

Hydrogen Adduct Radical Formation in γ -Irradiated α -, β -, and γ -Cycloamylose–Benzene Complexes

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Summary α -, β -, and γ -Cycloamyloses are suitable 'host' matrices for stabilising hydrogen adduct radicals formed by hydrogen atom addition to the benzene 'guest' during γ -irradiation and compare favourably with the extensively used adamantane matrix for the observation of extremely well resolved e.s.r. spectra.

ADAMANTANE has been extensively used as a 'host' matrix for the stabilisation of radicals produced by the removal of hydrogen or other atoms from organic 'guests' during irradiation. Recently it was demonstrated that hydrogen atom addition could also occur under favourable conditions.¹ Irradiated cycloamylose matrices are also capable of stabilising hydrogen adducts produced from included aromatic molecules,² in particular, benzene. The coupling constants reported were in reasonable agreement with those found for the cyclohexadienyl radical generated during the electron irradiation of liquid cyclohexa-1,4-diene.³

Here, we report e.s.r. results for α -, β -, and γ -cycloamylose–benzene complexes which demonstrate that these cyclic oligosaccharides form structures in which hydrogen adduct radicals trapped after γ -irradiation arise from aromatic 'guest' molecules specifically located within the network of voids.

TABLE. E.s.r. data for cyclohexadienyl radicals trapped in γ -irradiated α -, β -, and γ -cycloamylose–benzene complexes.

Host	Void size	Line width $\Delta H/G$	Coupling constant G			
			$a_{\text{H}}^{\text{CH}_2}(2)$	$a_{\text{H}}^{\alpha}(1)$	$a_{\text{H}}^{\beta}(1)$	$a_{\text{H}}^{\gamma}(2)$
α	0.6 nm	2.1	47.79	8.99	13.00	2.68
β	0.8 nm	1.6	"	"	"	"
γ	1.1 nm	0.9	"	"	"	"

Second-order splitting, 0.7 G

In the e.s.r. spectra, at 293 K, of hydrogen adduct radicals generated in these cycloamylose–benzene complexes γ -irradiated *in vacuo* at 77 K (see Figure A and B), the width of the individual lines decreases linearly ($\Delta H = 2.1$ – 0.9 G) as the size of the cycloamylose void is increased from 0.6 nm in α -cycloamylose to 1.1 nm in the γ -form. The line width for the radical in the α -cycloamylose complex is consistent with broadening the lines observed in the liquid phase to the width in the solid phase.³ For the γ -cycloamylose complex the line width is still appreciably larger than that reported by Fessenden and Schuler³ for the liquid state (0.2 G) indicating that even in the largest void the tumbling motion of the radical is not as rapid as in a solvent of low dielectric constant. This is probably due to the stronger interaction between the organic 'guest' and the hydrophobic core of the torus of the cycloamylose molecule.

The e.s.r. spectrum for the γ -cycloamylose–benzene complex is not explainable purely on the basis of a first-order approximation. Although the line width is greater than the reported second-order splitting³ (0.7 G) the simulated e.s.r. spectrum using this parameter, in addition to the observed line width and the relevant proton coupling con-

stants (see Table), fits the observed e.s.r. spectrum well. For the irradiated α - and β -cycloamylose complexes the e.s.r. spectra have individual line widths $\Delta H = 2.1$ and 1.6 respectively, and a better fit is also obtained by incorporating the same second-order splitting.

