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THERMAL DEGRADATION OF 3-DEOXY-D-*erythro*-HEXOSULOSE

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ABSTRACT

3-Deoxy-D-*erythro*-hexosulose is less stable than normal carbohydrates and polymerizes within the range 100–200°. The polymerization is accompanied by dehydration, fission, and rearrangement reactions which produce water, furan derivatives, carbonyl compounds of low molecular weight, saccharinic acid, carbon dioxide, and carbon monoxide. Heating at higher temperatures results in charring of the polymeric material, and further dehydration, fission, and disproportionation reactions which provide a variety of secondary pyrolysis products. The dehydration reactions are catalyzed by the addition of zinc chloride, and the fission reactions by the addition of sodium carbonate.

INTRODUCTION

Studies of the pyrolytic reactions of cellulose and a variety of model compounds[1–15] have shown that the addition of zinc chloride as a Lewis acid results in the enhanced formation of water, furan compounds, and char, whereas alkali catalysts promote the fission of the sugar moiety, and increase the formation of carbonyl compounds[3,4,10]. Isotopic tracing of the products formed on pyrolysis of 1,6-anhydro-β-D-glucopyranose (levoglucosan)[11] further indicated that the first dehydration product (3-deoxyhexosulose) of the sugar moiety could play a significant role in the pyrolysis of carbohydrates to various products, especially the furan compounds and char. The 3-deoxyaldosuloses are formed as general, intermediate products in the acid- and alkali-catalyzed reactions of carbohydrates[16–18], and have been identified among the pyrolysis products of cellulose, D-glucose, D-fructose, and D-xylose[19]. Moreover, the oligosaccharides formed from the pyrolytic transglycosylation of carbohydrate derivatives or the condensation of reducing sugars often show ultraviolet (u.v.) and infrared (i.r.) absorption bands that could be due to the presence of the 3-deoxyhexosulose unit or its tautomeric forms[4,13,14].

In view of these considerations, thermal reactions of 3-deoxy-D-*erythro*-hexosulose have been investigated in order to gain a better understanding of the pyrolytic reactions, particularly dehydration, charring, rearrangement, and decarboxylation, which could follow the initial formation of this compound.

RESULTS AND DISCUSSION

3-Deoxy-D-*erythro*-hexosulose was prepared by decomposition of *N*-butyl-D-glucosylamine[20,21], and purified by regeneration from the crystalline bis(benzoylhydrazone) derivative[22]. Dynamic thermal analysis of the amorphous material (see Fig. 1), including differential thermal analysis (d.t.a.), thermogravimetric analysis (t.g.a.), and derivative thermogravimetry (d.t.g.), shows that it starts to decompose at the early stages of heating and, after rapid endothermic decomposition at ~100 and 170°, ultimately leaves 43% of residue at 400°. The rapid decomposition results in a 22% loss of weight, but, in contrast to the thermal behavior of glycosides and polysaccharides which decompose at much higher temperatures (250–350°), a steady rate of weight-loss continues on further heating and is attributed to gradual charring of the residue.

