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A Redox-Metric Study of the Formation of Coloring Substances in the Synthesis of Pentaerythritol

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Abstract—The redox potentials of the reaction mixtures in the course of pentaerythritol synthesis and of transformations of formaldehyde and glucose in a NaOH solution without catalyst and in the presence of copper prepared by reduction of CuO were measured.

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When the synthesis of pentaerythritol is performed in the presence of a relatively small excess of formaldehyde, after the reaction completion it is necessary to remove residual aldehydes from the alkaline reaction mixture. To this end, the mixture is heated to the boiling point.

In the course of such treatment, at a minimal concentration of formaldehyde, a fast reaction yielding colored substances starts. These impurities impart color to pentaerythritol. The reaction can be stopped by neutralizing the reaction mixture with an acid. It is suggested to add an acid to the reaction mixture when the weight fraction of formaldehyde in it decreases to 0.1–0.3% [1] or when aldehydes are already practically absent and colored substances only start to form [2]. It is suggested to determine the moment of acid addition by monitoring the aldehyde concentration [3], redox potential [4], optical density [5], or electrical conductivity [6].

To avoid formation of colored substances or decrease their amount, it is suggested to use various additives, e.g., copper, chromium, manganese, iron, cobalt, or nickel oxalate [7], copper or silver hydroxide or oxide, active copper, nickel, or platinum [8], aluminum, zinc, or tin compounds [9], hydrogen peroxide [10], manganese compounds and atmospheric oxygen [11], and boron compounds [12]. According to published data, the use of additives does not eliminate the need for neutralization of the reaction mixture prior to evaporation and hence the need for determining the moment of acid addition.

In the above-cited papers, the nature of the phenomena noted and the effect of additives on them were not examined. In this paper we attempt to fill this gap.

EXPERIMENTAL

We used Formalin containing 37 wt % formaldehyde and 10 wt % methanol, NaOH, acetaldehyde, glucose, and copper prepared by reduction of CuO with formaldehyde in the presence of NaOH. The reactions were performed in a glass vessel submerged in a bath and equipped with a magnetic stirrer, a thermometer, and electrodes for measuring pH and redox potential. The temperature was maintained with an accuracy of $\pm 0.5^\circ\text{C}$.

The redox potentials were measured with a platinum electrode, and pH, with a glass electrode; as reference electrode we used a silver chloride electrode.

When preparing mixtures and in the course of the reactions, we took solution samples, transferred them into flasks with a known excess amount of 0.1 N HCl, and titrated excess HCl with a 0.1 N solution of NaOH in the presence of phenolphthalein to determine the NaOH concentration in the sample. Then a preset amount of an aqueous solution of hydroxylamine hydrochloride was added, and the concentration of aldehydes was determined by titration with 0.1 N alkali in the presence of Bromophenol Blue.

Three periods differing in the trend of variation of the redox potential (Fig. 1) can be distinguished in the

