during 20 hr. The solution was diluted with 25% aqueous potassium chloride to give a precipitate which was collected by filtration and dissolved in ether. The ethereal solution was washed with water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. Two recrystallizations of the residue from methanol afforded 21 mg. (35%) of needles, m.p. 161–165°. Additional recrystallizations from a mixture of dichloromethane and methanol gave the analytical sample: m.p. 162–167°; [α] −120°; infrared 5.80, 8.05 (3β-acetoxy), and 5.88 μ (23-acetyl).

Anal. Calcd. for $C_{31}H_{46}O_5$ (498.68): C, 74.66; H, 9.30. Found: C, 74.89; H, 9.44.

Acknowledgments.—The author is indebted to Dr. B. H. Walker of the Upjohn Research Laboratories for a gift of the diosgenin used as starting material and to the National Institutes of Health, U. S. Public Health Service, for financial support (H-2205 and M-2029).

Scrambling Equilibria on Carbon. I. Chloro- and Dimethylamino-Terminated Polyoxymethylenes

KURT MOEDRITZER AND JOHN R. VAN WAZER

Central Research Department, Monsanto Company, St. Louis, Missouri

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The chloromethyl groups of bis(chloromethyl) ether are readily scrambled (on the bridging oxygens) with the methylene groups of either trioxane or paraformaldehyde at 120°. Likewise, the dimethylamino groups of N,N,N′,N′-tetramethyldiaminomethane can be scrambled (on the methylene groups) with the bridging oxygens of paraformaldehyde at the same temperature. In both cases, equilibration is achieved within 1 to 3 days at 120° without a catalyst. There is a small amount of cyclic trioxane in equilibrium with the chain molecules. In all cases, a distribution of various sized chains is obtained, depending on the ratio of the reagents used. Proton n.m.r. was employed as the analytical procedure and the reaction products are quantitatively accounted for on the basis of the modern theory of equilibrium chemistry.

Because of the great success of reaction–mechanism theory in providing a rationale for most of organic chemistry on a kinetic basis, the role of equilibrium control in directly determining the kinds and amounts of products from chemical reactions in which there is extensive scrambling has, in our opinion, been neglected. Although such equilibrium-controlled reactions are of primary interest in inorganic chemistry (where investigations of this type are opening broad new fields of study), there are some areas[1] of organic chemistry to which this concept may be profitably applied and examples are presented here.

This paper describes a new organic reaction resulting in one new family of compounds, the α,ω-bis(dimethylamino)polyoxymethylenes, as well as another family, the α,ω-dichloropolyoxymethylenes, of which only the three smallest chains have been reported.[2] The work presented here is part of a broad theoretical[3,4] and experimental[5–7] program of investigation in the kind of equilibrium chemistry in which there is an exchange of parts between molecules. Since modern methods of analysis for molecular species have been employed in conjunction with a mathematical treatment to demonstrate the existence of the new compounds reported herein, we have felt that it was not necessary to isolate the relatively labile and difficultly separable individual compounds. As a result, the new compounds described in this study are characterized by their n.m.r. chemical shift instead of the usual parameters, such as boiling point and refractive index (which, by the way, may be estimated from semiempirical equations).

Experimental Section

Reagents.—Bis(chloromethyl) ether was purchased from Eastman Organic Chemicals and N,N,N′,N′-tetramethyldiaminomethane was obtained from Aldrich Chemicals. Both of these reagents were fractionally distilled and only the center cuts exhibiting the correct boiling points were employed. The trioxane and paraformaldehyde were used directly as obtained from Fisher Scientific Co. All reagents were examined for hydrogen-containing impurities by proton n.m.r. and were found to contain no observable contaminants (<0.5% of total H).

Reaction Mixtures and Equilibration.—Chosen proportions of the reagents were studied in 5-mm.-o.d. thin-walled precision Pyrex-glass n.m.r. tubes which were sealed with a torch. In all cases, more than half of the tube was filled with liquid so that at 120° the relative amount of material in the vapor phase would be small. The over-all composition (*i.e.*, the ratio of the reagents) is presented in terms of a composition ratio, *R*, which equals the ratio of the formula weight of total terminating groups (either chlorine or dimethylamino) to that of the total methylenes.

The kinetic runs were carried out by apportioning a previously prepared batch of starting ingredients into a number of different n.m.r. tubes which were then sealed and placed in the oven. Data corresponding to selected heating times were obtained by removing a tube and cooling it quickly (within 1 min.) to room temperature. The reported equilibrium data for the chloro-terminated polymethylene oxides correspond to 8 days at 120°. The same distribution of products was obtained after 3 days at the same temperature. The equilibrium data reported for the α,ω-bis(dimethylamino)polyoxymethylenes correspond to 48 hr. at 120°, there being no change from the data obtained after 24 hr. at the same temperature.

Analytical Method.—Analysis for the various molecular species was carried out by proton n.m.r. using a Varian A-60 spectrometer running at 60.000 Mc. For α,ω-dichloropolyoxymethylenes, a sweep width of 50 cycles was employed with a sweep rate

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(1) *E.g.*, N. E. Aubrey and J. R. Van Wazer, *J. Am. Chem. Soc.*, **86**, 4380 (1964).

