The Preparation and Acid-Catalyzed Hydrolysis of Polyoxymethylene Isopropyl Methyl Ethers

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Synopsis

The first four members of the polyoxymethylene ether series $(CH_3)_2CHO(CH_2O)_nCH_3$ were prepared, separated by fractional distillation and GLC, and characterized by NMR. Rate constants for the aqueous acid hydrolysis of the compounds were determined at 25°, 30°, and 35°C. Although the polyformals ($n > 1$) in this series hydrolyzed at essentially the same rate, they all hydrolyzed three times faster than the formal ($n = 1$). It is proposed that a mixed polyformal, $(CH_3)_2CHO(CH_2O)_{n>1}CH_3$, undergoes two concurrent fissions to yield (1) the stem $(CH_3)_2CHOCH_2$ with $CH_3O(CH_2O)_{n-1}$ as the leaving group and (2) the stem CH_3OCH_2 with $(CH_3)_2CHO(CH_2O)_{n-1}$ as the leaving group. Most of the fissions occur by the first path. An equation that can aid in predicting the rate of hydrolysis of a mixed polyformal was developed and tested.

INTRODUCTION

In a recent paper,[1] the present authors compared the rates of the acid-catalyzed hydrolysis of a number of symmetrical polyoxymethylene ethers (polyformals) $RO(CH_2O)_{n>1}R$ with the rates of hydrolysis of the parent oxymethylene ethers (formals) $ROCH_2OR$. The authors concluded that the rates of hydrolysis of the polyformals within a series (where R is the same group) were essentially the same and were equal to or up to four times greater than the rate for the parent formal.

In the present work the rates of hydrolysis of several mixed polyformals within the series $(CH_3)_2CHO(CH_2O)_{n>1}CH_3$ are compared with the rate for the parent mixed formal $(CH_3)_2CHOCH_2OCH_3$. Salomaa's hypothesis,[2] which has been used to calculate the contribution of the two possible fissions in a mixed formal, is applied to mixed polyformals to calculate the contribution of the two most likely fissions in the mixed polyformals.

EXPERIMENTAL

Materials

The methyl isopropyl formal was prepared from chloromethyl ether and isopropyl alcohol in pyridine by the method of Palomaa and Kantola.[3]

A mixture of the polyformals $(CH_3)_2CHO(CH_2O)_nCH_3$ was made by a modification of the method of Gresham and Brooks[4] for symmetrical polyformals. Methanol (6 moles), isopropanol (6 moles), paraformaldehyde (2 moles), and sulfuric acid (8.8 g) were refluxed together for an hour. Additional paraformaldehyde (2 moles) was added to the refluxing mixture every hour until a total of 14 moles had been added. After the last hour of refluxing, the solution was allowed to cool. The solution was filtered to remove precipitate and the filtrate was added to a solution containing 18 g sodium hydroxide and 24 ml water. This mixture was then refluxed to convert the excess formaldehyde to methanol and sodium formate. The upper layer was drawn off and fractionally distilled, under vacuum when necessary. Fractional distillation was carried out first with a Vigreaux column and then with a spinning band column. The separation was followed by injecting a sample of each fraction into a gas chromatograph equipped with a 6-ft silicone gum rubber column. A 125°C, the polyformals came out strictly in order of their molecular weights. Identification of the peaks was simplified because samples of the dimethyl polyformals and diisopropyl polyformals were available from the earlier work.[1]

Samples for NMR and elemental analysis were purified by GLC and collected at the exit by trapping in a capillary tube immersed in a Dry Ice–methanol bath. The boiling points of the formal and polyformals and their elemental analyses are given in Table I. The NMR data are summarized in Table II.