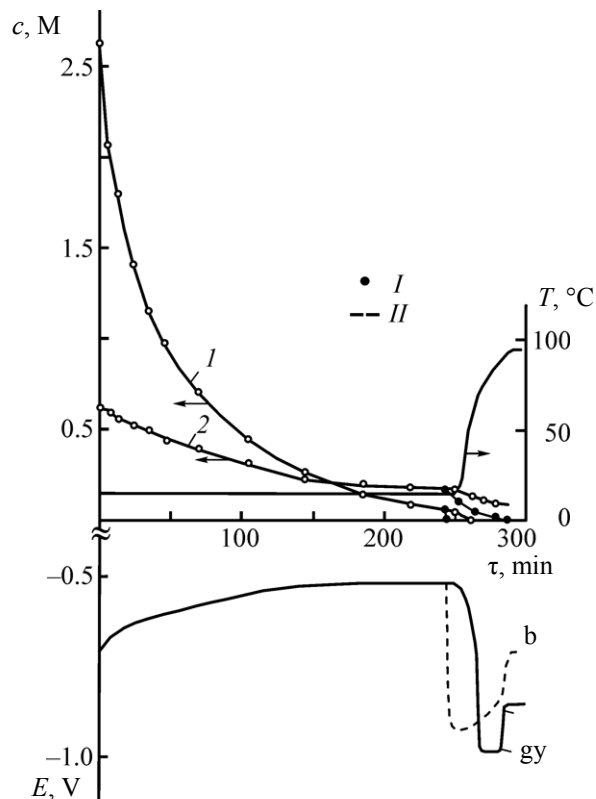


Fig. 1. Kinetic curves of the synthesis of pentaerythritol. (*c*) Concentration of aldehydes or NaOH, (*T*) temperature, (*E*) redox potential, and (τ) time; the same for Figs. 2 and 5. Initial concentration, M: formaldehyde 2.2 and acetaldehyde 0.44. (1) Aldehydes and (2) NaOH. (I, II) In the presence of 3.2 g l^{-1} copper (copper added on the 245th minute). The moments when the reaction mixture becomes greenish-yellow (gy) and brown (b) are indicated.

course of the pentaerythritol synthesis. In the first period, the negative redox potential decreases to a minimum; in the second, it increases to a maximum; and in the third, it rapidly decreases.

At the boundary between the second and third periods, the reaction mixture becomes greenish-yellow and loses the odor of aldehydes, and in the third period the mixture color changes from yellow to brown.

Similar changes of the redox potential and coloration of the reaction mixture are also observed in transformations of formaldehyde in an aqueous NaOH solution (Fig. 2). This fact suggests that the redox potential in the course of the pentaerythritol synthesis is primarily determined by the concentrations of formaldehyde, NaOH, and formaldehyde transformation products.

In the first period, the following main reactions occur:

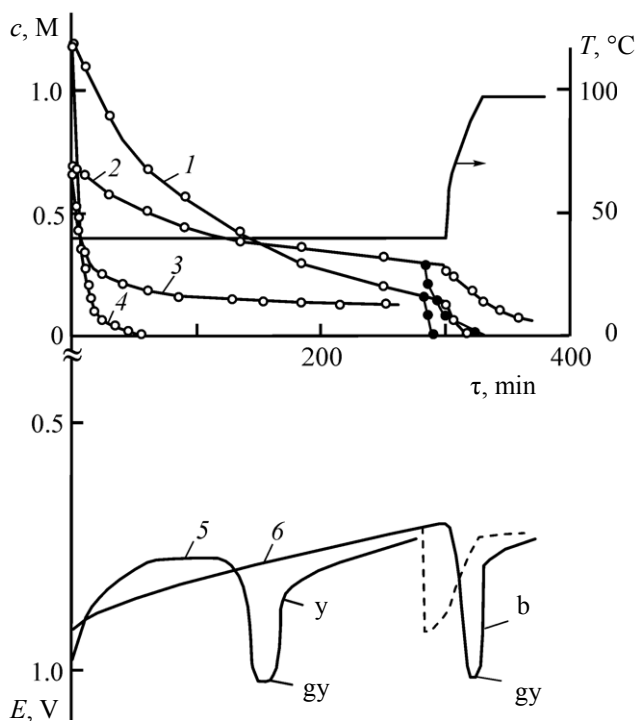
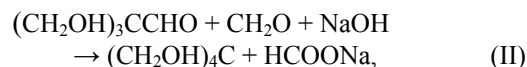
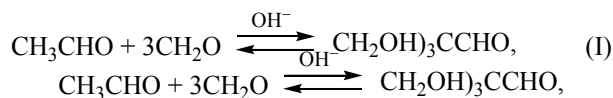


Fig. 2. Kinetic curves of formaldehyde transformations in aqueous NaOH solution. (1, 2) Formaldehyde and (3, 4) NaOH. (1, 2, 6) At programmed heating and (3–5) at a constant temperature of 70°C . (I, II) In the presence of 3.2 g l^{-1} copper (copper added on the 283rd minute). The moments when the reaction mixture becomes greenish-yellow (gy), yellow (y) and brown (b) are indicated.



as well as a number of side reactions including autocondensation of acetaldehyde [13], Cannizzaro reaction of formaldehyde [14]



and autocondensation of formaldehyde with the formation of sugars [15]. In the course of these reactions, the concentrations of aldehydes and NaOH decrease and those of pentaerythritol, sodium formate, and by-products increase.