(2) F. S. H. Head, *J. Chem. Soc.*, 2972 (1961).

(3) D. W. Matula, L. C. D. Groenweghe, and J. R. Van Wazer, *J. Chem. Phys.*, **41**, 3105 (1964).

(4) H. I. Weingarten, J. R. Van Wazer, and J. H. Letcher, manuscript in preparation.

(5) (a) K. Moedritzer and J. R. Van Wazer, *ibid.*, **86**, 802 (1964); (b) J. R. Van Wazer, K. Moedritzer, and D. W. Matula, *ibid.*, **86**, 807 (1964); (c) M. D. Rausch, J. R. Van Wazer, and K. Moedritzer, *ibid.*, **86**, 814 (1964); (d) J. R. Van Wazer and D. Grant, *ibid.*, **86**, 1450 (1964); (e) J. R. Van Wazer and K. Moedritzer, *J. Chem. Phys.*, **41**, 3122 (1964); (f) K. Moedritzer, J. R. Van Wazer, and C. H. Dungan, *ibid.*, **42**, 2478 (1965); (g) H. K. Hofmeister and J. R. Van Wazer, *J. Inorg. Nucl. Chem.*, **26**, 1201 (1964).

(6) D. Grant and J. R. Van Wazer, *J. Am. Chem. Soc.*, **86**, 3012 (1964).

(7) K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **3**, 139, 268 (1964); M. D. Rausch and J. R. Van Wazer, *ibid.*, **3**, 761 (1964); J. R. Van Wazer and K. Moedritzer, *J. Inorg. Nucl. Chem.*, **26**, 737 (1964); H. K. Hofmeister and J. R. Van Wazer, *J. Phys. Chem.*, **69**, 791 (1965); also see G. Calingaert and H. A. Beatty, *J. Am. Chem. Soc.*, **61**, 2748 (1939).

of 0.1 c.p.s./sec. The average of these chemical shifts is reported at the top of Table I. Deviation from the average was small, being no more than 0.1 p.p.m. Referencing was done on all of the equilibrated samples by adding a drop of tetramethylsilane (TMS) to each of the equilibrated tubes, opened after the quantitative n.m.r. data had been obtained. For the α,ω-bis(dimethylamino)polyoxymethylenes, a sweep width of 250 cycles was employed with a sweep rate of 0.5 c.p.s./sec. Referencing was carried out as reported above, but only on a single sample exhibiting an over-all $(CH_3)_2N/CH_2$ mole ratio of *ca.* 1.2. Chemical shifts downfield from TMS are given a negative sign.

N.m.r. peak assignments were made according to the techniques described in greater detail in other publications from our laboratory.[3,5,6,8] In brief, these consist of (a) material-balance calculations whereby the peak areas are compared to the starting composition in both equilibrium and kinetic runs; (b) the relative areas of related peaks, *e.g.*, the areas of the methylene resonance due to **e***me* is twice that of the corresponding *eme* resonance (see the following paragraph and footnote 9 for an explanation of the symbolism used here); (c) the over-all compositions at which the various resonances maximize; (d) the grouping of peaks in the spectra and their order within these groups; and, finally, (e) the theoretical calculation of peak areas from equilibrium constants as computed from the quantitative data obtained with the given assignments.

Results and Interpretation

As in other papers from this laboratory, we shall employ a shorthand notation for the various atomic arrangements, which correspond to the observed n.m.r. peaks and may be treated by equilibrium constants. Both systems studied here involve a collection of chain molecules of the formula $X(CH_2O)_{j-1}CH_2X$, where $X =$ Cl or $(CH_3)_2N$ or, perhaps in the case of paraformaldehyde, OH. In addition, there are trimeric and tetrameric ring molecules, trioxane and tetroxane, $(CH_2O)_z$. When $j = 1$ in the first formula, we have the *neso*[10] compound, *n;* when $j = 2$, the di chain, *ee;* when $j = 3$, the tri chain, *eme;* and when $j = 5$, the penta chain, *emmme*. Trioxane is symbolized as $(m)_3$. The end and middle groups, denoted by *e* and *m*, respectively, in these formulas have the following stoichiometry: $e = XCH_2O_{1/2}-$ and $m = -O_{1/2}CH_2O_{1/2}-$, in which $O_{1/2}$ represents an oxygen equally shared by the group in question and a neighboring methylene group.

