Radiation Chemistry of Carbohydrates, IX*  
γ-Radiolysis of N-Acetyl-glucosamine in Aqueous Solution  

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Radiolysis, NaBD₄ Reduction, Radical Reactions

The γ-radiolysis of N-acetyl-glucosamine in deoxygenated (N₂O saturated) and oxygenated (N₂O/O₂ saturated) solutions has been investigated. Eleven products have been characterised and their G-values estimated.

Deoxygenated conditions: The principal products identified are 1-acetamido-1,3-dideoxy-2-pentulose (4), 1-acetamido-1-deoxy-2-pentulose (5), 2-acetamido-2,3-dideoxy-hexos-4-ulose (6), 2-acetamido-2-deoxy-hexodialdose (7), 2-acetamido-2-deoxy-bios-5-ulose (8) and 2-acetamido-2-deoxy-gluconic acid (9). Products 1 to 3 contain 3–5 carbon atoms (acetamido group eliminated). Their yields are low.

Oxygenated conditions: G-values of 5, 7, 8 and 9 are increased, whereas compounds containing a deoxy-keto group (4 and 6) are absent. C-C-bond scission is more important in the presence of oxygen. 2-Acetamido-2-deoxy-tetrodialdose (10) has been identified and a number of products with 5 carbon atoms in the chain retaining the acetamido group (11) have been recognised.

Mechanisms for the formation of products are proposed.

Introduction

Although the radiation chemistry of neutral sugars is well on the way to being understood, little is known of the radiation behaviour of amino sugars and their acetyl derivatives¹⁻⁵. Amino sugars are present to a substantial amount in glycoproteins and their related mucopolysaccharides, and the high sensitivity of these biologically important polymers to ionising radiation is well known⁶⁻⁸. Such damage could also cause substantial functional changes of the cell membranes and connective tissue. Thus we have studied the γ-radiolysis of N-acetyl-glucosamine as it is a frequently occurring monosaccharide in these biopolymers.

In this paper we give details of the isolation, identification and determination of irradiation products from N-acetyl-glucosamine solutions. The solutions were either saturated with O₂-free N₂O or with a mixture of N₂O/O₂ (4:1). In both conditions the solvated electrons (eₐq⁻) generated by the radiolysis of water (reaction (1)) are converted into OH radicals (reaction (2)).

\[
\begin{align*}
H₂O & \rightarrow eₐq⁻ + H₂O₂ + H₂ + H⁺ + OH⁻ \\
eₐq⁻ + N₂O & \rightarrow OH + N₂ + OH⁻ \\
OH + RH & \rightarrow H₂O + R⁻ \\
R⁻ + O₂ & \rightarrow RO₂⁻
\end{align*}
\]

The OH radicals (and the H atoms in deoxygenated solution) abstract carbon bound hydrogen atoms from the solute N-acetyl-glucosamine as it is a frequently occurring monosaccharide in these biopolymers.

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Results

a) Deoxygenated solutions

Solutions of N-acetyl glucosamine (10^{-2} M in triply distilled water) were saturated with oxygen free N_{2}O by bubbling the gas through for 30 mins. Irradiations were carried out in the Co-60-\gamma-source from 0.9 to 3.4 \times 10^{19} \text{eV g}^{-1} at a dose rate of 4.3 \times 10^{18} \text{eV g}^{-1} \text{h}^{-1}. The products were fractionated using column chromatography, reduced with NaBD_{4}, trimethylsilylated and identified by GC–MS as described earlier\textsuperscript{9}. Fig. 1 shows a gas chromatogram of an irradiated derivatised sample but without enrichment of products by column chromatography.

GC-peak a (Fig. 1) is preceded by three peaks if the analysis is carried out at lower temperature. They have been assigned to the TMS ethers of glycerol, threitol and erythritol. The precursors of the glycerol can be glyceraldehyde and/or dihydroxyacetone and those of the tetritals, erythrose, threonse and/or erythrulose. As will be shown below, their yield is low and no special efforts have been made to exactly determine the precursors.

