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ANALYSIS OF HEMIFORMALS BY GAS CHROMATOGRAPHY

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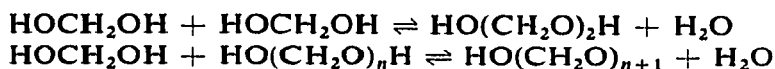
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SUMMARY

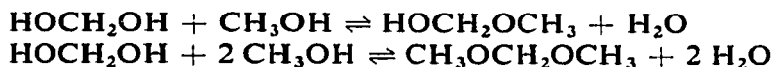
By reaction of formaldehyde with alcohols, various types of formals are formed. With the aid of gas chromatography, it was shown that, in addition to these compounds, hemiformals were also formed. We established that some hemiformals are not stable and exist in solution only under equilibrium conditions between the reactants and products, and therefore they cannot be determined by chemical analysis. By gas chromatography, these substances were identified in the form of their trimethylsilyl ethers.

INTRODUCTION

Formaldehyde exists in aqueous solution mainly as methylene glycol, which can readily polymerize to give poly(oxymethylene) glycols of various chain lengths¹:



The presence of methanol prevents the formation of high-molecular-weight poly(oxymethylene) glycols, as formals are formed:



Such formals are also formed from other alcohols as well, and their stability depends on the alcohol used². Some of these formals were identified by gas chromatography by Gruber and Plainer³.

Pentaerythritol is a product of the reaction of acetaldehyde and formaldehyde. By this reaction, various types of monoformals and diformals are formed⁴ and the analysis of these products is possible by gas chromatography⁵⁻⁸.

When we analyzed aqueous solutions of these products in the form of their trimethylsilyl ethers by gas chromatography, a number of the peaks were present on the chromatogram and many of these peaks disappeared when the water in the sample was evaporated before the analysis. We have investigated this problem.

EXPERIMENTAL

A Chrom-4 chromatograph (Laboratory Instruments N.E., Prague, Czechoslovakia) with a flame ionization detector was used. The column was made of stainless steel, with a length of 2.5 m and I.D. 3 mm. The column temperature was programmed from 125° to 300° at the rate of 6°/min. The injection port temperature was 280°. Some other temperature programs were also used. The carrier gas was nitrogen at the flow-rate of 24 ml/min, and the flow-rate of hydrogen was 50 ml/min. The stationary phases were 3% silicone rubber SE-30 on silanized Chromosorb W, 80–100 mesh, and OV-17 on the same carrier.

All samples were analyzed as their trimethylsilyl (TMS) ethers. The silylation was carried out by the following procedure: 50–100 μ l of aqueous solution were evaporated to one half of the original volume in a 5-ml conical flask. Then 5 μ l of a 5% solution of xylitol in dimethyl sulphoxide were added as an internal standard, 0.3 ml of silylation mixture (a 2:1 mixture of hexamethyldisilazane and trimethylchlorosilane) was added and the silylation was carried out for 30 min at normal temperature with intermittent shaking.

In the case of solid samples, a *ca.* 7–10% solution in dimethyl sulphoxide or water was prepared. The use of dimethyl sulphoxide as a solvent has the disadvantage that on the stationary phase OV-17 is eluted later than the silylation mixture and therefore it can overlap with the peaks of some lower-molecular-weight compounds. This silylation mixture gives better results as Trisil-Z (ref. 9).

As standards for the peak identification we used the following compounds: pentaerythritol (PE), m.p. 269°; dipentaerythritol (DPE), m.p. 221–223°; tripentaerythritol (TPE), m.p. 248–250°; pentaerythritol monoformal (PEMF), m.p. 61°; pentaerythritol diformal (PEDF), m.p. 51°; bispentaerythritol monoformal (bis-PEMF), a technical product; and *d*-xylitol (*d*-Xy), a commercial product (*pro analysi* grade). In the reactions with formaldehyde we used also 2-pentanol (BDH, Poole, Great Britain) and 1-octanol (Lachema, Brno, Czechoslovakia). According to the measured refractive index of 2-pentanol ($n_D^{20} = 1.4069$), it is a mixture of 2-pentanol ($n_D^{20} = 1.4127$) and 3-pentanol ($n_D^{20} = 1.40565$). The measured refractive index of 1-octanol was $n_D^{20} = 1.4300$ (theoretical value = 1.4295).

RESULTS AND DISCUSSION

The chromatogram of the above standards in the form of their TMS ethers is shown in Fig. 1. The elution temperature calculated according to the procedure of Schmit and Wynne¹⁰ and the elution indices calculated according to the classical equation of Kováts¹¹ are given in Table I. The reproducibility of the measured values was $\pm 1.8^\circ$.