Reactions Leading to Chloro-Terminated Polyoxymethylenes.—Bis(chloromethyl) ether is found to react with either the trimeric-ring or long-chain-polymeric forms of formaldehyde to give the same products at equilibrium. When trioxane is employed in reasonably large proportions in the reaction with bis(chloromethyl) ether, a white material having properties essentially the same as those of paraformaldehyde is found to precipitate after 1–5 hr. at 120°. This then redissolves in the reaction mixture, unless only very small amounts of bis(chloromethyl) ether were originally employed ($R \equiv Cl/CH_2 < 0.05$) in which case the equilibrium mixture contains solids or is solid at 120°. On the other hand, when paraformaldehyde is treated with bis(chloromethyl) ether, n.m.r. measurements on the liquid phase indicate that equilibrium is achieved about as fast as the paraformaldehyde dissolves. Thus it appears that, when either trioxane or paraformaldehyde are treated with bis(chloromethyl) ether, the rate-determining step is chemical attack on the precipitated long-chain polymer by the smaller molecules present in the liquid phase. This attack of the liquid on the solid, as well as a preponderance of the reactions occurring in the liquid phase, may be represented by the formal equation (1), where, for this case, X = Cl; $i < k, 2 \leq k < \infty$; and $2 \leq j < \infty$.

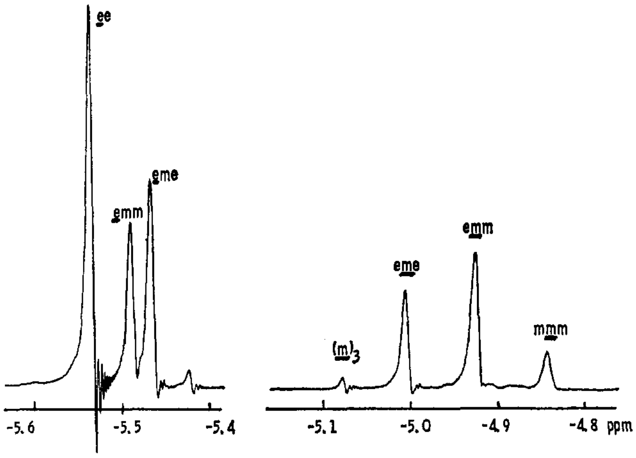

Figure 1.—Proton n.m.r. spectrum of an equilibrated mixture in the system $ClCH_2OCH_2Cl$ *vs.* $[CH_2O]$: $R = Cl/CH_2 = 0.659$.

$$X(CH_2O)_{k-1}CH_2X + X(CH_2O)_{j-1}CH_2X \rightleftharpoons X(CH_2O)_{k-i-1}CH_2X + X(CH_2O)_{j+i-1}CH_2X \quad (1)$$

The first attempts to study equilibria among the α,ω-dichloropolyoxymethylenes involved heating dichloromethane with trioxane or paraformaldehyde for as long as 120 hr. at 150°. However, no reaction was observed, and moreover, as shown in Table I, equilibrated mixtures of bis(chloromethyl) ether with either trioxane or paraformaldehyde contain no detectable amount of the *neso* compound, CH_2Cl_2. This means that chlorine atoms cannot be interchanged with the bridging oxygens under conditions where the latter are readily scrambled. This conclusion is supported by the fact that dichloromethane shows no sign of reaction with bis(chloromethyl) ether after heating for 4 days at 175° and that pure bis(chloromethyl) ether was not found to decompose into measurable amounts of formaldehyde plus methylene chloride after heating for 8 days at 120° or 4 days at 175°. Presumably higher temperatures, a catalyst, and/or longer periods of time should bring about *neso* equilibration, but side reactions may be important and might mask this reaction. A similar situation has been found in the α,ω-dimethyl polysulfides, where the sulfur-atom middle groups rearrange without involving the C–S bonds of the end groups.[6]

A kinetic study at 100° of a mixture of 3 moles of $ClCH_2OCH_2Cl$ with 1.4 moles of $(CH_2O)_3$ gave an average half-life with respect to equilibrium of *ca.* 2 hr. However, a severalfold variation was observed between replicate runs, a variation which we attribute to two causes: (a) differences in the rates of nucleation and state of compaction of the precipitated polymer appearing as an intermediate; and (b) variations in trace

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(8) J. R. Van Wazer and L. C. D. Groenweghe, "NMR in Chemistry," B. Pesce, Ed., Academic Press Inc., New York, N. Y., 1965.

(9) Boldface type is employed[5,7] to identify the particular end or middle group to which the specific resonance is assigned. The other groups shown in italic type denote the rearrangement of neighboring groups which determine the exact n.m.r. chemical shift.

(10) The term *neso*, which has been used for many years in silicate chemistry, refers to the smallest molecule of a family of compounds. Thus for the aliphatic hydrocarbons, the *neso* compound is methane, and for the α,ω-dichloro- and α,ω-bis(dimethylamino)poxymethylenees, it is dichloromethane and N,N,N′,N′-tetramethyldiaminomethane, respectively.

