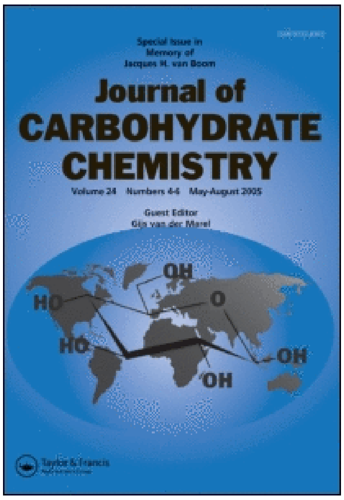
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Alkaline Degradation of Monosaccharides VI[1]: The Fhucto-Fobmose Reaction of Mixtures of D-Fructose and Formaldehyde

J. M. De Bruijn[ab]; A. P. G. Kieboom[a]; H. Van Bekkiun[a]
[a] Laboratory of Organic Chemistry, Delft University of Technology, BL Delft, The Netherlands [b] Central Laboratory, HL Breda, The Netherlands

To cite this Article De Bruijn, J. M. , Kieboom, A. P. G. and Van Bekkiun, H.(1986) 'Alkaline Degradation of Monosaccharides VI[1]: The Fhucto-Fobmose Reaction of Mixtures of D-Fructose and Formaldehyde', Journal of Carbohydrate Chemistry, 5: 4, 561 — 569

To link to this Article: DOI: 10.1080/07328308608062975

URL: http://dx.doi.org/10.1080/07328308608062975

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. CARBOHYDRATE CHEMISTRY, 5(4), 561-569 (1986)

ALKALINE DEGRADATION OF MONOSACCHARIDES VI[1]: THE FRUCTO-FORMOSE REACTION OF MIXTURES OF D-FRUCTOSE AND FORMALDEHYDE

J.M. de Bruijn[+], A.P.G. Kieboom and H. van Bekkum

Laboratory of Organic Chemistry, Delft University of Technology.
Julianalaan 136, 2628 BL Delft, The Netherlands

and

[+] Central Laboratory, CSM Suiker B.V.
Valveeken 6, 4815 HL Breda, The Netherlands

Received May 17, 1986 - Final Form June 17, 1986

ABSTRACT

The final product compositions of the alkaline (calcium hydroxide) degradation of D-fructose in the presence of formaldehyde at several D-fructose/formaldehyde ratios, and of the formose reaction were determined by HPLC and GC analysis. At decreasing D-fructose/formaldehyde ratio a gradual change of the composition was observed except for lactic acid and the oligomeric acidic products, which show a minimum and a maximum, respectively. A mechanistic explanation is given by the aldolization of formaldehyde both with saccharides and with their subsequent α-dicarbonyl intermediates, which favours the formation of oligomeric products at the cost of lactic acid. It is established both experimentally and theoretically that there is no essential mechanistic difference between the formose reaction and the alkaline degradation of monosaccharides.

The formose reaction[2], i.e. the oligomerization of formaldehyde in aqueous alkaline solution, results in a mixture of monosaccharides, called formose or formose sugars. The product mixture largely consists of both linear and branched aldo- and ketopentoses, and the respective hexoses. In addition, variable amounts of linear and branched alditols as well as hydroxycarboxylic

0732-8303/86/0504-0561$3.50/0

acids are irreversibly formed by (cross-)Cannizzaro reactions. Much research has been devoted to the improvement of the selectivity of the reaction. It has been reported that a proper choice of reaction conditions, catalysts, and additives leads to a preferential conversion of formaldehyde into ethylene glycol[3], 2-C-hydroxymethylglycerol[4], D,L-arabinitol[5], or 2,4-di-C-hydroxymethyl-3-pentulose[6], respectively.

