Organic Guest Radical and Radical Anion Trapping in Cycloamylose Host Matrices induced by γ-Irradiation at 77 K

By **Peter J. Baugh,*** **J. Ian Goodall,** and (in part) **Jeffrey Bardsley,** Cockcroft Building, Department of Chemistry, University of Salford, Salford M5 4WT

The e.s.r. spectra of a number of organic radicals and radical anions generated from organic ' guests ' in cycloamylose matrices by γ-irradiation at 77 K have been investigated. Both hydrogen addition to and hydrogen removal from guest molecules occurs, depending on the nature of the guest. Electron addition is observed only in certain instances, *i.e.* for highly electron affinic molecules, *viz.* hexafluorobenzene. The ability of these systems to stabilise organic radicals for the purpose of observing isotropic e.s.r. spectra at well below room temperature compares favourably with the extensively used adamantane systems. Furthermore, since the host void dimensions can be varied to a greater extent enhanced spectral resolution is observed in certain instances and the variations in line width with void size can be studied.

THE cycloamyloses (Schardinger dextrins or cyclodextrins) are a class of cyclic oligosaccharides [1,2] prepared by the action of bacillus macerans amylase on starch. They form a homologous series of non-reducing α 1 $\longrightarrow$ 4 linked D-glucopyranose oligomers containing six or more glucopyranose units of which the hexa (α)-, the hepta (β)-, and the octa (γ)-cycloamyloses are the most easily prepared.[1]

The cycloamyloses are torus-shaped enclosing central voids [diameters 50 (α), 75 (β), and 90—100 (γ) pm [1-3]] which enable inclusion complexes to be formed with a wide range of polar and non-polar organic and inorganic guests [1-6] both in aqueous solution and the solid state. Because of this complex-forming ability cycloamyloses have been used in a variety of studies as catalysis agents [7] and enzyme models.[8] As with other clathrate or inclusion forming compounds,[9,10] the cycloamyloses have also been utilised as traps for matrix-isolated radicals

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[1] D. French, *Adv. Carbohydrate Chem.*, 1957, **12**, 189.

[2] J. A. Thoma and L. Stewart, in ' Starch: Chemistry and Technology,' eds. R. L. Whistler and E. F. Paschall, Academic Press, New York, 1965, vol. 1, p. 209.

[3] F. R. Senti and S. Erlander, in ' Non-stoichiometric Compounds,' ed. L. Mandelcorn, Academic Press, New York, 1964, p. 588.

[4] F. Cramer, W. Saenger, and H.-C. Spatz, *J. Amer. Chem. Soc.*, 1967, **89**, 14.

[5] See for example W. Saenger and M. Noltmeyer, *Angew. Chem.*, 1974, **86**, 594; *Chem. Ber.*, 1976, **109**, 503; W. Saenger, K. Beyer, and P. C. Manor, *Acta Cryst.*, 1976, **32B**, 120.

[6] Y. Matsui, T. Kumta, and Y. Date, *Bull. Chem. Soc. Japan*, 1972, **45**, 3229; F. H. Trommsdorff, Ger. Offen. 2,260,536.

[7] F. Cramer and W. Dietsche, *Chem. Ber.*, 1959, **92**, 1739; F. Cramer and W. Kampe, *J. Amer. Chem. Soc.*, 1965, **87**, 1115; N. Heinrich and F. Cramer, *ibid.*, p. 1121.

[8] R. L. Van Etten, J. F. Sabastian, G. A. Clowes, and M. L. Bender, *J. Amer. Chem. Soc.*, 1967, **89**, 3242; D. L. Van Der Jagt, F. L. Killian, and M. L. Bender, *ibid.*, 1970, **92**, 1016.

[9] See for example G. B. Birrell and O. H. Griffith, *J. Phys. Chem.*, 1971, **75**, 3489 and previous papers cited therein.

