Radiation Chemistry of Carbohydrates. Part I

Radical Chain Reactions in Crystalline α-Lactose Monohydrate

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It has been known for some time that in the γ-radiolysis of some crystalline carbohydrates, *e.g.* α-D-glucose[1-3] and α-lactose · H_2O[2,4,5], acids are formed with high *G*-values*. From the magnitude of the *G*-values chain reactions are to be expected which largely seem to be restricted to the crystalline state[1]. PHILLIPS and BAUGH[1] found for polycrystalline α-D-glucose *G*(acid) = 13.2 whereas freeze-dried samples yield only *G*(acid) = 4. Even more pronounced is this effect in α-lactose · H_2O which gives *G*(acid) ≥ 40[2,4,5] while in the dehydrated form acid is produced with $G = 4.8$[2].

To elucidate the mechanism of such chain reactions we studied the γ-radiolysis of crystalline α-lactose · H_2O. As major products were identified 5-deoxy-lactobionic acid ($G = 40$), 2-deoxy-lactobionic acid lactone ($G = 20$), and galactonic acid lactone ($G = 4.5$) as well as 4-deoxyglucose ($G = 4.5$) (dose $< 4 \cdot 10^{20}$ eV/g, dose rate $1.35 \cdot 10^{18}$ eV/$g \cdot$ min). The products were identified by g.l.c. -m.s. after trimethylsilylation. The deoxy-lactobionic acids had to be hydrolized prior to this procedure. The structures were confirmed by reducing the product with $NaBD_4$ yielding deuterated polyalcohols with interpretable mass spectra[6,7].

The above products point to the existence of three chain reactions in α-lactose · H_2O, their nature being analogous or at least quite similar to that in ethylene glycol[8-12] (which even occurs in diluted aqueous solutions). This chain process is given by the Equs (1)–(3).

$$R\cdot + CH_2OH\text{-}CH_2OH \rightarrow RH + \underset{\mathbf{1}}{\cdot CHOH\text{-}CH_2OH} \quad (1)$$

$$\underset{\mathbf{1}}{\cdot CHOH\text{-}CH_2OH} \rightarrow H_2O + \underset{\mathbf{2}}{CHO\text{-}CH\cdot_2} \quad (2)$$

$$\underset{\mathbf{2}}{CHO\text{-}CH\cdot_2} + CH_2OH\text{-}CH_2OH \rightarrow CHO\text{-}CH_3 + \underset{\mathbf{1}}{\cdot CHOH\text{-}CH_2OH} \quad (3)$$

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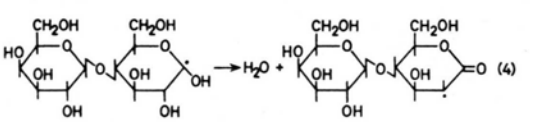
* The *G*-value is defined as number of molecules formed per 100 eV energy absorbed.

Hydrogen abstraction from ethylene glycol yields radical **1** which can eliminate water to give **2**. This radical is not stabilized by a hydroxyl group and is capable of abstracting hydrogen from another ethylene glycol molecule (reaction (3)) giving rise to the radical **1** which propagates the chain.

For chain propagation in a carbohydrate crystal there are three requirements, namely, the hydrogen abstracting radical (*e.g.* a radical not stabilized by hydroxyl groups), readily abstractable hydrogen, and sufficient proximity of these centers (this point will be discussed elsewhere). The most readily available hydrogens in lactose are those in the positions C-1 and C-1′, and since acids are formed these positions must be involved in the chain reaction.

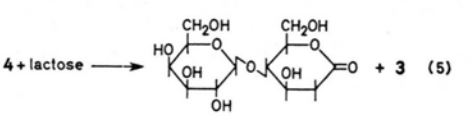
Route 1

In a water elimination process analogous to the one occurring with ethylene glycol (reaction (2)), radical **3** can split off water giving rise to radical **4** (reaction (4)). This process has been postulated by NORMAN and PRITCHETT[13] to interpret their ESR spectra obtained while reacting glucose with the Ti^{3+}-H_2O_2 reagent. Products from this type of radical were obtained in the γ-radiolysis of aqueous solutions of cellobiose[14,15], glucose[16,17] and ribose[18].



3 **4**

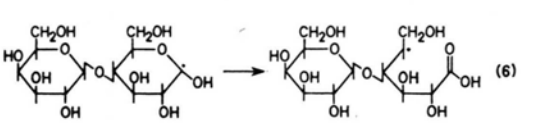
Radical **4** is a hydrogen abstracting radical similar to **2**. When abstracting hydrogen from C-1 at a neighbouring lactose molecule it is converted to 2-deoxy-lactobionic acid lactone ($G = 20$) regenerating the radical **3** (reaction (5)).



2-deoxy-lactobionic acid lactone

Route 2

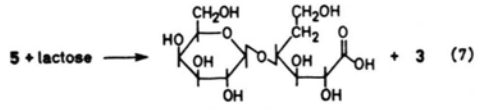
It has been shown in the radiolysis of 2-deoxy-ribose[19] and cellobiose[14,15] that radicals of the type of **3** easily rearrange to give radicals of the type of **5** (reaction (6)).



3 **5**

Radical **5** abstracting hydrogen from C-1 at a neighbouring lactose molecule is converted to

5-deoxy-lactobionic acid with the formation of **3** (reaction (7)).

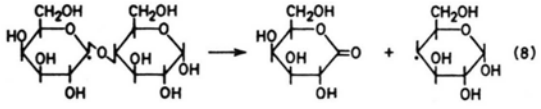


5-deoxy-lactobionic acid

5-Deoxy-lactobionic acid is the major product ($G = 40$).

Route 3

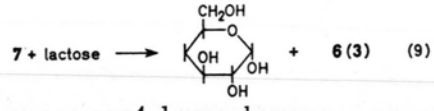
From radical **6** (at C-1') another chain starts involving a rearrangement (reaction (8)) similar to reaction (6). This type of rearrangement has been encountered in the radical-induced scission of the glycosidic linkage in aqueous cellobiose[14,15,20].



6 **7**

galactonic acid lactone

Radical **7** formed by rearrangement of radical **6** (reaction (8)) is again a hydrogen abstracting radical and propagates the chain, by which 4-deoxy-glucose ($G = 4.5$) and galactonic acid lactone ($G = 4.5$) are formed (reactions (8) and (9)).



4-deoxy-glucose

Although a G-value of 4.5 does not necessarily imply a chain reaction, it is believed that in this case 4-deoxy-glucose is indeed formed *via* a chain since in the γ-radiolysis of aqueous solutions of cellobiose (attack by OH radicals) this product has a G-value of only 0.27[15].

Preliminary results incidate that in crystalline α-D-glucose reactions similar to those above yield 5-deoxy-gluconic acid and 2-deoxy-gluconic acid.

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