[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

THE THERMAL DECOMPOSITION OF SOME POLYMETHYLOL COMPOUNDS[1]

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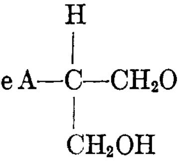
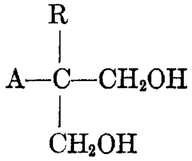
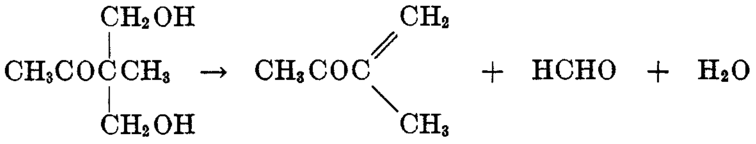
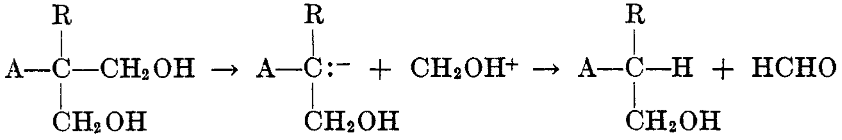
A number of investigators (1) have noted the relatively easy thermal decomposition, with and without catalysts, of compounds containing two or three methylol groups on the same carbon atom. In most cases these compounds were made by condensing formaldehyde with molecules containing hydrogen atoms made reactive by some adjacent activating group such as the carbonyl radical. In compounds of the type  $A{-}\overset{\displaystyle H}{\underset{\displaystyle CH_2OH}{C}}{-}CH_2OH$, where A is the activating group, dehydration by the usual methods applicable to aldols occurs readily. More interesting for the present discussion are molecules such as  $A{-}\overset{\displaystyle R}{\underset{\displaystyle CH_2OH}{C}}{-}CH_2OH$ where dehydration does not occur, at least at the first stage of the decomposition. Here, in almost every instance reported, the compounds decompose rather easily with the loss of formaldehyde. For example, the dimethylol derivative of methyl ethyl ketone apparently follows this course, for when distilled with potassium acid sulfate it yields, according to Morgan and associates (1b), methyl isopropenyl ketone, formaldehyde, and water:



$$CH_3CO\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}CH_3 \rightarrow CH_3COC\begin{matrix}{=}CH_2\\{-}CH_3\end{matrix} + HCHO + H_2O$$

Since these reactions are usually carried out in the liquid state in the presence of a catalyst it is not unreasonable to suppose that they are ionic in nature, and proceed in the following manner:

(I) 

$$A{-}\overset{\displaystyle R}{\underset{\displaystyle CH_2OH}{C}}{-}CH_2OH \rightarrow A{-}\overset{\displaystyle R}{\underset{\displaystyle CH_2OH}{C}}{:}^{-} + CH_2OH^{+} \rightarrow A{-}\overset{\displaystyle R}{\underset{\displaystyle CH_2OH}{C}}{-}H + HCHO$$

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[1] From a thesis submitted to the Faculty of the Graduate School in partial fulfillment of the requirements for the degree, Doctor of Philisophy.

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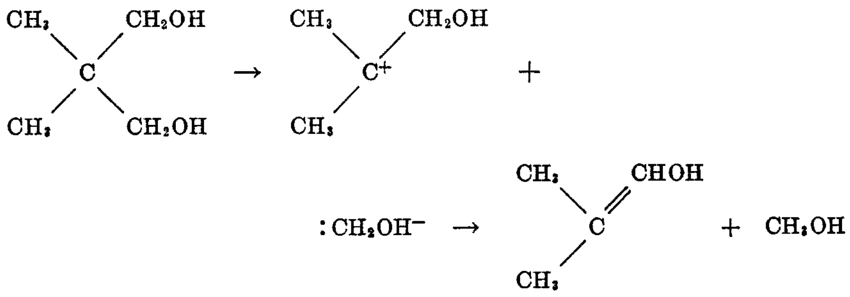
The positive methylol ion first formed loses a proton to the negative residue. The latter is then dehydrated to the final product. To facilitate later discussion this is called the type I reaction.