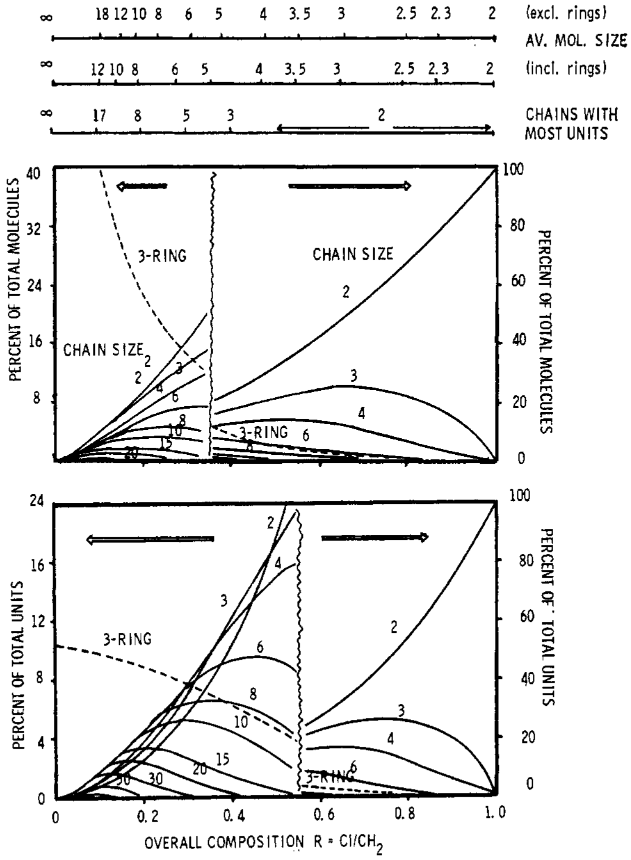

Figure 2.—Calculated molecular size distributions for the α,ω-dichloropolyoxymethylenes as a function of the over-all composition parameter $R = Cl/CH_2$. This theoretical graph includes the molecular distributions for $R < 0.4$ although precipitation of the long-chain polymers prevented experimental study in this composition range of the equilibrated single-phase system corresponding to the calculated values of this figure.

amounts of an acid catalyst, presumably HCl formed by undetectably slight thermal degradation of the bis(chloromethyl) ether (note: addition of *ca.* 0.1% of 85% H_3PO_4 was found to cause a large increase in the reaction rate). Another kinetic run was carried out at 120° by adding $ClCH_2OCH_2Cl$ to an equilibrated mixture of longer-chain α,ω-dichloropolyoxymethylenes exhibiting a composition corresponding to $R \equiv Cl/CH_2 = 0.39$. In this second kinetic study, in which R was raised from 0.39 to 0.80, no high-polymer precipitate was formed, and the amounts of the various measurable constituents were seen to change smoothly from the composition of the original equilibrium mixture to that of the new equilibrium mixture. To a reasonable approximation, the approach to the equilibrium value of the area of any given n.m.r. peak was logarithmic with time (pseudo-first-order kinetics). The half-life for this re-equilibration process was about 50 hr. We tentatively conclude from these limited kinetic data that the reaction shown in eq. 2 between tri-

$$(CH_2O)_3 + X(CH_2O)_{j-1}CH_2X \rightleftarrows X(CH_2O)_{j+2}CH_2X \quad (2)$$

oxane rings and the various chain species to give longer chains is very rapid compared with the reactions of eq. 1. It also appears that the precipitated polymer is in a highly reactive form, with the reactions of the form of eq. 1 occurring more rapidly at the polymer surface than in solution.

When the sealed n.m.r. tubes containing all-liquid equilibrated compositions for which $R < 0.6$ were allowed to stand for several weeks at room temperature, a precipitate of long-chain polymers was seen to form. Since, as will be shown later, the equilibria of eq. 1 are nearly random so that the respective enthalpies must be small,[3] this means that the longer-chain molecules are more soluble at 120° than at 25° in the liquid composed of the shorter-chain molecules (oligomers). Repetition of the previously described preparation[2] of the chloro-terminated tri- and tetra(oxymethylenes) from thionyl chloride and paraformaldehyde gave, prior to distillation, products which were essentially at equilibrium. After distillation, the allegedly pure products were contaminated with a rather wide range of other of the shorter-chain species. In this and several other unsuccessful attempts to separate cleanly various equilibrium mixtures by distillation, the high molecular weight polymer was always seen to coat the inside of the distilling head and condenser.

Equilibria in the Chloro-Terminated Polyoxymethylenes.—The experimental data obtained for a number of different compositions equilibrated at 120° are shown in Table I and a typical n.m.r. spectrum is shown in Figure 1. The n.m.r. resonances in the range of −5.6 to −5.3 p.p.m. were originally all assigned to end groups, and those in the range from −5.0 to −3.2 to middle groups on the basis of material balances. The *ee* and the $(\mathbf{m})_3$ resonances were known from previous n.m.r. measurements on pure bis(chloromethyl) ether and trioxane. The *emm* and *eme* resonances[9] were readily identified from the over-all composition where they maximized. One of the resonances at −4.93 or −4.85 p.p.m. likewise appeared to be due to an *emm* structure, while the remaining more upfield resonances were tentatively assigned to *mmm* arrangements.

