Formaldehyde Yield in Irradiated D-Fructose

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Irradiation of solid carbohydrates may give rise to molecular structures having C=O bonds as has been revealed by IR measurements in which absorption appears in the 1700–1740 cm⁻¹ region. Following dissolution of irradiated glucose in water, acetone and acetaldehyde have tentatively been suggested to occur. We have in this laboratory further studied the radiation-induced formation of keto-compounds in several carbohydrates by means of precipitation with 2,4-dinitrophenylhydrazine and subsequent analyses of the hydrazones by thin layer chromatography. Generally, at least 20–25 different spots can be detected. The separation as well as the evaluation of the analyses are, however, severely hampered by an instability of many of the hydrazones both during storage in solution and as solid dry material.

With the aid of a gas chromatographic method reported by Barrera et al., it is now possible to identify and quantify 2,4-dinitrophenylhydrazones of certain low molecular weight keto-compounds. Using this method we have studied the formation of formaldehyde in γ-irradiated solid D-fructose.

The solid D-fructose was irradiated at room temperature with 60Co γ-rays at a dose rate of 4 × 10¹⁵ eV/g. Ten grams of the irradiated sample were dissolved in 50 ml triple distilled water. Various amounts of 2,4-dinitrophenylhydrazine, dissolved in 150 ml of a 1:1 2 N aqueous HCl—ethanol solution, were added to the fructose solution. The precipitation was carried out at refrigerator temperature in order to avoid a reaction between 2,4-dinitrophenylhydrazine and unchanged fructose. After 2 h storage the precipitate was filtered off, washed, vacuum dried, and weighed. A weighed amount of the precipitate was mixed with a measured volume of CHCl₃, generally in the range of 2–10 % w/v. The slurry was thoroughly crushed and stirred after which the undissolved precipitate was separated from the supernatant. By this process, hydrazones of low molecular weight keto-compounds are concentrated in the supernatant over other hydrazones and bis-hydrazones occurring in the precipitate.

Volumes of the CHCl₃ solution of the order of µl were analyzed in a Perkin Elmer F 11 gas chromatograph with conditions described by Barrera et al. As references were used the 2,4-dinitrophenylhydrazone of formaldehyde dissolved in CHCl₃ as well as internal standards in which known amounts of formaldehyde were added to the solution of the irradiated fructose prior to precipitation of the keto-compounds. A comparison between the two references shows that the recovery of formaldehyde from the solution is about 70 %. The identification of formaldehyde relies on the identical retention time of reference and fructose sample and on the fact that all other hydrazones have longer retention times.

Irradiation of D-fructose and subsequent dissolution in water yields formaldehyde in

![Graph](image)

**Fig. 1.** The radiation-induced formation of formaldehyde from solid D-fructose. Filled circles, ⬤, give experimental results plotted against the linear scales on the left and at the bottom. Crosses, ×, give experimental results plotted against the logarithmic scales on the right and at the upper side. The dashed line, ——, joining the experimentally obtained results, has been calculated from the deduced second order dose dependence (cf. text).

an exponential dose response (Fig. 1), which may be expressed as

\[ \text{yield} = \text{constant} \times (\text{dose})^2 \]  

(1)

A log-log plot of the yield-dose curve shows that the exponent 2 well fits the results (Fig. 1). Least-square analyses of eqn. (1) in the logarithmic form give a constant of \(5 \times 10^{-14}\) or \(4 \times 10^{-14}\) molecules \(\text{HCHO} \times \text{g} \times (\text{eV})^{-2}\), using, resp., all doses or excluding the two lowest ones in the calculations. The dashed line in Fig. 1, joining the experimental results of the yield-dose data, has been calculated with a constant of \(4.5 \times 10^{-14}\) molecules \(\text{HCHO} \times \text{g} \times (\text{eV})^{-2}\).

Identification of the constant with the terms in the radiation hit theory equation for a two hit event\(^4\) gives the expression

\[ V/E^2 = 5.8 \times 10^{-24} \]

where \(V\) is the target volume in cm\(^3\) and \(E\) is the energy in eV per hit. If a target of size \(V\) is hit twice with \(E\), one molecule of formaldehyde is formed.

The complete target volume of solid fructose is not known. If, however, intermolecular hydrogen bonding is not involved, a target of 185 Å\(^3\) can be assumed; i.e. one fourth of the volume of the D-fructose unit cell which contains four molecules.\(^7\) With a value of \(V = 185\) Å\(^3\), \(E\) becomes 6 eV. If, instead, \(E\) is assumed to be about 30—33 eV, i.e. the energy per ionization, \(V\) becomes 5600 Å\(^3\). This would correspond to a target volume of about 30 molecules.

Radical formation in carbohydrates including fructose occurs with a G-value of \(3—5\); i.e. an energy consumption of 33—20 eV per radical formed.\(^5\)\(^6\) Further, the degradation of solid fructose occurs with G-values of 15—20 in the dose range \(15 \times 10^{16}\) to \(45 \times 10^{16}\) eV/g; corresponding to an energy consumption of \(5\) to \(7\) eV per degraded fructose molecule.\(^9\) The radiation-induced formation of formaldehyde in D-fructose, therefore, seems to be a rather efficient mode of degradation of those molecules which have absorbed radiant energy twice.

Acetaldehyde and acetone as well as formaldehyde have been detected qualitatively in irradiated sucrose and \(\alpha\)-D-glucose.

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