

61898-33-7; 1-adamantanol, 768-95-6; diamantane, 2292-79-7; 1-twistanol, 22635-86-5; 7-methyl-3-noradamantanol, 1905-16-4; 7-methylenebicyclo[3.3.1]nonan-3-one, 17933-29-8; (1-adamantyl)di-*tert*-butylcarbinol, 66951-98-2; 2-(1-adamantyl)-2-adamantanol, 38172-65-5; 2-(1-twistyl)-2-adamantanol, 81476-16-6; 2-(1-diamantyl)-2-

adamantanol, 69261-63-8; 2-(1-protoadamantyl)-2-adamantanol, 81476-17-7; adamantane, 281-23-2; 3-homoadamantane radical, 56263-72-0; 1-diamantane radical, 81476-18-8; 1-adamantane radical, 2819-03-6; 1-twistane radical, 56263-74-2; 7-methyl-3-noradamantane radical, 81476-19-9.

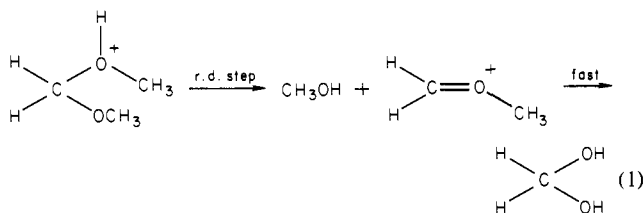
Methylal Hydrolysis: Reversal Reactions under Dilatometric Conditions and Invalidity of the Dilatometric Method

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Abstract: It has been found that serious kinetic complications render the standard dilatometric method of determining rate constants of methylal hydrolysis invalid and hence becloud interpretation of the H_0 dependence of the reaction. In 0.37–3.2 M hydrochloric acid under dilatometric conditions (0.2 M in initial methylal) both the composition of the product state and the acidity of the medium change substantially during a kinetic run. As established by NMR experiments, hemiacetal as well as formaldehyde hydrate is produced, and the former in increasing proportion during a kinetic run, up to 20% at the end of hydrolysis. The downward drift effect with time that this exerts on the apparent first-order dilatometric rate constant is counterbalanced in large part by an upward drift effect exerted by a considerable increase in the acidity of the medium during a run, by -0.09 to $-0.11 H_0$ units. A small amount of exchange between CD_3OH and methylal during hydrolysis was observed, indicating that under dilatometric conditions some reversal of the step of oxocarbenium ion formation occurs despite the abundance of water.

As illustrated in eq 1 for dimethylformal (methylal) the ac-



cepted mechanism for acetal and ketal hydrolysis is A-1, i.e., the rate-determining step is nucleophile-unassisted heterolysis of the carbonyl carbon to oxygen bond of the reversibly formed substrate conjugate acid. The conclusion is based on a wide variety and a great number of observations (for reviews, see ref 1).

The preferred method for following hydrolysis rates of alkyl acetals of formaldehyde has been the dilatometric one.²⁻⁴ Analytical methods of assaying formaldehyde production were cumbersome and lacked reproducibility.³ An ultraviolet spectrophotometric method cannot be used on alkyl acetals of formaldehyde since formaldehyde is extensively hydrated in water solution.

Unfortunately, the dilatometric method requires that a high concentration of acetal be employed, typically 0.20–0.25 M,²⁻⁴ in order that a sufficient volume change accompany the hydrolysis reaction. A volume change per se signals a change in the medium during reaction, and this could significantly affect the kinetics of a reaction, particularly one involving ions. Our suspicions were further aroused by finding that the Guggenheim method was generally employed to evaluate rate constants.⁵ Since the

Guggenheim method extrapolates in the limit to a two-point method of defining a line, deviations from first-order kinetics are obscured. Our view that the rate constants obtained by the dilatometric method might be unreliable was confirmed upon reading that the rate constant obtained in the hydrolysis of 0.2 M diethylformal in 0.5 M hydrochloric acid was 8% larger than that obtained when the same solution was recharged with 0.2 M diethylformal.² It occurred to us that the concentration dependence of the hydrolysis rate constant might be due to the alcohol being formed in sufficient amount during the hydrolysis to begin to compete with water in capturing the intermediate oxocarbenium ion, that is, that some reversal of the second step of eq 1 may be occurring, rendering the process no longer exclusively A-1 and first order. With this possibility in mind, we set out to examine the behavior of methylal in dilatometric concentrations in 0.37–3.21 M hydrochloric acid, only to find other serious kinetic complications as well.