GC-peak a (Fig. 1) is due to the TMS ether of arabitol. The precursor is arabinose\textsuperscript{4}.

The following two major peaks designated as b and c in the gas chromatogram (Fig. 1) show the same mass spectrum (Fig. 2). The fragment ions observed have been assigned to originate from the TMS ethers of 1-acetamido-1,3-dideoxy-pentitols-2-d_{1},

The dirigent effect of the deoxy-group typical for this class of compounds\textsuperscript{9} gives rise both to \alpha-fragments without the deoxy group (m/e 175 and 205) as well as \beta-fragments with the deoxy group (m/e 232 (322–90) and 201 (291–90)). m/e 289 (M–15–90) is present. The precursor of these two stereoisomeric...
polyalcohols is 1-acetamido-1,3-dideoxy-2-pentulose (4).

The substances corresponding to peaks d and e in Fig. 1 again show identical mass spectra (Fig. 3).

The carbonyl function present prior to reduction must have been somewhere in the middle of the molecule (two stereoisomers formed on reduction). The position must be next to the acetamido group (m/e 175). This is further evidenced by the ion m/e 320 (410–90) and the absence of m/e 319 (409–90), 218 (308–90) and 206. Elimination of acetamide (59 m.u.) from m/e 379 can also give rise to m/e 320. m/e 377 (M-15–90), 289 (M-103–90), 277 (M-205) are observed as well as the rearrangement ions m/e 260 (289–29) and 248 (277–29). Elimination of 29 m.u. (HCO) probably arises from the intramolecular transfer of a trimethylsilyl group to the amido nitrogen atom. The compounds are assigned to 1-acetamido-1-deoxy-pentitol-2-d1 TMS-ethers.

The precursor is, therefore, 1-acetamido-1-deoxy-2-pentulose (5).

The material from the GC peaks f and g shows identical mass spectra (Fig. 4). They are stereoisomers and their precursor must have a carbonyl function in the middle of the molecule. m/e 175 indicates one deuterium atom at C-1. The fragment ions m/e 292 (M-205) and 233 (292–59) give evidence for a deoxy-group at C-3 (β-fragmentation). The second deuterium atom is incorporated at C-4 as indicated by m/e 292, 233 and 218 (308–90). m/e 303 (393–90) and 304 (394–90) are also observed. The mass spectrum is assigned to originate from the TMS-ether of 2-acetamido-2,3-dideoxy-hexitol-1,4-d2.
The precursor is 2-acetamido-2,3-dideoxy-hexos-4-ulose 6.

Reduction of the starting material with NaBD₄ gives 2-acetamido-2-deoxy-glucitol-1-d₁. The mass spectrum of its TMS ether (h in Fig. 1) is shown in Fig. 5.

The fragmentation pattern is shown above. m/e 320 is thought to arise from m/e 379 by elimination of 59 m.u. (NH₂COCH₃). By column chromatography, material has been separated from N-acetyl-glucosamine which on NaBD₄ reduction and trimethylsilylation gave
mainly 2-acetamido-2-deoxyglucitol-TMS ether and some other stereoisomer (most likely 2-acetamido-2-deoxy-iditol-TMS ether, see below). The mass spectrum of the material from the 2-acetamido-2-deoxy-glucitol-TMS ether peak is given in Fig. 6. It differs from the preceding mass spectrum (Fig. 5) in the prominent fragment ions m/e 391, 308, 218 (308-90), 206, 204, and the absence of m/e 319. The presence of ions 308 and 206 shows that a second D-atom is incorporated. Since m/e 391, but not m/e 392, is present, this D-atom must be at C-6.

The mass spectrum has been assigned to the TMS ether of 2-acetamido-2-deoxy-glucitol-1,6-d_2. The precursor is 2-acetamido-2-deoxy-glucos-5-ulose (7).

The following mass spectrum (Fig. 7) taken from the material of peak i (Fig. 1) is due to a stereoisomer of h.

