

## Influence of Chain Length on the Rate of Hydrolysis of Polyoxymethylene Ethers

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### Synopsis

Four series of polyoxymethylene ethers (polyformals)  $[\text{RO}(\text{CH}_2\text{O})_n\text{R}]$  where R is isopropyl, ethyl, methyl, or methoxyethyl and  $n = 1-3$  have been prepared, examined by GLC, separated by fractional distillation, and characterized by NMR. Rate constants for the aqueous acid hydrolysis of all the compounds have been determined. The isopropyl series appears to be a special case, and as reported in the literature (but in aqueous dioxane), all members of this series hydrolyze at the same rate. In the other series, there is a definite increase in rate, which never exceeds fourfold, in going from  $n = 1$  to  $n = 2$ . This increase differs considerably from the 100-fold increase reported by others in going from  $\text{CH}_3\text{OCH}_2\text{OCH}_3$  to  $\text{CH}_3\text{O}(\text{CH}_2\text{O})_2\text{CH}_3$ . In all series, the  $n = 3$  compound hydrolyses at practically the same rate as the  $n = 2$  compound.

### INTRODUCTION

When formaldehyde reacts with an alcohol under acidic conditions, a mixture of the oxymethylene and polyoxymethylene ethers  $[\text{RO}(\text{CH}_2\text{O})_n\text{R}]$  ( $n = 1$ , formal;  $n > 1$ , polyformal) of the alcohol can be produced. This is generally true whether the alcohol is a low molecular weight compound with a single hydroxyl group<sup>1</sup> or a high polymer like cellulose with many hydroxyl groups.<sup>2</sup>

Over the years, a number of formals ( $n = 1$ ) and their homologous polyformals ( $n > 1$ ) have been isolated and their acid stabilities determined. However, there are enough conflicting statements in the literature to show that a question still exists concerning the relative stability of a given formal and its homologous polyformals. The purpose of this paper, then, is to improve the situation by determining the influence of  $n$  on the rate of hydrolysis of series of compounds of the type  $\text{RO}(\text{CH}_2\text{O})_n\text{R}$ .

Those who have studied the rate of hydrolysis of formals and polyformals usually give the pseudofirst-order rate constants and the second-order rate constants. Salomaa<sup>3</sup> has found that with strong acids at less than 0.15*N*, the normality can be used as the hydrogen ion concentration and that the second-order rate constants obtained by dividing the pseudofirst-order rate constants by the normality are true constants. With higher

normalities, the second-order rate constants obtained in this way tend to run high.

In 1937, Lobering and Fleischmann<sup>4</sup> reported on the hydrolysis of the formal and polyformals of methanol. They found almost a 100-fold increase in rate in going from  $n = 1$  to  $n = 2$ . However, for the polyformal with an average value of  $n = 3$ , they reported a rate which was only about three times that of the monoformal itself.

In 1963, Klein and co-workers<sup>5</sup> reported on the hydrolysis of isopropyl formal and its polyformals. Their rate studies were carried out in 50% dioxane-50% water and indicated that the formal ( $n = 1$ ) and polyformals ( $n = 2 \rightarrow 6$ ) all hydrolyzed at the same rate.

In 1964, Jones<sup>6</sup> studied the rate of hydrolysis of two cyclohexanediol derivatives, *cis*-hexahydrobenzo-1,3-dioxolane (I) and *trans*-hexahydrobenzo-1,3,5-trioxepin (II), which he selected as models for the mono- and dioxymethylene links in cellulose which had been reacted with formaldehyde. From the fact that compound II hydrolyzed twice as fast as I, he concluded that a dioxymethylene bridge is broken more readily than a monooxymethylene bridge. He went further and stated that for linear polyformals it is probable that their rate of hydrolysis would increase with an increase in the value of  $n$ .