The reaction conditions of the formose reaction are quite similar to those of the alkaline degradation of monosaccharides[7], i.e. $[HO^-] > 10^{-3}$ M, T = 40-90 °C, and 0.01-1 M reactant. It should be noted that in comparison with the fast conversion of formaldehyde, the alkaline degradation of formose sugars or monosaccharides is slow. For example, at 80 °C in aqueous saturated $Ca(OH)_2$, formaldehyde is converted within a few minutes, apart from a variable time of induction (see below), whereas the alkaline degradation of D-fructose takes about 2 hours. Thus, by the use of short reaction times subsequent degradation reactions can be largely prevented. Maximum conversion of formaldehyde together with a maximum yield of formose sugars has experimentally found to be attained at the so-called "yellowing point", based on colour development in the reaction mixture as an indication that irreversible alkaline degradation of the formose sugars starts to occur. The composition of the reaction mixture after complete alkaline conversion of the formose sugars is close to that of the product mixture of alkaline degradation of monosaccharides[8,9]. Furthermore, the formose reaction requires the initial presence of trace amounts of $\geq C_2$ aldehydes[10,11], which means that the processes taking place are "normal" aldolization and retro-aldolization reactions.

It is expected that monosaccharides, besides initiating the formose reaction, also might influence the selectivity of the reaction when present in higher concentrations. In addition, knowledge of the final reaction products of formaldehyde and monosaccharides in alkaline solution is of importance for the sugar manufacture. The formaldehyde used for controlling microbiological activity in the diffusion section is decomposed in the presence of invert sugar during the main liming. For these reasons, we have investigated the influence of monosaccharides, in particular D-fructose, on the formose reaction at various monosaccharide/formaldehyde ratios using HPLC and GC analysis[12] of the final carboxylic acid products.

The total concentration of carbohydrates, expressed as mol-C_6/L (e.g. 6 mol formaldehyde/L corresponds to 1 mol-C_6/L) was chosen between 0.025 mol-C_6/L and 0.050 mol-C_6/L in order to eliminate any concentration effects[13]. The reactions were performed in a thermostatted (78 °C) vessel (150 ml) under N_2. An excess of solid calcium hydroxide (590 mg in 100 ml water) was applied as the base, resulting in a constant HO^- concentration ($\sim$ 0.03 M) during the reaction. The composition of the final reaction mixtures as a function of the starting molar D-fructose/-formaldehyde ratio is depicted in Fig. 1. Going from the D-fructose alkaline degradation (left) to the formose reaction (right) there is a gradual change in the composition except for lactic acid and the $> C_6$ acids, i.e. the oligomeric acidic products[14], which show a minimum and a maximum, respectively, at D-fructose/-formaldehyde = 1/6. In addition, more branched C_4 and C_5 saccharinic acids are formed at higher formaldehyde concentrations.

Aldolization of formaldehyde with saccharides and their intermediate alkaline degradation compounds explains the observed change in composition of the final carboxylic acid products upon addition of formaldehyde (Fig. 2). Comparison of the degradation of D-fructose towards lactic acid (route A) with that including the interference by formaldehyde (routes A + B) clearly demonstrates the possible effects of formaldehyde on the degradation pattern. At a first approximation, there exists a direct correlation between the amounts of $> C_6$ acids and lactic acid formed (Fig. 1). Apparently, formaldehyde functions as a scavenger for C_3 enediol (anion) species - precursors of lactic acid - by the formation of the non-enolizable species $\underline{I}$ (Fig. 2). As a result, lactic acid formation decreases, whereas aldolization of $\underline{I}$ with other enolizable carbonyl compounds may be responsible for the enhanced $> C_6$ acid formation.