Prominent fragment ions at m/e 206, 379 and 392 indicate that the incorporated deuterium must be at the C-5 position and cannot be at C-4 or at C-6. The stereoisomer expected if the assignment is correct is the 2-acetamido-2-deoxy-iditol-1,5-d_2 TMS ether.

Its precursor is 2-acetamido-2-deoxy-hexos-5-ulose (8).

Peak k in the gas chromatogram (Fig. 1) is due to material from another stereoisomer of h and i. The mass spectrum is given in Fig. 8. It differs from those in Fig. 6 and 7 in the prominent fragment ions m/e 176 (no m/e 175), 319 (409-90) 307, 217 (307-90), 205, 105 and 103 (104 absent).
The mass spectrum has been interpreted to be due to the TMS ether of 2-acetamido-2-deoxy-hexitol-1,1-d₂.

Its precursor is a 2-acetamido-2-deoxy-hexonic acid lactone (9). In an enriched sample the major part elutes at the position of the 2-acetamido-2-deoxy-glucitol TMS-ether peak. The radiation product is most likely 2-acetamido-2-deoxy-gluconic acid lactone, which is known to be partly converted under weakly basic conditions into 2-acetamido-2-deoxy-mannonic acid lactone. An authentic
sample showed the same behaviour when subjected to our work up conditions. The 2-acetamido-2-deoxy-galactitol TMS-ether has the same retention time as peak i in Fig. 1 and the TMS-ether of the allitol derivative coincides with peak k. However, there was little indication from the mass spectra of isolated material that under our work up conditions the expected products, the 2-acetamido-2-deoxyhexos-4-(and 3)-uloses, have been isolated. On reduction with NaBD₄ they would give rise to 2-acetamido-2-deoxy-galactitol-1,4-d₂ and 2-acetamido-2-deoxy-allitol-1,3-d₂ and the respective glucitol derivatives.

b) Oxygenated solutions

In the presence of oxygen the compounds with a -CO-CH₂-function, 4 and 6, are absent. The yield of the other products is enhanced and further products with a shorter carbon chain than the starting material are observed. Fig. 9 gives the mass spectrum of the derivative of one of these products (GC-elution before arabitol).

The prominent fragment ions at m/e 366 (M-15), 281 (M-90), 277, 218 (277-59), 217, 206, 201 (M-90-90), 187 (277-90), 175 and 104 clearly indicate a tetritol TMS-ether with an acetamido group at C-2 and with D-atoms at C-1 and C-4.

| 104 | 175 |
| CHDOTMS | CHNHCOCH₃ |
| 277 | 277 |
| (187) | (187) |
| 206 | 205 |

Fig. 9. Mass spectrum assigned to TMS ether of 2-acetamido-2-deoxy-threitol-1,4-d₂.

c) Quantitative measurements

Products were determined quantitatively using glucitol or rhamnitol as internal standards.

Relative response factors can be calculated on an increment basis. The acetamido increment was determined by comparing the response of glucitol TMS ether with 2-acetamido-2-deoxy-glucitol TMS ether. Doses used were between 0.9 and 3.5 × 10¹⁹ eV g⁻¹ (~9-35% conversion based on G(OH)+
Table I. Co-60-y radiolysis products of N2O and N2O/O2 saturated aqueous solutions of N-acetyl-glucosamine (10^{-2} M, 25 °C, dose (0.9-3.4) \times 10^{19} \text{ eV} \times \text{g}^{-1}, \text{dose rate } 4.3 \times 10^{12} \text{ eV} \times \text{g}^{-1} \times \text{h}^{-1}).