Experimental Section

Dilatometric Kinetics. The apparatus and conditions were similar to those of Long and McIntyre.³ The dilatometers, volume about 60 mL, had one 0.5-mm precision-bore capillary and were fitted with a high-vacuum stopcock. The reaction solution, 0.20 M in methylal, was pressured into the dilatometer from a reservoir in the constant-temperature bath. Temperature was maintained at 25 ± 0.01 °C, uniform throughout the bath. The cathetometer readings of the meniscus heights, h , were corrected for small temperature fluctuations by simultaneous readings on an adjacent dilatometer, calibrated against the first and containing only the reaction solvent. Corrections thus made were less than 2% for each reading. Readings of h were duplicatable to ± 0.003 in., and the h decrease for total reaction was about 4 in. Readings were begun within 2.5 min of mixing of the reaction solutions, but only readings taken at greater than 5 min, to allow attainment of physical equilibrium, were considered significant. Usually, 15–20 readings per half-life were taken. Readings of h_∞ were stable for many half-lives beyond 10.

Exchange Experiment. A 200-mL solution of methylal (0.208 M) and CD_3OH (0.028 M) in 2.5 M hydrochloric acid was maintained at 25 °C for approximately 1 half-life of the hydrolysis. The solution was cooled,

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Table I. Values of Apparent First-Order Rate Constants Obtained Dilatometrically at 25 °C

[HCl], M	early $k \times 10^5$ ^a	later $k \times 10^5$ ^b	$k_G \times 10^5$ ^c
0.369	1.24	1.07 ^d	1.30
	1.22	1.15 ^d	1.15
	1.27	1.18 ^d	1.29
0.881	4.46	3.74	4.36
	4.35	3.92	4.12
	4.41	3.80	4.32
1.30	9.13	8.55	9.10
	9.30	8.63	9.48
	9.14	8.76	8.98
2.60	46.0	45.8	45.3
	47.9	46.4	48.2
	44.2	45.0 ^d	43.5
3.21	96.2	92.1	97.9
	98.3	90.3	101.0
	97.6		96.4

^a Value over approximately first 20% reaction. ^b Value at approximately 50% reaction. ^c Guggenheim rate constant. ^d Based on only two points.

Table II. Peak Height Percentages in the NMR Spectrum of Methylal (0.81 M) in 2.4 M DCl-D₂O at Various Times^a

time, min ^b	δ 3.19 (Ac) ^c	δ 3.27 (Hemi)	δ 3.39 (Hyd)
5	83	3	14
15	48	16	36
45	15	37	47
300	8	43	49

^a At ambient temperature in Varian Model V-4311 60-Hz spectrometer. ^b Time at beginning of scan. ^c The peaks at δ 3.19, 3.27, and 3.39 correspond to the methylene protons of methylal, hemiacetal, and formaldehyde hydrate, respectively, and are relative to the methyl protons of toluene.

basified, and extracted with chloroform (3 × 3 mL). About 0.4 mL of methylal was recovered from the extract by preparative VPC (Beckman GC-2) and subjected to mass spectral analysis (Consolidated Engineering Corp. Model 21-103 at 12 V).

NMR Experiments. The 60-Hz NMR spectra of methylal, methanol, and mixtures of methanol and formaldehyde in D₂O, 0.9 M DCl-D₂O, 2.4 M DCl-D₂O, and 1 M DClO₄-D₂O were taken in a Varian Model V-4311 instrument at ambient temperature, with toluene as an external marker. With reference to the methyl signals of toluene, methylene proton signals were assigned as follows: CH₂(OH)₂ 3.38–3.39, CH₂(O-CH₃)₂ 3.18–3.19, CH₂(OH)OCH₃ 3.26–3.27 ppm.

