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

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Received March 2, 1965

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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[1] G. Calingaert, H. A. Beatty, and H. R. Neal, *J. Am. Chem. Soc.*, **61**, 2755 (1939).

[2] G. Calingaert, H. Soroos, V. Hnizda, and H. Shapiro, *ibid.*, **62**, 1545 (1940).

[3] G. S. Forbes and H. H. Anderson, *ibid.*, **66**, 931 (1944).

$$CH_2(OCH_3)_2 + CH_2(OC_2H_5)_2 \rightleftarrows 2CH_2(OCH_3)(OC_2H_5) \quad (1)$$

cording to eq. 1 are presented in Table I. These data were employed to calculate[4] the equilibrium constant

$$K = \frac{[CH_2(OCH_3)_2][CH_2(OC_2H_5)_2]}{[CH_2(OCH_3)(OC_2H_5)]^2} = 0.30 \quad (2)$$

which has a standard error,[4] s, of 0.04. This equilibrium constant was used to calculate the values given in parentheses in Table I for the mole percentage of the various compounds at equilibrium. It is interesting to note that the equilibration according to eq. 1 does not proceed in the absence of a catalyst. Trace amounts of acids act as catalysts. A comparison of the equilibrium constant with that for the statistically random case ($K_{\text{rand}} = 0.250$) shows that the equilibrium of eq. 1 is quite close to this case as found earlier for ester–ester interchanges of some inorganic alkoxy compounds.[5]

TABLE I

EQUILIBRIUM DATA FOR SCRAMBLING OF OCH_3 WITH OC_2H_5 GROUPS IN THE SYSTEM $CH_2(OCH_3)_2$ *vs.* $CH_2(OC_2H_5)_2$ AT 65°

	Mole %		
$R = OCH_3/CH_2$	$CH_2(OCH_3)_2$	$CH_2(OCH_3)(OC_2H_5)$	$CH_2(OC_2H_5)_2$
0.250[a]	1.6	23.4	75.0
(0.266)[b]	(1.8)[c]	(21.4)	(76.8)
0.667	9.2	41.5	49.3
(0.599)	(12.0)	(42.7)	(45.3)
1.000	24.0	47.6	28.4
(0.956)	(26.1)	(47.8)	(26.1)
1.333	38.8	44.5	16.7
(1.221)	(45.3)	(42.7)	(12.0)
1.750	74.0	24.7	1.3
(1.727)	(76.8)	(21.4)	(1.8)

[a] From the ingredients. [b] Values in parentheses are calculated from the gas chromatographic data. [c] Values in parentheses are calculated using $K = 0.30$.

In a related study by others,[6] equilibrium constants were determined for the alcoholysis of diethyl- and dimethylacetal, $K_{\text{I}} = [CH_3CH(OCH_3)(OC_2H_5)][C_2H_5OH]/[CH_3CH(OC_2H_5)_2][CH_3OH] = 4.61$ with $s = 0.09$ and $K_{\text{II}} = [CH_3CH(OCH_3)_2][C_2H_5OH]/[CH_3CH(OCH_3)(OC_2H_5)][CH_3OH] = 1.01$ with $s = 0.04$. It is seen that $K_{\text{II}}/K_{\text{I}} = K = 0.22$. This indirectly measured value of the constant of eq. 2 has a standard error of 0.003 and is in fair agreement with our value, and the concept[1,2] that exchange reactions of this type follow the statistics of random sorting.

