An h.p.l.c. study of the initial stages of dextrose decomposition in neutral solution

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The decomposition of dextrose in acid and alkaline solution has been extensively studied (Wolfrom, Shuetz & Cavalieri, 1948; Anet, 1960; Heimlich & Martin, 1960; Tahir & Cates, 1974) and mechanisms suggested for the reactions involved. The main product in acid solution is 5-hydroxymethylfurfural (5-HMF); in basic solution various saccharinic acids result. Evidence for intermediates in the acid decomposition is the appearance of a maximum at 230 nm in solutions of degraded dextrose (Wolfrom & others, 1948; Taylor, Jappy & Neil, 1972). From basic solutions a derivative of an intermediate 3-deoxyhexosone has been isolated (Anet, 1960). Few studies have been made of thermal decomposition under neutral conditions although analogies have been drawn with decomposition in acid solution. It has also been suggested (Taylor & others, 1972) that the absorbance at 230 nm arises from an acidic intermediate in line with the observed fall in pH on autoclaving neutral solutions of dextrose (Wing, 1960).

In this work, using h.p.l.c., we have followed the progress of dextrose decomposition to 5-HMF in neutral solution. With a reverse phase C-18 column and an aqueous eluting solvent resolution of two intermediate compounds as well as 5-HMF was obtained. The rapid production of a second product identified as an acid by ion-pairing methods is also reported. These findings are interpreted on the basis of previously suggested mechanisms for the acid and basic decompositions.

The decomposition was followed by heating 0·278 M aqueous dextrose solutions (0·5 cm^3 samples) in sealed ampoules for various times at tempertures varying from 90 to 140°, the changes reported being general over this temperature range. The reaction mixture (50 μl) was applied to a 250 mm × 4·3 mm i.d. Partisil ODS (10 μm) column and absorbance was monitored at 254 nm in an 8 μl, 10 mm flow cell. Water was used as the eluting solvent as was an aqueous solution of 0·2 %w/v tetrabutylammonium phosphate (TBAP) to increase the retention time of the anticipated acid anion. Such a chromatographic system minimizes the effect of the large excess of unreacted dextrose while the C-18 stationary phase effects a high degree of separation of the closely related species produced initially in the reaction.

The chromatograms obtained after heating for 50 min at 120° showed five major peaks. The ultraviolet spectra of these were obtained using the 'stopped flow' technique by incorporating a Pye-Unicam SP1800 double beam spectrophotometer with an 8 μl flow cell into the chromatographic system and data are recorded in

* Correspondence.

Table 1. *Retention times relative to dextrose, capacity factors and wavelengths of maximum absorption for chromatographic peaks observed in degraded dextrose solution.*

	Eluant-water		Eluant-0·2% TBAP		Max in water
Peak	Rt/Rt dextrose	k^1	Rt/Rt dextrose	k^1	(nm)
P-1	0·70	0	1·93	1·62	<200
P-2	1·00	0·439	1·00	0·359	<200
P-3	1·09	0·573	1·05	0·483	235
P-4	1·49	1·15	1·23	0·685	235
P-5	4·39	5·32	2·31	2·134	235, 285

* The Rt value of furfuraldehyde (FA) is longer than that of 5-HMF. In our investigation we have consistently observed this compound being produced during decompositions and have labelled it P-6 Since it is present in very small quantities and appears later in the reaction scheme than 5-HMF, we have not included it as part of the initial stages. We do not know yet if it arises from 5-HMF or independently from one of the intermediates.
k^1 5-HMF = 5·32 k^1 P-6 (FA) = 7·8.
Relative peak height after 6 h at 120° 5-HMF/FA = 20·3.

