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Features of Acetal Interchange of 1,1-Dialkoxyalkanes with 1,2-Propylene Glycol in Neutral Solutions

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Abstract—Reactions fo 1,1-dimethoxymethane, 1,1-dimethoxyethane, and 1,1-dimethoxypropane with 1,2-propylene glycol at 25°C in neutral solutions were studied by ^{13}C NMR spectroscopy. Under these conditions, 1,1-dimethoxymethane does not react with the glycol. Only the primary OH group of the glycol participates in the acetal interchange. The reactions of 1,1-dimethoxyethane and 1,1-dimethoxypropane with the glycol, along with the linear acetals, yielded 2-alkyl-4-methyl-1,3-dioxolanes. The product ratio depends on the molar ratio 1,1-dialkoxyalkane : glycol. In the system 1,1-dimethoxypropane–1,2-propylene glycol, the equilibrium concentration of the cyclic acetal slightly increases with temperature in the range 25–80°C.

Acetal interchange of linear acetals (1,1-dialkoxyalkanes) with 1,2-glycols is a convenient route to 1,2-dioxolanes [1, 2]. The advantage of this procedure over the other routes is that significant amounts of the target product are formed already on mixing the reactants in a neutral solution [3]. Previously we studied the reaction of linear acetals with ethylene glycol [3] and elucidated the influence of the structure of the linear acetal on the composition of the reaction mixture. With increasing volume of the alkoxy group in the initial acetal, the reaction selectivity with respect to 1,3-dioxolane increases. Variation of the structure of the alkyl radical in the aldehyde moiety has virtually no effect on the equilibrium yield of the cyclic acetal.

To elucidate the influence of the structure of 1,2-glycol on its reactivity in acetal interchange and on the composition of the reaction products, we studied in this work, using ^{13}C NMR spectroscopy, the reactions of 1,1-dimethoxyalkanes $RCH(OCH_3)_2$ [R = H (**I**), CH_3 (**II**), C_2H_5 (**III**)] with 1,2-propylene glycol (**IV**) in neutral solution at 25–80°C.

Previously it was suggested [1] that the mechanism of acetal interchange is similar to the mechanism of formation and hydrolysis of acetals. Study of the reactions of carbonyl compounds with ethylene glycol and 1,2-propylene glycol in neutral solution showed that the major reaction products are various hemiacetals [4, 5]. On mixing of 1,2-propylene glycol with an aldehyde, the OH groups of the glycol participate in the reaction with the carbonyl group, with the secondary OH groups being less reactive.

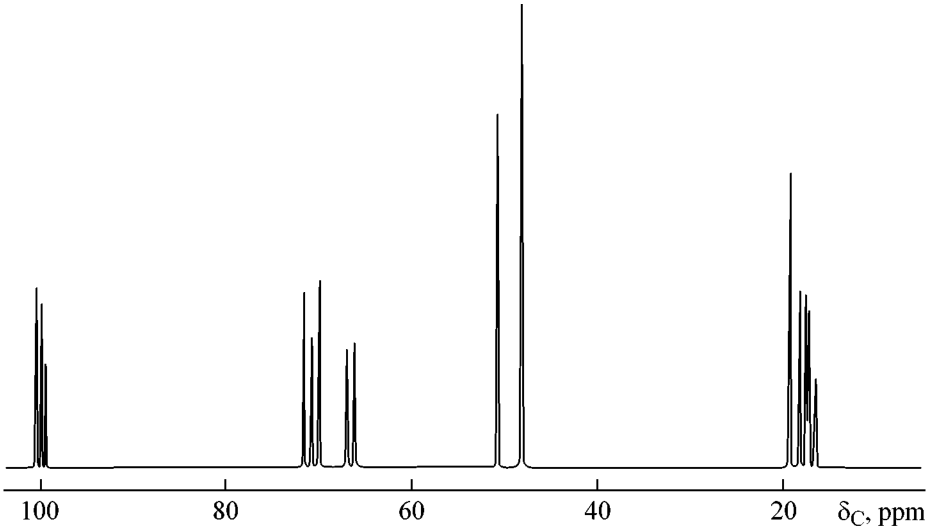


Fig. 1. ^{13}C NMR spectrum of the mixture 1,1-dimethoxyethane (**II**)–1,2-propylene glycol (**IV**) (25°C, $c^0_{\mathbf{II}}$ 5.457, $c^0_{\mathbf{IV}}$ 5.479 M).