## EXPERIMENTAL

### Materials

The formals and their homologous polyformals were prepared readily by the method of Gresham and Brooks.<sup>1</sup> Paraformaldehyde was mixed with the alcohol, and a trace of sulfuric acid was added. The mixture was stirred and heated. It was found that the progress of the reaction could be followed by withdrawing a sample from time to time, neutralizing, and then running a GLC analysis using a 6-foot Carbowax 1000/Chromosorb

TABLE I  
Boiling Points of the Formals and Polyformals,  $\text{RO}(\text{CH}_2\text{O})_n\text{R}$

R	$n$	bp, °C/mm (found)	bp, °C/mm (lit)	ref.
$(\text{CH}_3)_2\text{CH}-$	1	116-118/760	117-119/760	5
$(\text{CH}_3)_2\text{CH}-$	2	59/15	39.5-41/23	5
$(\text{CH}_3)_2\text{CH}-$	3	71/6	68.2/68.5/3	5
$\text{CH}_3\text{CH}_2-$	1	86-87/760	86-87/760	Reagent
$\text{CH}_3\text{CH}_2-$	2	140-144/760	72/76	1
$\text{CH}_3\text{CH}_2-$	3	82-84/19	71/13	1
$\text{CH}_3-$	1	41-43/760	41-43/760	Reagent
$\text{CH}_3-$	2	104-105/760	105/760	7
$\text{CH}_3-$	3	153/760	155/760	7
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	1	69-72/3	100/21	3
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	2	100/2	—	—
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	3	167/19	—	—

W (80–100 mesh) column with a helium flow of 60 ml/min. For good separation and to keep the retention times for the  $n = 3$  polyformals below 10 min, the column temperatures were: R = methyl, 60°C; R = ethyl, 75°C; R = isopropyl, 80°C; R = methoxyethyl, 165°C. When the chromatogram was no longer changing appreciably with time, the reaction was stopped by the addition of base. The mixture was then heated to destroy the excess formaldehyde. The upper organic layer was drawn off and fractionally distilled, under vacuum when necessary. When required, a given fraction was redistilled until it gave a single peak on the gas chromatogram. The boiling points of the various compounds are given in Table I. The structure of the individual formals and polyformals used in this study were verified by NMR. The pertinent nmr data are given in Table II.

TABLE II  
NMR Spectra\* (Neat) of  
(b) (a) (b)  
R(OCH<sub>2</sub>)<sub>c</sub>(OCH<sub>2</sub>)<sub>p</sub>OCH<sub>2</sub>OR

R	OCH <sub>2</sub> O		RO		
	a	b	CH <sub>3</sub>	CH <sub>2</sub>	CH
CH <sub>3</sub> ; $c = 0, p = 0$	—	267	195	—	—
CH <sub>3</sub> ; $c = 1, p = 0$	—	278	200	—	—
CH <sub>3</sub> ; $c = 1, p = 1$	290	282	201	—	—
C <sub>2</sub> H <sub>5</sub> ; $c = 0, p = 0$	—	272	68(m) <sup>c</sup>	209(m)	—
C <sub>2</sub> H <sub>5</sub> ; $c = 1, p = 0$	—	279	68(m)	211(m)	—
C <sub>2</sub> H <sub>5</sub> ; $c = 1, p = 1$	288	282	69(m)	213(m)	—
(CH <sub>3</sub> ) <sub>2</sub> CH; $c = 1, p = 0$	—	275	65(m)	—	228(m)
(CH <sub>3</sub> ) <sub>2</sub> CH; $c = 1, p = 0$	—	281	67(m)	—	228(m)
(CH <sub>3</sub> ) <sub>2</sub> CH; $c = 1, p = 1$ <sup>b</sup>	286	281	67(m)	—	228(m)
CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> ; $c = 0, p = 0$	—	276	196	210(m)	—
CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> ; $c = 1, p = 0$	—	282	196	211(m)	—
CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> ; $c = 1, p = 1$	289	283	197	211(m)	—

\* Position of peaks are given in Hz downfield from TMS internal reference using a Jeolco MH-60-II spectrometer.

<sup>b</sup> Integration of spectrum of this compound showed that ratio of b:a was 2:1.

<sup>c</sup> Center of expected multiplet.

