Tetrahedron Letters No.14, pp. 1297-1300, 1967. Pergamon Press Ltd. Printed in Great Britain.

THERMAL DECOMPOSITION OF D-GLUCOSE LABELLED WITH ^{14}C AT VARIOUS POSITIONS

Yoram Houminer and Saul Patai
Department of Organic Chemistry, The Hebrew University,
Jerusalem, ISRAEL

(Received 27 January 1967)

The thermal decomposition mechanism of D-glucose and other related sugars is a very complicated one (1). Roughly it consists of two different types of reactions: inter- or intra-molecular dehydration (2) and fragmentation of the carbon skeleton of the D-glucose molecule (1,3). It is not yet clear whether these two reactions are parallel or consecutive, but it is known that at the beginning of the thermal decomposition the dehydration is much faster than the fragmentation process (4). A large variety of decomposition products from D-glucose were identified (1,3,5) and based on the nature of these, a mechanism was proposed (5,6).

Continuing our investigation on the pyrolytic reactions of carbohydrates (7), we obtained basic information regarding the pethways through which the carbon skeleton of the glucose molecule is cleaved during its thermal decomposition, using glucose labelled with ^{14}C either uniformly or at the positions 1, 2 or 6.

The materials used were obtained by dilution of commercially available ^{14}C labelled D-glucose samples (Radiochemical Center, Amersham, U.K.) with D-glucose (Analar). Recrystallization twice was esential and critical since very small amounts of impurities were found to have a significant catalytic effect on the reaction. One gram of D-glucose with a specific activity of about 1 μc/g. was taken for each experiment and heated in vacuo ($<10^{-3}$ mm.Hg) for 4 hours at various temperatures. In each run, three fractions were separated and collected: carbon monoxide, carbon dioxide and a volatile liquid fraction consisting mainly of water. The amount and radioactivity of each fraction was measured, using a liquid scintillation counting method. A special device was developed by us enabling the absorption of carbon dioxide into Hyamine directly in the counting vial <u>in vacuo</u>. Carbon monoxide was oxidized to carbon dioxide and determined by the same method.

Table 1 shows the relative contribution of the different carbon atoms in the glucose molecule to the formation of carbon dioxide and carbon monoxide at different temperatures.

Obviously the formation of carbon oxides may occur through several different pathways: probably each of the carbon atoms in the glucose molecule can form carbon dioxide as well as carbon monoxide in varying amounts depending on the temperature at which the reaction is carried out. Manifestly, the contribution of C-1 is dominant at all temperatures studied and that of C-2 is quite big at 200°C but falls at 225°C and at 250°C. The relative contributions of the different carbon atoms to the formation of carbon monoxide and of carbon dioxide are similar.

Examination of the total radioactivity of the aqueous fraction showed that from the decomposition of C - 1 and C - 2 labelled glucose comparatively much more activity reaches this fraction than in the case of the C - 6 labelled or uniformly labelled substrates, showing that the volatile fragments are formed preferentially with the involvment of C - 1 and C - 2

We carried out thin layer chromatography of the aqueous fraction

TABLE 1

Contribution of the Different Carbon Atoms in the Glucose Molecule to the Formation of CO and CO_2 in % During the Thermal Decomposition of D-Glucose.

$T^{o}C$	Labelling position in the glucose molecule	Contribution to the formation of CO_2 in %.(a)	Contribution to the formation of CO in %. (b)
200	C - 1	47	(c)
	C - 2	22	(c)
	C - 6	10	(c)
225	C - 1	57	67
	C - 2	12	16
	C - 6	7	9
250	C - 1	51	60
	C - 2	11	14
	C - 6	11	12

(a) Reliability of these determinations was about ± 3%.

(b) Reliability of these experiments (since they involved much smaller volumes of gas, followed by a combustion process) was about ± 5%.

(c) The amount of CO formed in these experiments was only 2-3 times larger than the expected experimental error, hence no calculations were made.

in each experiment and identified some of the products and also measured their radioactivity. It was found that in the spot containing furfural, practically no activity was present if the starting material was labelled only at C - 6 and practically all of the activity was retained with the other labelled substrates.

The above mentioned facts emphasize the complexity of the processes involved in the thermal decomposition of glucose. Much further basic research is needed in order to elucidate the routes and mechanisms of these processes.

Acknowledgement: This research has been financed in part by a grant made by the United States Department of Agriculture.

REFERENCES

1. K. Heyns, R. Stute and H. Paulsen, Carbohydrate Research, 2, 132 (1966).
2. J.W. Liskowitz, Diss. Abs., 23 1945 (1962)
3. H. Sugisawa, J. Food Sci., 31, 381 (1966).
4. I.E. Puddington, Canad. J. Res., B,26, 415 (1948).
5. D. Gardiner, J. Chem. Soc. (C), 1473 (1966).
6. D.J. Bryce and C.T. Greenwood, Die Stärke, 359, (1963).
7. A. Broido, Y. Houminer and S. Patai, J. Chem. Soc. (B), 411 (1966).