In the above example it seemed possible that the primary dissociation was conditioned by the electrophilic properties of the carbonyl or other activating group present, and it was therefore of interest to study the behavior of other polymethylol compounds in which such a group was absent. For this purpose the following were chosen: 2,2-dimethyl-1,3-propanediol, 2,2-dihydroxymethyl-1-propanol, and 2,2-dihydroxymethyl-1-butanol.

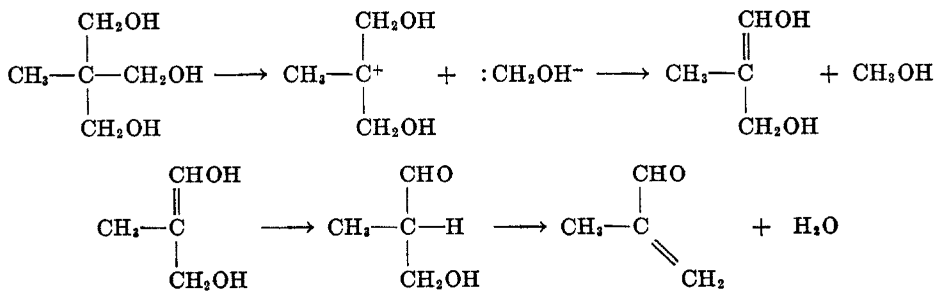
When 2,2-dimethyl-1,3-propanediol was heated with activated alumina at 200–210° the principal products were methanol and isobutryaldehyde. The latter was obtained in 70% yield. No isobutylene or isobutyl alcohol could be isolated, and only a trace of formaldehyde was detected. It is again a reasonable assumption that the first step in this process is the loss of a methylol group from the diol, but, if the reaction is ionic, it must in this case leave as the negative ion, since it acquires a proton from the residue and appears as methanol.

(II)



This may be called the type II reaction.

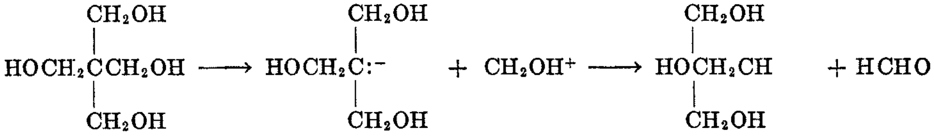
The 2,2-dihydroxymethyl-1-propanol decomposed completely to volatile products on heating at 240–270° with alumina. There was no tar formation, and the catalyst at the end of the reaction was dry and powdery. The principal products isolated were α-methylacrolein, methanol, and water. The yield of the acrolein derivative was 70% of theory. Formaldehyde was detected, but no isobutyraldehyde or α-methylallyl alcohol, to which the aldehyde has been shown to rearrange (2), could be found. Here also it appears that the proton goes to the methylol group or ion, and the residue then rearranges and loses water to give the final product:



The 2,2-dihydroxymethyl-1-butanol, as might be expected, gave results entirely analogous to those obtained from the lower homolog; α-ethylacrolein was obtained in 60% yield, accompanied by methanol and water.

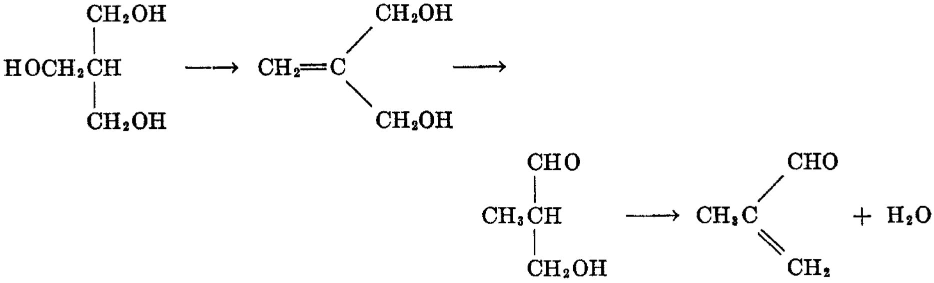
It is clear that the behavior of the two types of polymethylol compounds upon heating to the decomposition point in the presence of alumina differs sharply. The theoretical quantities of end products in the Type II reactions were never approached in any experiments, but the yields were surprisingly good considering the possibilities for complex condensations and polymerizations. The small amount of formaldehyde found indicated that the Type I decomposition could have occurred only to a very slight extent.