### Acid-Catalyzed Hydrolyses in Aqueous Solutions

The formal or polyformal solution and the hydrochloric acid were brought to the desired temperature, and then equal volumes were mixed to start the reaction. At selected time intervals, 1-ml portions were withdrawn and added to water containing enough base to neutralize the acid. In a typical experiment, the final volume was then adjusted to 100 ml. A 10-ml aliquot of the neutralized solution was then mixed with an equal volume of Nash's reagent for formaldehyde analysis.<sup>8</sup> After heating for 5 min at 60°C, the absorbance using a 1-cm path was determined at 412 nm against

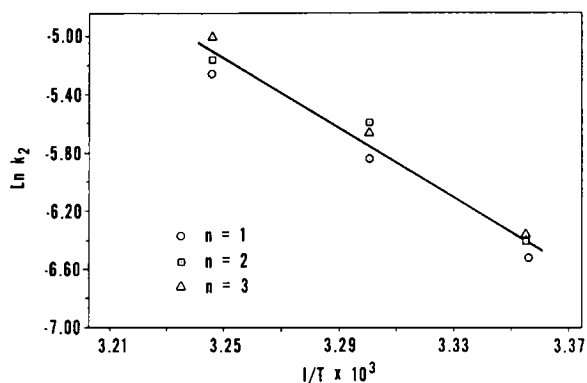


Fig. 1. Temperature dependence of the second-order rate constants for the acid-catalyzed hydrolysis of  $(\text{CH}_3)_2\text{CHO}(\text{CH}_2\text{O})_n\text{CH}(\text{CH}_3)_2$ .

a blank made by heating 10 ml water and 10 ml Nash's reagent for 5 min at  $60^\circ\text{C}$ .

Typical absorbance ( $A$ ) and time ( $t$ ) data are given in Table III. From a plot of  $\ln(A_\infty - A_t)$  versus  $t$ , the slope or pseudofirst-order rate constant is obtained, which is converted to the second-order rate constant by dividing by the hydrogen ion concentration. The rate data for the formal and polyformal experiments are summarized in Table IV. The temperature dependence of the second order rate constants for each homologous series is illustrated in Figures 1-5.

TABLE III  
Typical Hydrolysis Data  
The Hydrolysis of Isopropyl Formal (0.015M) in  
Hydrochloric Acid (0.104N) at  $25^\circ\text{C}$

Time, sec	Absorbance $A_t$	$A_\infty - A_t$	$\ln(A_\infty - A_t)$
0	0.000	0.513	-0.668
1200	0.090	0.423	-0.860
2400	0.158	0.355	-1.036
3600	0.212	0.301	-1.201
4800	0.263	0.250	-1.386
6000	0.312	0.201	-1.605
7200	0.345	0.168	-1.784
8400	0.376	0.137	-1.988
$\infty^a$	0.513	—	

<sup>a</sup> Before taking the final sample, the reaction mixture is heated to speed completion of reaction and then cooled to the original temperature.

### Effect of Dioxane on Rate of Hydrolysis

Kreevoy and Taft<sup>9</sup> reported a value of  $4.13 \times 10^{-5}$  l. mole<sup>-1</sup>sec<sup>-1</sup> for the second-order rate constant when diethyl formal was hydrolyzed in 50% dioxane-50% water at  $25^\circ\text{C}$ . This is considerably smaller than the  $1.38 \times 10^{-4}$  l. mole<sup>-1</sup>sec<sup>-1</sup> found by Salomaa<sup>8</sup> or the  $1.25 \times 10^{-4}$  l. mole<sup>-1</sup>sec<sup>-1</sup>

TABLE IV  
Rate Data Using Aqueous Solutions for the Acid-Catalyzed Hydrolysis  
of Compounds of the Type  $\text{RO}(\text{CH}_2\text{O})_n\text{R}$