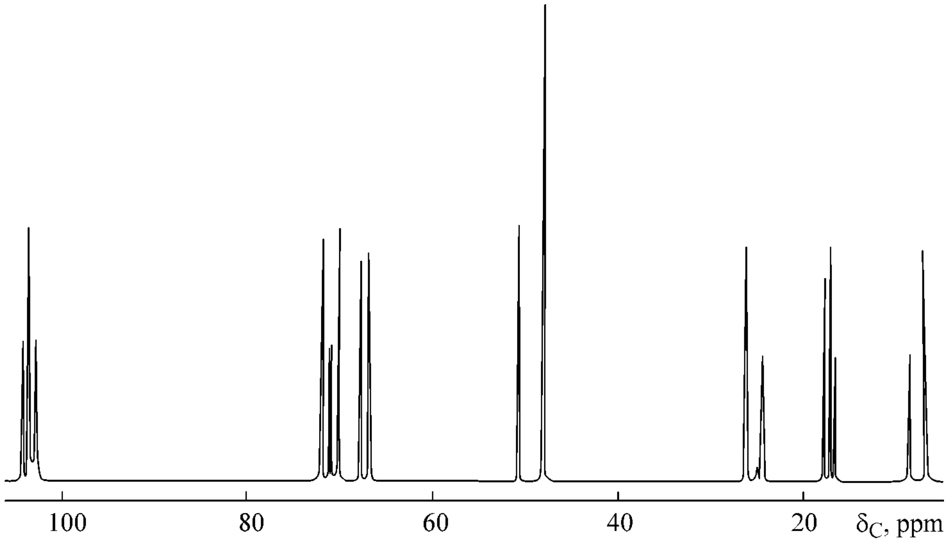
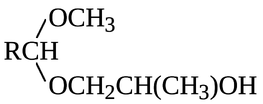


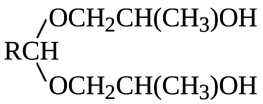
Fig. 2. ^{13}C NMR spectrum of the mixture 1,1-dimethoxypropane (**III**)–1,2-propylene glycol (**IV**) (25°C, c^0_{III} 4.802, c^0_{IV} 5.459 M).

The spectra of the equilibrium mixtures **II**–**IV** and **III**–**IV** are shown in Figs. 1 and 2. In analysis of the composition of the equilibrium mixtures and structure of the products, we leaned upon the spectra of the pure reactants and of equilibrium reaction mixtures of linear acetals with ethylene glycol [3] and of carbonyl compounds with ethylene glycol and 1,2-propylene glycol [4, 5]. Table 1 gives the assignments for the groups of signals whose integral intensities were used to obtain quantitative data on the composition of the reaction mixtures. Among the reaction products, we detected mixed acetal **V**, acetal **VI**, and the cyclic acetal, 2-alkyl-4-methyl-1,3-dioxolane **VII**.



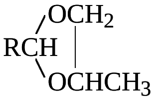
$$\mathrm{RCH}\begin{array}{l}/\mathrm{OCH_3}\\ \backslash\mathrm{OCH_2CH(CH_3)OH}\end{array}$$

V



$$\mathrm{RCH}\begin{array}{l}/\mathrm{OCH_2CH(CH_3)OH}\\ \backslash\mathrm{OCH_2CH(CH_3)OH}\end{array}$$

VI



VII

Table 1. Signal assignment in the ^{13}C NMR spectra of mixtures 1,1-dimethoxyethane–1,2-propylene glycol and 1,1-dimethoxypropane–1,2-propylene glycol at 25°C (the carbon atoms giving the indicated signal are printed italic)