Results and Discussion

Dilatometric Kinetics. The usual first-order rate equation (eq 2) was applied to the readings of the meniscus height, h . The

$$-\ln(h - h_\infty) = kt + \text{constant} \quad (2)$$

infinity readings, h_∞ , were stable; i.e., there is no necessity to use

Table III. Relative NMR Areas and Values of K_1 and K_2

solution	[Ac] ₀ ^a	[Hyd] ₀ ^a	[CH ₃ OH] ₀ ^a	[Hemi]/[Hyd] ^b	[Ac]/[Hemi] ^b	K_1 ^c	K_2 ^d
2.4 M DCl	0.87	0	0	0.98	0.19	6.2	1.2
	0.81	0	0	0.82	0.23	5.0	1.4
	0.81	0	0	0.83	0.21	5.5	1.4
0.9 M DCl	1.04	0	0	1.08	0.25	5.5	1.3
	0.87	0	0	0.94	0.23	5.2	1.3
	1.04	0	0	1.08	0.28	4.8	1.2
	0.87	0	0	0.69	0.24	5.2	1.8
	0.87	0	0	0.71	0.25	4.6	1.7
1.0 M DClO ₄	1.02	0	0	1.06	0.18	7.7 ^e	1.3
2.4 M DCl	0	1.14	1.07	0.50	0.14	4.2	1.2
	0	0.84	3.34	2.0	0.50	5.0	1.3
0.9 M DCl	0	0.84	3.35	2.4	0.48	5.2	1.1
						av 5.1	1.4

^a Initial molarities. ^b Ratio of NMR areas at equilibrium. ^c Equilibrium constant of eq 4. ^d Equilibrium constant of eq 5. ^e Omitted from average.

the Guggenheim method (eq 3) of evaluating rate constants.

$$-\ln(h - h') \text{ at constant } \Delta t = k_G t + \text{constant} \quad (3)$$

Except for runs in 2.60 M HCl, the plots of $\ln(h - h_\infty)$ against time were consistently concave (decreasing apparent k), though not dramatically so. This is illustrated in Table I, which lists values of the first-order rate constant during the first 20% of the decrease in h and then again early in the second half-life.

As revealed below, the kinetic complications are more serious than indicated by the mild curvature of the first-order plots. The curvature is minimized because the kinetic complications exert a counterbalancing effect on the decrease in $h - h_\infty$ with time.

In contrast to the straightforward treatment of the data, the Guggenheim method failed to hint of any deviation from first-order kinetics. That is, plots of the Guggenheim equation (eq 3) were generally quite linear.

NMR Results. The NMR spectra of solutions of methylal, formaldehyde, methanol, and mixtures thereof in 0.9 M DCl-D₂O, 2.4 M DCl-D₂O, and 1.0 M DClO₄ established that hemiacetal as well as formaldehyde hydrate is a significant product of the hydrolysis of methylal. There was no detectable formaldehyde or chloromethyl ether in these solutions.

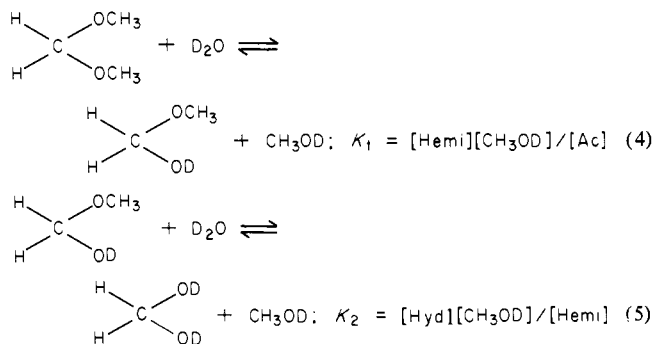
Table II, for a run on methylal (0.81 M) in 2.4 M DCl-D₂O, summarizes how the absorption in the methylene proton region of the NMR spectrum changes with time. It is seen that the initial decline in the intensity of the peak for methylal is accompanied mainly by an increase in the intensity of the peak due to formaldehyde hydrate. However, a peak due to hemiacetal soon makes its appearance and increases in intensity faster than the peak due to hydrate. At the end of hydrolysis, hemiacetal and hydrate peaks are of comparable intensity and the acetal peak does not completely disappear. Parallel results were obtained on runs in 0.9 M DCl-D₂O and 1.0 M DClO₄-D₂O.

Hemiacetal and hydrate are in rapid equilibrium relative to the rate of acetal hydrolysis. This was verified by the finding that solutions prepared from formaldehyde and methanol showed the constant equilibrium ratio of hemiacetal to hydrate peaks at the first fast NMR scan, 45 s after the solution was prepared.

The fact that the hemiacetal is an appreciable product of the hydrolysis and that even some methylal remains at the end of reaction is indeed surprising in view of the much greater abundance of water than methanol. It suggests that methanol is a much better nucleophile than water.