It was of interest to subject a compound midway between Type I and Type II to catalytic thermal decomposition. For this the easily available pentaerythritol and dipentaerythritol were chosen. Nef (3) reported, that in addition to much carbon monoxide and solid residue, a small amount of liquid boiling at 60–70° was obtained from the destructive distillation of pentaerythritol. He assumed that the liquid was acrolein. We have found that at 250–320° in the presence of activated alumina, pentaerythritol is decomposed into gaseous products containing much carbon dioxide, and a distillate consisting of α-methylacrolein, methanol, formaldehyde, and water. The amounts of α-methylacrolein were not high, ranging from 12 to 20%. However, when the reaction was conducted in the presence of copper-bronze rather than alumina the yield of unsaturated aldehyde rose to 50% while that of methanol dropped sharply. The fact that the methanol decreases as the amount of α-methylacrolein increases strongly suggests that the latter is formed by a Type I mechanism:



$$\mathrm{HOCH_2}\overset{\mathrm{CH_2OH}}{\underset{\mathrm{CH_2OH}}{\mathrm{C}}}\mathrm{CH_2OH} \longrightarrow \mathrm{HOCH_2}\overset{\mathrm{CH_2OH}}{\underset{\mathrm{CH_2OH}}{\mathrm{C}}}\mathrm{:^-} + \mathrm{CH_2OH^+} \longrightarrow \mathrm{HOCH_2}\overset{\mathrm{CH_2OH}}{\underset{\mathrm{CH_2OH}}{\mathrm{CH}}} + \mathrm{HCHO}$$

The 2-hydroxymethyl-1,3-propanediol is then assumed to undergo dehydration to a molecule of a type which has been shown (2) to rearrange to an aldehyde under the conditions of the pyrolysis. A second dehydration then leads to the final product.



The formation of substantial amounts of methanol indicates that part of the pentaerythritol decomposed according to the Type II mechanism, in which the negative methylol group takes a proton from the residue. However, no other fragment was found which might have resulated from the loss of methanol. The first product would be 2-hydroxymethyl-1-propanol-3-al. This is a β-hydroxy aldehyde with a hydrogen on the α carbon atom, and would be expected to undergo dehydration to 2-hydroxymethylpropenal-1. As no evidence for the presence of the latter compound, or of acrolein, to which it could revert by loss of formaldehyde, was found, it is postulated that due to the strong hydrogen bond acting between pentaerythritol molecules the escaping methylol group captures a proton from an adjacent molecule, causing condensation of the residues and accounting in part for the considerable amounts of polymeric material formed.

The decomposition of dipentaerythritol was not found to differ significantly from that of the monomer. Over alumina at 245–300° the same products were obtained, and the maximum yield of α-methylacrolein was 25%. Over copper powder the yield of aldehyde increased to 44%. Apparently the existence of one ether bond between two molecules of pentaerythritol does not materially change the course of decomposition.

EXPERIMENTAL PART[3]

Materials. The pentaerythritol, dipentaerythritol, 2,2-dihydroxymethyl-1-propanol, and 2,2-dihydroxymethyl-1-butanol were supplied by the Heyden Corporation. The 2,2-dimethyl-1,3-propanediol was prepared by the action of an excess of formaldehyde on isobutyraldehyde in the presence of potassium hydroxide (4).

Pyrolysis. As the compounds studied all decompose at or below their boiling points pyrolysis in a static system was found to be satisfactory. Pentaerythritol, dipentaerythritol, and the trimethylol compounds were distilled from a Claisen flask heated in a metal-bath. The diol, which distils at atmospheric pressure without decomposition was decomposed in a flask surmounted by a short Vigreux column. A thermometer was inserted at the top of the column to give a rough check of the temperature of the distilling vapor. In the compounds investigated the maximum temperature of distillation was not above 110°.

