The Review of Physical Chemistry of Japan Vol. 20 (1946)

METHYLOL CONDENSATION OF ACETALDEHYDE.

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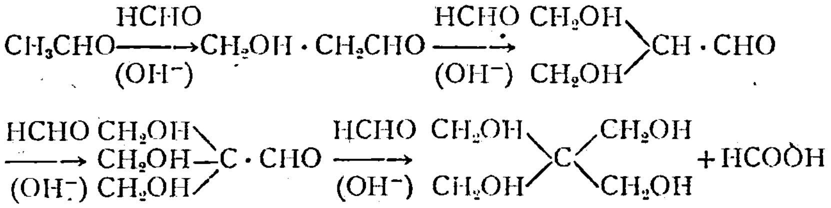
(1) Since Tollens[1] found that pentaerythritol was formed by the action of alkalis from acetaldehyde and formaldehyde, several investigations[2] on this condensation have been made. But even nowadays the yield of pentaerythritol is less than 70% and its melting point is variously described. The mechanism of this condensation is very interesting to chemists but it has rarely been studied.

Mc. Leod[3] reported that pentaerythritol is formed by the following scheme:



i. e. acetaldehyde successively condenses with 3 mol. of formaldehyde and finally pentaerythritol is formed as 4th mol. of formaldehyde is consumed.

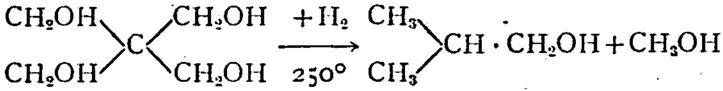
The present writer has studied on the condensation by analysing high-pressure hydrogenation products of the condensates of these two aldehydes in various ratios.

(2) Hydrogenations of the condensation product of 1 mol. acetaldehyde with 2.2—2.5 mol. formaldehyde.

44 grs. of acetaldehyde and 70 grs. of formaldehyde in 500 c.c. water were stirred at about 40°, being added 10 grs. of CaO little by little. After the reaction had been complete, the product was concentrated in vacuo to a syrup. This syrupy product weighted about 110 grs. and contained usually some crystalline substances.

a) Hydrogenation at 250°.

H. Adkins[4] obtained isobutanol and methanol from pentaerythritol by a high-pressure hydrogenation with the Cu-Cr-oxide catalyst.


......(1)

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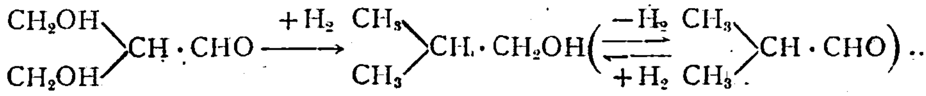
[1] B. Tollens, *Ann.*, **265**, 316 (1891).

[2] P. Rave & B. Tollens, *Ann.*, **276**, 58 (1893); B. Friedrich & B. Brün, *Ber.*, **63**, 2681 (1930); Backer & S. Schrink, *Rec. Trav. Chim.*, **50**, 923 (1931).

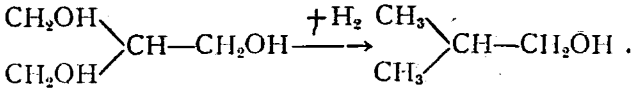
[3] A. F. McLeod, *Am. Chem. Jour.*, **37**, 37 (1907).

[4] *Jour. Am. Chem. Soc.*, **54**, 4678 (1932).

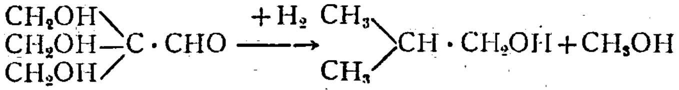
Following this process, the writer tried to hydrogenate the syrup and got isobutanol (and isobutanal) in a good yield. This product can be formed according to either of the four equations described above and below.



$$\left.\begin{matrix}CH_2OH\\CH_2OH\end{matrix}\right\rangle CH\cdot CHO \xrightarrow{+H_2} \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH\cdot CH_2OH\left(\underset{+H_2}{\overset{-H_2}{\rightleftharpoons}}\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH\cdot CHO\right)\ldots(2)$$