TABLE I
Data for $(CH_3)_2CHO(CH_2O)_nCH_3$

n	Boiling point, °C	Calcd C, %	Found C, %	Calcd H, %	Found H, %
1	76	57.66	56.97	11.62	11.16
2	130	53.70	53.81	10.52	10.50
3	165	51.20	50.52	9.82	9.46
4	93/3 mm	49.46	50.07	9.34	9.79

Acid-Catalyzed Hydrolyses

The formal or polyformal solution and the hydrochloric acid were brought to the desired temperature, and equal volumes were mixed to start the reaction. At selected time intervals, samples were withdrawn, neutralized, and analyzed for liberated formaldehyde by the Nash procedure.[5] In this method, formaldehyde is converted to 3,5-diacetyl-1,4-dihydrolutidine, which absorbs strongly at 412 nm. The absorbance at a given time (A_t) is a measure of the freed formaldehyde, which is proportional to the formal or polyformal that has hydrolyzed. The absorbance at the end of the reaction (A_∞) minus the absorbance at a given time (A_t) is a measure of the formal or polyformal remaining at a given time (t). From a plot of $\ln (A_\infty - A_t)$ versus t, the slope or pseudofirst-order rate constant is obtained. Further details are given in an earlier paper.[1] The pseudofirst-order rate con-

TABLE II
NMR Data on $(CH_3)_2CHO(CH_2O)_nCH_3$[a]

n	Type of proton	Shift, Hz	Proton count
1	$(CH_3—)_2$	70	6
	$—OCH_3$	202	3
	$>CH—$	232	1
	$—OCH_2—$	280	2
2	$(CH_3—)_2$	70	6
	$—OCH_3$	202	3
	$>CH—$	232	1
	$—OCH_2—$	283)→	4
	$—OCH_2—$	286)	
3	$(CH_3—)_2$	70	6
	$—OCH_3$	202	3
	$>CH—$	233	1
	$—OCH_2—$	282)	
	$—OCH_2—$	287)→	6
	$—OCH_2—$	291)	
4	$(CH_3—)_2$	69	6
	$—OCH_3$	200	3
	$>CH—$	231	1
	$—OCH_2—$	281	2
	$—O—CH_2—$	286	2
	$—O—CH_2—$	291	4

[a] Positions of peaks are given in Hz downfield from TMS internal reference in $CDCl_3$ using a Varian A-60A spectrometer.

TABLE III
Rate Data for the Hydrolyses of $(CH_3)_2CHO(CH_2O)_nCH_3$

n	M, $(CH_3)_2CHO$-$(CH_2O)_nCH_3$	N, HCl	t, °C	k_2, l. mole^{-1} sec^{-1}	k_2^p/k_2^{f} [b]
1	0.015	0.1038	25	3.22×10^{-4}[a]	—
1	0.015	0.1038	30	5.96×10^{-4}	—
1	0.015	0.1038	35	1.24×10^{-3}	—
2	0.015	0.1038	25	9.74×10^{-4}	3.0
2	0.015	0.1038	30	1.71×10^{-3}	2.9
2	0.015	0.1038	35	3.58×10^{-3}	2.9
3	0.0015	0.1002	25	1.02×10^{-3}	3.2
3	0.0015	0.1002	30	2.02×10^{-3}	3.4
3	0.0015	0.1002	35	3.85×10^{-3}	3.1
4	0.0075	0.1038	25	9.49×10^{-4}	2.9
4	0.0075	0.1038	30	1.63×10^{-3}	2.7
4	0.0075	0.1038	35	3.45×10^{-3}	2.8

[a] Salomaa[2] found 3.08×10^{-4}.