[10] (*a*) See D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, 1970, **52**, 3840 and subsequent papers in the series; (*b*) R. E. Linder and A. C. Ling, *Canad. J. Chem.*, 1972, **50**, 3981.

generated from organic guests[11,12] by irradiation and for nitroxide spin labels.[13,14] In the former, for non-polar organic guests, the e.s.r. spectra are isotropic at low temperatures due to the random tumbling of the radicals in voids, and line widths approach those observed in solution[12] as the void size increases ($\alpha < \beta < \gamma$). In the latter, both X/Y[13a] and Z[13b] preferential anisotropic motion have been observed due to the nitroxide guests rapidly rotating about central axes of an extended arrangement of cycloamylose voids.

The application of α-, β-, and γ-cycloamyloses in investigations on trapped guest radicals may allow the effects of variation in matrix dimensions on radical tumbling to be studied which is often a handicap with other matrices, *viz.* adamantane.[15,16] However, the types of organic radicals which may be investigated may not be as widespread as for adamantane since the rotational motion of organic radicals which are able to hydrogen bond to the host may be severely restricted[5,17] (also adamantane may be more versatile from a preparative standpoint).

Initially the emphasis in radiation studies on cycloamyloses and their organic complexes was in the possible protective influence of the organic guest toward the host[11,18] although e.s.r. spectra were investigated[11] [in fact, Phillips and Young in 1966 were the first to observe well resolved hydrogen adduct (cyclohexadienyl) radical e.s.r. spectra in this type of solid phase, well before that for adamantane]. At that time no e.s.r. facilities were available to these particular investigators for observing radicals at low temperature which have been subsequently found to be vital in investigations using adamantane[10] and cycloamyloses.[12] The earlier work has been extended here to include radicals generated by hydrogen removal from organic guests, as well as hydrogen adduct radicals and anion radicals which are formed in one or two special instances. The results demonstrate that these matrices have similar radical trapping properties to the extensively used adamantane systems.

EXPERIMENTAL

Materials.—The cycloamyloses (α-, β-, and γ-CA) were prepared selectively by the method of French *et al.*[19a] as modified by Cramer and Henglein[19b] after initially obtaining CA mixtures by enzymically degrading potato starch (bacillus macerans amylase was isolated using bacterium strains obtained from the National Collection of Industrial Bacteria, Aberdeen). The crude products obtained by precipitation[19] were purified by further selective precipitation using organic reagents and repeated recrystallisation from water (properties such as water content, optical rotation, and crystal geometry were as reported in the literature[1,19a]). The complexes for irradiation were prepared by vigorously stirring a saturated aqueous solution of α-, β-, or γ-CA with an excess of the appropriate organic liquid (benzene, perdeuteriobenzene, toluene, *m*-fluorotoluene, *p*-xylene, cyclohexa-1,4-diene, cyclohepta-1,3,5-triene, cyclo-octa-1,3,5,7-tetraene, and hexafluorobenzene) for several hours at constant temperature (*ca.* 293 K) to achieve equilibrium. The acetone complexes were prepared somewhat differently as explained in the text later. The precipitated complex was filtered, washed with methanol or methanol–water, dried in the oven at 50 °C for 10 min, and finally *in vacuo* over P_2O_5 for several days. Before transferring to radiation-resistant quartz tubes the complexes were finely ground in an agate mill.

Irradiation.—Samples of the complexes were evacuated in the irradiation tubes (3 mm i.d.) to 5×10^{-3} Torr and flame-sealed (or sealed under vacuum using high vacuum taps). The tubes were then placed in a Dewar containing liquid nitrogen and irradiated at 77 K on a ^{60}Co source at a dose rate of *ca.* 10^{17} eV g^{-1} min^{-1} for up to 45 min.