In the quantitative treatment of data of the type reported in Table I, it is assumed, unless otherwise shown,[3] that the oxymethylene middle groups are randomly sorted between the chloromethyl end groups to form the observed distribution of chain molecules, using what Flory[11] calls the "principle of equal reactivity of (exchangeable) groups." From testing all reasonable peak assignments made on this basis, we found it necessary to conclude that the relatively small resonances (given in Table I), seen at −5.44, −5.33, −4.56, −3.45, −3.35, and −3.37 p.p.m., must be due to by-products, *i.e.*, reactions other than the sorting of middle groups between end groups in the α,ω-dichloropolyoxymethylenes. (Treating these peaks as by-products caused no problems with the material balance.) It should be noted that further testing involving the theoretically acceptable deviations from the equal-reactivity principle [due to thermodynamic effects transmitted through a molecular chain (*i.e.*, a reorganization heat order[3] greater than unity) or to solution nonidealities] did not justify any alternative assignment of the n.m.r. peaks attributed to by-products in Table I to atomic arrangements appearing in the chloro-terminated polyoxymethylenes. However, it is possible that some of the "by-product" resonances might be due to polyoxymethylene ring structures larger than trioxane.

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(11) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 102, 103.

TABLE I

PROTON N.M.R. DATA IN PERCENTAGE OF TOTAL HYDROGEN FOR THE SYSTEM $ClCH_2OCH_2Cl$ *vs.* $[CH_2O]$ AT EQUILIBRIUM AT 120°

	N.m.r. shift, p.p.m										
	−5.55	−5.51	−5.48	−5.44	−5.08	−5.02	−4.93	−4.85	−4.56	−3.45	−3.35
	Assignment										
$R = Cl/CH_2$	*ee*	*emm*	*eme*	By-product	$(m)_3$	*eme*	*emm*	*mmm*	By-products		
0.976[a]	89.8	1.2	3.6	...	...	3.6	1.8	...	...	...	...
(0.946)[b]	(84.9)[c]	(1.0)	(8.7)			(4.4)	(1.0)	(0.1)			
0.953	85.1	1.9	7.5	...	...	4.3	1.2	...	...	...	...
(0.944)	(84.4)	(1.1)	(8.9)			(4.5)	(1.1)	(0.1)			
0.921	79.4	3.8	6.8	...	1.0	3.3	4.7	1.0	...	...	...
(0.901)	(74.0)	(2.9)	(13.2)		(0.1)	(6.6)	(2.9)	(0.3)			
0.794	51.2	9.3	16.9	1.0	0.5	9.3	9.0	1.4	...	1.4	...
(0.793)	(51.5)	(8.7)	(17.2)		(0.7)	(8.5)	(8.8)	(2.2)			
0.659	31.5	14.8	17.1	2.1	1.5	8.7	15.5	5.8	1.6	1.4	...
(0.668)	(32.8)	(14.7)	(15.9)		(2.0)	(7.9)	(14.7)	(6.9)			
0.571	21.8	19.4	15.3	0.8	2.5	7.4	19.8	10.3	1.9	0.8	...
(0.586)	(24.6)	(18.1)	(13.9)		(3.1)	(6.9)	(18.1)	(11.8)			
0.484	15.1	19.9	11.9	2.5	4.0	5.6	21.7	16.5	...	1.9	0.9
(0.495)	(16.4)	(19.8)	(10.6)		(4.5)	(5.3)	(19.8)	(18.3)			
0.388	11.5	19.0	8.0	4.3[d]	5.4	4.0	21.0	21.2	0.9	0.9[e]	3.8[f]
(0.427)	(11.3)	(19.3)	(8.0)		(5.0)	(4.0)	(19.3)	(23.2)			

[a] From ingredients. [b] From n.m.r. peak areas, omitting the by-product resonances. [c] Calculated from $K_3° = 3.4$ moles of CH_2 groups/l. (see eq. 35 in ref. 3 for definition, $\rho = 1$). [d] Two peaks: one equaling 2.9% of total H at −5.44 p.p.m., the other 1.4% at −5.33 p.p.m. [e] Correct shift is −3.53 p.p.m. [f] Two peaks: one equaling 2.2% of total H at −3.35 p.p.m., the other 1.6% at −3.27 p.p.m.

TABLE II

PROTON N.M.R. DATA IN PERCENTAGE OF TOTAL HYDROGEN FOR THE SYSTEM $CH_2[N(CH_3)_2]_2$ *vs.* $[CH_2O]$ AT EQUILIBRIUM AT 120°