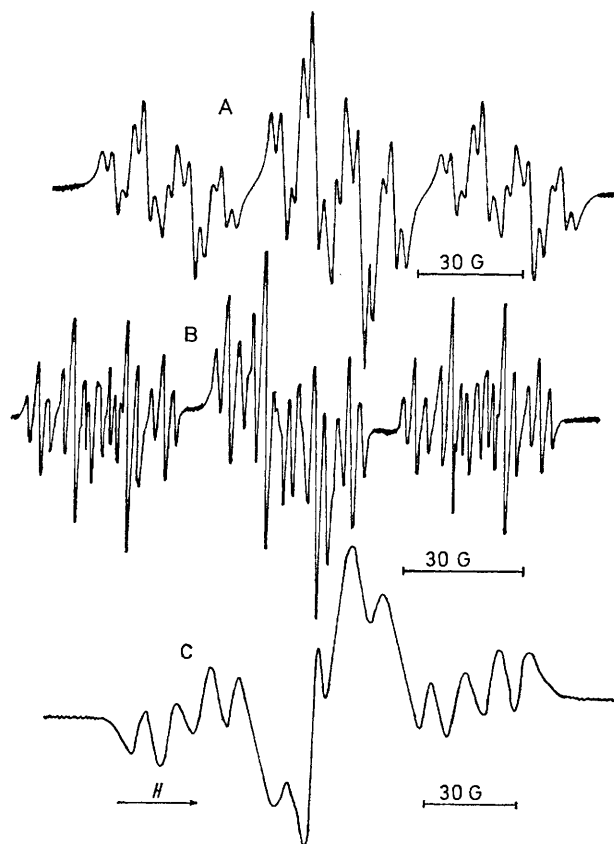


FIGURE. E.s.r. spectra of cyclohexadienyl radicals trapped in cycloamylose–benzene complexes γ -irradiated *in vacuo* at 77 K. A: α -Cycloamylose at 293 K after annealing from 77 K. B: γ -Cycloamylose at 293 K after annealing from 77 K. C: γ -Cycloamylose at 77 K observed directly or after recoiling complex from 293 K.

The stability of these radicals trapped in the γ -irradiated cycloamylose–benzene complexes was studied in the temperature range 77–293 K. Below 150 K the spectra are poorly resolved, similar to those observed for irradiated benzene-methanol binary mixtures⁴ at this temperature (Figure C). From 150 to 210 K, considerable line narrowing occurs, with some decay of these or other radical species present. At 210 K the e.s.r. spectra are well resolved and comparable to those observed for the cyclohexadienyl radical in an adamantane matrix.¹ On recoiling the irradiated complexes to 77 K, the spectra observed are

identical to the original spectra at 77 K (Figure C), indicating that the radicals which disappear during thermal annealing are in fact cyclohexadienyl radicals.

Information about the structures of the complexes can be obtained from the e.s.r. data. The e.s.r. line width decreases rapidly with increasing void dimensions and shows a linear dependency which indicates that the cyclohexadienyl radicals are located within individual cycloamylose voids. The benzene 'guest' molecules would fit more easily into the voids in the β - and γ -cycloamylose matrices which would form more rigid contiguous (cage) networks⁵ than the α -cycloamylose complex. However, a channel-type structure⁵ could just as easily explain the differing e.s.r. line widths observed.

From the decay of the cyclohexadienyl radicals it appears that some radicals are more rigidly trapped within these structures than others. Radicals trapped at 293 K after thermal annealing from 77 K are relatively stable *in vacuo* and $G(\text{radical})_{293\text{K}}$ is 1.4. Yet between these temperatures diffusion of some of the radicals occurs since $G(\text{radical})_{77\text{K}}$ is 2.4. This decrease in radical concentration on annealing could be due to radical-radical recombination which would require a degree of mobility of the radicals.

However, residual trapped oxygen could be responsible for the scavenging of radicals.

Our chromatographic analysis of various prepared complexes indicates that the benzene-cycloamylose molecular ratio is as high as 3:1, *i.e.* more 'guest' molecules are present than can be accommodated in a cage system unless each cage contains more than one benzene molecule. A higher ratio of 'guest' to 'host' could possibly prevail if a channel-type structure predominated and, furthermore, diffusion of radicals would be facilitated here.

The complexes are prepared by precipitation from an aqueous solution saturated with benzene. The structures which are formed may contain different amounts of trapped oxygen and, furthermore, may be unstable to freezing and annealing over large temperature ranges, which may account for the varying stability of the trapped radicals. Preliminary e.s.r. observations for the β -cycloamylose-toluene complex suggest that both hydrogen adduct and benzyl radicals can be trapped but their relative concentrations appear to be critically dependent on the preparation of the complex and the trapped oxygen levels.

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⁵ For references see R. K. McMullan, W. Saenger, J. Fayos, and D. Mootz, *Carbohydrate Res.*, 1973, **31**, 37.