The redox potential of aqueous solutions of formaldehyde and NaOH depends on the concentration of formaldehyde anion, pH, and temperature. The

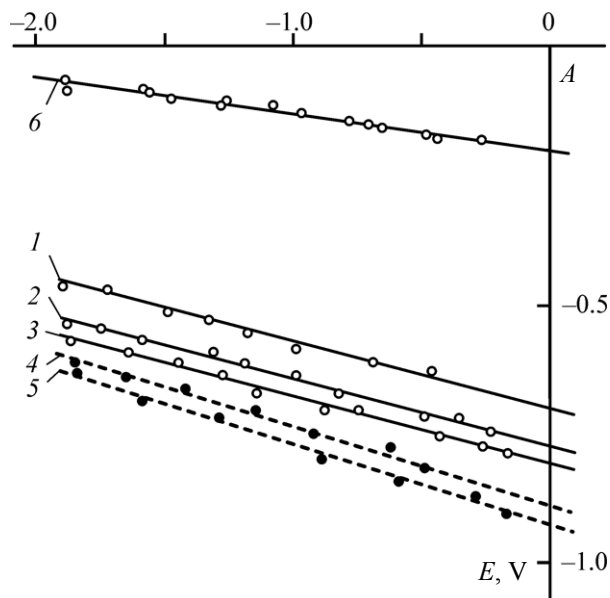


Fig. 3. Redox potential E as a function of the activity of methylene glycol anion and glucose. (A) Logarithm of activity. Aqueous solution of (1–5) formaldehyde + NaOH and (6) glucose + NaOH. T , °C: (1–3, 6) 10 and (4, 5) 40. pH: (1) 11.9 ± 0.05 , (2) 13.2 ± 0.05 , (3) 13.8 ± 0.05 , (4) 12.1 ± 0.05 , (5) 12.8 ± 0.05 , and (6) from 11.5 to 13.8.

dependence of the redox potential on the logarithm of the activity of the methylene glycol anion at constant pH is linear (Fig. 3). However, it differs from the dependence described by the Nernst equation in that the slope of the straight line is 2.2 times larger than the calculated value, $(2.3RT)/(nF)$. The pH dependence of the redox potential at a constant concentration of methylene glycol anions is also linear. The influence of temperature is more complex. The slopes of the straight lines vary with temperature in accordance with the relationship $(2.3RT)/(nF)$, but an increase in the temperature leads also to an increase in the portion intercepted on the E axis.

The dependence of the redox potential E (V) of aqueous solutions of formaldehyde and NaOH on the activities of the methylene glycol anion and hydrogen ions and on the temperature is described by an empirical equation based on the Nernst equation:

$$E = 3.5 \times 10^{-3}(T - 273) + (2.3RT)/(nF) \log \{ \{a_{H^+}\} / \{a[CH_2(OH)O^-]\} \}, \quad (1)$$

where a_{H^+} and $a[CH_2(OH)O^-]$ are the activities of hydrogen ions and methylene glycol anion, respectively (M).

Sodium formate, pentaerythritol, methanol, and products of aldol condensation of acetaldehyde, when

introduced into these solutions, do not noticeably affect the redox potential.

The above-described features show that methylene glycol and formic acid anions are not components of the redox system that determines the redox potential and that one of components of this system is formed in a reaction involving methylene glycol anion.

In view of data on hydrogenation of methylene glycol anion on a metal surface [16], it can be assumed that the redox potential is determined by the redox reactions



Then the methylene glycol anion is merely a source of the hydride ion. Equation (1) is consistent with this assumption, but a special study is required for more complete explanation.