Values of the equilibrium constants K_1 and K_2 (eq 4 and 5, respectively) were determined from the relative areas of the NMR peaks for hydrate, hemiacetal, and acetal at the end of the hydrolysis reaction and also for reactions between formaldehyde and methanol allowed to come to equilibrium with acetal. The relevant data and values of K_1 and K_2 are given in Table III.

The concentrations of substrates used in the NMR measurements were of necessity higher than those used in the dilatometric kinetics. However, assuming that the value of K_2 applies to dilatometric conditions, i.e. $[\text{Ac}]_0 = 0.20$ M, one calculates that



at 25% disappearance of methylal in a dilatometric run, the product would consist of 6.5% hemiacetal and 93.5% formaldehyde hydrate.⁶ At 50% disappearance of methylal, the product would consist of 11.8% hemiacetal and 88.2% hydrate. At the end of total reaction, the product mixture would consist of 19.9% hemiacetal and 78.7% hydrate, and even 1.4% methylal would be left (based on the value of K_1).

It is clear from the above that the dilatometric method suffers very seriously as a means of determining the rate constants of the hydrolysis of methylal or for that matter of any other acetal yielding significant hemiacetal under dilatometric conditions. That is, for the dilatometric method to be valid requires that the product or products be constant in composition throughout the kinetic run. Otherwise, the meniscus height difference, $h - h_\infty$, will not remain in constant proportion to $[\text{Ac}]_0 - [\text{Ac}]$.

The fact that there is a decrease in h during a dilatometric run implies that the net overall process, methylal \rightarrow hydrate + $2\text{CH}_3\text{OH}$, results in a volume decrease. This further implies that both of the forward processes, acetal \rightarrow hemiacetal + CH_3OH and hemiacetal \rightarrow hydrate + CH_3OH , give a volume decrease, since the structural changes in the two processes are comparable. Thus the reverse reaction, hydrate + methanol \rightarrow hemiacetal, would give a volume increase. Since this reverse reaction is occurring appreciably to an increasing extent during the hydrolysis of the acetal, it follows that there is an increasing suppression of the h decrease, and further that the h_∞ value is substantially greater than it would be had the final product consisted only of formaldehyde hydrate. This means that the hydrate-hemiacetal equilibrium acts in the direction of imparting a substantial downward drift in the value of the apparent first-order rate constant; i.e., it imparts a concave curvature to the plot of $\log(h - h_\infty)$ against time. Although definite concavity of the rate plots was obtained in most kinetic runs, it was not nearly as bad as one might have supposed, and indeed, the runs in 2.6 M HCl gave rate plots that were reasonably linear for 2 half-lives. This leads to the suspicion that there may be at least one other kinetic complication.

Acidity Change during Reaction. There is a significant increase in the acidity of the medium during methylal hydrolysis under dilatometric conditions, as shown by indicator base measurements. The indicator used was 2,6-dichloro-4-nitro-*N,N*-dimethylaniline, $\text{p}K_a = -0.17$,^{7,8} which does not react with formaldehyde. The ultraviolet spectrum of a solution of 0.21 M methylal in 1.30 M HCl also containing indicator base (1.04×10^{-4} M) was determined at 25 °C in a Cary 14 spectrophotometer at various times. A significant decrease in absorption of free base occurred during the hydrolysis of methylal. Data obtained at 390 nm, where absorption by the amine is strong (ϵ 8200) and that of its conjugate acid is weak (ϵ 780), are shown in Table IV. The increase in indicator ratio, $[\text{BH}^+]/[\text{B}]$, corresponds to an acidity increase in

(6) The calculations were made starting with the quadratic equation $2[\text{Hyd}] = C_1 - C_2 + K_2 + ((C_1 - C_2 + K_2)^2 - 4K_2C_2)^{1/2}$, where C_1 is the stoichiometric concentration of methanol not in the form of methylal, and $C_2 = [\text{Ac}]_0 - [\text{Ac}]$. For calculations of final equilibrium concentrations, a short iterative procedure was applied until the calculated concentrations of all normal and deuterated species were constant and reproduced stoichiometric concentrations.

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(8) The primary amine, *o*-nitroaniline, gave a Schiff base reaction.

Table IV. Indicator Base Ratios of 2,6-Dichloro-4-nitro-*N,N*-dimethylaniline^a in a Solution of Methylal^b in 1.30 M HCl at 25 °C

time, min	D at 390 nm	$[\text{BH}^+]/[\text{B}]$
5	0.377	1.60
20	0.371	1.65
50	0.362	1.73
100	0.358	1.77
387	0.342	1.94
1040	0.331	2.08

^a 1.036×10^{-4} M. ^b 0.21 M.