R	n	$M_{\text{RO}(\text{CH}_2\text{O})_n\text{R}}$	$N_{\text{HCl}}$	$t, ^\circ\text{C}$	$k_1, \text{sec}^{-1}$	$k_2, \text{l. mole}^{-1}\text{sec}^{-1}$
$(\text{CH}_3)_2\text{CH}-$	1	0.015	0.104	25	$1.55 \times 10^{-4}$	$1.49 \times 10^{-3}$ ( $1.32 \times 10^{-3}$ ) <sup>a</sup>
$(\text{CH}_3)_2\text{CH}-$	1	0.015	0.104	30	$3.08 \times 10^{-4}$	$2.96 \times 10^{-3}$
$(\text{CH}_3)_2\text{CH}-$	1	0.015	0.105	35	$5.52 \times 10^{-4}$	$5.24 \times 10^{-3}$
$(\text{CH}_3)_2\text{CH}-$	2	0.015	0.104	25	$1.77 \times 10^{-4}$	$1.71 \times 10^{-3}$
$(\text{CH}_3)_2\text{CH}-$	2	0.0075	0.105	30	$3.97 \times 10^{-4}$	$3.77 \times 10^{-3}$
$(\text{CH}_3)_2\text{CH}-$	2	0.0075	0.105	35	$6.07 \times 10^{-4}$	$5.76 \times 10^{-3}$
$(\text{CH}_3)_2\text{CH}-$	3	0.015	0.104	25	$1.80 \times 10^{-4}$	$1.73 \times 10^{-3}$
$(\text{CH}_3)_2\text{CH}-$	3	0.005	0.105	30	$3.75 \times 10^{-4}$	$3.56 \times 10^{-3}$
$(\text{CH}_3)_2\text{CH}-$	3	0.005	0.105	35	$6.83 \times 10^{-4}$	$6.49 \times 10^{-3}$
$\text{CH}_3\text{CH}_2-$	1	0.015	0.104	25	$1.30 \times 10^{-5}$	$1.25 \times 10^{-4}$ ( $1.38 \times 10^{-4}$ ) <sup>a</sup>
$\text{CH}_3\text{CH}_2-$	1	0.015	0.104	30	$2.73 \times 10^{-5}$	$2.63 \times 10^{-4}$
$\text{CH}_3\text{CH}_2-$	1	0.015	0.104	35	$6.06 \times 10^{-5}$	$5.82 \times 10^{-4}$
$\text{CH}_3\text{CH}_2-$	2	0.015	0.104	25	$3.75 \times 10^{-5}$	$3.62 \times 10^{-4}$
$\text{CH}_3\text{CH}_2-$	2	0.015	0.104	30	$7.79 \times 10^{-5}$	$7.50 \times 10^{-4}$
$\text{CH}_3\text{CH}_2-$	2	0.015	0.104	35	$1.49 \times 10^{-4}$	$1.44 \times 10^{-3}$
$\text{CH}_3\text{CH}_2-$	3	0.015	0.104	25	$3.99 \times 10^{-5}$	$3.84 \times 10^{-4}$
$\text{CH}_3\text{CH}_2-$	3	0.015	0.104	30	$7.97 \times 10^{-5}$	$7.68 \times 10^{-4}$
$\text{CH}_3\text{CH}_2-$	3	0.015	0.104	35	$1.59 \times 10^{-4}$	$1.53 \times 10^{-3}$
$\text{CH}_3-$	1	0.015	0.104	25	$2.71 \times 10^{-6}$	$2.61 \times 10^{-5}$ ( $2.50 \times 10^{-5}$ ) <sup>a</sup>
$\text{CH}_3-$	1	0.015	0.104	30	$5.32 \times 10^{-6}$	$5.13 \times 10^{-5}$
$\text{CH}_3-$	1	0.015	0.104	35	$1.14 \times 10^{-5}$	$1.10 \times 10^{-4}$
$\text{CH}_3-$	2	0.015	0.104	25	$9.21 \times 10^{-6}$	$8.88 \times 10^{-5}$
$\text{CH}_3-$	2	0.015	0.104	30	$2.05 \times 10^{-5}$	$1.98 \times 10^{-4}$
$\text{CH}_3-$	2	0.015	0.104	35	$3.95 \times 10^{-5}$	$3.80 \times 10^{-4}$
$\text{CH}_3-$	3	0.015	0.104	25	$1.01 \times 10^{-5}$	$9.72 \times 10^{-5}$
$\text{CH}_3-$	3	0.015	0.104	30	$1.90 \times 10^{-5}$	$1.83 \times 10^{-4}$
$\text{CH}_3-$	3	0.015	0.104	35	$3.86 \times 10^{-5}$	$3.73 \times 10^{-4}$
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	1	0.015	0.104	25	$8.22 \times 10^{-7}$	$7.92 \times 10^{-6}$ ( $7.61 \times 10^{-6}$ ) <sup>a</sup>
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	1	0.015	1.038	25	$1.85 \times 10^{-5}$	$1.78 \times 10^{-5}$
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	1	0.015	1.038	30	$3.80 \times 10^{-5}$	$3.66 \times 10^{-5}$
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	1	0.015	0.104	35	$2.27 \times 10^{-6}$	$2.19 \times 10^{-5}$
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	1	0.015	1.038	35	$8.98 \times 10^{-5}$	$8.65 \times 10^{-5}$
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	1	0.015	0.104	55	$8.98 \times 10^{-5}$	$8.65 \times 10^{-4}$
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	1	0.015	0.104	65	$2.38 \times 10^{-4}$	$2.29 \times 10^{-3}$
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	2	0.015	0.104	25	$1.04 \times 10^{-8}$	$9.98 \times 10^{-6}$
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	2	0.015	1.038	25	$3.92 \times 10^{-5}$	$3.78 \times 10^{-5}$
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	2	0.015	1.038	30	$9.51 \times 10^{-5}$	$9.16 \times 10^{-5}$
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	2	0.015	1.038	35	$1.85 \times 10^{-4}$	$1.78 \times 10^{-4}$
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	2	0.015	0.104	55	$9.67 \times 10^{-5}$	$9.32 \times 10^{-4}$
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	2	0.015	0.104	65	$4.82 \times 10^{-4}$	$4.65 \times 10^{-3}$
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	3	0.015	1.038	30	$9.72 \times 10^{-5}$	$9.37 \times 10^{-5}$
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	3	0.015	0.104	55	$1.55 \times 10^{-4}$	$1.49 \times 10^{-3}$
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	3	0.015	0.104	65	$5.50 \times 10^{-4}$	$5.30 \times 10^{-3}$
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	3	0.015	1.038	25	$4.69 \times 10^{-5}$	$4.52 \times 10^{-5}$
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	3	0.015	1.038	35	$2.19 \times 10^{-4}$	$2.11 \times 10^{-4}$