Fig. 2 shows the chromatogram of the reaction product of formaldehyde with pentaerythritol. Elution temperatures are given in parentheses above the peaks. By comparing these values with those in Table I, the presence of PE and PEMF can be identified. It should be noted that the elution temperatures of adjacent peaks 4, 7, 10, 11 and 12 increase by 16–19°.

In order to identify the other components of the mixture, we analyzed 100 μ l of formaldehyde solution that had been concentrated by evaporation to one half

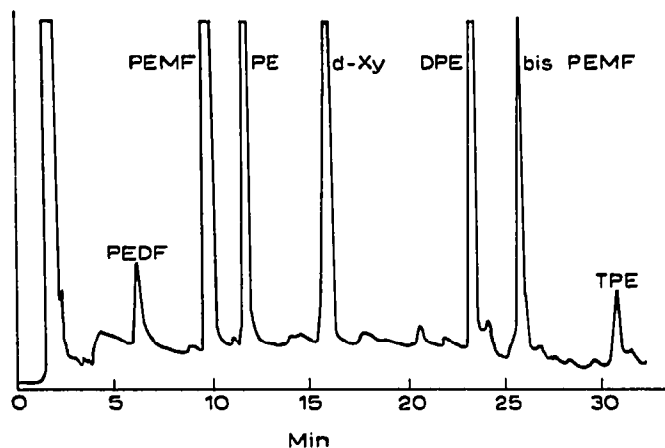


Fig. 1. Chromatogram of pentaerythritol and some of its derivatives (as TMS ethers). Stationary phase, 3% SE-30; temperature programme, 125–300° at 6°/min. For abbreviations, see text.

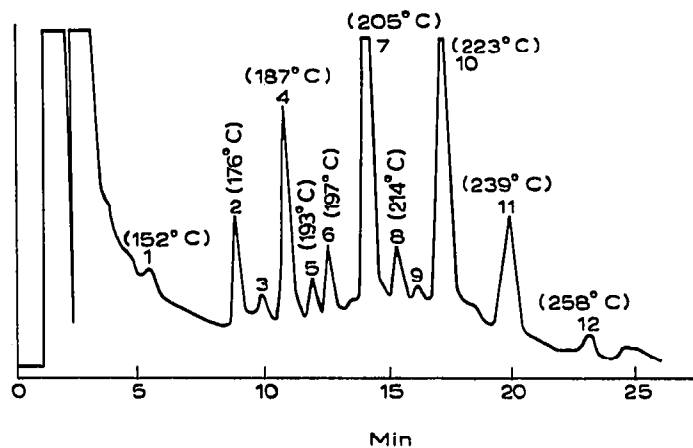


Fig. 2. Chromatogram of the reaction product of pentaerythritol with formaldehyde (as TMS ethers). Conditions as in Fig. 1. Numbers on peaks are as in Table III.

TABLE I

ELUTION VALUES OF STANDARDS (AS TMS ETHERS)

Elution times are not corrected. Helium elution time was 1.00 min.

Compound*	SE-30			OV-17	
	Elution time (min)	Elution temperature (°C)	Elution index	Elution time (min)	Elution temperature (°C)
PEDF	5.2	153		6.1	162
PEMF	8.5	176	1450	11.9	193
PE	10.6	188	1553	9.6	183
d-Xy	14.3	211	—	18.0	233
DPE	21.4	253	2212	20.8	247
bis-PEMF	24.3	271		23.8	268
TPE	28.5	296		28.1	293

* For abbreviations, see text.

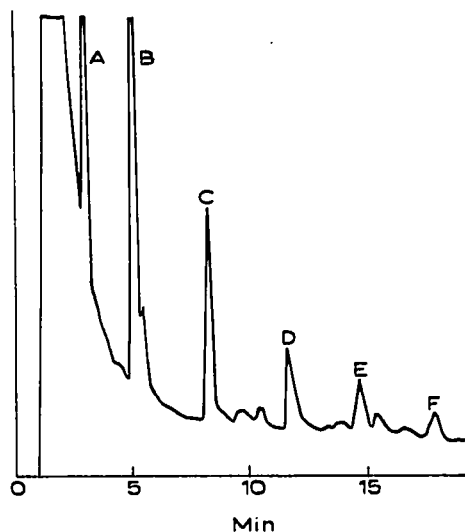


Fig. 3. Chromatogram of formaldehyde solution (as TMS ethers). Conditions as in Fig. 1. Letters on peaks correspond to substances in Table II.

of its volume prior to the silylation. As can be seen from Fig. 3, we obtained a chromatogram in which peaks of methylene glycol and also its higher oligomers are present. The elution temperatures of the substances increase on both stationary phases by a regular value: on OV-17 by 24° and on SE-30 by 18° per CH_2O group. The only exception is the second member of the series.