H_0 units of -0.11 . For a reaction following H_0 , i.e., $\log k = -H_0 + \text{constant}$, this would correspond to an increase in k of 29% from the beginning to the end of the reaction.⁹ In a repeat experiment, the acidity increase was $-0.10 H_0$ units. The corresponding experiment in 0.50 M HCl gave an increase in acidity in H_0 units of -0.09 .

The effect that the increase in acidity during a kinetic run has on the first-order rate plots is opposite to that of the hemiacetal-hydrate equilibrium; i.e., it would of itself make the plots convex (increasing apparent first-order rate constant). These two factors are evidently in approximate balance in the nearly linear rate plots for 2.6 M HCl and the latter a somewhat larger factor in the other HCl solutions.

CD₃OH Exchange. Under conditions closely simulating the dilatometric ones, a solution of methylal (0.208 M) and CD₃OH (0.028 M) in 2.5 M HCl was allowed to react for 33 min and methylal was then recovered from the reaction mixture. The reaction time would correspond to 57% disappearance of initial methylal if the dilatometrically derived rate constant, $4.26 \times 10^{-4} \text{ s}^{-1}$, were truly the rate constant for a first-order hydrolysis.¹⁰ Mass spectral analysis of recovered methylal (parent peaks) indicated that it contained $0.61 \pm 0.02\%$ CH₂(OCH₃)OCD₃.¹¹

The question arises as to the timing of the CD₃ incorporation into the methylal, that is, to what extent incorporation arose prior to or after formation of hemiacetal-hydrate product. If CH₂(OCH₃)OCD₃(Ac^H) were formed *solely* after hemiacetal, then the *maximum* concentration that it could possibly attain would be that pertaining once initial and product states had finally reached total equilibrium. On the basis of the equilibrium constant values of K_1 and K_2 of Table II, the equilibrium concentration is calculated to be $[\text{Ac}_D^H]_e = 4.1 \times 10^{-4}$ M. The calculation was made as per ref 6 and eq 6, small possible secondary isotope effects on K_1 and K_2 being neglected. The statistical factor of 2 in eq 6 arises because Ac^H has only one CD₃ group.^{12,13}

$$[\text{Ac}_D^H]_e = 2[\text{Hemi}_H]_e[\text{CD}_3\text{OH}]_e/K_1 = 2[\text{Hemi}_D]_e[\text{CH}_3\text{OH}]_e/K_1 \quad (6)$$

Calculation of the concentration of Ac^H that was actually present at the time the methylal hydrolysis was stopped depends on knowing the extent of hydrolysis at that time. On the basis of an assumed 57% disappearance of original methylal and the mass spectral analysis, the concentration of Ac^H at that time would be 5.4×10^{-4} M, comparable to the value for the entire system at total equilibrium. Since the assumption of 57% reaction derives from using the dubious dilatometric rate constant,¹⁰ one could

(9) The actual plot of $\log k_{\text{obsd}}$ against $-H_0$ is linear with slope 1.28, which would correspond to a 38% increase in k from beginning to end of reaction. However, since the dilatometric k values have no quantitative significance, the slope that the true first-order constants would give is unknown.

(10) The "rate constant" in 2.5 M HCl was interpolated from the linear Hammett plot, $\log k_{\text{obsd}} = -1.28H_0 + \text{constant}$, where the k_{obsd} values are the initial apparent first-order rate constants obtained dilatometrically (Table I). Since the dilatometric rate constants were shown to be inaccurate, the calculated "percent reaction" is correspondingly inaccurate.

(11) Prior to this, exchange between ethylal and methyl alcohol during hydrolysis of ethylal was observed, but not quantitatively evaluated.

(12) Since hemiacetal is in rapid equilibrium with hydrate + methanol, normal hemiacetal (Hemi_H) and deuterated hemiacetal (Hemi_D) can be assumed to be in rapid equilibrium.

(13) The concentration of H₂C(OCD₃)₂ at equilibrium is calculated to be 1.4×10^{-5} M.

make instead the conservative assumption that hydrolysis had been stopped at as late as 70% disappearance of methylal; i.e., one could apply a first-order rate constant that is 1.4 times the dilatometric "rate constant". The actual concentration of Ac_5^{H} produced would then be 3.8×10^{-4} M, still comparable to the value for the entire system at equilibrium.