[b] This ratio of the second-order rate constants shows how many times greater the rate constant for the polyformal (k_2^p) is than the rate constant for the formal (k_2^{f}) at the same temperature.
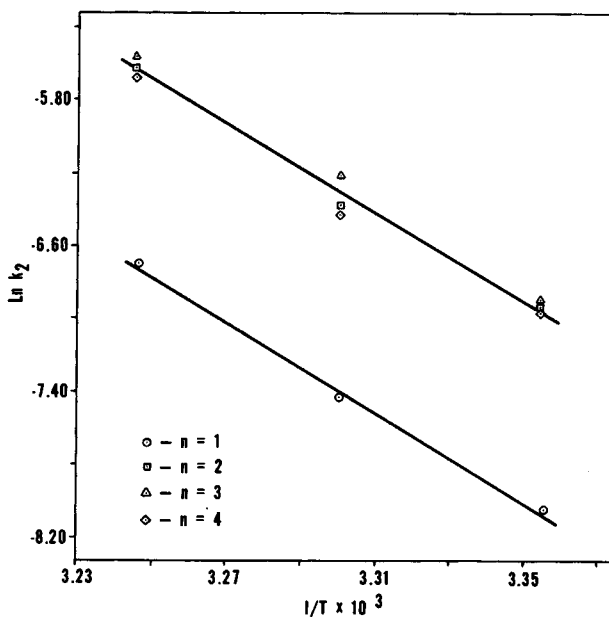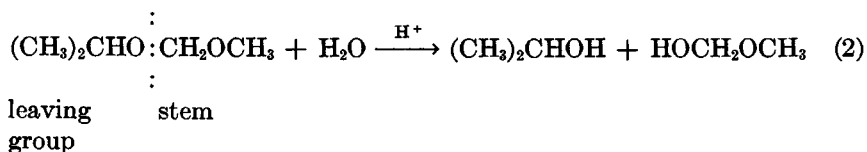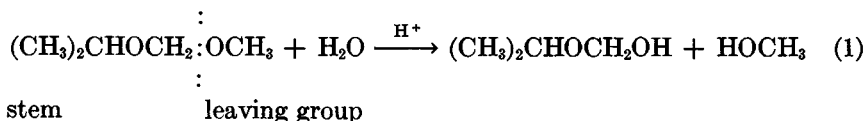
Fig. 1. Temperature dependence of the second-order rate constants for the acid-catalyzed hydrolysis of $(CH_3)_2CHO(CH_2O)_nCH_3$.

stant is converted to the second-order rate constant by dividing by the hydrogen ion concentration. The rate data for the formal and polyformal hydrolyses are given in Table III.

The temperature dependence of the second-order rate constants for the acid catalyzed hydrolyses of the mixed formal $(CH_3)_2CHOCH_2OCH_3$ and the mixed polyformals $(CH_3)_2CHO(CH_2O)_{n>1}CH_3$ is illustrated in Figure 1.
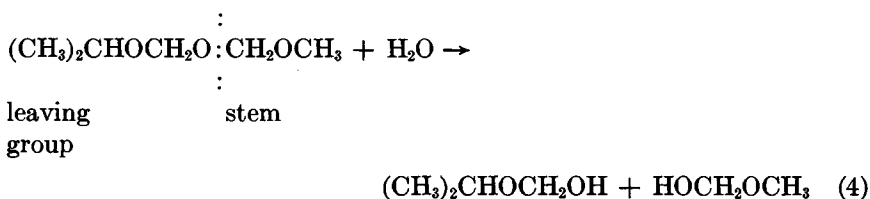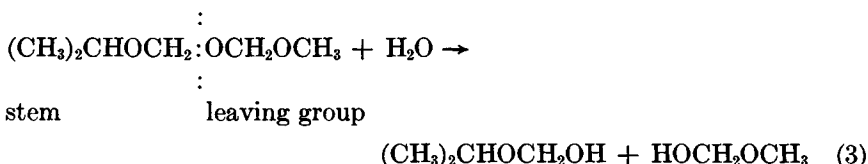
DISCUSSION AND CONCLUSIONS