In Table II, the elution values of poly(oxymethylene) glycols on both stationary phases are given. It is obvious that, owing to the increase in regular elution values, the dependence of the net elution times of the poly(oxymethylene) glycols *versus* their molecular weights is linear, with the exception of the first two members.

We used these results for the identification of the components of the chromatogram in Fig. 2. By comparing the calculated and measured elution temperatures we found that substances 7, 10, 11 and 12 (Table III) are PE derivatives, having the basic molecule

TABLE II

ELUTION VALUES OF METHYLENE GLYCOL OLIGOMERS (AS TMS ETHERS)

Elution times are not corrected.

Peak symbol	Compound	SE-30			OV-17
		Elution time (min)	Elution temperature ($^\circ\text{C}$)	Elution index	Elution temperature ($^\circ\text{C}$)
A	HOCH_2OH	2.2	138		
B	$\text{HO}(\text{CH}_2\text{O})_2\text{H}$	3.5	146	1251	156
C	$\text{HO}(\text{CH}_2\text{O})_3\text{H}$	6.3	163	1429	180
D	$\text{HO}(\text{CH}_2\text{O})_4\text{H}$	9.3	181	1591	205
E	$\text{HO}(\text{CH}_2\text{O})_5\text{H}$	12.5	200	1760	230
F	$\text{HO}(\text{CH}_2\text{O})_6\text{H}$	15.5	218	1924	255

TABLE III
IDENTIFICATION OF COMPOUNDS FROM CHROMATOGRAM IN FIG. 2

Peak No.	Compound	Elution temperature ($^{\circ}\text{C}$)	
		Measured	Calculated
1	PEDF	152	—
2	PEMF	176	—
3	Not identified	184	—
4	PE	187	—
5	PEMF + CH_2O	193	$177 + 18 = 195$
6	$\text{HO}(\text{CH}_2\text{O})_5\text{H}$	197	
7	PE + CH_2O	205	$189 + 18 = 207$
8	$\text{HO}(\text{CH}_2\text{O})_6\text{H}$	214	
9	Not identified	221	
10	PE + $2 \times \text{CH}_2\text{O}$	223	$189 + (2 \times 18) = 225$
11	PE + $3 \times \text{CH}_2\text{O}$	249	$189 + (3 \times 18) = 243$
12	PE + $4 \times \text{CH}_2\text{O}$	258	$189 + (4 \times 18) = 261$

enlarged by one, two, three or four CH_2O groups. In the same manner, substance 5 is a PEMF derivative, with the molecule enlarged by one CH_2O group. These compounds are named in the literature as hemiformals². The results of the identification are given in the Table III.

We prepared the same products with 2-pentanol and 1-octanol. Fig. 4 shows the chromatogram of the reaction product of formaldehyde with 2-pentanol. The lower chromatogram represents 2-pentanol without silylation. As the starting product

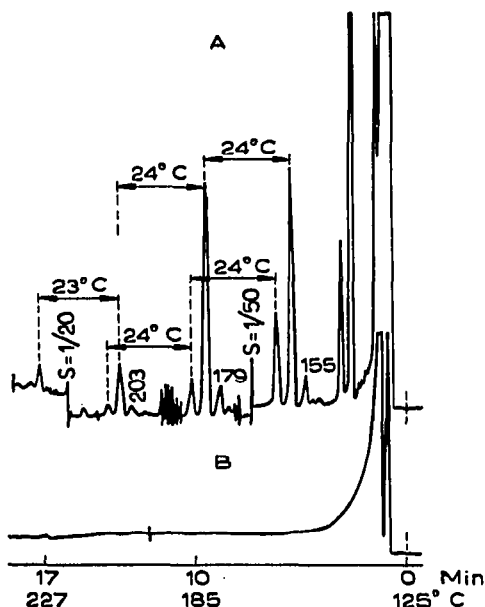


Fig. 4. A, chromatogram of the reaction product of 2-pentanol with formaldehyde (as TMS ethers). Stationary phase, OV-17; temperature programme as in Fig. 1. Numbers on peaks are elution temperatures of oligomers of formaldehyde. B, Chromatogram of 2-pentanol.