Table 1. The variation of each peak height with time is given in Fig. 1. When the ion-pairing agent TBAP was included an identical behaviour pattern was observed. Peak P-2 was confirmed as dextrose by comparison with an authentic sample. P-3 and P-4 showing increased retention times over dextrose and reaching steady state conditions, with P-4 showing sigmoidal rise to the steady state, are attributed to intermediate products appearing in that order. Both have identical ultraviolet

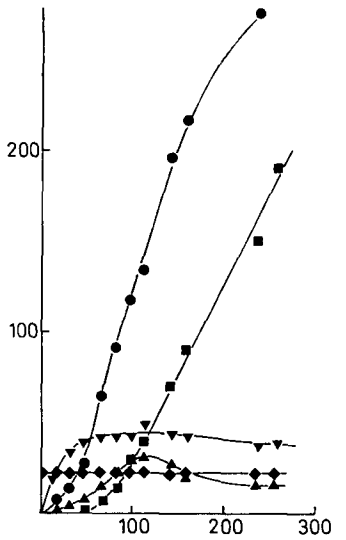
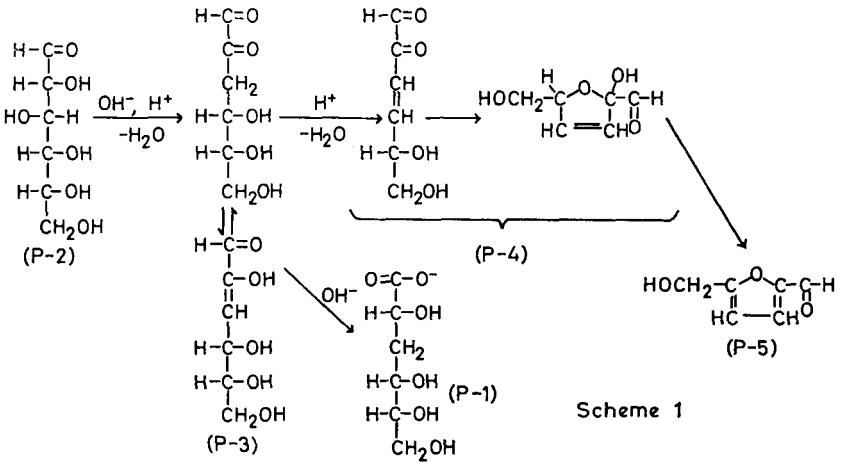


FIG. 1. Variations of peak heights (corrected to full scale deflection of 0·01 absorbance units) of dextrose decomposition products with time at 120°. ● P-1; ◆ P-2; ▼ P-3; ▲ P-4; ■ P-5. Ordinate: Peak height (cm). Abscissa: Time (min).



Scheme 1

spectra with a maximum at 235 nm. Thus two intermediates, rather than one, are responsible for the previously reported ultraviolet absorption at 230 nm. Such a value is consistent with the 3-deoxyhexosone structure previously isolated from basic solutions. P-5, identified as 5-HMF by comparison with an authentic specimen, was not detected until after significant quantities of the compounds producing P-3 and P-4 were present. For solutions heated at 120° this time lapse is in the region of 20 min.

P-1 is attributed to an acid anion since in aqueous solution it is not retained on the column while in dilute TBAP solution its retention time is markedly increased. It appears early in the reaction scheme after the production of the first intermediate and its rate of production appears to decrease after 100 min at 120°. This behaviour parallels closely the rapid drop in pH to a value between 3 and 4. Species P-1 exhibits no characteristic maxima above 200 nm and is therefore unlikely to be the intermediate acetylacrylic acid postulated by Tahir & Cates (1974).

The data presented here for neutral solution suggest a modification to the mechanism proposed by Taylor & others (1972). At the beginning of the decomposition it is the alkaline degradation mechanism which is predominant and the 3-deoxyhexosone (P-3) formed first by dehydration rearranges (Sowden, 1957) to form metasaccharinic acid (P-1). This acid has not been identified in the present work but the absence of characteristic ultraviolet maxima is consistent with the nature of this acid. At longer times when the acid product has reduced the pH of the solution, the acid decomposition is favoured and 5-HMF (P-5) continues to be formed as the main product. The acidity in autoclaved dextrose solutions cannot reasonably be considered as arising from the further decomposition of 5-HMF to formic, levulinic or acetylacrylic acids since the acid product clearly occurs before appreciable concentrations of 5-HMF exist in the solution. The combined reaction is shown in Scheme 1.

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