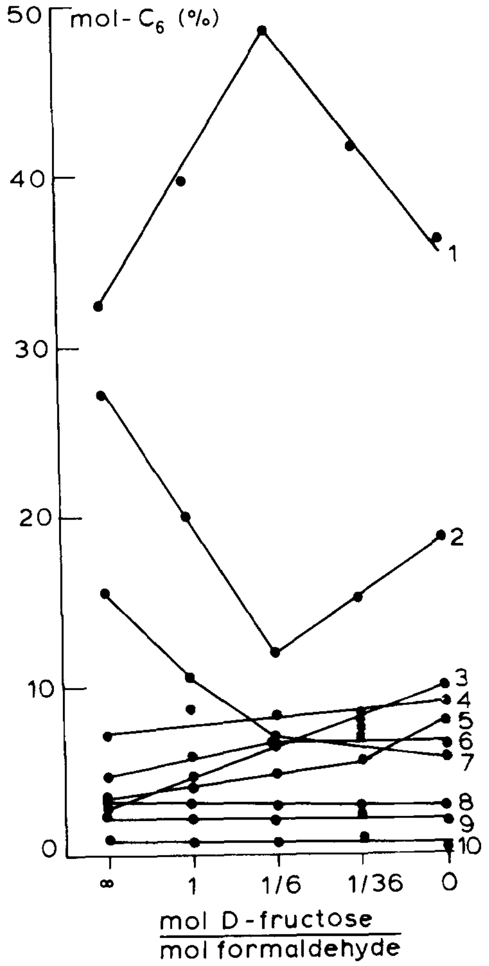


Fig. 1. Carboxylic acid products as a function of the molar D-fructose/formaldehyde ratio. Reaction conditions: 0.025 M D-fructose (except at the ratios 1/36 (0.0042 M) and 0 (0.15 M formaldehyde)); 590 mg $Ca(OH)_2$ in 100 ml H_2O, 78 °C, N_2, 7 h, 100% conversion.

1. $> C_6$ acids
2. lactic acid
3. 2-methylglyceric acid
4. 2,4-dihydroxybutyric acid
5. formic acid
6. C_5-saccharinic acids
7. C_6-saccharinic acids
8. acetic acid
9. glycolic acid
10. glyceric acid