The side arm of the flask or column led into a condenser which was connected to a receiver cooled in ice, followed by a trap immersed in acetone-Dry Ice. In experiments where decomposition into geseous products was suspected a gas burette was connected to the Dry Ice trap.

In order to minimize polymerization of the unsaturated aldehydes the distillate was collected on about 0.2 g. of hydroquinone in each receiver, and the apparatus was flushed out with nitrogen before heating was begun.

Determination of α-methylacrolein. In reactions in which both α-methylacrolein and methanol were produced, it was found that the two distilled together as an azeotrope boiling at 59–61°. When the alcohol was removed by drying with calcium chloride, only small amounts of α-methylacrolein, b.p. 67–69° could be isolated, apparently because of polymerization and acetal formation. Partition between ether and water or between toluene and water was also not successful in separating the two. The amount of α-methylacrolein in the azeotrope was determined by distilling a middle cut of the azeotrope (b.p. 59.9–60.1°) onto a small amount of hydroquinone in a tared tube. The sample was weighed and transferred to a 250-ml. volumetric flask. Aliquots were analyzed for total carbonyl compounds with Brady's reagent according to the procedure of Iddles and Jackson (5). Analysis for formaldehyde with dimedone gave no weighable precipitate. A sample of the azeotrope was allowed to stand with saturated sodium bisulfite solution for two days, made alkaline to litmus, and distilled. The distillate gave a positive test for formaldehyde, and a

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[3] All melting points are corrected.

light precipitate with Brady's reagent, which was identified as the 2,4-dinitrophenylhydrazone of formaldehyde. Since no saturated aldehydes appear to be present, and the amount of formaldehyde is very small, it was assumed that the total carbonyl compound found was equal to the α-methylacrolein present. Two samples from different runs gave 75.5% and 77.0% aldehyde in the azeotrope.

2,2-Dimethyl-1,3-propanediol. Thirty-nine g. of the glycol was heated at 200–210° with 16 g. of activated alumina. Distillation took place slowly, the temperature of the distilling vapor remaining below 100°. The small amount of liquid which collected in the Dry Ice trap was allowed to come to room temperature with the trap connected to a wash bottle containing Brady's reagent, and another containing a very dilute solution of bromine in carbon tetrachloride. No decoloration of the bromine took place. Fractionation of the distillate after the addition of 10 ml. of water gave 28 g. of material boiling at 58–66°. Preliminary experiments had shown that two fractions came over in this range; an azeotrope of isobutyraldehyde and methanol, and methanol at 64–66°. In this run no attempt was made to separate the two. A weighed sample of the distillate was diluted and analyzed for isobutyraldehyde as described above. The 2,4-dinitrophenylhydrazone crystallized in yellow needles from ethyl acetate, m.p. 181–182°. A test for formaldehyde with resorcinol and sulfuric acid was negative. A sample of the distillate was dried with calcium chloride, the drying agent filtered off, dissolved in water, and distilled. The presence of methanol in the distillate was proved by oxidation to formaldehyde with a heated copper spiral and detection of the latter with resorcinol and sulfuric acid.

The aqueous solution remaining after removal of isobutyraldehyde and methanol was extracted with an equal volume of ether, the extract washed twice with saturated sodium bisulfite and dried over magnesium sulfate. Removal of the ether left only a small amount of oil, which did not distil at 160°. Distillation of the residual aqueous solution gave a distillate which contained formaldehyde, identified as the 2,4-dinitrophenylhydrazone, m.p 164–165° after recrystallization from dilute alcohol (0.4 g. of derivative isolated).

2,2-Dihydroxymethyl-1-propanol. Twenty-five g. of 2,2-dihydroxymethyl-1-propanol and 10 g. of 100-mesh activated alumina were heated together at 240–250°. At the end of three hours the catalyst was completely dry. The distillate amounted to 25 g. Fractionation gave 13.7 g. of a fraction boiling at 59–63° and 2.0 g. boiling at 63–67°. No further distillate appeared until the temperature reached 94°, when a mixture of oil and water distilled.