<table>
<thead>
<tr>
<th>No.</th>
<th>Product</th>
<th>Identified as</th>
<th>N2O</th>
<th>N2O/O2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Three carbon fragments</td>
<td>Glycerol-TMS</td>
<td>0.02</td>
<td>0.08</td>
</tr>
<tr>
<td>2</td>
<td>Four carbon fragments</td>
<td>Erythritol-TMS, Threitol-TMS</td>
<td>0.01</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ribitol-TMS</td>
<td>&lt;0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>3</td>
<td>Five carbon fragments</td>
<td>Anabitol-TMS</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ribitol-TMS</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>4</td>
<td>1-Acetamido-1,3-dideoxy-pentitol-2-d1-TMS</td>
<td>0.07</td>
<td>absent</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1-Acetamido-1-deoxy-pentitol-2-d1-TMS</td>
<td>0.02</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2-Acetamido-2,3-dideoxy-hexitol-1,4-d2-TMS</td>
<td>0.35</td>
<td>absent</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2-Acetamido-2-deoxy-hexitol-1,6-d2-TMS</td>
<td>0.5</td>
<td>absent</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2-Acetamido-2-deoxy-hexitol-1,5-d2-TMS</td>
<td>0.4</td>
<td>absent</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>2-Acetamido-2-deoxy-mannitol-1,5-d2-TMS</td>
<td>0.15</td>
<td>absent</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2-Acetamido-2-deoxy-mannitol-1,4-d2-TMS</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Five carbon fragment products containing the acetamido group in 2-position</td>
<td>2-Acetamido-2-deoxy-pentitol-TMS</td>
<td>absent</td>
<td>0.09</td>
</tr>
</tbody>
</table>

\(a\) Probably contains contributions from other deoxyketo sugars. \(b\) Determined from sample of enriched products. \(c\) Estimated from iditol isomer (GC peak i). \(d\) Estimated from mannitol isomer (GC peak k).

G(H) = 6). G-values were calculated and plotted against dose. The values given in Table I are obtained by extrapolation to zero dose. G(6) is overestimated and gives rather the total yield of the group of 2-acetamido-2-deoxy-hexoses carrying a further –CO–CH₂-function. The G-values of 7, 8 and 9 are not accurate but represent the order of magnitude. To estimate the yield of 8 it has been assumed that 8 is reduced by NaBD₄ into equal amounts of the stereoisomeric alcohols. This reduction is somewhat selective but it has been shown that the ratio of polyalcohols (glucitol and stereoisomer) obtained from hexosuloses never exceeds 1.75.\(^{13}\) Calculations of G(8) are based on the yield of the iditol derivative multiplied by two. The yield of 7 has been estimated by measuring in an enriched sample (free of starting material) the relative yields of the glucitol derivative and the iditol derivative making the above corrections for a contribution of 8 but not for a possible contribution of the 2-acetamido-2-deoxy hexos-3-(and 4)-uloses, which have not been identified but are most likely present. However, the value obtained in the presence of oxygen agrees well with the value of gluco-hexodialdose in the radiolysis of glucose under the same conditions.\(^{13}\)

G(9) has been calculated on the basis of the mannitol derivative. NaBD₄ reduction of an authentic sample of 2-acetamido-2-deoxy-glucono-lactone in aqueous solution gave a 2-acetamido-2-deoxy mannitol/2-acetamido-2-deoxy-glucitol ratio of 1:2. This value was used to calculate G(9).

**Discussion**

**a) Deoxygenated solutions**

The free radical chemistry of N-acetyl-glucosamine appears to follow similar lines to those of other carbohydrates, *e.g.* glucose\(^{14}\) and ribose-5-phosphate\(^{15}\). The primary radicals are mainly transformed by three types of reactions:

i) Water elimination from \(\alpha,\beta\)-dihydroxy alkyl radicals (reaction (9) in Scheme 1).

ii) Water elimination from \(\beta,\gamma\)-dihydroxy alkyl radicals (reaction (5) in Scheme 1).

iii) Loss of carbon monoxide from radicals of the type –CHX–CO or its hemiacetal (ring closed) analogue (reaction (2) in Scheme 1).
The primary and the secondary radicals undergo combination and disproportionation reactions. Only those products which arise from disproportionation reactions were accessible by the technique applied. The derivatives of the combination products were insufficiently volatile for analysis.

