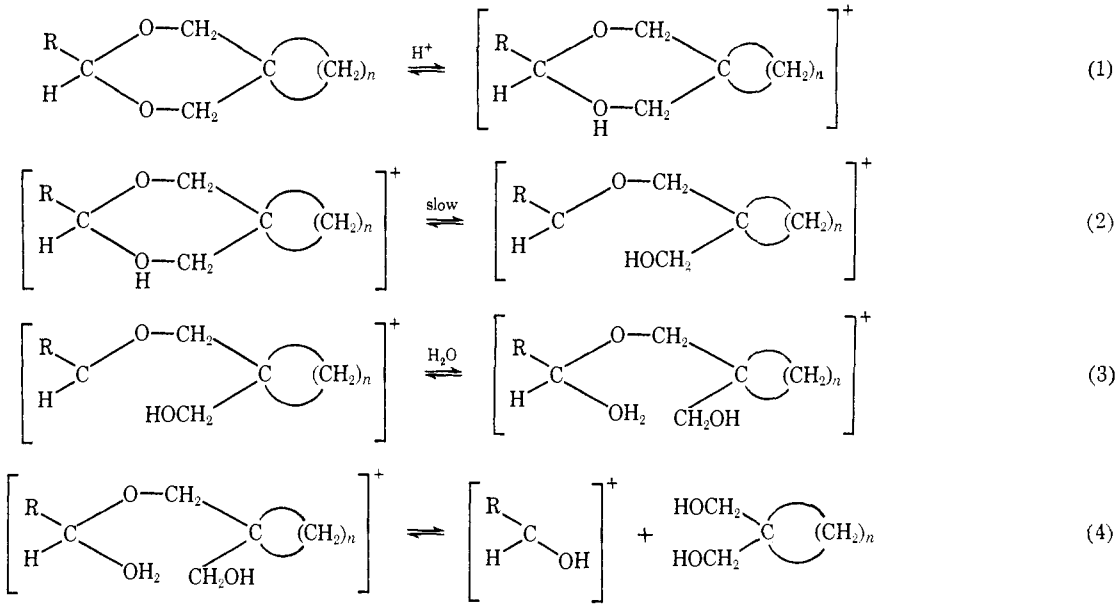
If the rate-determining step is that shown in eq 2 then the order of rates observed may be explained by ascribing the major effect to release of strain in the ring-opening step. Stabilization of the carbonium ion shown at the right in eq 2 is not important since the greater resonance stabilization of a carbonium ion attached to the 1 position of naphthalene[12] as compared to that at the 2 position is counteracted by the lesser solvation stabilization at the 1 position due to greater steric hindrance. The subtle interplay of steric effects on resonance stabilization and solvation of carbonium ions at the 1 and 2 positions of naphthalene is illustrated by the facts

(9) See von R. Schleyer, footnote *b*, Table IV.

(10) J. M. O'Gorman and H. J. Lucas, *J. Amer. Chem. Soc.*, **72**, 5489 (1950); J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1962, p 120; K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, p 397.

(11) H. K. Garner and H. J. Lucas, *J. Amer. Chem. Soc.*, **72**, 5497 (1950), and E. R. Alexander, *ibid.*, **74**, 3173 (1952).

(12) V. Gold, *Advan. Phys. Org. Chem.*, **1**, 64 (1963).



(1)

(2)

(3)

(4)

that the ratio of the solvolysis of 1-naphthylcarbinyl chloride to 2-naphthylcarbinyl chloride in aqueous acetone is 6.9 whereas the similar ratio involving the isomeric 1- and 2-naphthyldimethylcarbinyl chlorides is 1.0.[13]

The equilibrium data summarized in Table VI show the expected qualitative order of stability for the 1- and 2-naphthyl acetals, the least stable being the acetals derived from 1,1-(bishydroxymethyl)cyclopropane. Interestingly, the calculated values for the rate of formation of the acetals (see Table VI) show no significant trend in relation to the *gem*-dialkyl effect. Although the kinetic and equilibrium data were obtained in different media, they suggest that the mechanism of hydrolysis in which ring opening (eq 2) is rate determining may be in error in the case of cyclic acetals. If ring opening were rate determining for hydrolysis, the principle of microscopic reversibility requires that ring closure be the rate-determining step in the formation of acetals. The lack of the *gem*-dialkyl effect on k_f requires that the slow step in formation of these acetals occurs prior to ring closure. It is suggested[14] that the cleavage shown in eq 4 is the slow step. Proper evaluation of various factors already mentioned on the equilibria which precede the slow step allows for rationalization of our results within the framework of the new mechanism[15] but because of the different media involved further discussion will not be made at this time.

Ketals. Because of our inability to prepare pure samples of 3-1-K and 3-2-K, interest in the study of ketal hydrolysis was decreased. Accordingly the rates of hydrolysis of only 4-1-K, 6-1-K, 4-2-K, and 6-2-K were measured. Interestingly, the 1-naphthyl ketals hydrolyzed at about the same rate as the corresponding 1-naphthyl acetals whereas the 2-naphthyl ketals hydrolyzed about 7–8 times faster than the corresponding 2-naphthyl acetals (see Table IV).

Since ketals usually hydrolyze faster than related acetals[16] the fact that 4-1-K and 6-1-K hydrolyze at about the same rates as 4-1-A and 6-1-A, respectively, may be explained by assuming that the rates for the 1-naphthyl ketals are slowed because of steric factors; *e.g.*, steric inhibition of resonance of the incipient carbonium ion in the transition state and of solvation of this ion.

Also 4-2-K and 6-2-K hydrolyzed about 6 and 14 times more rapidly than 4-1-K and 6-1-K, respectively. The increased rates for the 2-naphthyl ketals are probably due to increased resonance stabilization of the incipient carbonium ion in the transition states, compared to the stabilization for the 1-naphthyl ketals, since there should be some steric inhibition of resonance in the 1-naphthyl ketal cases. Also, in the 1-naphthyl cases steric hindrance to solvation might be contributory.[17] An additional factor which may act to accelerate the hydrolysis of 4-2-K and 6-2-K relative to 4-2-A and 6-2-A may be the release of strain when ring opening occurs (ground state of higher energy) due to the axial methyl groups. In this connection 2-methyl-2-phenyl-1,3-dioxane has been shown to hydrolyze 6 times faster than 2-phenyl-1,3-dioxane.[18]

(13) Y. Okamoto and H. C. Brown, *J. Amer. Chem. Soc.*, 79, 1903 (1957).

(14) We thank Professor Jack Hine for his help in interpreting our data and for suggesting this mechanism. A referee suggests that the results may be accounted for by assuming that step 2 is rate determining for hydrolysis but that a large amount of C–O bond stretching is involved in the C–O bond which is protonated in the transition state. This bond lengthening largely relieves the strain.

(15) For further discussion of the factors involved see ref 2b.

(16) M. M. Kreevoy and R. W. Taft, Jr., *J. Amer. Chem. Soc.*, 77, 5590 (1955).

(17) According to T. H. Fife and L. Hagopian, *J. Org. Chem.*, 31, 1772 (1966), steric hindrance to solvation plays a minor role in hydrolysis of 2-methyl-2-phenyldioxolane.

(18) O. Cedar, *Ark. Kemi*, 6, 523 (1954).