Total equilibrium is very far from being established at 57% or 70% disappearance of original methylal. Hence the amount of Ac_5^{H} arising *solely* from reversal of the overall hydrolysis should be much smaller than the equilibrium value. Since at *partial* hydrolysis the concentration of Ac_5^{H} has already reached a value comparable to the equilibrium value, we conclude that a substantial proportion of the Ac_5^{H} must have been found formed *prior* to hemiacetal. In other words, there is partial reversal of the step of oxocarbenium ion formation, eq 1, in the overall forward reaction. It is of interest that this should occur despite the fact that water was by far the most abundant nucleophile present.

The extent of exchange of methylal with 0.028 M CD_3OH was quite small. However, it is to be noted that the reversal of the step of oxocarbenium ion formation with CH_3OH would be substantially more extensive than with CD_3OH , since an amount of CH_3OH equal to the CD_3OH concentration used was generated by the time hydrolysis had proceeded to the extent of only 7%. In other words, the hydrolysis of methylal under dilatometric conditions is not strictly of the A-1 mechanism and hence also inherently not strictly first order.¹⁴

Acidity Dependence of k_{obsd} . It is of interest that, despite the dubious nature of the dilatometric rate constants, a plot of $\log k_{\text{obsd}}$ against $-H_0$ is nevertheless linear with a slope of 1.28. The k_{obsd} values used are the apparent first-order rate constants listed in Table I that were obtained over about the first 20% of the total decrease in meniscus heights. Long and McIntyre obtained a slope of 1.25 with their dilatometric rate constants (Guggenheim method) for methylal hydrolysis in hydrochloric acid solutions at 25 °C³ and found that earlier dilatometric values (Guggenheim method) for ethylal hydrolysis at 10 °C, reported by Kilpatrick and Leininger,² gave a linear Zucker-Hammett plot of slope 1.38.

In keeping with standard practice at the time, Long and McIntyre presumed that the linearity of the Zucker-Hammett plot showed the reaction mechanism to be A-1, despite the significant departure from the postulated ideal slope of unity, and

(14) The sum total of all of the other evidence seems conclusive that acetal hydrolyses do proceed, at least in the main, via the oxocarbenium ion intermediate, $\text{R}_2\text{C}=\text{OR}$. Significant reversal of the step of oxocarbenium ion formation would also act in the direction of imparting a downward drift with time of the apparent first-order rate constant.

assigned the deviation from unit slope to the behavior of the activity coefficient of the acetal relative to that of the free indicator bases used to measure H_0 . However, at about that time it was shown that a reaction which was not A-1, aromatic deformylation, showed the postulated behavior of an A-1 reaction over a very wide range of molarity of strong sulfuric acid, thus casting first doubts on the validity of the Zucker-Hammett hypothesis.^{15a-c} Shortly thereafter, Koskikallio and Whalley showed another failure of the hypothesis, specifically in the hydrolysis of epoxides.¹⁶ The studies of the Schubert group were extended to demonstrate that proven A-1 reactions can deviate considerably from the postulated A-1 behavior; i.e., in nondilute mineral acid, the change in k_{obsd} with acid percentage depends significantly on substrate structure as well as mechanism. The change with acid percentage in the solvent stabilization of transition states relative to initial states, both of the composition SH^+ , was attributed to differential specific water solvation of the ions.^{15d,e} Moreover, several groups have shown that the change with acid percentage in indicator concentration ratios, $[\text{BH}^+]/[\text{B}]$, is dependent on specific structure.¹⁷

It now seems to be widely accepted that the behavior of $\log k_{\text{obsd}}$ against an acidity function is an insufficient criterion of mechanism, even assuming that the k_{obsd} values are valid. Such plots can only reveal how many protons have entered into the activated complex but not how many water molecules are covalently involved. However, as an adjunct to other data that do provide a mechanistic assignment, the behavior of $\log k_{\text{obsd}}$ vs. acidity functions may provide information as to the detailed nature of the transition state and its solvation.^{15d,e,18}

As to the Zucker-Hammett plot obtained herein, little can be made of its linearity or its slope. That is, the dilatometric method does not provide true rate constants for a purely A-1 hydrolysis of methylal.

Registry No. Methylal, 109-87-5; methanol, 67-56-1; formaldehyde, 50-00-0.

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