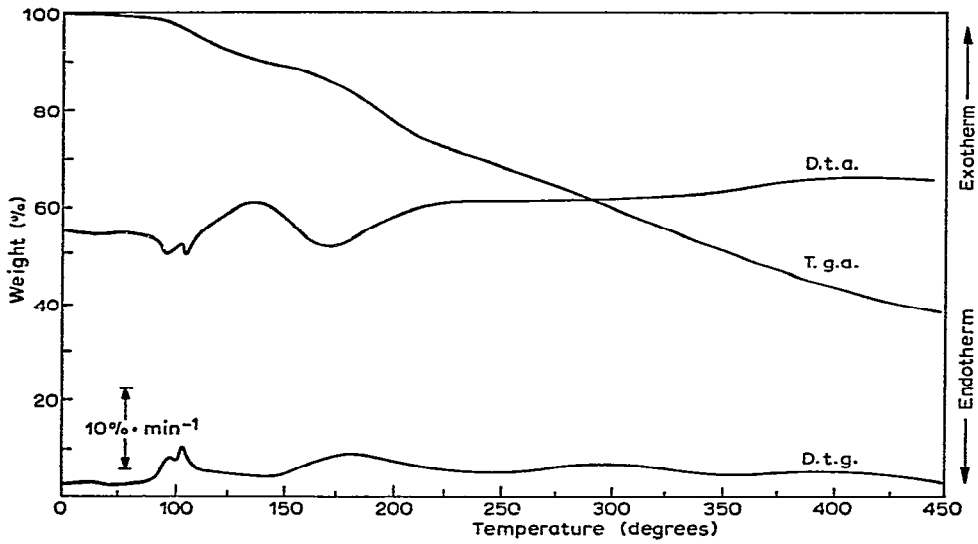


Fig. 1. Thermograms of 3-deoxy-D-*erythro*-hexosulose: D.t.a. is given on the right-hand scale, T.g.a. on the left-hand scale, and D.t.g. on the scale indicated.

The sequence of the thermal reactions was studied by g.l.c. of the products, and by mass spectroscopy (m.s.) of the gases formed at different temperatures. The m.s. data presented in Fig. 2 showed evolution of water, carbon monoxide, and carbon dioxide during both the decomposition and charring periods, with maximum rates associated with the latter.

For chemical investigation of the products formed within the range 70–170°, the reaction mixtures were first reduced (to prevent tautomerization of the carbonyl compounds, particularly the intact 3-deoxy-D-*erythro*-hexosulose which was determined as the corresponding 3-deoxy-D-hexitols[23]) and then trimethylsilylated and

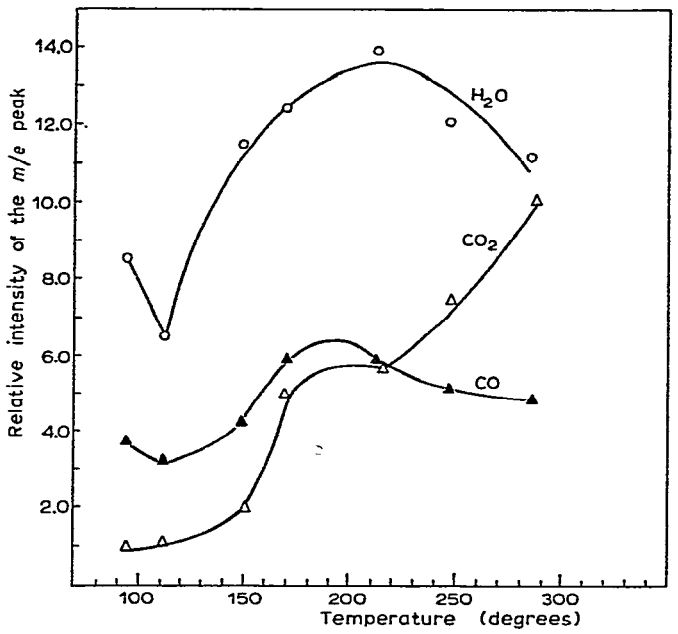


Fig. 2. Evolution of H_2O, CO_2, and CO on heating of 3-deoxy-D-*erythro*-hexosulose.

analyzed by g.l.c. As listed in Table I, small quantities of 2,5-dihydroxymethylfuran, α- and β-D-glucometasaccharinic acid (3-deoxy-D-*ribo*-hexonic and 3-deoxy-D-*arabino*-hexonic acids, respectively), glycerol, propane-1,2-diol, and ethylene glycol were detected as the monomeric reaction products which, with the exception of the saccharinic acid, are derived from the corresponding carbonyl compounds. These data indicate that the sugar moiety undergoes a variety of reactions including dehydration, rearrangement, and fission. Addition of zinc chloride enhanced the dehydration and rearrangement reactions, resulting in increased formation of 5-hydroxymethyl-2-furaldehyde and glucometasaccharinic acid, whereas the addition of sodium carbonate enhanced the fission and rearrangement reactions leading to the formation of glyceraldehyde, 1-hydroxy-2-propanone or pyruvaldehyde, and glycolaldehyde. These changes in the course of the reactions could also be detected by thermal analysis of the samples of 3-deoxy compound containing zinc chloride or sodium carbonate. As seen in Fig. 3, addition of zinc chloride lowers the decomposition temperature within the broad range 95–155°, and produces more char (52% at 400°).