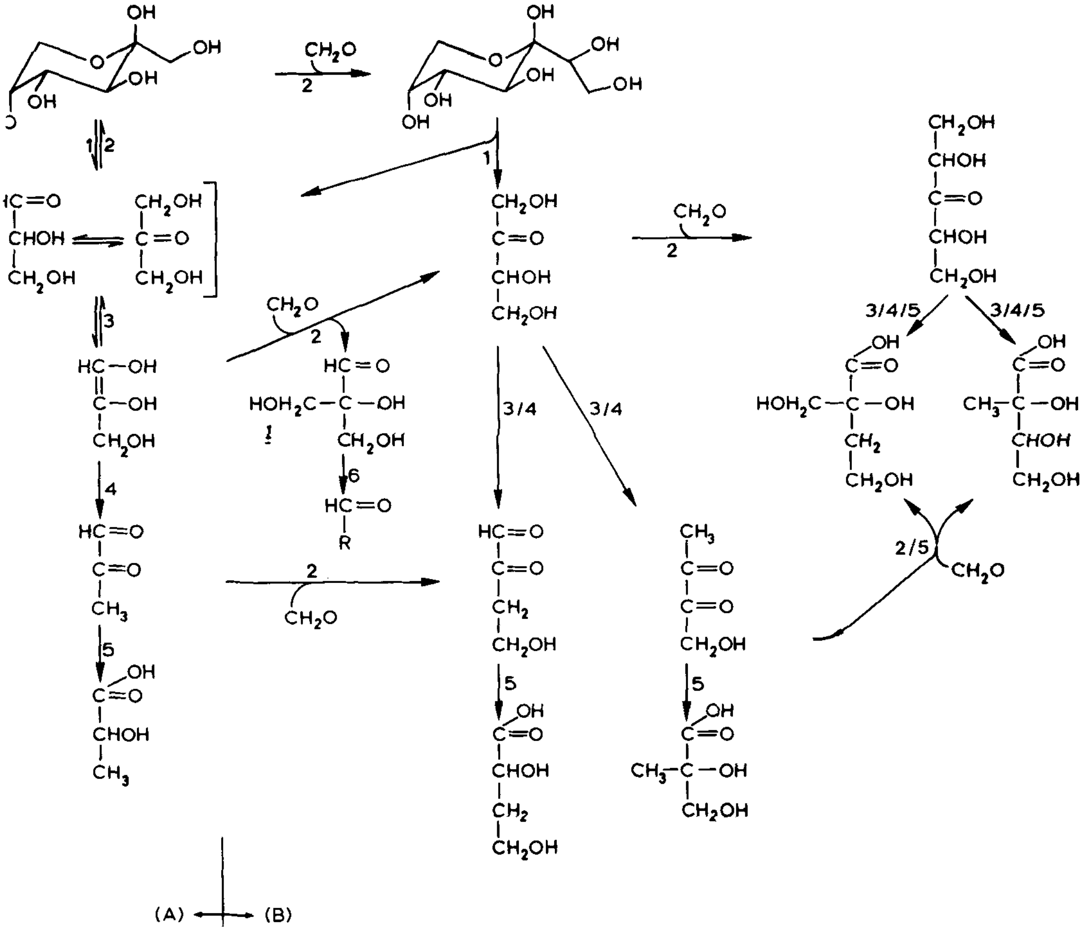


Fig. 2. Simplified reaction sequence for the alkaline degradation of D-fructose into lactic acid without (A) and in the presence of formaldehyde (A + B).

Numbering of reaction types:

1. retro-aldolization,
2. aldolization,
3. enolization,
4. β-elimination,
5. benzilic acid rearrangement,
6. aldolization with other enolizable carbonyl compounds.

Furthermore, aldolization of enols with formaldehyde will compete with the β-elimination to dicarbonyls, which in turn may aldolize with formaldehyde in stead of other carbonyl compounds. As dicarbonyls are assumed to be the main precursors of coloured compounds[14], these reactions explain the retardment of colour formation upon addition of formaldehyde (Fig. 3). The rate of colour formation is indicated by the time elapsed until the yellowing point (t_{yp}). Up to the yellowing point, the formation of acidic products can be neglected and, consequently, only formaldehyde and saccharides derived thereof will be present in the reaction mixture[2]. At the yellowing point formaldehyde is almost completely converted (Fig. 4) and concomitantly a maximum concentration of saccharides is attained.

The various fructo-formose reactions carried out can be also considered as normal formose reactions since the initial composition of these mixtures reflects more or less that of the formose reac-

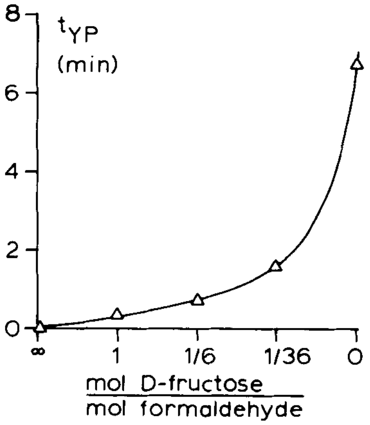


Fig. 3. Time elapsed until the yellowing point (t_{yp}) as a function of the molar D-fructose/formaldehyde ratio. Reaction conditions: see Fig. 1.

tion mixture between t = 0 and t_{yp}. Indeed, the t_{yp} of the various fructo-formose reactions versus their initial formaldehyde-saccharide compositions, as indicated by Δ in Fig. 4, correlate quite well with the conversion curve of formaldehyde in the formose reaction. The results also confirm the earlier conclusion[10,11] that the formose reaction has to be considered as an autocatalytic reaction sequence consisting of aldolization and retro-aldolization steps and that the first step of the formose reaction ($C_1 + C_1 \longrightarrow C_2$) does not occur at all. Using the derived relation[11]