E.s.r. Spectroscopy.—The irradiated samples were transferred to a Dewar insert in the e.s.r. cavity, the temperature of which could be varied between 77 K and room temperature.[20,21] Dry air was continuously driven into a sealed plastic surround to the e.s.r. cavity to reduce the condensation to a minimum. The e.s.r. spectra were normally recorded at a temperature as close as possible to the temperature at which the radicals disappeared in order to achieve maximum spectral resolution. The e.s.r. spectrometer system and facilities have been previously described.[20,21] The errors in measuring coupling constants were of the order of $\pm$0.005 mT for spectra with line widths of 0.05 mT and $\pm$0.02 mT for those with line widths of 0.2 mT. For the anion radical observed in hexafluorobenzene–CA complexes the error in coupling constant was estimated to be $\pm$0.05 mT (see later).

RESULTS AND DISCUSSION

(i) *Trapped Electrons* (e_t^-).—The trapping of electrons in hydrated CA matrices γ-irradiated at 77 K has previously been communicated.[22] No change in line width (ΔH 1.25 $\pm$ 0.05 mT) with void size is observed. Replacing H_2O by D_2O in these structures leads to a narrowing of the e.s.r. line (ΔH 0.44 $\pm$ 0.03 mT) consistent with e_t^- interacting with eight protons from four tetrahedrally located water molecules. The line widths are comparable in magnitude to those observed at 77 K in γ-irradiated frozen aqueous solutions containing carbohydrates.[20,21]

If the traps are predominantly water-walled[23] then

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[11] G. O. Phillips and M. Young, *J. Chem. Soc. (A)*, 1966, 393.

[12] J. Bardsley, P. J. Baugh, J. I. Goodall, and G. O. Phillips, *J.C.S. Chem. Comm.*, 1974, 890.

[13] (*a*) G. B. Birrell, S. P. Van, and O. H. Griffith, *J. Amer. Chem. Soc.*, 1973, **95**, 2451; (*b*) G. B. Birrell, O. H. Griffith, and D. French, *ibid.*, p. 8172.

[14] K. Flohr, R. M. Patton, and E. T. Kaiser, *J. Amer. Chem. Soc.*, 1975, **97**, 1209.

[15] R. V. Lloyd and D. E. Wood, *J. Amer. Chem. Soc.*, 1974, **96**, 659.

[16] M. B. Yim and D. E. Wood, *J. Amer. Chem. Soc.*, 1975, **97**, 1004.

[17] R. K. McMullan, W. Saenger, J. Fayos, and D. Mootz, *Carbohydrate Res.*, 1973, **31**, 37.

[18] G. O. Phillips and P. J. Baugh, *J. Chem. Soc. (A)*, 1966, 387.

[19] (*a*) D. French, M. L. Levine, J. H. Pazur, and E. Norberg, *J. Amer. Chem. Soc.*, 1949, **71**, 353; (*b*) F. Cramer and F. M. Henglein, *Chem. Ber.*, 1958, **91**, 308.

[20] P. J. Baugh, K. Kershaw, and G. O. Phillips, *J. Chem. Soc. (B)*, 1970, 1482.

[21] J. Bardsley, P. J. Baugh, and G. O. Phillips, *J.C.S. Perkin II*, 1975, 614.

[22] J. Bardsley, P. J. Baugh, and G. O. Phillips, *J.C.S. Chem. Comm.*, 1972, 1335.

[23] G. V. Buxton, F. S. Dainton, T. E. Lantz, and F. P. Sargent, *Trans. Faraday Soc.*, 1970, **66**, 2962.

they must be formed by water molecules not located in voids since it has been demonstrated,[24] at least for hexahydrated α-CA [α-CA$(H_2O)_2,4H_2O$], that only two water molecules can be accommodated in voids, the other four being externally associated with CA molecules in a hydrogen bonded network. It was found that the yield of e_t^- was linearly dependent on water content (D_2O, see Figure 1) in the range 2—14% w/w indicating trapping efficiency within this range to be directly proportional to water content, the lower limit of which corresponds to a D_2O : CA molecular ratio of *ca.* 1 : 1 (one D_2O per void).