The primary radicals when oxidised in a disproportionation reaction are converted into the carbonyl compounds (e.g. reactions (1), (3) and (4) in Scheme 1, similarly product 7 from the radical at C-6 and product 8 from the radical at C-5). Enols may well be intermediates in these disproportionation reactions. An enol is expected to be the intermediate in reaction (3) (Scheme 1) leading to product 5. An acetimido compound may be the precursor of arabinose (3).

The secondary radicals derived from the water elimination processes i) and ii) are usually reduced in disproportionation reaction (e.g. reactions (6) and (10) in Scheme 1) if they do not combine. Their oxidation into products of the type $-\text{CO-CH}_2-\text{CO-}$ has not yet been observed.

Elimination reactions of type i) are more general. The leaving group might not only be $-\text{OH}$ but also $-\text{OR}$, $-\text{NH}_3^+$, $-\text{Cl}$, $-\text{Br}$, $-\text{OAc}$ and $-\text{OPO}_3^{2-}$. The mechanism has been studied in detail with $-\text{OAc}$ as leaving group. $-\text{NHCOCH}_3$ appears to be a poor leaving group and there is no indication that under our experimental conditions $\text{NH}_2\text{COCH}_3$ is eliminated (e.g. reaction (7) in Scheme 1) at a rate to compete successfully with radical radical reactions (formation of products). This is suggested by the fact that 2-deoxy-gluconic acid lactone, a major product in the case of glucose, has not been found as a product in the present study.

Although a number of products has been identified here it is obvious that of the products with six or five carbon atoms in the chain, only the most prominent have been recognised. The previous work on glucose suggests a number of products which must be expected when rigorously applying all free radical reactions known to occur in carbohydrates. However, yields of such products may have been too low to allow detection. This view is supported by the quantitative measurements. The G-value of primary radicals is about $G \approx 6$ and although the consumption of N-acetyl-glucosamine has been found to be $G \approx 5$, the sum of the G-values of all products measured is only around 1.3. It is possible that much of the material is in the dimer fraction (which has not been analysed) or underwent secondary (non-radical) reactions yielding products not accessible by the technique used.

Although $G(\text{-N-acetyl-glucosamine})$ cannot be measured very accurately, its value of $\approx 5$ suggests the absence of an efficient chain reaction, as has been reported for $5 \cdot 10^{-2} \text{ M}$ aqueous solutions of N-acetyl-glucosamine saturated with $\text{N}_2$. An earlier study concluded the absence of $-\text{CH}_2-\text{CO-}$ functions in the irradiation products. The identification of products 4 and 6 contradicts this view. However, it must be noted that these products are not accessible to the $-\text{CH}_2-$ determination employed in the earlier investigation.

b) Oxygenated solutions

In the presence of oxygen the primary radicals are scavenged by the molecular oxygen giving rise to the corresponding peroxy radicals. Only very
fast first order processes can compete with this reaction. The formation of products 3 and 5 even in the presence of oxygen does not necessarily mean that reaction (2) in Scheme 1 still occurs. It has been generally observed\textsuperscript{13,22}, that in the presence of oxygen, reactions occur which lead to a scission of the carbon chain. Under certain conditions this reaction may be due to the intermediate formation of oxylradicals (reaction (5))\textsuperscript{23,24}.

$$2 \text{RO}_2^+ \rightarrow 2 \text{RO}^- + \text{O}_2$$

(5)

Oxyl radicals are known to decompose by the scission of the neighbouring C–C bond. Although this mechanism may contribute to the enhanced (compared to deoxygenated solutions) formation of shorter carbon chain products, it is doubtful that this fragmentation occurs to a significant extent via reaction (5).