The Orthoformate System.—Data for the scrambling of alkoxy groups in orthoformates are given in Table II. The resulting equilibria obtained after 7 days at 120° without a catalyst are expressed by eq. 3 and 4

$$HC(OCH_3)_3 + HC(OCH_3)(OC_2H_5)_2 \rightleftarrows 2HC(OCH_3)_2(OC_2H_5) \quad (3)$$

$$HC(OC_2H_5)_3 + HC(OCH_3)_2(OC_2H_5) \rightleftarrows 2HC(OCH_3)(OC_2H_5)_2 \quad (4)$$

and the experimental data in Table II were used to calculate[4] the equilibrium constants K_1 and K_2 which

$$K_1 = \frac{[HC(OCH_3)_3][HC(OCH_3)(OC_2H_5)_2]}{[HC(OCH_3)_2(OC_2H_5)]^2} = 0.46 \quad (5)$$

$$K_2 = \frac{[HC(OC_2H_5)_3][HC(OCH_3)_2(OC_2H_5)]}{[HC(OCH_3)(OC_2H_5)_2]^2} = 0.33 \quad (6)$$

have standard errors $s_1 = 0.03$ and $s_2 = 0.02$, respectively. This system is also quite close to the statistically random case ($K_{1(\text{rand})} = K_{2(\text{rand})} = 0.333$). The constants K_1 and K_2 quantitatively describe all possible exchange equilibria in the orthoformate system, a system which has been studied earlier in a qualitative manner by Post and Erickson.[7]

TABLE II

EQUILIBRIUM DATA FOR THE SCRAMBLING OF OCH_3 WITH OC_2H_5 GROUPS IN THE SYSTEM $HC(OCH_3)_3$ *vs.* $HC(OC_2H_5)_3$ AT 120°

	Mole %			
$R = OCH_3/C$	$HC(OCH_3)_3$	$HC(OCH_3)_2$-(OC_2H_5)	$HC(OCH_3)$-$(OC_2H_5)_2$	$HC(OC_2H_5)_3$
0.375[a]	0.1	3.0	35.9	61.0
(0.420)[b]	(0.3)[c]	(4.1)	(28.5)	(67.1)
1.000	3.5	23.5	41.5	31.5
(0.990)	(4.5)	(21.3)	(43.8)	(30.4)
1.500	15.1	35.2	37.9	14.0
(1.503)	(14.3)	(34.9)	(37.3)	(13.5)
2.000	33.9	40.2	20.5	5.4
(2.025)	(31.6)	(40.9)	(23.0)	(4.4)
2.625	68.4	27.5	3.9	0.2
(2.641)	(67.4)	(27.4)	(4.9)	(0.3)

[a] From the ingredients. [b] Values in parentheses are calculated from the gas chromatographic data. [c] Values in parentheses are calculated using $K_1 = 0.46$ and $K_2 = 0.33$.

Attempts to extend these studies to the systems $CH_3C(OCH_3)_3$ *vs.* $CH_3C(OC_2H_5)_3$ and $C(OCH_3)_4$ *vs.* $C(OC_2H_5)_4$ failed owing to difficulties in finding a suitable support–substrate combination for the gas chromatographic analysis and formation of low-boiling side products, respectively.

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(5) K. Moedritzer, G. M. Burch, J. R. Van Wazer, and H. K. Hofmeister, *Inorg. Chem.*, **2**, 1152 (1963); K. Moedritzer and J. R. Van Wazer, *ibid.*, **3**, 268 (1964); J. R. Van Wazer and K. Moedritzer, *J. Inorg. Nucl. Chem.*, **26**, 737 (1964).

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Ketene Acetals. II. The Synthesis of Ketene Acetals from Dichloro Olefins and Sodium β- and γ-Alkoxy Alcoholates[1]

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Received May 11, 1965

Simons and Vebanc[2] observed the formation of an acetate ester as the terminal product in the reaction of vinylidene chloride with a polyoxypropylene glycol in the presence of a base. Evidence for the intermediates or a choice of proposed mechanisms was not offered, however, by these authors. Earlier work by Coleman, Wiley, and Hadler[3] suggested the formation

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(1) Paper I: W. C. Kuryla and D. G. Leis, *J. Org. Chem.*, **29**, 2773 (1964).

(2) D. M. Simons and J. J. Verbanc, *J. Polymer Sci.*, **44**, 303 (1960).

(3) G. H. Coleman, R. M. Wiley, and B. C. Hadler (to the Dow Chemical Co.), U. S. Patent 2,245,962 (June 17, 1941).