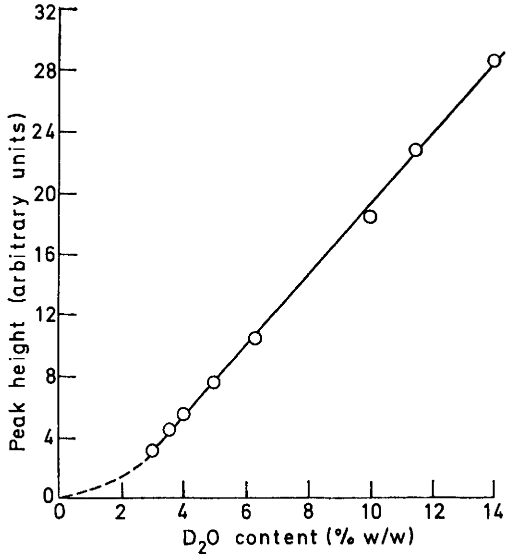

FIGURE 1 Variation in e_t^- yields with D_2O content for β-CA–D_2O γ-irradiated at 77 K

The fact that e_t^- are observed indicates that CA molecules orient water molecules to form suitable trapping sites thus imposing a glass-like (hydrogen bond disordered) structure at least on part of the CA matrix. This may occur during cooling to 77 K since α-CA hexahydrate is considered to have a wholly crystalline structure.[24] However, e_t^- are observed whether the CA is initially in a hydrated or an anhydrous state and allowed to take up water.

The yields of e_t^- are low with $G(e_t^-)_{77} - 0.7$ determined from the difference between $G(\text{CA radical} + e_t^-)_{77\ \text{K}}$ for anhydrous CA in which no e_t^- are stabilised. The yields are consistent with the lower yields predicted for glassy aqueous solutions containing carbohydrate concentrations above 80% w/w [21] and an observation of $G(e_t^-)$ 0 for pure carbohydrate glasses.[25] The effects of photobleaching are similar to previous observations in glassy aqueous solutions containing sugars [21] and alcohols [26] with an increase in sugar radicals of *ca.* 43%.

(ii) *Hydrogen Adduct Radicals.*—(a) *Benzene.* E.s.r. spectra of the cyclohexadienyl radical ($C_6H_7\cdot$) stabilised in γ-irradiated benzene–CA complexes have also been reported [12] and the coupling constants were in good agreement with those reported previously.[27,28] The line width was found to decrease from 0.21 mT for α-CA to 0.09 mT for γ-CA. A line width of 0.06 mT has been observed here for this radical generated from cyclohexa-1,4-diene in γ-CA matrix [see section (iii)]. The line width observed in solution is 0.02 mT [27] for this radical generated in irradiated cyclohexa-1,4-diene and 0.21 mT for the solid at low temperature, the latter suggesting that α-CA void could correspond approximately to solid cyclohexa-1,4-diene in restricting the motion of the radical.

A reversible effect is observed for the line widths in all three complexes on annealing to 293 K and recooling to low temperature. Thus the broadening can be explained purely in terms of a liquid–solid line width effect [12,27] at least for the radicals in β- and γ-CA complexes. Because of the smaller size of the α-CA void (*ca.* 50 pm) the radical may be subject to anisotropic motion due to rapid rotation (at least from 233 K since there is little change in line width between this temperature and 293 K) about the axis of symmetry of the void. The cyclohexadienyl radical can be likened in shape to the benzyl radical which is severely restricted in its motion in α-CA (see later). It is difficult to identify such motion [13] here since the anisotropy and line width are of the same order of magnitude.

According to Takeo and Kuge [29] benzene–CA complexes form channel structures, even the α-CA complex. However, we would expect the line width variation with void dimensions to be independent of the structural nature of the complexes (isolated void-cage or channel type).