	N.m.r. shift, p.p.m.							
	$N(CH_3)_2$– region			CH_2– region				
	−2.15	−2.28	−2.33	−2.58	−3.98	−4.15	−4.65	−4.73
	Assignment							
$R = N(CH_3)_2/CH_2$	*neso**[a]	e**e*[a]	e**m*[a]	*neso*	*ee*	e*m*	*eme*	*emm*
1.935[b]	79.1	4.3	...	15.1	1.6	...	...	...
(1.910)[c]	(81.3)[d]	(3.7)	(0.2)	(13.6)	(1.2)	(0.1)	(0.0)	(0.0)
1.897	79.4	5.8	...	13.1	1.6	...	...	...
(1.890)	(80.3)	(4.5)	(0.2)	(13.4)	(1.5)	(0.1)	(0.0)	(0.0)
1.758	74.4	7.7	1.9	12.9	2.6	0.5	...	...
(1.810)	(76.4)	(7.4)	(0.7)	(12.7)	(2.5)	(0.2)	(0.1)	(0.0)
1.615	65.8	11.7	5.2	11.5	4.1	1.1	0.7	...
(1.620)	(67.0)	(13.2)	(2.8)	(11.2)	(4.4)	(0.9)	(0.4)	(0.2)
1.413	54.5	14.5	10.0	11.0	5.0	2.9	1.4	0.7
(1.430)	(57.8)	(17.2)	(6.1)	(9.6)	(5.7)	(2.0)	(0.6)	(0.5)
1.197	43.2	18.6	14.7	8.8	7.1	4.3	2.0	1.3
(1.230)	(48.3)	(19.6)	(10.8)	(8.1)	(6.5)	(3.6)	(1.2)	(1.3)

[a] The asterisk indicates that the resonating hydrogen does not stay with the CH_2 moiety under the reaction conditions. [b] From ingredients. [c] From n.m.r. peak areas of $-CH_2-$ region. [d] Calculated from $K_1 = 0.22$ (see footnote 14) and $K_3° = 3.4$ moles of CH_2 groups/l. (see eq. 35 in ref. 3).

The equal-reactivity principle leads to an equilibrium constant of unity for the generalized chain–chain reaction given in eq. 1, as long as k and j in these equations are larger than 2. There is one other equilibrium constant needed to describe the system reported in Table I and this is the ring–chain equilibrium constant for the reaction of eq. 2. For a neat single-phase liquid, this constant[12] was shown to exhibit the value $°K_3 = 1.1$ mole/l. with a standard deviation[13] of 0.2. When trioxane is dissolved without reaction at room temperature in one of the equilibrium mixtures or in pure bis(chloromethyl) ether, cooling is observed. Thus the value of $°K_3$ should reflect an enthalpy contribution due to nonideal solution of the trioxane ring in the α,ω-dichloropolyoxymethylene chains.

On the basis of the above pair of equilibrium constants, we have computed the percentage of total hydrogen corresponding to the areas of the observed n.m.r. peaks, as shown in Table I, from which it can be seen that the calculated values in parentheses are in good agreement with experimental values given above. This pair of equilibrium constants was also used to compute the amounts of the various molecules present in an equilibrated mixture as a function of the over-all composition of the mixture. This information is plotted in Figure 2.

The Dimethylamino-Terminated Polyoxymethylenes.—N,N,N′,N′-Tetramethyldiaminomethane was found to react with paraformaldehyde at elevated temperatures but not with trioxane. This probably means that the reactions shown in eq. 1 for $i < k$, $2 \leq k < \infty$,

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[12] The constant $°K_3$ dealing with molecules equals one-third of the ring–chain constant $K_3°$ dealing with exchangeable molecular segments (*i.e.*, building units). This latter constant is one used in the majority of our previous papers[3,5] (only the ref. 5e and f deal with rings).

[13] L. C. D. Groenweghe, J. R. Van Wazer, and A. W. Dickinson, *Anal. Chem.*, **36**, 303 (1964).

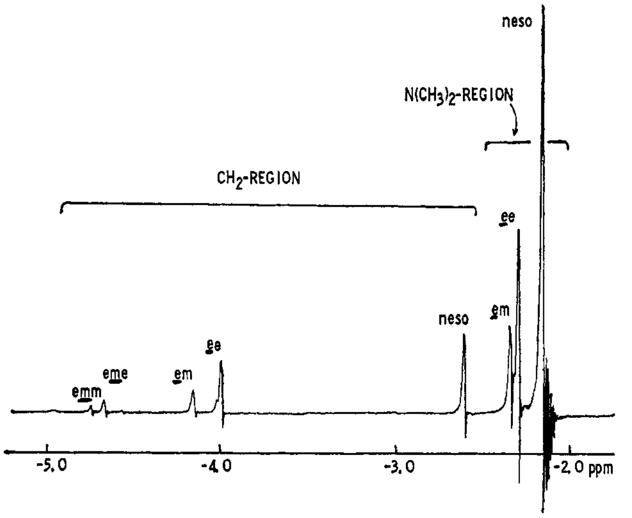

Figure 3.—Proton n.m.r. spectrum of an equilibrated sample in the system $CH_2[N(CH_3)_2]_2$ *vs.* $[CH_2O]$: $R = N(CH_3)_2/CH_2 = 1.197$.

and $1 \leq j < \infty$, with $X = (CH_3)_2N$ can proceed under conditions where there is no mechanism for ring opening, as defined by eq. 2.

