

Radiation Degradation of Crystalline D-Fructose and α -Lactose Monohydrate

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Crystalline D-fructose and α -lactose monohydrate are considerably more sensitive towards ionizing radiations than other studied carbohydrates.^{1,2} Initial G-values of about 40 for D-fructose¹ and about 50–55 for α -lactose monohydrate^{1,2} have been recorded. The method employed in the determination of the degradation includes, however, dissolution of the irradiated solid sample in water as a primary step, followed by isotope dilution and synthesis of a suitable derivative.^{1,2} Hence, the measured breakdown may also comprise possible degradative reactions during the dissolution in water in addition to the effects already present in the solid state. We have now measured the degradation of D-fructose and α -lactose monohydrate irradiated in the solid state by a technique which may exclude dissolution in water.

Experimental. Pyridine was added to a weighed amount of the irradiated (or unirradiated) sample and to a weighed amount of a suitable internal standard (mannitol for fructose and trehalose for lactose). The trimethylsilyl derivatives were then prepared as described by Sweeley *et al.*³ The pyridine solution of the derivatives was analyzed by gas chromatography on a Perkin Elmer F 11 with FID detection and a 1.4 m \times 2.2 mm glass column packed with 2 % SE 30 on Chromosorb W 60–80 mesh. The column temperature was 165°C for the monosaccharide and 230°C for the disaccharide analysis. The amount of fructose and lactose in relation to the internal standards was determined by planimetry of the chromatograms.

This technique has certain limitations. The derivative synthesis and the gas chromatographic analysis introduce experimental errors of one or a few per cent, and these errors become amplified in the final result as the measured degradation is a difference between two large values. In the present case, it seems to us that the

analyses of fructose were less variable than those of lactose; this might be due to the fact that fructose readily dissolves in the pyridine whereas lactose does not dissolve until after the silylating reagents have been added. Also, the possibility exists that some silyl derivative(s) of the degradation products may chromatograph within the fructose and lactose peaks, which would result in a degradation yield lower than the true value.

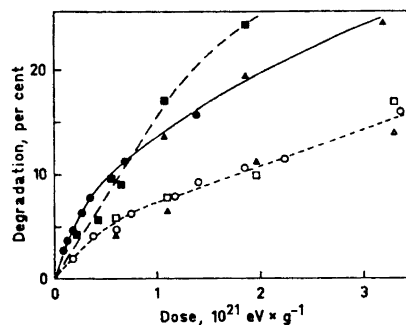


Fig. 1. γ -Radiation induced degradation yield vs. dose for crystalline D-fructose (open symbols) and α -lactose monohydrate (filled symbols): \circ , \bullet , determined by ^{14}C -isotope dilution after dissolution in water (Ref. 1); \triangle , \blacktriangle , determined by gas chromatography of the trimethylsilyl derivative prepared after dissolution in water and subsequent freeze-drying; \square , \blacksquare , determined by gas chromatography of the trimethylsilyl derivative with pyridine as the only solvent for the samples.

In Fig. 1 the radiation induced degradation of D-fructose and α -lactose monohydrate, as determined by gas chromatography of the trimethylsilyl derivatives, is compared with the previously reported degradation, as determined by ^{14}C -isotope dilution. The gas chromatographic determination has been applied to samples directly after the irradiation as well as to samples which were first dissolved in water after the irradiation and then freeze-dried. The results for D-fructose show that the degradation is independent of the mode of dissolution and method of analysis. For α -lactose monohydrate the results are similar, although it is indicated that the degradation might be more linearly dependent on the dose when pyridine is the solvent than when water is the solvent. A

G-value of about 26 can be calculated from the assumed linear part of the degradation curve for pyridine as solvent. This is not significantly different from the average slope of the degradation curve for dissolution in water within the same dose interval, *i.e.* $0.3 \times 10^{21} - 10^{21}$ eV g^{-1} .

It therefore seems most likely that the dissolution in water is not a reason for the high radiation induced degradation of these crystalline carbohydrates but that the major part or all of the degradation is present already in the solid state. Ahmed *et al.*² have inferred a similar conclusion indirectly by means of spectroscopic studies of irradiated lactose samples.

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2. Ahmed, N. U., Baugh, P. J. and Phillips, G. O. *J. Chem. Soc. Perkin Trans. 2* **1972** 1305.
3. Sweeley, C. C., Bentley, R., Makita, M. and Wells, W. W. *J. Am. Chem. Soc.* **85** (1963) 2497.

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Polychlorinated Biphenyls

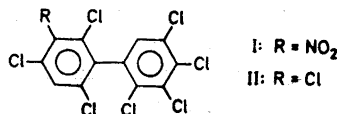
IV.* Synthesis of 2,2',3,3',4,4',5,6'-Octachlorobiphenyl-¹⁴C from 3-Nitro-2,2',3',4,4',5,6'-heptachlorobiphenyl-¹⁴C and Tetrachloromethane**

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As a part of an investigation concerning the distribution and metabolism in mice and quails of the industrial chemical and environmental pollutant PCB (polychlorinated biphenyls)¹⁻³ we recently reported the syntheses of some ¹⁴C-labelled tetra- and hexachlorobiphenyls.^{4,5} The simple syntheses of some unlabelled tetra- and pentachlorobiphenyls were also reported.⁶

The present paper describes the synthesis of 2,2',3,3',4,4',5,6'-octachlorobiphenyl-¹⁴C (II) labelled in the 2,3,4,6-substituted ring. Acetylation of aniline-¹⁴C hydrogen sulphate followed by chlorination⁶ gave 2,4,6-trichloroacetanilide-¹⁴C⁶ which was nitrated to give 3-nitro-2,4,6-trichloroacetanilide-¹⁴C.⁷ Hydrolysis of the anilide gave 3-nitro-2,4,6-trichloroaniline-¹⁴C, which was coupled with 1,2,3,4-tetrachlorobenzene by the method of Cadogan⁸ (*cf.* Refs. 5, 6) to yield 3-nitro-2,2',3',4,4',5,6'-heptachlorobiphenyl-¹⁴C (I). The nitroheptachlorobiphenyl I on treatment with tetrachloromethane at 280–290° for 70 min gave 2,2',3,3',4,4',5,6'-octachlorobiphenyl-¹⁴C (II) (isotope yield from I, 72 %).



The labelled compound was chromatographically identical (TLC, GLC) with 2,2',3,3',4,4',5,6'-octachlorobiphenyl as

* Part III, Ref. 5.

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