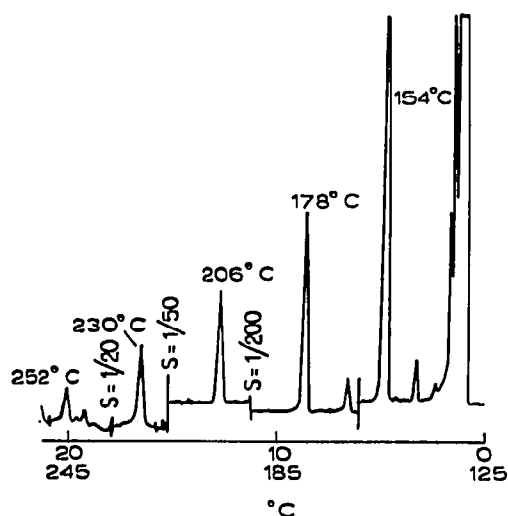


Fig. 5. Chromatogram of the reaction product of 1-octanol with formaldehyde (as TMS ethers). Conditions as in Fig. 4. Numbers on peaks are elution temperatures of hemiformals of 1-octanol: 1 = monohemiformal; 2 = bishemiformal; 3 = trishemiformal; 4 = tetrakishemiformal; 5 = pentakishemiformal.

was a mixture of 2- and 3-pentanol, derivatives of both of these alcohols are formed. The elution temperature increased by a regular value of 24° , with the exception of the first member. The chromatogram also contains poly(oxymethylene) glycol peaks and their elution temperature agrees with those in Table II. Fig. 5 shows the chromatogram of the reaction product of formaldehyde with 1-octanol. Enlargement of the molecule by one CH_2O group also caused an increase in elution temperature of 24° .

On the basis of these results we can say that the enlargement of a molecule by

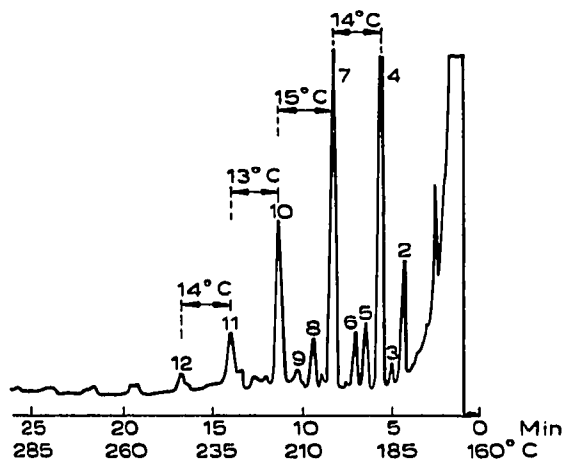


Fig. 6. Chromatogram of reaction product of pentaerythritol and formaldehyde (as in Fig. 2). Stationary phase, SE-30; temperature programme, $160\text{--}300^\circ$ at $5^\circ/\text{min}$. Numbers on peaks correspond to compounds in Table III.

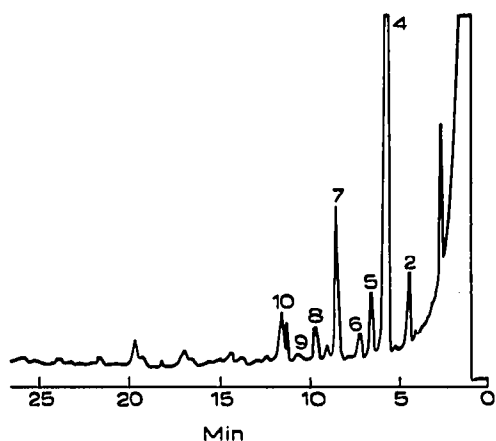


Fig. 7. Chromatogram of reaction product of pentaerythritol and formaldehyde (as in Fig. 2) after evaporation of water and drying at 100° for 6 h. Conditions as in Fig. 6.

one CH_2O group causes the elution temperature to increase by a constant value regardless of the shape of the molecule in which this group is bound.

When we changed the column temperature programme, the elution temperatures and incremental values also changed, but the increment for one group CH_2O remained regular (Fig. 6).

Study of hemiformal properties

The chromatogram in Fig. 6 was obtained by direct silylation of the aqueous solution of the reaction product. When the water was evaporated on a water-bath prior to the silylation and the dry residue was silylated, then hemiformals were partially decomposed and the peak of PE increased (Fig. 7). By heating the dried residue at 100° for 6 h and at 150° for 3 h, the hemiformals were completely decomposed (Fig. 8). When an equal volume of a 26% aqueous solution of ammonia,