The combination of the data in Table I and Figs. 1 and 3 shows that the 3-deoxy compound disappears much faster than could be accounted for by the loss in weight (due to volatilization) and the formation of the above monomeric products. Also, reaction mixtures formed within the range 100–185°, after reduction, gave a continuous strip between the starting point and the location of 3-deoxyhexitols in t.l.c., suggesting that other non-volatile compounds of high molecular weight must be produced.

TABLE I

MONOMERIC PRODUCTS FORMED BY HEATING 3-DEOXY-D-*erythro*-HEXOSULOSE TO VARIOUS TEMPERATURES AFTER REDUCTION WITH SODIUM BOROHYDRIDE

Conditions		*3-Deoxy-D-hexitols* (%)	*2,5-Dihydroxymethylfuran* (%)	*Glucometasaccharinic acid*		*Glycerol* (%)	*1,2-Dihydroxypropane* (%)	*Ethylene glycol* (%)
Additive	*Temperature of samples (degrees)*			*1,4-lactone* (%)	*free acid* (%)			
None	70	97.3	—	—	—	—	—	—
	95	90.5	—	—	T[a]	—	—	—
	105	77.5	—	T	0.2	—	—	—
	120	59.5	T	T	1.0	—	—	—
	145	41.8	0.3	T	1.3	T	T	T
	163	36.0	0.6	T	1.5	0.1	0.2	0.1
	170	20.1	0.8	T	0.8	0.3	0.3	0.1
5% of $ZnCl_2$	70	95.5	—	—	—	—	—	—
	90	70.8	T	T	4.0	—	—	—
	100	63.0	2.5	0.1	5.0	—	—	—
	120	36.5	6.3	T	3.2	—	—	—
	150	5.1	0.6	T	2.6	T	T	T
5% of Na_2CO_3	80	94.0	—	—	—	—	—	—
	95	85.2	—	T	1.4	—	—	—
	120	30.1	—	T	6.4	0.3	0.4	0.1
	155	8.0	—	T	7.4	0.5	0.6	0.2

[a]T = trace amounts.

