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POTENTIOMETRIC ANALYSIS OF THE FORMOSE REACTION

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The course of the calcium hydroxide-catalyzed reaction of formalin to give monosaccharides was potentiometrically followed. Changes of the oxidation-reduction potential curve obtained were found to correspond satisfactorily to the reaction phases; induction period, accumulation of C_3 products, saccharide formation, and gradual decomposition of saccharides, successively.

The formose reaction, which results in the formation of monosaccharides from formaldehyde in the presence of an alkaline catalyst in aqueous media, has drawn much attention as a possible model for the prebiotic synthesis of saccharides,1,2) since its discovery by Butlerow.3) Among a large number of catalysts calcium hydroxide is most widely used. The reaction proceeds with an induction period which is believed to be necessary for the accumulation of the initially formed C_2 and C_3 products such as glycolaldehyde, glyceraldehyde, and dihydroxyacetone.4) Over this period, the formation of monosaccharides increases rapidly and their total yield reaches to the maximum immediately after the so-called yellowing point at which the reaction mixture turns to pale yellow,5) and then the yield of total saccharides decreases gradually because of the decomposition of the formed saccharides under the conditions. The nature of the yellow point has not yet been clarified. We now wish to report on the potentiometric behaviour of the formose reaction which may be a useful tool for the analysis of this reaction.

The formose reaction was carried out in an apparatus attached to a potentiometer in the usual manner: the reaction mixture maintained at 60°C initially consisted of 90 ml of 37% formalin, 8.5 g of calcium hydroxide, and 790 ml of water. The reaction was potentiometrically followed and aliquots withdrawn from the mixture at intervals were quantitatively analyzed for formaldehyde,6) total saccharides,7) and organic acids (neutralization titration). Some aliquots were qualitatively analyzed by paper chromatography8) for C_2 and C_3 products and hexoses. The results are shown in Figs.1and 2.

As seen from the oxidation-reduction potential (ORP) curve, the reaction was found to show four distinct steps (a-d). In the first step (a), ORP stayed almost constant and no production of saccharides could be detected, although slow formation of organic acids (mainly formic acid) comparative to the consumption of formaldehyde. After this step, the ORP curve turned downward to a minimum point (b). The accumulation of C_3 products appeared to occur in this step, as seen from the paper chromatographic analysis of the reaction mixture (Fig. 2; No. 1-3), but the saccharide formation was only less than 10% at the end of this period. Next, the ORP curve turned upward to a small maximum (c), where the colour of the mixture became yellow. During this period the burst of the saccharide production was observed simultaneouly with the comparative consumption of formaldehyde and the temperature of the mixture was raised up to 70-75°C. The highest yield of saccharides (ca. 70%) was obtained at the maximum point of ORP (Fig. 2; No. 4-5). Over the third period, ORP increased very slowly while the formed saccharides began to decompose resulting in the colour change of the mixture from pale yellow to light brown (d).

The utility of the ORP analysis of the formose reaction was examined under various conditions. The appearance of the ORP minimum and maximum was observed whenever the formose reaction took place smoothly. However, under such conditions that the reaction did not take place, ORP did not show significant change but rather increased slowly. For example, treatment of glucoreductone with calcium hydroxide under similar conditions gave no saccharide formation and a plain ORP curve with a small downward tendency.

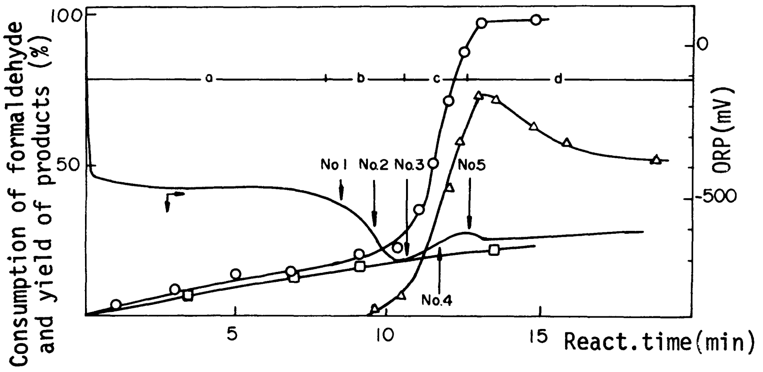

Fig. 1 Potentiometric and product analyses of the formose reaction.

○, formaldehyde; △, total sugars; □, organic acids.

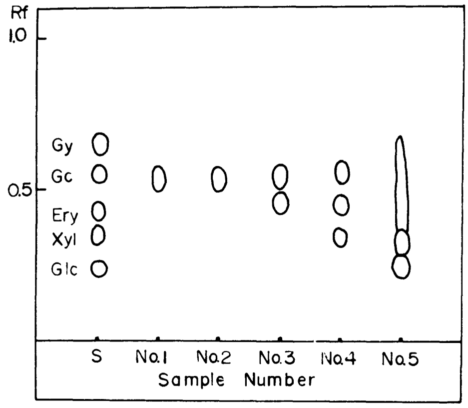

Fig. 2 Paperchromatographic analysis of products.

S, standard sugars; Gy, glycolaldehyde; Gc, glyceraldehyde; Ery, erythrose; Xyl, xylose; Glc, glucose.

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