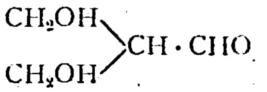


$$\left.\begin{matrix}CH_2OH\\CH_2OH\end{matrix}\right\rangle CH-CH_2OH \xrightarrow{+H_2} \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH-CH_2OH \ldots\ldots\ldots\ldots(3)$$



$$\left.\begin{matrix}CH_2OH\\CH_2OH\\CH_2OH\end{matrix}\right\rangle C\cdot CHO \xrightarrow{+H_2} \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH\cdot CH_2OH+CH_3OH \ldots\ldots\ldots\ldots(4)$$

It is, however, very likely that equation (2) is the principal reaction, because the actual production of methanol was not so appreciable in amount and the yield of isobutanol was much more than 70% of the value calculated from the quantity of formaldehyde used in the condensation. Consequently the main condensation product in the syrup should be the so-called tetraglycerose.



$$\left.\begin{matrix}CH_2OH\\CH_2OH\end{matrix}\right\rangle CH\cdot CHO .$$

The experimental results suggest a new method for the industrial preparation of isobutanol and support among all Morgan's idea for the mechanism[5] of isobutanol formation in the synthol process.

b) Hydrogenation at 220°.

When the temperature of hydrogenation of the syrup was intentionally raised slowly (5°/15 min.), there was no difference in the yields of isobutanol, but the pressure-temperature-curve (2) was markedly altered from the usual one (1) as seen in the following diagram, indicating that hydrogen was in step wise absorbed at about 160°, 220° and 250°.

The product of hydrogenation at 220° was composed of two parts, one of which was ether soluble and the other water-soluble. The former gave isobutanol and the latter pentaerythritol of high purity. Even in a hydrogenations at 250°, the same analytical results were obtaind, when the hydrogenation-time was too short, or the catalyst too small in quantity or in activity.

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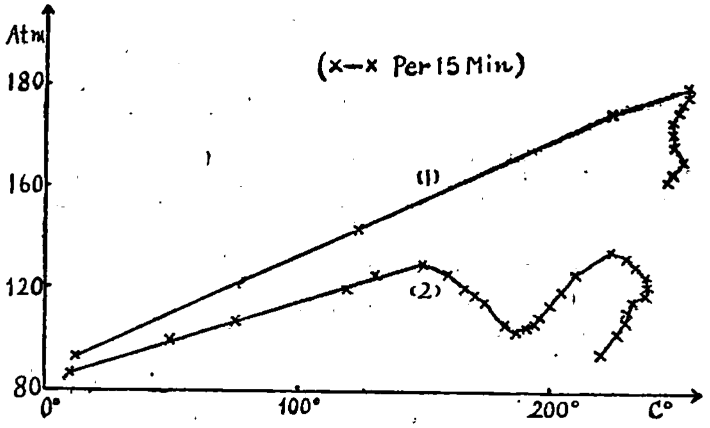
5) F. Fischer, *Ind. & Eng. Chem.*, 17, 546 (1925); G. T Morgan, *Proc. Roy. Soc.*, **127A**, 246 (1930); M. Marcel Guerbet, *Compt. Rend.*, 133, 1221 (1901).



These facts indicate that tetraglycerol is decomposed while pentaerythritol remains unattacked by a hydrogenation under these conditions, and the syrupy condensation product contains certain amounts of pentaerythritol and perhaps pentaerythrose also.

c) Hydrogenation at 160°.

When the condensate was hydrogenated at 160°, the result was quite different from those of a) and b). The product was completely soluble in water, from which two kinds of crystals were separated, one melting at 178°, the other at 258°. A complete fractionation was very difficult, and the melting points of all of the fractions lay between 178° and 258°. On hydrogenation, these fractions gave isobutanol at 250°, and isobutanol and pentaerythritol at 220°, hence these fractions are thought to be mixtures of pentaerythritol [258°] and tetraglycerol [178°].

Benzoylation: Some of these fractions were benzoylated according to Schotten-Baumann's method[6] and the products were fractionated by means of alcohol. They gave always a soft resinous matter and a crystalline solid which was identified as pentaerythritol-tetrabenzoate.

Yields of the solid, counterbalancing with those of the resinous product, depended on the melting points of the samples used in the benzoylation, about 90% for the sample [240°] and less than 10% for that [190°]. Only the resinous product was obtained, when the sample melting at 178° was benzoylated. Using benzene as solvent in stead of alcohol, pentaerythritol-tetrabenzoate crystallised out with crystal-benzene and was more easily separated from the resious part.