The first fraction gave a precipitate upon reaction with 2,4-dinitrophenylhydrazine. Recrystallization from ethyl acetate gave short reddish needles, m.p. 200–201° (dec.). Semicarbazone, white needles from water, m.p. 196–197°. Shriner and Fuson (6) give 206° (dec.) and 198° respectively as the melting points of these derivatives of α-methylacrolein, but Nicholls and Pritchett (7) report 198–202° (dec.) and 194°. The decomposition point of the first depends markedly on the rate of heating.

The amount of aldehyde in the azeotrope was determined as described above. The presence of methanol was proved as in the decomposition of 2,2-dimethyl-1,3-propanediol.

The residue remaining after removal of α-methylacrolein and methanol was extracted with ether, dried over sodium sulfate, and the ether removed on a water-bath. The oily liquid remaining gave no distillate below 150° at atmospheric pressure. It was heated to 250° under 12 mm. pressure in an atmosphere of nitrogen. No distillate was obtained, and the oil had thickened to such an extent that bubbles no longer emerged from the capillary.

2,2-Dihydroxymethyl-1-butanol. Twenty-one g. of 2,2-dihydroxymethyl-1-butanol and 10 g. of alumina were heated at 250–260°. The distillate weighed 17 g. Two fractionations with an intervening drying gave 3.8 g. (76%) of methanol, b.p. 63–66°, and 7.9 g. (60%) of α-ethylacrolein, b.p. 75–82°, semicarbazone, white needles from dilute alcohol, m.p. 184–184.5°.

Pentaerythritol. In a typical run, 32 g. of pentaerythritol and 20 g. of 8-14-mesh activated alumina were heated at 270–280° until distillation ceased. The distillate was homogeneous, with a strong acrolein-like odor. It weighed 22.5 g., or 70% of the starting material. Fractionation gave 4.4 g. of material boiling at 57–63° and 2.1 g. of a fraction boiling at 63–68°. The products were identified as α-methylacrolein and methanol as described above. Mixed m.p. of semicarbazone of product with that of crotonaldehyde, 176–179°.

Treatment of the residue as described above gave what was apparently the same intractable oil. The aqueous solution left after ether extraction was analyzed for formaldehyde with dimethyldihydroresorcinol. The amount found corresponds to 11 mole per cent of the pentaerythritol used.

Decomposition over copper powder. Forty g. of pentaerythritol and 8 g. of copper-bronze powder were heated together at 250–260° for two hours. At the end of this time, distillation had nearly ceased. The distillate consisted of two layers. They were separated and the aqueous layer extracted with 15 ml. of ether. The combined organic layers were dried over magnesium sulfate and fractionated. After removal of the ether, 2.5 g. of α-methylacrolein-methanol azeotrope and 9.0 g. of α-methylacrolein, b.p. 67–69° were obtained.

Dipentaerythritol. Thirty-two g. of dipentaerythritol was heated at 280–290° with 20 g. of 8–14-mesh alumina until distillation ceased. Twenty-two g. of homogeneous distillate was collected. Fractionation gave 5.7 g. of azeotrope, corresponding to 24% conversion to α-methylacrolein, and a methanol fraction of 1.1 g. As it appeared that fractionation might not be efficient in separating the azeotrope and methanol, the two fractions were combined, diluted to one liter and analyzed with Brady's reagent. The amount of aldehyde found in this manner corresponded to 25% of the theoretical.

Decomposition over copper powder. Thirty-two g. of dipentaerythritol and 5.5 g. of copper-bronze powder were heated at 250–260° until distillation ceased. The distillate formed two layers. They were separated and fractionated as described in the similar experiment with pentaerythritol. The fractionation gave 1.7 g. of azeotrope and 6.3 g. of α-methylacrolein.

SUMMARY

A study has been made of the decomposition of a series of polymethylol compounds in the presence of alumina and copper metal catalysts. Thermal decomposition of the methylol group has been shown to take place in two distinctly different ways, depending on the electronegativity of other groups in the molecule.

PRINCETON, N. J.

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