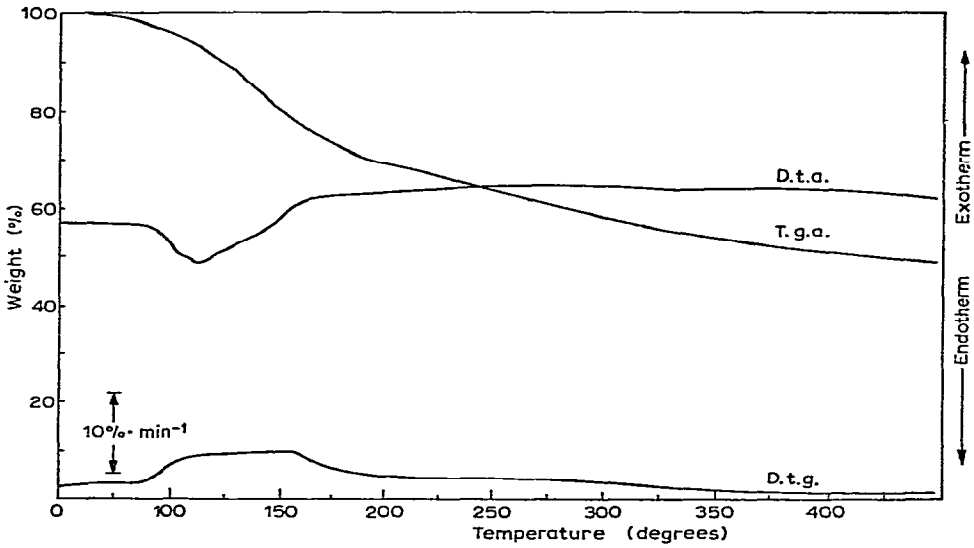


Fig. 3. Thermograms of 3-deoxy-D-*erythro*-hexosulose in the presence of 5% of $ZnCl_2$: D.t.a. is given on the right-hand scale, T.g.a. on the left-hand scale, and D.t.g. on the scale indicated.

To investigate the nature of the polymeric products, 3-deoxy-D-*erythro*-hexosulose was heated to 185° and then fractionated into methanol-soluble (*A*) and -insoluble (*B*) portions. These fractions were then reduced and analyzed by g.l.c. (see Table II). Fraction *A* contained ~20% of monomeric materials, including 17.5% of the 3-deoxyhexitols, and gave an insoluble residue and ~40% of additional monomeric compounds on acid hydrolysis. The hydrolysis products consisted mainly of D-glucitol (17.5%) and two unknown compounds (15%) which appear to be isomers or closely related derivatives of 3,6-anhydro-D-glucose. There was also an additional proportion of the 3-deoxyhexitols (2.8%) and a small proportion of 3,6-anhydro-D-glucose (1.8%).

Fraction *B* did not contain any monomeric compound, but, on hydrolysis with acid, yielded ~40% of monomeric products consisting mainly of α- and β-D-glucopyranose (11.5 and 7.8%, respectively), D-glucitol (9.3%), the unknowns (9%), 3,6-anhydro-D-glucose (4%), and some insoluble condensation products. The unknown compounds gave mass spectra closely similar to that of 3,6-anhydro-D-glucose, and were formed by treatment of the latter compound with aqueous acid[24].

Formation of 3,6-anhydro-D-glucose and D-glucose derivatives on hydrolysis of the polymeric materials with acid indicates that heating not only results in elimination of the substituents (dehydration), but also effects the reverse process, namely, inter- and intra-molecular addition involving the enolic double bond.

As noted before, further heating resulted in continued evolution of water, carbon dioxide, and carbon monoxide, and also charring of the residue. A sample heated to 210° contained very little 3-deoxy and other monomeric compounds, was

TABLE II

ACID HYDROLYSIS OF THE REACTION PRODUCTS (AFTER REDUCTION WITH SODIUM BOROHYDRIDE) FORMED BY HEATING 3-DEOXY-D-*erythro*-HEXOSULOSE TO 185°

Fraction	*3-Deoxy-D-hexitols* (%)	*2,5-Dihydroxymethylfuran* (%)	*Saccharinic lactone* (%)	*Saccharinic acid* (%)	*Glycerol* (%)	*2-Deoxy-D-erythro-pentitol* (%)	*Unknowns* (%)	*3,6-Anhydro-D-glucose* (%)	*3-Deoxy-D-hexose* (%)	*3,6-Anhydro-D-glucitol* (%)	*D-Glucitol* (%)	*α-D-Gluco-pyranose* (%)	*β-D-Gluco-pyranose* (%)
A. Methanol-soluble													
Before hydrolysis	17.5	1.5	0.5	0.3	1.3	1.1	—	T[a]	—	—	—	—	—
After hydrolysis	20.3	1.0	0.6	0.2	1.2	0.8	15	1.8	0.1	T	17.5	T	T
B. Methanol-insoluble													
Before hydrolysis	—	—	—	—	—	—	—	—	—	—	—	—	—
After hydrolysis	T	—	T	T	—	—	9	4.0	T	T	9.3	11.5	7.8

[a]T = trace amounts.