The data corresponding to equilibrium at 120° are shown in Table II, where it should be noted that there are two regions of the n.m.r. spectrum—one corresponding to the hydrogens of the dimethylamino group and the other corresponding to those of the methylene hydrogens. This is exemplified by the n.m.r. spectrum of Figure 3. Assignment of resonance peaks was very simple since only the *neso* molecule, $CH_2[N(CH_3)_2]_2$, and end groups can show up in the dimethylamino region. The methylene resonance at −2.58 p.p.m. was known to be due to the *neso* molecule and the resonances at −3.98 and −4.15 p.p.m. were readily assigned to end groups from the over-all material balance and the 1:3 ratio they bear to the end-group peaks in the dimethylamino region of the spectrum. This pair of resonances and the two remaining ones at −4.64 and −4.73 p.p.m. are readily assigned to molecular arrangements from the region of over-all composition at which they maximize. The resonance at −5.08 p.p.m. was not noted in any of the equilibrated samples so that we must assume that ring-chain equilibration is either kinetically excluded or is such that the trioxane ring does not appear in detectable amounts at equilibrium. However, since this system must be identical with the chloro-terminated polyoxymethylenes at $R = 0$, all calculations were carried out using the value[12] of $°K_3 = 1.1$ found for the latter system where rings were actually observed. For the experiments of Table II, the maximum amount (at $R = 1.91$) of trioxane was calculated to represent only 0.4% of the total hydrogen and hence was too small to be detected in the n.m.r. spectra.

In Table II, equilibrium data for R values ranging from 2 to 1.2 are reported. Although compositions with R values ranging from 1.0 to 0.5 were found to give homogeneous solutions upon heating, it was seen that reactions other than those of the type described by eq. 1 and 2 were significant. Thus, series of n.m.r. peaks in the range of −2.6 to −3.9 p.p.m. totaling about 10–30% of the total methylene hydrogens was seen. Since all these peaks lie in a range which is between the resonances for the CH_2 group in the *neso* compound and the *ee* molecule (where no other resonances are to be expected), they must represent products of other reactions. Therefore, these latter data were not considered in the equilibrium constant calculations and are also not included in Table II.

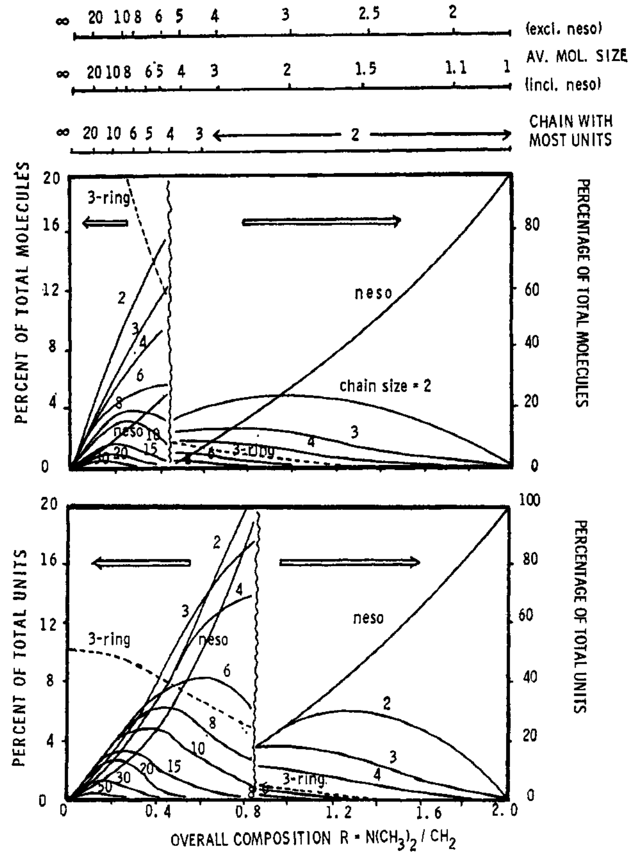

Figure 4.—Calculated molecular size distributions for the α,ω-bis(dimethylamino)polyoxymethylenes as a function of the over-all composition parameter $R = N(CH_3)_2/CH_2$. Since side reactions became important for $R < 1.2$ and precipitation of long-chain polymers occurred at $R <$ *ca.* 0.4, the left half of this figure represents a theoretical extrapolation.

For the chloro-terminated system, we have no information about the equilibrium constant of eq. 1 for a value of $j = 1$. On the other hand, it is found that, for the dimethylamino-terminated polyoxymethylenes, the equilibrium constant of eq. 1 is always nearly equal to unity, even[14] for $j = 1$. The values given in parentheses in Table II are calculated for this case ($K_1 = 0.22$ and $K_3° = 3.4$ moles of CH_2 groups/l.) and the good agreement between experimental and theoretically calculated "yields" is apparent. These equilibrium constants were also employed to calculate the molecular distribution shown in Figure 4, a distribution which corresponds to essentially random scrambling at all levels of exchangeable molecular fragments and molecules.