<sup>a</sup> From Salomaa.<sup>1</sup>

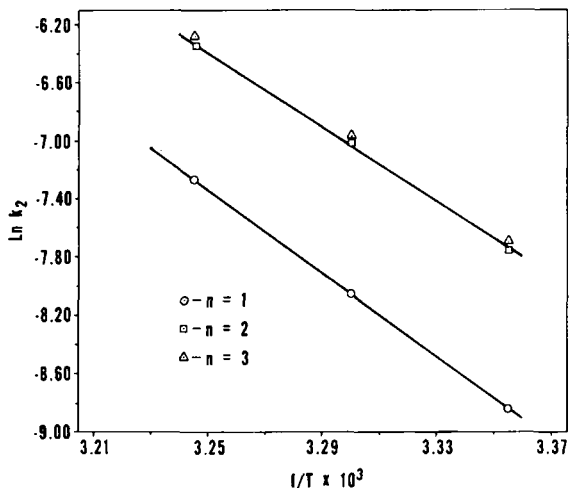


Fig. 2. Temperature dependence of the second-order rate constants for the acid-catalyzed hydrolysis of  $\text{CH}_3\text{CH}_2\text{O}(\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_3$ .

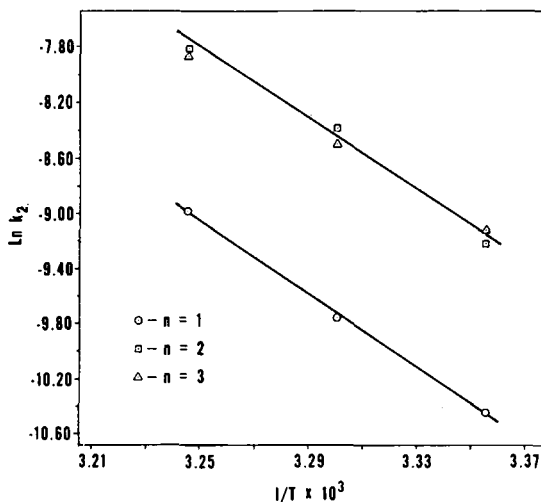


Fig. 3. Temperature dependence of the second-order rate constants for the acid-catalyzed hydrolysis of  $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$ .

found by the present authors with water as the solvent. Klein et al.,<sup>5</sup> on the other hand, have reported a much larger second-order rate constant for the hydrolysis of diisopropyl formal in 50% dioxane-50% water at 25°C than that obtained by Salomaa and the present authors with water as the solvent. Although Klein used a higher concentration of acid (greater than the 0.15*N* recommended for true constants), it was doubtful that the stronger acid could cause such a large difference. In order to clarify this discrepancy, some of the work of Klein et al. was repeated.