The cycloamylose complexes with perdeuteriobenzene as a guest were also investigated. The radicals were more difficult to stabilise and e.s.r. spectra were poorly resolved due to the reduced coupling to deuterons (a_D^{CHD}, a_D^{CD}) but were indicative of the hydrogen adduct radical, $C_6D_6H\cdot$, with a_H^{CHD} 4.84 and a_D^{CHD} 0.8 mT. Similar '*a*' values have been previously reported for this radical produced from C_6D_6 in irradiated methanolic glasses.[30] An attempt was made to deuteriate the CA hydroxy-groups (using a complex prepared by precipitation of α-, β-, and γ-CA from D_2O saturated with benzene) to ascertain if the hydroxy-hydrogen is involved in the formation of the adduct (involving protonation of an intermediate anion [31]) as with benzene–CH_3OD mixtures reported previously.[30] The deuteron

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[24] P. C. Manor and W. Saenger, *Nature*, 1972, **237**, 393; *J. Amer. Chem. Soc.*, 1974, **96**, 3630.

[25] I. E. Makarov, B. G. Ershov, and A. K. Pikaev, *Izvest. Akad. Nauk, S.S.S.R., Ser. Khim.*, 1972, 106(1).

[26] F. S. Dainton, G. A. Salmon, and P. Wardman, *Proc. Roy. Soc.*, 1968, **A313**, 1.

[27] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **38**, 773.

[28] S. Di Gregorio, M. B. Yim, and D. E. Wood, *J. Amer. Chem. Soc.*, 1973, **95**, 8455.

[29] K. Takeo and T. Kuge, *Agric. Biol. Chem.*, 1970, **34**, 568, 1787.

[30] J. A. Leone and W. S. Koski, *J. Amer. Chem. Soc.*, 1966, **88**, 224.

[31] T. Shida and W. Hamill, *J. Amer. Chem. Soc.*, 1966, **88**, 5371.

or deuterium addition to benzene appears to be less efficient (isotope effect); however, we would have expected to observe a hydrogen adduct radical [31] if a hydrogen atom transfer reaction predominates, the hydrogen atom being produced *via* scission of a C_α–H bond in CA molecule or transferred from a CA radical.[32] Thus it is tentatively suggested that a cycloamylose hydroxy-hydrogen is involved in adduct radical formation. The main question that arises in trying to deduce how the hydrogen adduct is formed concerns the absence in the e.s.r. spectrum of a large contribution from CA radicals that can be stabilised in anhydrous CA γ-irradiated *in vacuo* [18] or hydrated CA at low temperatures.[33] This is a common feature of other matrices, *i.e.* adamantane.[10] If benzene acts as a charge scavenger (electron) after a CA molecule is ionised then the geminate $CA^{+\cdot}$ (positive ion) should lead to a radical by dissociation or by undergoing an ion–molecule reaction. It is possible that such radicals [34] are reactive enough to transfer a hydrogen atom to benzene as suggested earlier. If this is the case, little molecular hydrogen would be observed when benzene is present. However, $G(\mathrm{H}_2)$, although reduced, is still appreciable. Alternatively, if benzene acts as a hydrogen atom scavenger with CA being the source $G(\mathrm{H}_2)$ would again be small with the absence of the CA radical also explained as above. With $G(\mathrm{H})_2$ still being appreciable and the CA radical yield being small it is possible that a process of molecular elimination of hydrogen may be involved whichever mechanism is operative. An attempt was made to correlate $G(\mathrm{H}_2)$ with $G(\mathrm{C_6H_7}\cdot)$ but the results were inconclusive.