Discussion

Since to a rather close approximation the distributions of chain molecules in both the chloro- and dimethyl-

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(14) When the constant involving molecules $K_{mol} = [neso][k\text{-chain}]/[\{k + 1)/2\}\text{-chain}]^2 = 1$ for a reorganization heat order of one, it can be shown[3] that the building-unit equilibrium constant $K_1 = [neso][\text{middles in chains}]/[\text{ends}]^2$ has the "random" value of 1/4. Evaluation of $K_1 = 0.22$ with a standard deviation, *s*, of 0.03 shows that the equilibrium constant of eq. 1 is 1.1 with $s = 0.1$ for $j = 1$.

amino-terminated polyoxymethylenes are random, we conclude that the chain–chain equilibria discussed in this paper are entropy controlled and, thus, essentially independent of temperature. This means that the relative amounts of chain molecules in Figures 2 and 4 should apply to all temperatures where the chemistry described herein may be studied, as long as the reaction products are present in the form of a homogeneous liquid and the methylene, chloromethyl, and dimethylamino groups are not disrupted in the reactions whereby the equilibria are achieved.

A check of the effect of doubling or halving the equilibrium constants underlying the calculations of Figures 2 and 4 showed that the gross features of the distribution curves were insensitive to these changes, which are greater than several standard deviations. The major effect of the twofold change in K_1 is about a 30% variation in the amount of di- and trichain species for the larger R values—those R values corresponding to the composition region in which the best experimental data were obtained in the work reported above. Moreover, the amounts of "3-ring" shown in Figures 2 and 4 were even more affected by the given change in the ring–chain equilibrium constant. Since this constant was obtained from experiments involving the reaction of bis(chloromethyl) ether with trioxane, it seems improbable that the equilibrium would correspond to a larger amount of "3-ring" than shown in the figures. In the unlikely event that our measurements poorly represent true equilibrium (*i.e.*, the trioxane is present in insignificant amounts at all R values at equilibrium), the distribution of the various chain species (except for the *neso* compound) on the left side of Figures 2 and 4 would not be greatly affected. This is true because the CH_2O groups now considered to be present at equilibrium as trioxane would then be incorporated into a wide range of different-sized chains so that their proportions would be little changed.

Notes

Scrambling Equilibria on Carbon. II. Alkoxy Group Exchange Reactions in Acetals and Orthoformates

KURT MOEDRITZER AND JOHN R. VAN WAZER

Central Research Department, Monsanto Company,
St. Louis, Missouri

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Scrambling of substituents on a single carbon atom and the resulting equilibria have been studied previously by separating equilibrated molecules through distillation. Calingaert and co-workers[1,2] have investigated the systems $C_2H_4Cl_2$ *vs.* $C_2H_4Br_2$, CH_3COOCH_3 *vs.* $C_3H_7COOC_2H_5$, and $(COOCH_3)_2$ *vs.* $(COOC_4H_9)_2$, and Forbes and Anderson[3] the system CCl_4 *vs.* CBr_4. In all these cases, the resulting scrambling equilibria were classified as random although the deviations from randomness might have been quite large, since distillation is a very crude method of quantitatively assaying a mixture of closely related chemical compounds. In this paper, we report the results of a study of scrambling equilibria in acetals (dimethyl *vs.* diethylformal) and orthoformates (trimethyl *vs.* triethyl orthoformate), using gas chromatography as a precise method for the quantitative separation of the resulting mixtures of compounds.

Experimental Section

Reagents.—Dimethoxymethane, diethoxymethane, trimethyl orthoformate, and triethyl orthoformate were purchased from Eastman and were fractionated before use.

Apparatus.—The gas chromatography studies were performed using a Perkin-Elmer vapor fractometer, Model 154D, with a printing integrator. A 3-m. column containing C-22 firebrick (30–60 mesh) supporting 10% of Tween 80 was employed at temperatures of 58° for the system $CH_2(OCH\ )_2$ *vs.* $CH_2(OC_2H_5)_2$, and 75° for the system $HC(OCH_3)_3$ *vs.* $HC(OC_2H_5)_2$. The retention times of the starting materials were identified through runs on the pure samples. The assignment of the chromatographic peaks to the mixed compounds were made from their sequence and checked by material-balance calculations. For each series of compounds, the peaks were found to be spaced practically linearly with increasing replacement of OCH_3 for OC_2H_5.

Equilibrations.—The desired proportions of starting materials were sealed in 7-mm.-o.d. Pyrex glass tubes which were then heated for the desired length of time. Pilot runs were used to establish the conditions for reaching equilibrium. The reaction products of the ester–ester interchange were quantitatively determined by gas chromatography.

In the system $CH_2(OCH_3)_2$ *vs.* $CH_2(OC_2H_5)_2$, equilibrium was reached in less than 21 days at room temperature and 7 days at 65° in the presence of trace amounts of concentrated H_2SO_4 as catalyst. The reported equilibrium data correspond to 7 days at 65°. No reaction was observed in this system in the absence of a catalyst after 48 hr. at 120°. Longer heating times and higher temperatures resulted in decomposition of the starting materials.

The data for the system $HC(OCH_3)$ *vs.* $HC(OC_2H_5)_3$ were obtained after holding the samples for 7 days at 120°. Pilot runs did not show any further change in the composition of the reaction product after 3 additional days at this temperature.

Results and Discussion

The Acetal System.—The experimental data for the scrambling equilibria in dialkoxymethanes ac-

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