soluble in water, and was immobile on t.l.c. It showed u.v. absorption with maxima at 220 and 285 nm, and i.r. absorption bands at 3100 and 1590 cm^{-1} for unsaturation, and at 1750 and 1850 cm^{-1} for carbonyl functions. The u.v. and i.r. absorptions were stronger in the condensation products obtained on addition of zinc chloride, and weaker when sodium carbonate was added. The residue left at 225° was highly condensed, and could not be hydrolyzed under acidic conditions. An e.s.r. investigation of pyrolysis wihin the range 70–280° indicated that the initial decomposition reactions are heterolytic, but the charring reactions which take place above 200° are accompanied by the formation of stable free-radicals. Again, this process is facilitated by the addition of zinc chloride, and the increasing intensity of the free-radical signals within the range 160–240° is shown in Fig. 4, which shows results very similar to those obtained for levoglucosan[11].

Heating at elevated temperatures not only effects charring of the residue by further condensation and elimination of substituents, but also results in further rearrangement and disproportionation of the initial, dehydration, and fission products. As shown in Table III, pyrolysis of the neat sample at 550° gives ~10% of organic volatile products, 38% of char, 18.5% of water, 12.5% of carbon dioxide, and 4% of carbon monoxide. The balance of 17% is accounted for by a tar fraction. Detailed analysis of the pyrolysis products (Table III) indicated a preponderance of dehydration reactions resulting in the formation of furan derivatives, including

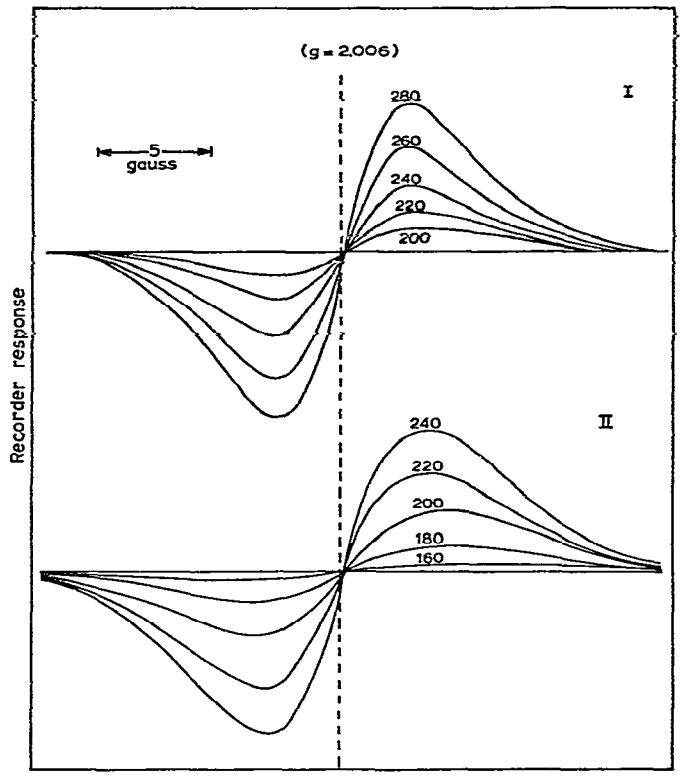


Fig. 4. E.s.r. signals formed on heating 3-deoxy-D-*erythro*-hexosulose in the absence (I) and presence (II) of zinc chloride to various temperatures at the rate of $\sim 10°.min^{-1}$.

2-furaldehyde, 2-methylfuran, 5-methyl-2-furaldehyde, 2-furfuryl alcohol, and furan, plus water and char. Formation of these products was further enhanced by the addition of zinc chloride. The volatile fraction also contained some acetaldehyde, propenal, 2-butenal, 1-hydroxy-2-propanone, glyoxal, and carbon monoxide, and these compounds, considered as fission products, were increased by the addition of sodium carbonate.

G.l.c. analysis of the tar fraction produced in absence of any additives (Table IV) gave 24% of the 3-deoxyhexitols (amounting to 4% of the original material), 10% of the primary pyrolysis products, and ~65% of condensation products which had evaporated and escaped further decomposition.