(b) *Toluene.* Although the hydrogen adduct could be stabilised in complexes with toluene the predominating species was the benzyl radical formed by hydrogen removal from the included molecule. The e.s.r. spectrum of the adduct was poorly resolved but could be identified from the outer groups of lines (M_I ± 1) as a methylcyclohexadienyl radical substituted in the *para*-position. The overall line width (*ca.* 13.6 mT) and coupling constants were in reasonable agreement with those reported by Wood and his co-workers [28] for [4-^{2}H]toluene taking $a_\mathrm{H}^{para} \sim a_\mathrm{D}^{para}$ given in ref. 28 as 0.042 mT for the deuteron in the *para*-position. As with the preparation of hydrogen adducts in adamantane [28] these radicals are more difficult to stabilise than radicals formed by hydrogen removal, probably due to their enhanced susceptibility to oxygen.[12]

TABLE 2

E.s.r. data for the benzyl radicals stabilised in toluene and *m*-fluorotoluene–cycloamylose complexes at low temperature

Matrix	T/K	Coupling constants (mT) $a_\mathrm{H}^{\mathrm{CH_2}}$	a_H^{o}	a_H^{m}	a_H^{p}	a_F^{m}	Line width ΔH/mT
Toluene–β-CA	77—293	1.64(2)	0.516(2)	0.176(2)	0.608(1)		0.107
Toluene–γ-CA	77—293	1.62(2)	0.517(2)	0.172(2)	0.625(1)		0.052
m-Fluorotoluene–γ-CA	77—293	1.622(2)	0.53(2)	0.178(1)	0.644(1)	0.489(1)	0.09

No. of equivalent nuclei in parentheses.

(c) p-*Xylene.* Surprisingly for *p*-xylene complexes the hydrogen adduct was easier to stabilise than the *p*-methylbenzyl radical. The radical stabilised in the γ-CA complex exhibited the smallest line width (0.04 mT) for any organic radical we have studied. Due to the complexity of the spectrum and the inability of INDO calculations to derive the correct or relative spin densities the absolute assignment of coupling constants other than for the methylene group ($a_\mathrm{H}^{\mathrm{CH_2}}$ *ca.* 4.8 mT) is difficult. Data, as far as we are aware, are not available in the literature for this radical.

(d) *Acetone.* Although solid complexes with acetone as ' guest ' could not be prepared directly by the precipitation method due to acetone–water miscibility, quite unexpectedly acetone could be incorporated during washing other organic–CA complexes with this solvent. This procedure can thus be adopted, in some instances, for obtaining solid preparations of complexes that are water-soluble.

TABLE 1

E.s.r. data for 1-hydroxy-1-methylethyl radicals stabilised in γ-irradiated acetone–cycloamylose complexes at low temperatures

Matrix	T/K	$a_\mathrm{H}^{\mathrm{CH_3}}$/mT	ΔH/mT
α-CA	77—293	1.93	0.2
β-CA	77—193	1.93	0.2
γ-CA	77—148	1.93	0.2

The radical stabilised in α- β-, and γ-CA–acetone complexes was the 1-hydroxy-1-methylethyl radical formed by hydrogen addition to the acetone guest (see Figure 2A). The line width did not vary with void size but the stability markedly decreased in the order $\alpha > \beta > \gamma$. The temperature range for observation of the radicals, the line widths and coupling constants are summarised in Table 1. The coupling constants agree well with those reported by Zeldes and Livingston [35] [$a_\mathrm{H}^{\mathrm{CH_3}}$ 1.948 and 1.996 mT for $(\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{OH}$ generated during photolysis of acetone and acetone–water, respectively]. The greater stability of these radicals in the α-CA complex probably arises because the acetone molecule is more rigidly accommodated in the α-CA void thus giving rise to a more stable structure. The observation of an invariant line width, however, appears to be in conflict although hydrogen bonding may

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[32] J. S. Moore, personal communication.

[33] J. Bardsley and P. J. Baugh, unpublished results communicated in P. J. Baugh, J. I. Goodall, G. O. Phillips, C. von Sonntag, and M. Dizdaroglu, *Carbohydrate Res.*, 1976, **49**, 315.

[34] For solid state and aqueous solution reactions of sugar radicals see M. Dizdaroglu, D. Henneberg, K. Neuwald, G. Schomburg, and C. von Sonntag, *Z. Naturforsch.*, 1977, **32b**, 213.

[35] H. Zeldes and R. Livingston, *J. Chem. Phys.*, 1966, **45**, 1946.

restrict the motion of these radicals to a similar extent in all three complexes and wherever they are located.