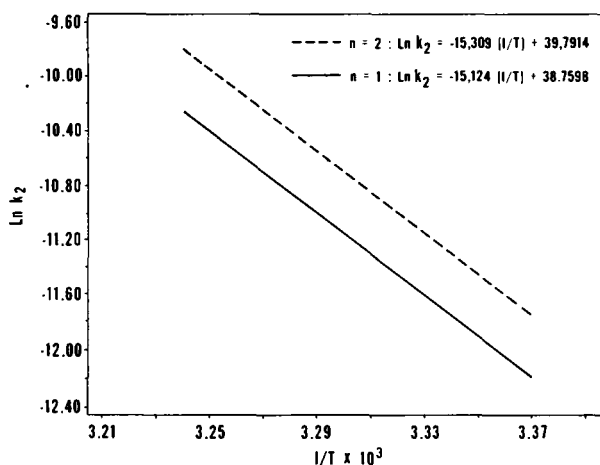


Fig. 4. Temperature dependence of the second-order rate constants for the acid-catalyzed hydrolysis of  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{O}(\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{OCH}_3$ .

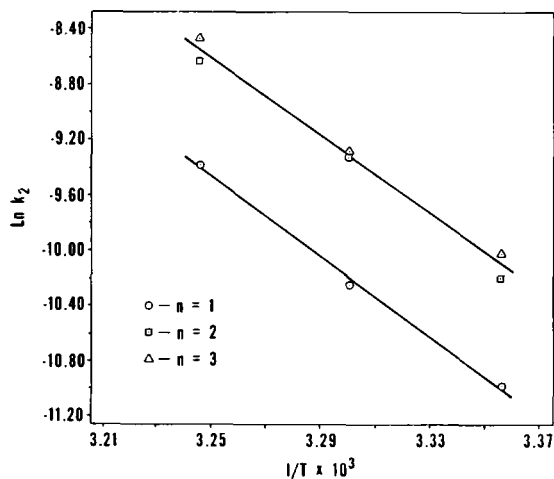


Fig. 5. Temperature dependence of the apparent second-order rate constants for the acid-catalyzed hydrolysis of  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{O}(\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{OCH}_3$  using 1.04*N* hydrochloric acid.

When 0.5*N* hydrochloric acid in 50% dioxane–50% water was used, the rate constant found by the present investigators was lower, being about  $1/60$  of that previously reported. Apparently the time unit in the earlier work was the minute and not the second as reported. When the earlier value was divided by 60, relatively good agreement was obtained. These data are shown in Table V. Just as Kreevoy and Taft<sup>9</sup> found with diethyl formal, the presence of dioxane decreases the rate of hydrolysis of diisopropyl formal.

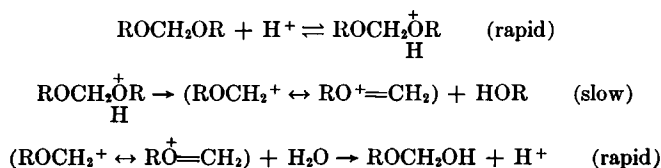
TABLE V  
Comparison of Rate Data for the Hydrolysis of Diisopropyl Formal in Water  
and in 50% Dioxane-50% Water

Investigators	<i>t</i> , °C	Solvents	<i>N</i> of acid	<i>k</i> <sub>2</sub> , l. mole <sup>-1</sup> sec <sup>-1</sup>
Klein et al.	25	(50% water) (50% dioxane)	0.5	4.00 × 10 <sup>-2a</sup>
Salomaa	25	Water	0.1	1.32 × 10 <sup>-3</sup>
Present	25	Water	0.1	1.49 × 10 <sup>-3</sup>
Present	25	(50% water) (50% dioxane)	0.1	4.44 × 10 <sup>-4</sup>
Present	25	(50% water) (50% dioxane)	0.5	6.84 × 10 <sup>-4</sup>

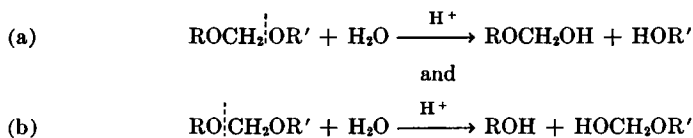
\* Apparently the time units are min<sup>-1</sup> rather than sec<sup>-1</sup>. Corrected *k*<sub>2</sub> = 4.00 × 10<sup>-2</sup> l. mole<sup>-1</sup> min<sup>-1</sup>, or 6.67 × 10<sup>-4</sup> l. mole<sup>-1</sup> sec<sup>-1</sup>.