Using Eq. (1), it is possible to calculate the redox potential for the first period of the pentaerythritol synthesis and for the reaction of formaldehyde in an aqueous NaOH solution, taking into account the fact that the formaldehyde concentration $c(CH_2O)$ [M] in the reaction mixture in the course of the pentaerythritol synthesis is as follows:

$$c(CH_2O) = c(Al) - [c(CH_2CHO)_{in} - \{c(NaOH)_{in} - c(NaOH)\}], \quad (2)$$

where $c(Al)$ is the concentration of aldehydes (M); $c(CH_2CHO)_{in}$, initial concentration of acetaldehyde (M), $c(NaOH)_{in}$ and $c(NaOH)$, initial and running concentrations of NaOH (M); the concentration of methylene glycol anions $c[CH_2(OH)O^-]$ (M) is described by the equation [17]

$$c[CH_2(OH)O^-] = c(CH_2O) \{ \{6c(OH^-)\} / (1 + 6c(OH^-)) \}. \quad (3)$$

The calculated and experimental redox potentials agree with each other. This means that, in the first period of the reactions, the redox potential is indeed determined by the concentration of methylene glycol anions, pH, and temperature.

Rapid increase in the negative redox potential in the second period of the pentaerythritol synthesis and formaldehyde transformations cannot be attributed solely to the effect of temperature, because a similar increase in the negative redox potential is also observed in formaldehyde transformations at a constant temperature (Fig. 2). Hence, heating of the reaction system generates a new redox system. In view of the fact that the side reaction of formaldehyde

autocondensation (Butlerov reaction) yields sugars [15], which, when heated in an alkaline solution, undergo retro-aldol cleavage with the formation of glyceraldehyde and dihydroxyacetone transforming successively into 2-oxopropionaldehyde (methylglyoxal) and levulinic acid [18], it can be assumed that the components of this redox system are products of retro-aldol cleavage of sugars and products of their subsequent reactions.

This assumption is confirmed experimentally. The redox potential of aqueous solutions of glucose and NaOH at a low temperature depends on the glucose concentration in accordance with the Nernst equation (Fig. 3), but in the course of heating (conditions of retro-aldol cleavage of glucose) the time dependence of the negative redox potential passes through a maximum (Fig. 4), similarly to the curves for the second and third periods of the pentaerythritol synthesis and formaldehyde transformations.

The difference is that, in transformations of glucose, colored substances appear before the maximal value of the redox potential is reached, and in the synthesis of pentaerythritol and transformations of formaldehyde they appear simultaneously with the peak of the redox potential. However, on adding a small amount of formaldehyde into an alkaline solution of glucose, colored substances also appear at the moment when the redox potential reaches a maximum (Fig. 4), and the redox potential in the region of the maximum decreases compared to the experiment without formaldehyde. Apparently, formaldehyde enters into cross Cannizzaro reactions with products of retro-aldol cleavage of glucose, which occur at higher rates than the reactions between the decomposition products. As a result, the concentration of decomposition products and the rate of reactions yielding colored products decrease.

In the third period of the pentaerythritol synthesis and formaldehyde transformations in aqueous NaOH solution, apparently, products of retro-aldol cleavage of sugars undergo aldol condensation. Under the reaction conditions, the equilibrium of the reversible reaction is strongly shifted toward products of retro-aldol cleavage, glycolaldehyde and glyceraldehyde; at the same time, conditions are created for the condensation of these aldehydes and dehydration of condensation products with the formation of compounds with extended carbon chain including a conjugation chain.

