ON THE MECHANISM OF AUTOCATALYSIS IN CARBOHYDRATE SYNTHESIS FROM FORMALDEHYDE

T. I. Khomenko, O. A. Golovina, M. M. Sakharov, O. V. Krylov
and A. H. Weiss

1 Institute of Chemical Physics, Moscow, USSR
2 Department of Chemical Engineering, Polytechnic Institute, Worcester, Massachusetts, USA

Received December 19, 1979
Accepted January 25, 1980

From the analysis of kinetic behaviour in carbohydrate synthesis from formaldehyde and spectral data on the structure of catalytically active Ca(OH)$_2$ complexes with carbohydrates a step-wise mechanism of autocatalysis of formaldehyde condensation to carbohydrates in the presence of Ca(OH)$_2$ is proposed. A kinetic equation to describe the initial step of autocatalysis is given.

In the past decade carbohydrate synthesis from formaldehyde has been studied by kinetic methods in non-gradient /1-3/ and static /4-15/ reactors and by UV /15, 16/, NMR /11, 15, 17, 18/, IR /11, 19/ and XPS /19/ techniques. The successful application of gas-liquid chromatography /1/, particularly, in combination with mass spectrometry /20/, and the above studies have provided a large body of information on the product composition and the reaction kinetics and permitted to find new catalysts for this process /21/.

The most detailed information on its kinetics has been obtained with Ca(OH)$_2$ as catalyst. 1) At low conversion ($\alpha$) of CH$_2$O the carbohydrate synthesis is an
autocatalytic reaction. 2) According to their effect (reduction or complete elimination of the induction period) carbohydrate cocatalysts are arranged as $C_2 > C_3 > C_4 > C_5 > C_6$. 3) Beginning with $\alpha = 10-20$ to 80-90%, the synthesis is zero order with respect to $C_2H_2O$, its rate being independent of the initial concentration of carbohydrate added as cocatalyst. 4) At pH < 9.5 and pH > 12 the synthesis rate sharply drops, which indicates that the actual catalyst is CaOH$^+$ ion /3/. 5) Synthesis is a homogeneous catalytic process; the highest rates are obtained by adding a homogeneous solution which contains Ca(OH)$_2$ and carbohydrate, to the solution of $C_2H_2O$; the induction period can also be eliminated by adding (at optimum pH) complexes of Ca(OH)$_2$ with carbohydrates prepared by the Roy-Mitra method /22/. Synthesis is accompanied by the Cannizzaro reaction without induction period; at $\alpha = 100\%$ the $C_2H_2O$ consumption is below 25% without cocatalyst and 6-8% in the presence of carbohydrate cocatalysts.

The above kinetic studies have confirmed the previous conclusion /23/ that the rate-determining step of the synthesis is $C_2H_2O$ dimerization to glycolaldehyde governing the duration of the induction period. All other molecules of carbohydrates can readily be formed due to the much faster aldol condensations of $C_2H_2O$ with glycolaldehyde and other carbohydrates /24/ and auto- and co-condensation of lower carbohydrates /25/. Aldol condensations, which proceed mainly at medium $\alpha$, are responsible for the observed zero order kinetics.

Spectral studies have permitted to clarify the structure of catalytically active Ca(OH)$_2$ complexes with carbohydrates. UV spectra of the solutions containing Ca(OH)$_2$ and carbohydrates, and of the reaction mixture /15/ indicate that the carbohydrate in the complex is of the ene-diol form. With increasing pH, a marked long-wave shift of the ene-diol complex band /15/ indicates that the complexed carbohydrate is ionized. Its ionization is also confirmed by ESCA data /19/, showing the proximity of polarization of the Ca$^{2+}$-carbohydrate bond to that for calcium.