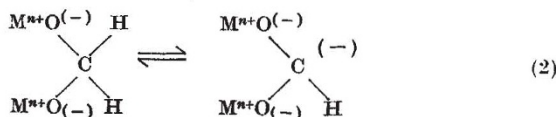
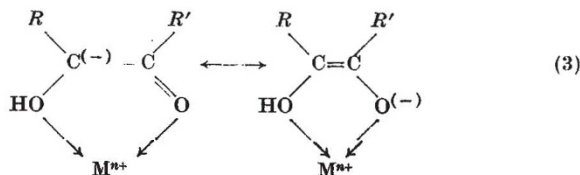


attached to carbon. Co-ordination of the oxygens with divalent cations (2) would greatly enhance this effect, which would explain in part the greater efficacy of divalent oxides as catalysts. It should be noted that the



microcrystalline clay minerals usually have alkaline earths, alkali metals and protons adsorbed as cations on their surfaces<sup>18</sup>. Franzen and Hauck<sup>20</sup> have reported that alkaline earth cations form salts with aqueous formaldehyde, and although Staudinger *et al.*<sup>21</sup> have shown that there is no definite composition to these materials, they are probably co-ordination complexes of the metals with water, hydroxide ions, and a variety of chain lengths of partially polymerized formaldehyde.

The polyvalent cations, which are Lewis acids, also co-ordinate with the carbonyl oxygen atom of non-hydrated formaldehyde, rendering the carbon atom much more subject to nucleophilic attack. It can further be expected that the polyvalent cations would also stabilize the enolate anions of the hydroxy aldehydes and ketones (3).



In this work, it has been shown that a dilute ( $10^{-2}$  molar) solution of formaldehyde can be condensed to a mixture of sugars in conditions designed to simulate a primordial hydrothermal spring. An alkaline medium is unnecessary for this condensation to take place. The reaction takes place at mildly acid and neutral pH. The basic sites on the crystal lattice of the alumina and aluminosilicates probably serve to remove protons from the formaldehyde and various intermediates adsorbed on the mineral surfaces, thereby providing the necessary reactant molecules.

A reasonable rationale for the production of hexoses in  $10^{-2}$  molar solution of formaldehyde and not in a 0.33 molar solution is that in dilute solution an individual reaction intermediate will be adsorbed for a longer time on the mineral surface. Conversely, in a more concentrated solution, the reaction intermediate is more quickly displaced from the mineral surface by the other solute molecules. It can be expected that the longer any given reactant remains on the active surface of the catalyst the greater are its chances of undergoing further reactions to form products of higher molecular weight.

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## Synthesis of Sugars in Potentially Prebiotic Conditions

THE formation of sugars from formaldehyde has been studied extensively<sup>1</sup>, but the reaction has usually been carried out in conditions too extreme to have existed on the primitive Earth. The claim that relatively pure ribose can be obtained by boiling formaldehyde with a suspension of calcium carbonate<sup>2</sup> led us to investigate the catalytic activity of "carbonate-apatite". Hydroxy-apatite, a very common phosphate mineral, is inactive; we argued that if carbon dioxide was abundant at any stage in the evolution of the ocean, carbonate incorporation into apatite must have been extensive.

A slurry of "carbonate-apatite" prepared freshly by the method of Hayek *et al.*<sup>3</sup>, was found to have a pH of 8.5. On boiling with 0.5 molar formaldehyde, it gave yields of up to 40 per cent of sugars. There was an initial induction period of several hours during which no sugars could be detected, then glycolaldehyde, trioses, tetroses, pentoses and hexoses appeared successively. Sugars were separated by chromatography in butanol-acetic acid-water (4 : 1 : 5, upper phase) and in acetic acid-pyridine-water (7 : 3 : 2) and estimated using the acid aniline phthalate spray<sup>1</sup>. Pentoses are present in maximal amount after about 12 h and hexoses after about 24 h. When boiling was continued for longer periods the solution darkened and the sugars gradually disappeared; the hexoses persisted longest. We obtained similar results when we used calcium carbonate as a catalyst, but the whole sequence of reactions proceeded more slowly.

When this experiment was repeated using more dilute formaldehyde, we could still detect sugars from 0.01 molar solution but not from 0.001 molar. The minimum detectable yield in the latter experiment was 1-2 per cent. In these experiments, we used formaldehyde labelled with carbon-14 to obtain greater sensitivity in our analyses. The experiment was discontinued after 14 days. These results are similar to those reported by Gabel and Ponnampuruma<sup>4</sup>, who used a suspension of  $Al_2O_3$  as catalyst.

We do not believe that the formose reaction as we and others have carried it out is a plausible model for the prebiotic accumulation of sugars. First, it requires concentrated formaldehyde solutions and, second, the sugars formed are decomposed quite quickly. If formaldehyde is the prebiotic precursor of ribose, some method of stabilizing the sugars is essential. The formation of ribosides of the natural bases—for example, adenine—is one possibility, but attempts to bring about this condensation have not been successful. Instead, rather unstable adducts were formed<sup>5</sup>.

The formation of sugars in plausible conditions and their incorporation into nucleosides have not been achieved. Until the problem is solved or by-passed it remains a weakness in theories of abiotic nucleic-acid synthesis.

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