Salomaa[2] states that the acid catalyzed hydrolysis of methyl isopropyl formal in molar hydrochloric acid at 25°C occurs by two concurrent fission processes (1) and (2):

$$(CH_3)_2CHOCH_2 \colon OCH_3 + H_2O \xrightarrow{\ H^+\ } (CH_3)_2CHOCH_2OH + HOCH_3 \quad (1)$$

stem   leaving group

$$(CH_3)_2CHO \colon CH_2OCH_3 + H_2O \xrightarrow{\ H^+\ } (CH_3)_2CHOH + HOCH_2OCH_3 \quad (2)$$

leaving   stem
group

and that fission (1) accounts for 90.7% of the cleavage and fission (2), for the remaining 9.3%. From his second-order rate constant for CH_3OCH_2-OCH_3, $(CH_3)_2CHOCH_2OCH(CH_3)_2$, and $(CH_3)_2CHOCH_2OCH_3$, in dilute hydrochloric acid (0.1–0.15N) at 25°C, the values are 90.5% for (1) and 9.5% for (2). From the present authors' second-order rate constants for the two symmetrical formals and the mixed formal, the values are 89.6% for (1) and 10.4% for (2).

The authors now propose that the equations which Salomaa[2] used to calculate the fractions of fission in a mixed formal can be used to calculate the fractions of the two most likely fissions in a mixed polyformal such as $(CH_3)_2CHOCH_2OCH_2OCH_3$ if the rate constants for its hydrolysis and for the two symmetrical polyformals $CH_3OCH_2OCH_2OCH_3$ and $(CH_3)_2CHO$-$CH_2OCH_2O(CH_3)_2$ are known.

In the hydrolysis of isopropyl methyl dioxymethylene ethers, there are two nonequivalent fission points that lead to the same stems as those produced during the hydrolyses of the symmetrical dimethyl and diisopropyl dioxymethylene ethers. That part of a molecule not in the stem is the replaced or leaving group. These points are illustrated in eqs. (3) and (4):

$$(CH_3)_2CHOCH_2 \vdots OCH_2OCH_3 + H_2O \rightarrow$$

stem   leaving group

$$(CH_3)_2CHOCH_2OH + HOCH_2OCH_3 \quad (3)$$

$$(CH_3)_2CHOCH_2O \vdots CH_2OCH_3 + H_2O \rightarrow$$

leaving   stem
group

$$(CH_3)_2CHOCH_2OH + HOCH_2OCH_3 \quad (4)$$

In the following part of the discussion, letters will be used to represent the compounds (polyformals and formals) and the leaving groups. These letters and their equivalents are shown in Table IV.

The rate constant for fission (3) is denoted by ^ak_C, where the superscript refers to the leaving group and the subscript to the intact molecule and the rate constant for fission (4), ^bk_C. The overall rate constant for both fissions k_C is then:

$$k_C = {}^ak_C + {}^bk_C \quad (5)$$

Salomaa's hypothesis applied to the system yields eq. (6):

$$^ak_A/{}^bk_C = {}^ak_C/{}^bk_B \quad (6)$$

TABLE IV
Letters and Their Equivalents

Letter	Compound	Letter[1]	Leaving Group
A = $CH_3OCH_2OCH_2OCH_3$		a = CH_3OCH_2O
B = $(CH_3)_2CHOCH_2OCH_2OCH(CH_3)_2$		b = $(CH_3)_2CHOCH_2O$
C = $CH_3OCH_2OCH_2OCH(CH_3)_2$		
D = $RO(CH_2O)_{n>1}R$		d = $RO(CH_2O)_{n-1}$
E = $R'O(CH_2O)_{n>1}R'$		e = $R'O(CH_2O)_{n-1}$
F = $RO(CH_2O)_{n>1}R'$		
G = $ROCH_2OR$		g = RO
H = $R'OCH_2OR'$		h = $R'O$
I = $ROCH_2OR'$		
J = $CH_3OCH_2OCH_3$		j = CH_3O
K = $(CH_3)_2CHOCH_2OCH(CH_3)_2$		k = $(CH_3)_2CHO$
L = $CH_3OCH_2OCH(CH_3)_2$		

[1] The letters, c, f, i, and l are not used because C, F, I, and L produce a and b, d and e, g and h, or j and k, respectively.