There is increasing evidence\textsuperscript{25–27}, that in aqueous solution, \(\alpha\)-hydroxy-peroxyl radicals readily decompose according to reaction (6) with rate constants of a few hundred \(s^{-1}\)\textsuperscript{27}.

\[
\begin{align*}
\text{COH}^- & \rightarrow \text{C}=\text{O} + \text{O}_2^- + \text{H}^+ \\
\text{O}_2^- & \rightarrow \text{O}^- + \text{H}_2\text{O}
\end{align*}
\]

(6)

The lifetime of the \(\alpha\)-hydroxy-peroxyl radicals is then too short to build up a sufficient steady state concentrations to undergo reaction (5) at the dose rates of the Co-60-\(\gamma\) source. However, there is the possibility that the \(\text{O}_2^-\) (or HO\(_2\)) radical, whose lifetime is fairly long and can build up higher steady state concentrations, may play a role (e.g. substitution of HO\(_2\)) for one of the RO\(_2\) radicals in reaction (5).

Although the radiolysis of the oxygenated solution is less well understood than that of the deoxygenated, it appears that the increase in the yield of products 7, 8 and 9 is due to the fast addition of oxygen to the primary sugar radicals, preventing reactions i)–iii) as well as the formation of dimeric compounds. The peroxy radicals formed in this process then decay via reaction (6).

c) Conclusions

The free radical chemistry of N-acetyl-glucosamine largely follows the routes observed with glucose, where, in deoxygenated aqueous solution, \(\alpha, \beta\) water eliminations predominate. However, the acetamido group is not as readily eliminated as OH and a \(\beta,\gamma\) water elimination, paralleled by similar results from ribose-5-phosphate, is observed.

Fragmentation of the carbon skeleton is only noticeable between C-1 and C-2 in deoxygenated solutions but is more general in the presence of oxygen.

Experimental

Materials: Nitrous oxide (Farbwerke Hoechst), 2-acetamido-2-deoxy-glucose, hexamethyldisilazane and chlorotrimethylsilazane (Fluka), 2-acetamido-2-deoxy-gluconolactone and 2-acetamido-2-deoxy-galactose (Koch-Light), 2-deoxy-glucose (Serva), glyceraldehyde, erythrose, ribose, arabinose, NaBH\(_4\), NaBD\(_4\) and Dowex 50 WX 8 (200–400 mesh H\(^+\) form) (Roth) were available.

An aqueous solution of methyl 2-acetamido-2-deoxy-\(\alpha\)-d-ribo-hexopyranosid-3-ulose\textsuperscript{28} was reduced with NaBH\(_4\). TLC showed the \(R_f\) values of one of the products to be the same as methyl 2-acetamido-2-deoxy-\(\alpha\)-d-glucopyranoside (prepared according to KUHN et al.\textsuperscript{29}). Treatment with Dowex 50 WX 8 (H\(^+\)) at 70 °C gave a small yield of product which, after reduction (NaBH\(_4\)) and silylation gave two new GC peaks, attributed to the 2-acetamido-2-deoxy-glucitol and 2-acetamido-2-deoxy-allitol TMS-ethers. 2-Acetamido-2-deoxy-galactitol was obtained by reducing 2-acetamido-2-deoxy-galactose with NaBH\(_4\).

Irradiations and analysis: Irradiations were carried out in a Nuclear Engineering Ltd. 60-Co-\(\gamma\)-source. Products were separated on a Kieselgel (0.06–0.2 mm, Merck) column, (2 m, 4 cm i.d.) using ethyl acetate-acetone-water (4:5:1)\textsuperscript{30} as eluting agent. NaBD\(_4\) reduction and trimethyl-silylation were carried out as described in previous work\textsuperscript{31}.

DC 560 capillary columns\textsuperscript{32} have been used for GC and GC–MS separations. GC analyses were carried out on a 40 meter column operating isothermally at 160 °C and a 57 meter column was temperature programmed between 125 and 250 °C at 5 °C per minute. For mass spectral analysis, the samples were centrifuged and the clear supernatent liquid evaporated to remove excess silylating agent and then redissolved in pyridine. The mass spectrometer (Atlas CH-4) was linked to a DC 560 25 meter column (operating isothermally at 180 °C). The details of the instrumentation including the computer link-up are given elsewhere\textsuperscript{33}.

The quantitative determinations were carried out by GC using L-rhamnose as an internal standard.

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