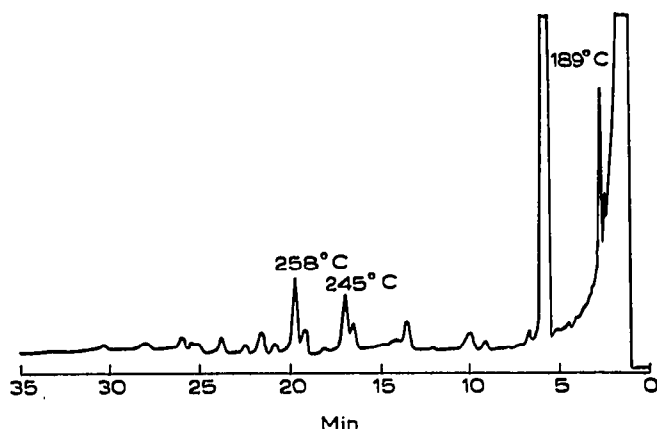


Fig. 8. Chromatogram of reaction product of pentaerythritol and formaldehyde (as in Fig. 2) after heating the residue at 100° and 150°. Conditions as in Fig. 6.

TABLE IV

DETERMINATION OF PENTAERYTHRITOL IN REACTION PRODUCTS WITH AND WITHOUT ADDED AMMONIA (AQUEOUS SOLUTION, 26%)

Sample No.	PE (g per 100 ml)		
	With ammonia	Without ammonia	Δ
1	2.84	0.37	2.47
	2.81	0.28	2.53
2	4.28	0.55	3.73
	4.32	0.55	3.77
3	5.23	3.20	2.03
	5.16	2.32	2.84
4	5.75	3.96	1.79
	5.78	4.37	1.41
5	7.40	6.16	1.24
	7.43	6.21	1.22

which reacts with formaldehyde to give hexamethylenetetramine was added to the solution, the hemiformals decomposed rapidly and quantitatively. The chromatogram obtained was the same as before. The effect of the addition of ammonia on the quantitative determination of pentaerythritol in solution at various concentration of pentaerythritol in solution at various concentrations is shown in Table IV. It is evident that after the addition the hemiformals were decomposed and the free pentaerythritol content increased.

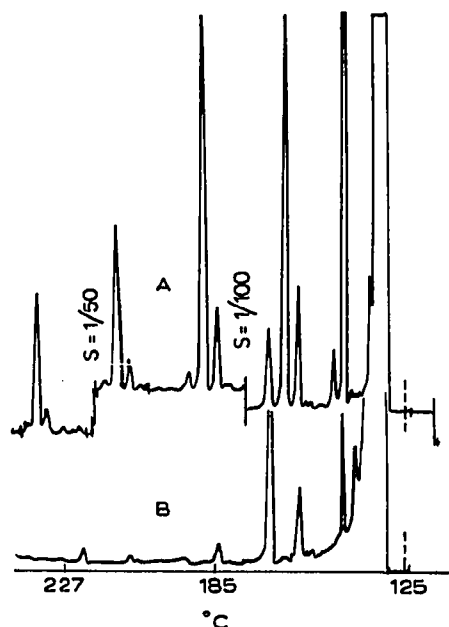


Fig. 9. Chromatogram of reaction product of 2-pentanol and formaldehyde. A, After heating for 1 h at 80°; B, after addition of a 26% aqueous solution of ammonia. Conditions as in Fig. 4.

The hemiformals obtained from 2-pentanol and 1-octanol have different properties. As can be seen from Fig. 9, which is the chromatogram of the reaction product of formaldehyde with 2-pentanol, the concentration of the hemiformals did not decrease, although the product was heated for 1 h at 80° (chromatogram A). But when 15 μ l of a 26 % aqueous solution of ammonia were added to 5 μ l of solution and this solution was silylated, the hemiformals decomposed completely (chromatogram B). The hemiformals from octanol had the same properties.

We determined the hydroxyl group content in these products by acetylation with a mixture of acetic anhydride and pyridine. The hemiformals decomposed and the determined hydroxyl group content corresponded to the concentration of the alcohols (Table V). The solution after esterification became dark.

It is obvious from the results that linear aliphatic alcohol hemiformals have high thermal stability, but are decomposed by the chemical reaction to give the starting materials.

TABLE V

HYDROXYL GROUP CONTENT IN REACTION PRODUCTS OF FORMALDEHYDE WITH ALCOHOLS

Solution of alcohol	OH (%)	
	Calculated	Determined
50 % of 1-octanol	6.53	7.05
65 % of 2-pentanol	12.55	12.23

CONCLUSION

It has been shown that, in the reaction of formaldehyde with alcohols, in addition to the well-known products, hemiformals are also formed. As these compounds are labile, they cannot be determined by chemical methods. Gas chromatography proved to be a very useful method that not only permitted these compounds to be identified, but also to be determined quantitatively.

ACKNOWLEDGEMENT

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