δC, ppm	Assignment	Correction factor	δC, ppm	Assignment	Correction factor
1,1-Dimethoxyethane–1,2-propylene glycol			1,1-Dimethoxypropane–1,2-propylene glycol		
48.33	$\mathit{C}\mathrm{H_3OH}$	0.9969	48.33	$\mathit{C}\mathrm{H_3OH}$	1.0404
51.06	$\mathrm{CH_3CH(O}\mathit{C}\mathrm{H_3)_2}$	1.0042	51.32	$\mathrm{CH_3CH_2CH(O}\mathit{C}\mathrm{H_3)_2}$	0.9299
66.81	$\mathrm{HO}\mathit{C}\mathrm{H_2CH(CH_3)OH}$	0.8293	66.89	$\mathrm{HO}\mathit{C}\mathrm{H_2CH(CH_3)OH}$	0.6938
67.31	$\mathrm{HOCH_2}\mathit{C}\mathrm{H(CH_3)OH}$	0.6453	67.36	$\mathrm{HOCH_2}\mathit{C}\mathrm{H(CH_3)OH}$	0.7994
70.00	$\mathrm{CH_3CH(OCH_3)O}\mathit{C}\mathrm{H_2CH(CH_3)OH}$ $\mathrm{CH_3CH(O}\mathit{C}\mathrm{H_2CH(CH_3)OH)_2}$	0.8240	70.06	$\mathrm{CH_3CH_2CH(OCH_3)O}\mathit{C}\mathrm{H_2CH(CH_3)OH}$ $\mathrm{CH_3CH_2CH(O}\mathit{C}\mathrm{H_2CH(CH_3)OH)_2}$	1.1303
70.89	$\mathrm{CH_3CHO}\mathit{C}\mathrm{H_2CH(CH_3)O}$	0.9955	70.87	$\mathrm{CH_3CH_2CHO}\mathit{C}\mathrm{H_2CH(CH_3)O}$	1.1155
71.00	$\mathrm{CH_3CHOCH_2}\mathit{C}\mathrm{H(CH_3)O}$	1.7103	71.13	$\mathrm{CH_3CH_2CHOCH_2}\mathit{C}\mathrm{H(CH_3)O}$	1.4260
72.11	$\mathrm{CH_3CH(OCH_3)OCH_2}\mathit{C}\mathrm{H(CH_3)OH}$ $\mathrm{CH_3CH(OCH_2}\mathit{C}\mathrm{H(CH_3)OH)_2}$	1.4557	71.96	$\mathrm{CH_3CH_2CH(OCH_3)OCH_2}\mathit{C}\mathrm{H(CH_3)OH}$ $\mathrm{CH_3CH_2CH(OCH_2}\mathit{C}\mathrm{H(CH_3)OH)_2}$	1.4471
99.68	$\mathrm{CH_3}\mathit{C}\mathrm{HOCH_2CH(CH_3)O}$	1.3066	103.71	$\mathrm{CH_3CH_2}\mathit{C}\mathrm{HOCH_2CH(CH_3)O}$	1.1284
100.45	$\mathrm{CH_3}\mathit{C}\mathrm{H(OCH_3)_2}$	0.9353	104.56	$\mathrm{CH_3CH_2}\mathit{C}\mathrm{H(OCH_3)_2}$	1.0047
100.67	$\mathrm{CH_3}\mathit{C}\mathrm{H(OCH_2CH(CH_3)OH)_2}$	1.0335	105.02	$\mathrm{CH_3CH_2}\mathit{C}\mathrm{H(OCH_2CH(CH_3)OH)_2}$	0.9087

Table 2. Equilibrium composition of reaction mixtures obtained by mixing of linear acetals with 1,2-propylene glycol at 25°C

Initial concentrations of reactants, M		Concentrations of components of equilibrium reaction mixture, M					
linear acetal	1,2-propylene glycol	linear acetal	1,2-propylene glycol	methanol	acetal **V**	acetal **VI**	dioxolane **VII**
Compound **II**							
1.541	11.33	–	8.828	3.082	–	0.9609	0.5801
2.978	9.014	0.2811	4.723	5.048	0.3461	1.594	0.7573
4.285	7.068	0.9865	2.520	6.084	0.5127	1.249	1.537
5.457	5.479	2.181	0.9656	5.856	0.6964	1.238	1.341
Compound **III**							
1.261	11.25	–	9.144	2.522	–	0.8454	0.4156
2.630	9.039	0.2114	5.187	4.779	0.0579	1.433	0.9278
3.661	7.389	0.6415	2.709	5.819	0.2197	1.660	1.140
4.802	5.459	1.493	0.7026	6.011	0.6074	1.448	1.253
4.802[a]	5.459	1.300	0.1396	6.520	0.4844	1.817	1.201
4.802[b]	5.459	1.209	0.0057	6.877	0.3093	1.86	1.424

[a] Reactants mixed at 65°C. [b] Reactants mixed at 80°C.

Similar to the system with ethylene glycol, the spectrum of the mixture dimethoxymethane (**I**)–compound **IV** contains only the signals of the initial components; no reaction products are detected.