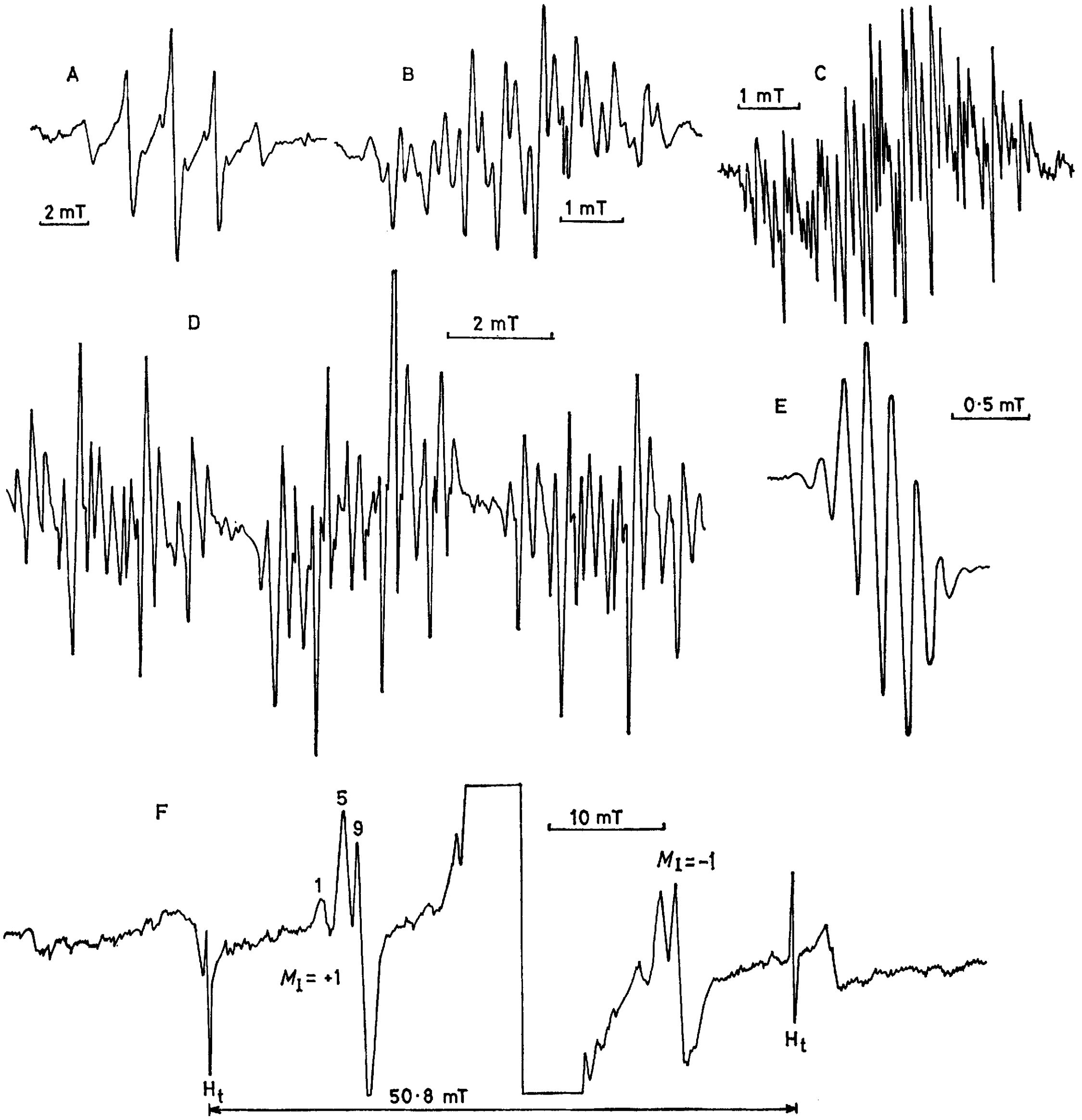

FIGURE 2 E.s.r. spectra of organic radicals generated in organic guest–cycloamylose matrices at 77 K: A, 1-hydroxy-1-methylethy in acetone–β-CA; B, benzyl in toluene–β-CA; C, benzyl in toluene–γ-CA; D, cyclohexadienyl in cyclohexa-1,4-diene–γ-CA; E, cycloheptatrienyl in cycloheptatriene–β-CA; F, hexafluorobenzene anion in hexafluorobenzene–β-CA