### DISCUSSION AND CONCLUSIONS

According to the generally assumed mechanism of formal hydrolysis, the reaction proceeds as follows:



For simplicity, the mechanism is illustrated with a symmetrical formal where both oxygens attached to the central (originally the formaldehyde) carbon atom are equivalent. For unsymmetrical formals, two concurrent processes,



can occur and each contributes to the overall rate of hydrolysis. If  $k_{\text{ROCH}_2\text{OR}'}$  is the overall rate constant and  ${}^{\text{RO}}k_{\text{ROCH}_2\text{OR}'}$  is defined as the rate constant for the concurrent reactions in which RO is the leaving group (and CH<sub>2</sub>OR' is necessarily the stem), then the following relationship holds:

$$k_{\text{ROCH}_2\text{OR}'} = {}^{\text{RO}}k_{\text{ROCH}_2\text{OR}'} + {}^{\text{R}'\text{O}}k_{\text{R}'\text{OCH}_2\text{OR}'}$$

The relative rate of hydrolysis of a symmetrical formal compared to that of dimethyl formal as unity can be obtained by dividing the rate constant of the former by the rate constant for dimethyl formal. For example, to compare the rate of hydrolysis of diisopropyl formal with dimethyl, we write

$$\frac{k_{(\text{CH}_3)_2\text{CHOCH}_2\text{OCH}(\text{CH}_3)_2}}{k_{\text{CH}_3\text{OCH}_2\text{OCH}_3}} = \frac{269 \times 10^{-5} \text{ l. mole}^{-1}\text{sec}^{-1}}{5.37 \times 10^{-6} \text{ l. mole}^{-1}\text{sec}^{-1}} = 50.1.$$



In his extensive study on the acid-catalyzed hydrolysis of formals, Salomaa<sup>3</sup> provided strong evidence that the structure of the stem (the fission product which retains the formaldehyde carbon atom) exerts a more decisive influence upon the rate than the structure of the leaving group. For instance, the relative effect on the rate of changing the stem from  $\text{CH}_3\text{OCH}_2$  to  $(\text{CH}_3)_2\text{CHOCH}_2$  is

$$\frac{\text{CH}_3\text{O}k_{\text{CH}_3\text{OCH}_2\text{OCH}(\text{CH}_3)_2}}{\text{CH}_3\text{O}k_{\text{CH}_3\text{OCH}_2\text{OCH}_3}}$$

fraction of fission of  $\text{CH}_3\text{OCH}_2\text{OCH}(\text{CH}_3)_2$   
with  $\text{CH}_3\text{O}$  as leaving group  $\times k_{\text{CH}_3\text{OCH}_2\text{OCH}(\text{CH}_3)_2}$

$$= \frac{\text{fraction of fission of } \text{CH}_3\text{OCH}_2\text{OCH}_3 \text{ with } \text{CH}_3\text{O} \text{ as leaving group} \times k_{\text{CH}_3\text{OCH}_2\text{OCH}_3}}{0.907 \times 67.1 \times 10^{-5} \text{ l. mole}^{-1}\text{sec}^{-1}}$$

$$= \frac{0.50 \times 5.37 \times 10^{-5} \text{ l. mole}^{-1}\text{sec}^{-1}}{0.907 \times 67.1 \times 10^{-5} \text{ l. mole}^{-1}\text{sec}^{-1}} = 22.6$$