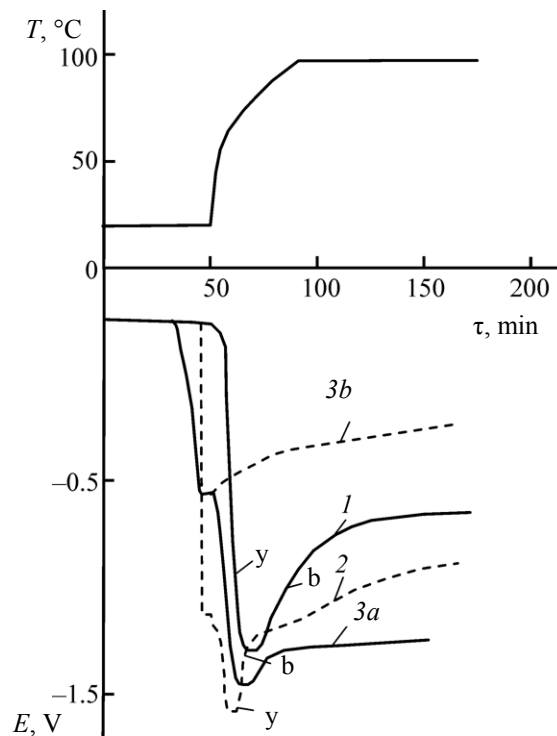


Fig. 4. Variation with time τ of the redox potential E of an aqueous solution of glucose and NaOH. Initial concentration, M: glucose 0.011, NaOH 0.14, formaldehyde 0.085, and copper 3.2 g l^{-1} . (T) Temperature. (1) Without additives, (2) with addition of formaldehyde, and ($3a$, $3b$) in the presence of copper. (1 , 2 , $3a$) At programmed heating and ($3b$) at 20°C . The moments when the reaction mixture becomes yellow (y) and brown (b) are indicated.

The observed change in the color of the reaction mixtures from greenish-yellow to brown suggests a shift of the absorption maxima of the colored products from 400 to 595 nm.

Taking into account data on the dependence of the absorption maxima of hydrocarbons on the number of double bonds in conjugation chains and on the nature of substituents [19], we can tentatively estimate the number of double bonds in the conjugation chain of molecules of products imparting the color to the reaction mixtures.

To have greenish-yellow color (absorption maximum at 400–435 nm), the molecules of the products should have more than five double bonds in the conjugation chain, which corresponds to products of successive addition of four and more glyceraldehyde molecules. The products imparting brown color to the reaction mixture (absorption maxima at 400 to 595 nm) should have more than ten double bonds in the

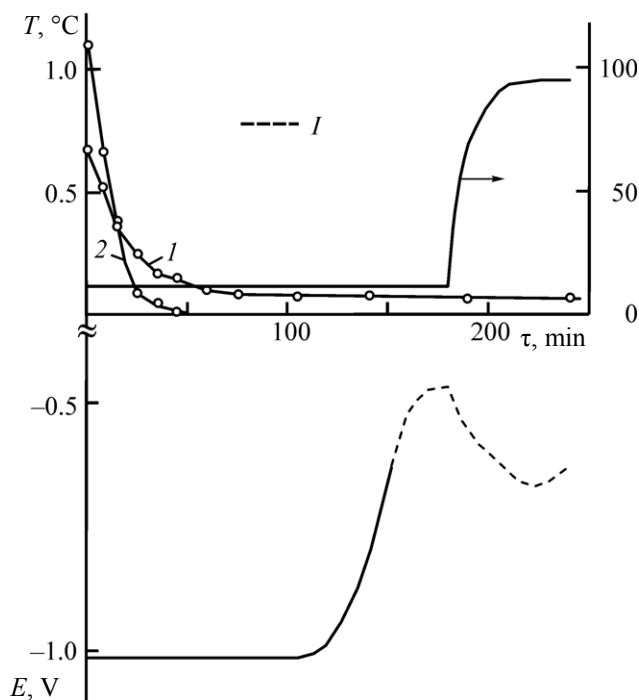


Fig. 5. Kinetic curves of formaldehyde transformations in an aqueous NaOH solution in the presence of copper (3.2 g l^{-1}). (1) Formaldehyde and (2) NaOH. (I) Without copper (removed on the 150th minute).

molecule, which corresponds to products of successive addition of more than seven glyceraldehyde molecules.