The concentrations of the components of the reaction mixtures, calculated from the integral intensities of the appropriate signals, are listed in Table 2. Similar to the system with ethylene glycol [3], an increase in the molar ratio dialkoxyalkane–compound **IV** (*A*) results in increased concentrations of the linear acetal, alcohol, mixed acetal **V**, and dioxolane **VII**. The equilibrium conversion of the linear acetal decreases with increasing its initial concentration (Fig. 3). In going from ethylene glycol to 1,2-propylene glycol, the equilibrium conversion of the linear acetal changes insignificantly. Such a low sensitivity to the structure of 1,2-glycol was observed previously in direct acetalization of carbonyl compounds with 1,2-glycols [4–7]. With both glycols, replacement of the C_2H_5 group in the aldehyde moiety of dimethoxyalkane by C_3H_7 has virtually no effect on its equilibrium conversion in acetal interchange.

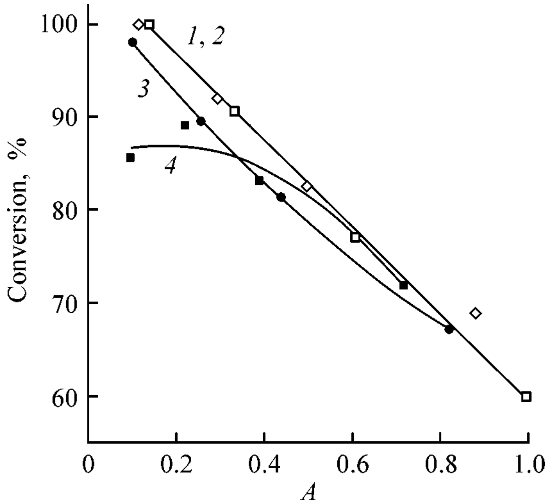


Fig. 3. Influence of the initial molar ratio [linear acetal] : [glycol] (*A*) on the equilibrium conversion of linear acetals **II** and **III**: (*1*) 1,2-propylene glycol + **II**, (*2*) 1,2-propylene glycol + **III**, (*3*) ethylene glycol + **II** [3], and (*4*) ethylene glycol + **III** [3].

In going from dimethoxyethane to dimethoxypropane, the equilibrium yield of the corresponding 2-alkyl-4-methyl-1,3-dioxolane, acetal **V**, and acetal **VI** in the reaction with 1,2-propylene glycol slightly increases (Table 2), which is well consistent with data obtained for the reaction of linear acetals with ethylene glycol [3]. In going from ethylene glycol to propylene glycol, the equilibrium yields of the products change dramatically: The equilibrium yields of the cyclic product and acetal **V** decrease, and the yield of acetal **VI** increases.

Increase in the temperature in the range 25–80°C also affects to some extent the equilibrium composition of the reaction mixture. The equilibrium concentrations of the linear acetal and compound **IV** decrease and that of free methanol increases, which indicates that the equilibrium conversion of the reactants increases. With increasing temperature, the concentrations of the products vary differently: The content of acetal **V** decreases, whereas the equilibrium concentrations of acetal **VI** and dioxolane somewhat increase.

Thus, formation of cyclic acetals in reactions of 1,1-dialkoxyalkanes with 1,2-glycols is favored by equal reactivity of the hydroxy groups in the glycol and by elevated temperatures. If a glycol contains both primary and secondary hydroxy groups, the CH_2OH group is more reactive, and along with the heterocycle (reactant ratio 1 : 1) the reaction yields large amounts of linear acetal **VI** (reactant ratio 1 : 2).

EXPERIMENTAL

Linear acetals were prepared from alcohols and aldehydes by standard procedures. The acetals were washed with aqueous NaOH and distilled twice in a column. Chemically pure grade 1,2-propylene glycol was used without additional purification (weight fraction of water 0.2–0.3%, as determined by Fischer titration). After mixing, the reaction solutions were kept at 25°C for no less than 24 h.

The ^{13}C NMR spectra were taken on a Varian Gemini-300 Fourier spectrometer at 25°C using the INEPT technique. For stabilization of the resonance conditions, a thin ampule of D_2O was placed inside the ampule with the reactants. The internal reference was $(CD_3)_2SO$ (Δ_C 39.7 ppm). In quantitative analysis, correction factors were introduced to allow for incomplete spin relaxation and the nuclear Overhauser effect.

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