The above data clearly show that 3-deoxy-D-*erythro*-hexosulose decomposes rapidly within the range 100–200° (see Fig. 1), as compared to D-glucose[3], levoglucosan[10], and various glycosides[3–7] which decompose at much higher temperatures (250–350°). Within this range, a small fraction of the compound gives monomeric products of dehydration, fission, and rearrangement (see Table I), whereas most of the compound undergoes condensation. The condensation reactions involve more than

TABLE III

PRODUCTS OF THE PYROLYSIS OF 3-DEOXY-D-*erythro*-HEXOSULOSE AT 550°

Pyrolysis product	*Yield* (%)		
	Neat	$+ZnCl_2$	$+Na_2CO_3$
Acetaldehyde	1.5	0.5	2.1
Furan	0.6	0.2	0.5
Acrylaldehyde	T[a]	T	0.6
2-Methylfuran	2.0	5.8	1.1
2,3-Butanedione	T	T	1.3
2-Butenal	0.8	0.4	1.0
1-Hydroxy-2-propanone, Glyoxal	0.8	0.1	2.6
Acetic acid	0.2	0.1	0.6
2-Furaldehyde	3.1	6.5	0.1
5-Methyl-2-furaldehyde	0.8	0.9	0.6
2-Furfuryl alcohol	0.1	T	T
Carbon monoxide	4.0	3.3	4.4
Carbon dioxide	12.4	8.1	16.1
Water	18.4	22.3	16.8
Char	38.2	45.1	35.2
Balance (tar)	17.1	6.7	17.0

[a]T = trace amounts.

TABLE IV

MONOMERIC PRODUCTS OF THE TAR FRACTION FORMED BY PYROLYSIS OF 3-DEOXY-D-*erythro*-HEXOSULOSE AT 550° AFTER REDUCTION WITH SODIUM BOROHYDRIDE

Product	*Yield* (%)
3-Deoxy-D-hexitols	24.7
Glycerol	8.3
3,6-Anhydro-D-glucose	2.6
2-Deoxy-D-*erythro*-pentitol	1.3
2,5-Dihydroxymethylfuran	0.5
Glucometasaccharinic acid 1,4-lactone	T[a]
3,6-Anhydro-D-glucitol	T

[a]T = trace amounts.

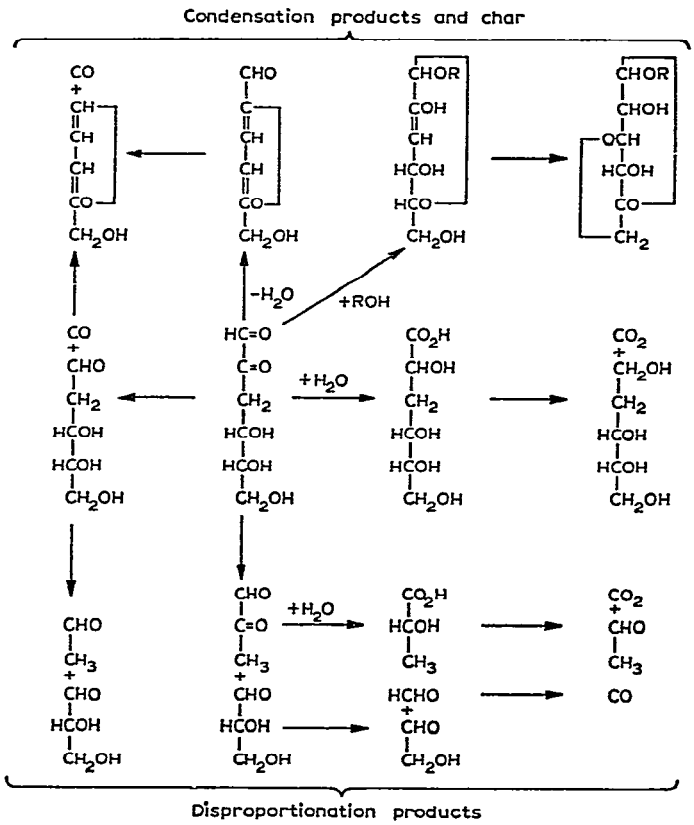
acetal or glycosyl polymerization, because only a portion of the products could be hydrolyzed to monomeric compounds, which include 3,6-anhydro-D-glucose and D-glucose derivatives, indicating the formation of intramolecular ether bonds and an addition reaction through the enolic double bond.