This can be seen to be greater than the relative effect on the rate of changing the leaving group from  $\text{CH}_3\text{O}$  to  $(\text{CH}_3)_2\text{CHO}$ :

$$\frac{(\text{CH}_3)_2\text{CHO}k_{(\text{CH}_3)_2\text{CHOCH}_2\text{OCH}_3}}{\text{CH}_3\text{O}k_{\text{CH}_3\text{OCH}_2\text{OCH}_3}}$$

fraction of fission of  $(\text{CH}_3)_2\text{CHOCH}_2\text{OCH}_3$  with  $(\text{CH}_3)_2\text{CHO}$   
as leaving group  $\times k_{(\text{CH}_3)_2\text{CHOCH}_2\text{OCH}_3}$

$$= \frac{\text{fraction of fission of } \text{CH}_3\text{OCH}_2\text{OCH}_3 \text{ with } \text{CH}_3\text{O} \text{ as leaving group} \times k_{\text{CH}_3\text{OCH}_2\text{OCH}_3}}{0.093 \times 67.1 \times 10^{-5} \text{ l. moles}^{-1}\text{sec}^{-1}}$$

$$= \frac{0.5 \times 5.37 \times 10^{-5} \text{ l. moles}^{-1}\text{sec}^{-1}}{0.093 \times 67.1 \times 10^{-5} \text{ l. moles}^{-1}\text{sec}^{-1}} = 2.27.$$

The fact that a formal, which hydrolyzes at a relatively fast rate, gives rise to a series of polyformals each of which hydrolyzes at the same or only slightly faster rate indicates that predominantly the same stem is produced from the formal and from each of its polyformals. Within a series, it is then a simple matter to explain an increase in rate upon going from  $n = 1$  to  $n = 2$  as a change to a better leaving group with a fixed stem. Thus, within the series  $\text{RO}(\text{CH}_2\text{O})_n\text{R}$ , where R is methyl,

$$\frac{\text{CH}_3\text{OCH}_2\text{O}k_{\text{CH}_3\text{OCH}_2\text{OCH}_2\text{OCH}_3}}{\text{CH}_3\text{O}k_{\text{CH}_3\text{OCH}_2\text{OCH}_3}}$$

fraction of fission of  $\text{CH}_3\text{OCH}_2\text{OCH}_2\text{OCH}_3$  with  $\text{CH}_3\text{OCH}_2\text{O}$   
as leaving group  $\times k_{\text{CH}_3\text{OCH}_2\text{OCH}_2\text{OCH}_3}$

$$= \frac{\text{fraction of fission of } \text{CH}_3\text{OCH}_2\text{OCH}_3 \text{ with } \text{CH}_3\text{O} \text{ as leaving groups} \times k_{\text{CH}_3\text{OCH}_2\text{OCH}_3}}{0.5 \times 8.88 \times 10^{-5} \text{ l. mole}^{-1}\text{sec}^{-1}}$$

$$= \frac{0.5 \times 2.61 \times 10^{-5} \text{ l. mole}^{-1}\text{sec}^{-1}}{0.5 \times 8.88 \times 10^{-5} \text{ l. mole}^{-1}\text{sec}^{-1}} = 3.4,$$

a value which is reasonable for a leaving group change with a fixed stem.

It is probably safe to predict that the rate of hydrolysis for compounds within a series with  $n > 2$  will be essentially the same as the rate for the  $n = 2$  compound. That is, if any significant change in leaving group effect occurs within a series, it will occur in going from RO to ROCH<sub>2</sub>O. The authors have included the  $n = 3$  compound in this study, and the findings in each case lend validity to such predictions. The increase in rate in going from  $n = 1$  to  $n = 2$  within a series may be as high as fourfold, but the 100-fold increase reported by Lobering and Fleischmann<sup>4</sup> for the methyl series is much too high.

There was no evidence encountered in this work which would establish a buildup of hemiformals, RO(CH<sub>2</sub>O) <sub>$n-1$</sub> H, during the hydrolysis. Presumably, these materials, when formed, break down immediately into formaldehyde and the alcohol.

In general, the recent literature<sup>10-12</sup> indicates that the subject of acid-catalyzed hydrolyses of acetals, ketals, and orthoformates is being re-examined, and the protonation step is suggested as being partially or completely rate determining in some instances. As a final thought, one should visualize an extremely inert formal and then its homologous polyformals. In such compounds, this polyoxymethylene chain itself might contain relatively weak links. Conceivably, these could play an important role during the hydrolysis of such a compound. To gain some additional knowledge of the stability of the polyoxymethylene chain itself, the authors have begun a study of the acid-catalyzed hydrolysis of a number of cyclic polyoxymethylene compounds or oxocanes.

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