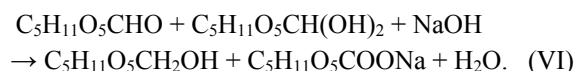
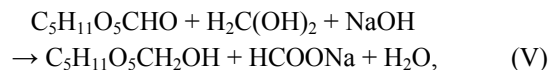
On adding to the reaction mixtures, prior to heating, metallic copper prepared by the reduction of CuO with formaldehyde in a NaOH solution (Figs. 1, 2, 4), the time dependence of the redox potential noticeably changes. These dependences appear to be similar for the synthesis of pentaerythritol and for transformations of formaldehyde and glucose in aqueous NaOH solutions.

On introducing copper into reaction mixtures, the negative redox potential at constant temperature rapidly increases, suggesting the formation of a new redox system (Figs. 2, 4, 5).

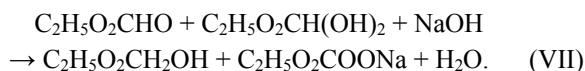
The data we obtained do not allow us to determine the composition of this system. Presumably, it includes the products of the copper formation reaction, adsorbed by the surface of crystals and retained on washing with water. Also, possible effect of copper particles and copper ions on the platinum electrode cannot be ruled out.

On heating copper-containing reaction mixtures, an increase in the negative redox potential is primarily associated with an increase in temperature, the effect of retro-aldol cleavage products is considerably weaker than in the copper-free mixtures, and colored products are not formed: the reaction mixtures always remain colorless.

The fact that the effect of formaldehyde on the redox potential in the reaction with glucose is associated with the cross Cannizzaro reaction has already been noted (Fig. 4). In the presence of copper, the formaldehyde disproportionation is strongly accelerated (Figs. 2, 5), and under the conditions when sugars do not yet undergo retro-aldol cleavage the reactions of sugars are accelerated (Fig. 5), e.g., the reduction of aldoses with formaldehyde and the disproportionation of aldoses:



The similar reactions of retro-aldol cleavage products, primarily of glyceraldehyde, are probably also accelerated:



This reduces or fully eliminates the possibility that hydroxy aldehydes formed by retro-aldol cleavage of sugars will undergo dehydration to form products containing a large number of unsaturated bonds in conjugation chains, and alkaline reaction mixtures remain colorless even under severe conditions of evaporation.

In the course of evaporation of the reaction mixture from the pentaerythritol synthesis, prepared without copper and neutralized with acid at the moment of weak greenish-yellow coloration, a colorless distillate is obtained. However, on adding NaOH and heating, the distillate rapidly becomes brown, which indicates that a part of products of retro-aldol cleavage of sugars have been distilled off with steam.

The mother liquor obtained after cooling of the evaporated mixture and crystallization and filtration of pentaerythritol has a weak yellow color, but on adding NaOH and heating it becomes black. Hence, only a minor fraction of products of retro-aldol cleavage of sugars have been distilled off with steam.

When the same operations are performed with the alkaline reaction mixture obtained by evaporation in the presence of copper, both the distillate and mother liquor remain colorless. Hence, in the presence of copper, sugars and products of their retro-aldol cleavage fully transform into substances that do not yield colored products.

The use of copper after the completion of the reactions of pentaerythritol formation is advantageous because of the following facts: A product with low coloration is formed; it becomes unnecessary to neutralize the reaction mixture prior to evaporation and to properly choose the moment of acid addition; the alkaline reaction mixture does not cause corrosion of evaporation equipment; the distillate and mother liquor contain no substances that can yield colored products, which allows the distillate to be used instead of water and simplifies deep processing of the mother liquor.

CONCLUSIONS

(1) Introduction of copper in the final step of pentaerythritol synthesis considerably decreases the coloration of the final product and simplifies the process as a whole.

(2) The final step involves the reactions of the retro-aldol cleavage of sugars into hydroxy aldehydes and of their condensation and dehydration.

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