$$[CH_2O] = \frac{\alpha}{1+\beta e^{kt}},$$

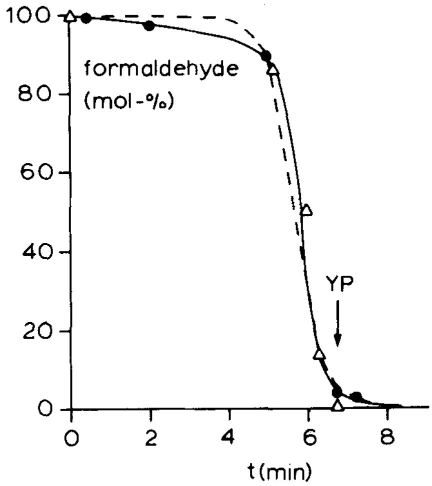


Fig. 4. Reaction course of formaldehyde (0.15 M) in alkaline medium (590 mg $Ca(OH)_2$ in 100 ml H_2O, 78 °C, N_2): ●, experimental data; Δ, initial compositions of the fructo-formose mixtures versus their corresponding t_{yp} observed (data from Fig. 3); YP, yellowing point.
The dotted line is the theoretical conversion curve of formaldehyde calculated according to the kinetic relation for an autocatalytic reaction sequence (see text).

in which α is the initial CH_2O concentration and $\beta = \frac{[C_n]}{[CH_2O]}$ with $C_n > C_2$ carbonyl species, the experimental data in Fig. 4 correlate with a pseudo first order reaction rate constant $k = 2.7$ min^{-1} and $\beta = 2 * 10^{-7}$ (see dotted line in Fig. 4).

The results clearly show that (retro-)aldolization reactions are of major importance for both the formose reaction and the alkaline degradation of monosaccharides. In other words, there is no essential mechanistic difference between these two reactions.

References

1. Part V: J.M. de Bruijn, A.P.G. Kieboom, and H. van Bekkum, Carbohydr. Res., to be published.
2. T. Mizuno and A.H. Weiss, Adv. Carbohydr. Chem. Biochem., 29, 173 (1974).
3. A.H. Weiss, S. Trigerman, G. Dunnells, V.A. Likholobov, and E. Biron, Ind. Eng. Chem. Process Des. Dev., 18, 522 (1979).
4. T. Matsumoto and S. Inoue, J. Chem. Soc. Perkin Trans., 1, 1975 (1982).
5. Y. Shigemasa, A. Matsuba, N. Ueda, and R. Nakashima, Carbohydr. Res., 134, C4 (1984).
6. Y. Shigemasa, S. Akagi, and R. Nakashima, Carbohydr. Res., 80, C1 (1980).
7. J.M. de Bruijn, A.P.G. Kieboom, H. van Bekkum, and P.W. van der Poel, Sugar Techn. Rev., 13, 21 (1986).
8. E. Reinefeld, K.-M. Bliesener, P. Kowitz-Freynhagen, and E. Brandes, Zuckerind., 104, 504 (1979).
9. A. Carruthers and J.F.T. Oldfield, Int. Sugar J., 66, 355 (1964).
10. R.F. Socha, A.H. Weiss, and M.M. Sakharov, React. Kinet. Catal. Lett., 14, 119 (1980).
11. A.P.G. Kieboom and H. van Bekkum, Recl. Trav. Chim. Pays-Bas, 103, 1 (1984).

12. J.M. de Bruijn, A.P.G. Kieboom, H. van Bekkum, and P.W. van der Poel, Int. Sugar J., 86, 195 (1984).

13. J.M. de Bruijn, A.P.G. Kieboom, and H. van Bekkum, Recl. Trav. Chim. Pays-Bas, in press.

14. J.M. de Bruijn, A.P.G. Kieboom, H. van Bekkum, P.W. van der Poel, N.H.M. de Visser, and M.A.M. de Schutter, Int. Sugar J., to be published.