From our previous paper,[1] $^ak_A = \frac{1}{2}k_A = 4.44 \times 10^{-5}$ and $^bk_B = \frac{1}{2}k_B = 8.55 \times 10^{-4}$. From this paper, $k_C = 9.74 \times 10^{-4}$. Substituting these values into (5) and (6), one obtains

$$9.74 \times 10^{-4} = {}^ak_C + {}^bk_C \tag{7}$$

$$4.44 \times 10^{-5}/{}^bk_C = {}^ak_C/8.55 \times 10^{-4} \tag{8}$$

from which

$${}^ak_C = 9.335 \times 10^{-4} \quad (95.8\%)$$

$${}^bk_C = 0.405 \times 10^{-4} \quad (4.2\%)$$

In the present work, the rate constant for the acid-catalyzed hydrolysis of $(CH_3)_2CHO(CH_2O)_{n>1}CH_3$ was determined experimentally. Theoretically, it should be possible to calculate this rate constant or the rate constant for any other mixed polyformal $R'O(CH_2O)_{n>1}R$ from the rate constants for the mixed formal $R'OCH_2OR$, the symmetrical formals $R'OCH_2OR'$ and $ROCH_2OR$, and the symmetrical polyformals $R'O(CH_2O)_{n>1}R'$ and $RO(CH_2O)_{n>1}R$, to which it is related.

The overall rate constant for the hydrolysis of a mixed polyformal is equal to the sum of the rate constants for the two concurrent fissions:

$$k_F = {}^dk_F + {}^ek_F. \tag{9}$$

However, by hypothesis,

$${}^dk_F/{}^gk_I = {}^dk_D/{}^gk_G = 0.5k_D/0.5k_G = r_1 \qquad {}^dk_F = r_1{}^gk_I \tag{10}$$

where r_1 is the factor by which the rate constant for the hydrolysis of $ROCH_2OR$ must be multiplied to obtain the rate constant for the hydrolysis of $RO(CH_2O)_{n>1}R$, and

$${}^ek_F/{}^hk_I = {}^ek_E/{}^hk_H = 0.5k_E/0.5k_H = r_2 \qquad {}^ek_F = r_2{}^hk_I \tag{11}$$

where r_2 is the factor by which the rate constant for the hydrolysis of $R'OCH_2OR'$ must be multiplied to obtain the rate constant for the hydrolysis of $R'O(CH_2O)_{n>1}R'$.

By substituting from (10) and (11) into (9), one obtains

$$k_F = r_1{}^g k_I + r_2{}^h k_I \text{ (General Equation)} \tag{12}$$

The value k_C, which was determined experimentally above, will now be calculated. For compound C, the general equation becomes

$$k_C = r_1{}^j k_L + r_2{}^k k_L. \tag{13}$$

But $^j k_L = 28.85 \times 10^{-5}$ and $^k k_L = 3.35 \times 10^{-5}$ (by application of Salomaa's equation to rate data on J, K, and L given above and in the recent paper[1]). Also, $r_1 = 3.4$ (from the fact that the dimethyl polyformals hydrolyze 3.4 times faster than the dimethyl formal[1]) and $r_2 = 1.0$ (from the fact that the diisopropyl polyformals hydrolyze at the same rate as the diisopropyl formal[1]). Substituting these values into equation (13) one finds

$$k_C = (3.4 \times 28.85 \times 10^{-5}) + (1 \times 3.35 \times 10^{-5}) = 1.01 \times 10^{-3}. \tag{14}$$

This calculated value of 1.01×10^{-3} should be valid for any members of the series $(CH_3)_2CHO(CH_2O)_{n>1}CH_3$ and compares well with the found values 9.74×10^{-4} $(n = 2)$, 1.02×10^{-3} $(n = 3)$, and 9.49×10^{-4} $(n = 4)$ given in Table III.

Summary

The relationship between size of a formaldehyde crosslink and its stability toward acid is clarified. Thus, with two different groups at the ends of a formaldehyde crosslink, a link containing one formaldehyde unit is more stable than a crosslink containing two units. Larger links have essentially the same stability as the two-unit crosslink. This information is useful in designing acid-catalyzed crosslinking reactions between formaldehyde derivatives and cotton for making durable press fabrics.

References

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