On further heating, the condensation products became resistant to hydrolysis by aqueous acid, and could not be broken down by thermal transglycosylation, which occurs on pyrolysis of glycosides and polysaccharides, because of the absence of hemiacetal or glycosidic bonds. Consequently, gradual charring occurred, leaving a

large proportion of carbonaceous residue (see Fig. 1). Accordingly, the charring process involves initial condensation of the monomeric materials followed by elimination of water and homolytic cleavage of carbon-chain substituents. It has been shown already that the free radicals associated with char are quite stable, and form new carbon–carbon bonds at still higher temperatures[1]; amino sugar derivatives give a similar dehydration pattern and substantial proportions of char[25].

Higher temperatures also enhance the concurrent dehydration and fission of the sugar moiety to monomeric compounds, and their further disproportionation and randomization products.

Reactions of carbohydrates in aqueous systems[16–18,26], such as dehydration and the formation of furan compounds, residual char, and saccharinic acid, which require interaction of the 3-deoxy compound with water, are catalyzed by the addition of Lewis acid. Addition of alkali promotes the fission of the molecule through dealdolization. In addition to the reactions observed in aqueous system, there are some decarbonylation, decarboxylation, and disproportionation reactions which may be considered to be peculiar to pyrolytic reactions[10,11].



Scheme 1. The pyrolytic reactions of 3-deoxy-D-*erythro*-hexosulose.

The above concurrent and consecutive reactions have been summarized in Scheme 1. Since, at high temperatures, the energy barrier becomes less significant, this scheme is much more complex than a single pathway generally postulated for reactions in aqueous system, and shows the phenomena common in the thermal decomposition of carbohydrates.

EXPERIMENTAL

Preparation of samples. — 3-Deoxy-D-*erythro*-hexosulose was prepared by a combination of previously described methods[20–22]. D-Glucose (30 g) was reacted with butylamine (12 g) in methanol to produce *N*-butyl-D-glucosylamine, which was converted into the corresponding 3-deoxyhexosulose on treatment with glacial acetic acid[21,22]. The mixture was then treated with benzoylhydrazine, and the resulting 3-deoxy-D-*erythro*-hexosulose bis(benzoylhydrazone) was recrystallized from ethanol; yield, 6 g; m.p. 191–192°; lit.[22] m.p. 191–192°). Treatment of the product with benzaldehyde[22] gave 3-deoxy-D-*erythro*-hexosulose as an amorphous powder. The product showed no u.v. absorption at 210–360 nm, indicating the absence of any enolic form[16].

A sample of 3-deoxy-D-hexosulose containing 5% of sodium carbonate was obtained by grinding the calculated proportions of the two compounds to a fine powder in a mortar. A sample of 3-deoxy compound containing 5% of zinc chloride was prepared by adding the calculated proportion of zinc choride in ether and evaporating the solvent under vacuum. The samples were stored under anhydrous conditions.

Analytical methods. — The thermal analysis, u.v. and e.s.r. spectroscopy, and g.l.c. of the 3-deoxy compound and its transformation products were performed as described previously[3,5,12]. The thermal analysis was programmed at the rate of 15°.min^{-1}. T.l.c. was performed on silica IB-F (Bakerflex), using 1-butanol–pyridine–water (6:4:3).

3-Deoxy-D-*erythro*-hexosulose and other samples for chromatographic analyses were reduced with sodium borohydride, as previously described[14,23].