Debenzoylation: When the resinous part obtained above was hydrolysed by boiling with 20% caustic-soda, a substance melting at 178° was obtained and

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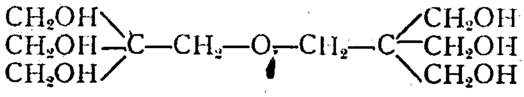
6) *Ann.*, 301, 95 (1895).

identified as tetraglycerol by an ultimate analysis. By the same hydrolysing process pentaerythritol was naturally obtained from its tetrabenzoate. It is noteworthy that the melting points of any mixtures of tetraglycerol and pentaerythritol lay always between 178° and 258°.

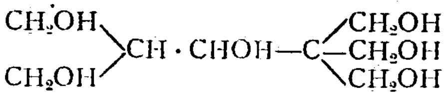
Nitration: The same crystal fractions as used for benzoylation were now nitrated by Tollen's method[7]. Yields and melting points of the crystalline products were almost equal, being independent of the melting points of samples used. It was observed under a microscope that the crystalline products are composed of two kinds of crystals, one of which was tablet form and identified as pentaerythritol-tetranitrate [142°] and the other needle form, as tetraglycerol-trinitrate [137°]. The nitration product of a commercial pentaerythritol melted at neighbourhood of 140° and was also observed to be composed of the same two forms of crystals as described above. It is, therefore, inferable that the ordinary samples of pentaerythritol may more or less be contaminated with tetraglycerol.

Dipentaerythritol: On leaving a mother-liquor from which no more the nitrates separated, stand in an ice-box for several days, a small amount of crystals was separated out. After recrystallisation, it melted at 71~73° and was identified as dipentaerythritol-hexanitrate which is a nitrate of so-called dipentaerythritol—a by-product of pentaerythritol:



$$\begin{array}{r} CH_2OH\diagdown \\ CH_2OH- \\ CH_2OH\diagup \end{array}C-CH_2-O-CH_2-C\begin{array}{l}\diagup CH_2OH\\ -CH_2OH\\ \diagdown CH_2OH\end{array}$$

This chemical structure of dipentaerythritol, however, has not been settled. It is doubtful that such an ether structure may be formed in the reaction of an alkaline medium, and also survived through high pressure-and high temperature-hydrogenation. The writer ventures to give it rather a structure



$$\begin{array}{r}CH_2OH\diagdown\\ \\ CH_2OH\diagup\end{array}CH\cdot CHOH-C\begin{array}{l}\diagup CH_2OH\\ -CH_2OH\\ \diagdown CH_2OH\end{array}$$

which could be formed by an aldol-condensation of tetraglycerose and survived through a drastic hydrogenation.

(3) Hydrogenation of the condensation products of both aldehydes in other ratios.

When a condensation product of 1 mol. acetaldehyde and 1 mol. formaldehyde

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[7] *Ann.*, 265, 316 (1891); 276, 58 (1893); *D.R.P.*, 265025 (C 1913, II. 1445).

was subjected to the high-pressure hydrogenation, it gave at 250° isobutanol and a little of propanol whose 3.5-dinitrobenzoate melted at 73°, and at 160° a mixture [200–220°] of tetraglycerol and pentarrythritol, and some other unknown substances. The condensation product of 1 mol. acetaldehyde and 3 mol. formaldehyde was obtained as a crystalline paste. On catalytic hydrogenation this product gave tetraglycerol and pentaerythritol at 160°, isobutanol and pentaerythritol at 220°. This fact suggests a new method for synthesizing pure pentaerythritol.

(4) The experimental results described above support not only Mc. Leod's scheme for the pentaerythritol formation, but show that tetraglycerose may be formed quickly and reduced by formaldehyde to tetraglycerol easily. So, much more than the theoretical amount of formaldehyde is demanded in order to get a good yield of pentaerythritol by the condensation of acetaldehyde and formaldehyde.

The present paper is contributed to the Sexagint of Dr. S. Horiba who is the Head of the 15th Special Committee of Japan Society for the Promotion of Scientific Research by R. Nodzu—a member of the Committee.

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