Mass spectrometry. — Water, carbon monoxide, and carbon dioxide evolved on gradual heating of samples were monitored by mass spectrometry, using a Varian-Mat III spectrometer at 80 eV. A sample (2 mg) of the 3-deoxy compound was placed in a small pan, and heated, at the rate of 15°.min^{-1}, in a current of helium directly connected to the mass spectrometer. The rates of release of water, carbon monoxide, and carbon dioxide were determined by the changes in the ratio of the peaks at *m/e* 17, 28, and 44, respectively, to the peak at *m/e* 32 for background oxygen. These ratios were found to be constant in blank experiments. The results are shown in Fig. 2.

Thermal reaction. — Samples (~2 mg) of 3-deoxy-D-*erythro*-hexosulose, either neat or containing the additives, were heated in a d.t.a. instrument at the rate of 15°.min^{-1} to temperatures corresponding to the various thermal events. The heated samples were then reduced with sodium borohydride and trimethylsilylated, and the

products were analyzed by g.l.c., using D-glucitol as an internal standard. The results are summarized in Table I.

The reference compounds α- and β-D-glucometasaccharinic acid and the 1,4-lactones were prepared as previously described[27]; 3-deoxy-D-hexitols and 2,5-bis(hydroxymethyl)furan were obtained by the reduction of 3-deoxy-D-*erythro*-hexosulose and 5-(hydroxymethyl)-2-furaldehyde, respectively, with sodium borohydride.

Isolation and investigation of the thermal condensation products. — A sample (76 mg) of 3-deoxy-D-*erythro*-hexosulose was placed in a small ampoule (5 ml), which was flushed with nitrogen, and heated to 185°, at the rate of $\sim 15°.min^{-1}$, in a Fisher–Johns melting-point apparatus. The heated mixture was separated into two fractions with methanol (3 ml): a methanol-soluble fraction (*A*, 60 mg), and a methanol-insoluble, but water-soluble fraction (*B*, 4.7 mg). Both fractions were subsequently reduced with sodium borohydride, trimethylsilylated, and analyzed for monomeric compounds by g.l.c. Each fraction, after reduction, was hydrolysed with boiling M hydrochloric acid for 4 h. Small proportions of these materials became insoluble after the acid treatment. The solution was neutralized with Amberlite IR-45(HO^-) resin, filtered, and evaporated to dryness. The residues, after trimethylsilylation, were then analyzed by g.l.c., and the results are summarized in Table II.

The reference compounds 3,6-anhydro-D-glucose[28] and 3-deoxy-D-*ribo*-hexose[25] were obtained by previously described methods; 3,6-anhydro-D-glucitol and 2-deoxy-D-*erythro*-pentitol were prepared by reduction of 3,6-anhydro-D-glucose and 2-deoxy-D-*erythro*-pentose, respectively, with sodium borohydride.

Thermal degradation. — Samples (100 mg) of the 3-deoxy compound, either neat or treated with zinc chloride or sodium carbonate, were heated under nitrogen for 8 min at 550° in a modified Sargent microcombustion unit attached to a series of receptacles[11]. This gave a charred residue, a tar fraction that condensed on the pyrolysis tube, an aqueous pyrolysate that was collected in a Dry Ice–acetone trap, and uncondensed gases.

Among the gases, carbon dioxide was recovered as barium carbonate in traps containing a solution of barium hydroxide, and was analyzed by titration with dilute oxalic acid (0.02M); carbon monoxide was oxidized with iodine pentaoxide[29], and then analyzed as carbon dioxide in the same manner.

The tar fraction, after reduction with sodium borohydride and trimethylsilylation, was analyzed for monomeric products by g.l.c.

For direct analysis of the volatile products, samples (5 mg) of the 3-deoxy compound in the absence or presence of catalysts were pyrolyzed at 550° in a modified Perkin–Elmer pyrolysis unit connected to a gas chromatograph. The peaks were identified by established methods[4,10]. The results are summarized in Tables III and IV.

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