(iii) *Hydrogen Removal Radicals*.—(a) *Toluene*. The benzyl radical produced by hydrogen removal from the toluene guest was observed in all three complexes but the spectrum was poorly resolved for the α-CA complex. Table 2 summarises the e.s.r. data obtained for benzyl radical. Space filling models demonstrate that the benzyl radical in the α-CA void is unable to fulfil the requirement for isotropic motion due to steric effects resulting from interaction with the void. Such effects will promote anisotropic motion preferentially as previously described. For β-CA the e.s.r. spectrum begins to resolve at 110 K and the same spectrum is observed up to 293 K (Figure 2B). The line width decreases to 0.052 mT in γ-CA with the result that spectral resolution is optimised here (Figure 2C). The radicals power saturate and the spectral resolution is increased at low power ($<10^{-4}$ W). It is possible that the radicals from the CA host are more pronounced at high power as a result of the more rapid saturation of the benzyl radicals. Such an effect is observed for radicals generated from cyclopentadiene in irradiated adamantane.[36] The coupling constants are in good agreement with those previously reported,[36] but differ slightly from the data reported by Lloyd and Wood.[37a] The

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[36] See P. Neta and R. H. Schuler, *J. Phys. Chem.*, 1973, **77**, 1368 and references therein.

[37] R. V. Lloyd and D. E. Wood (*a*) *Mol. Phys.*, 1971, **20**, 735; (*b*) *J. Amer. Chem. Soc.*, 1974, **96**, 659.

spectral resolution is superior here for the γ-CA complex as a result of a reduction in line width by a factor of almost two and thus a better computer fit is obtainable. However, the coupling constants may differ because adamantane may be a considerably less polar matrix than γ-CA, although the void core is considered to be hydrophobic.[8]

(b) *m-Fluorotoluene.* The *m*-fluorobenzyl radical could be observed in *m*-fluorotoluene–γ-CA complexes (see Table 2). The line width is *ca.* 1.8 times larger than for the benzyl radical in the toluene–γ-CA complex, demonstrating that the motion of the radical in the void is sensitive to small substituent changes in the guest. The fluorine coupling constant is 0.489 mT, in good agreement with that reported previously[37b] and is a factor of >2 larger than the hydrogen it has replaced. INDO calculations[37b] predict a somewhat higher value for a_F^{meta} and in general do not give correlatable values for fluorine coupling constants.[38]

(c) *Cyclohexa*-1,4-*diene.* The well characterised[11,12,27,28] cyclohexadienyl radical (see before) was generated in cyclohexa-1,4-diene–α-, β-, and γ-CA complexes by hydrogen removal from the guest. The smallest line width observed, 0.06 mT, for this radical in the γ-CA complex (Figure 2D) is considerably less than for the same radical observed in the benzene–γ-CA complex (0.09 mT). Since both complexes are likely to have a channel structure[29] it is evident that the complexing agent may control the way in which the cycloamylose molecules aggregate together to form a void with an optimum geometry and stability to accommodate the guest molecules.

(d) *Cyclohepta*-1,3,5-*triene.* The e.s.r. spectra observed (see Table 3 and Figure 2E) for all three complexes were characteristic of the cycloheptatrienyl radical formed by hydrogen removal from the guest. For this radical there is a slight decrease in line width even at 77 K on increasing the void dimensions. At room temperature the changes are more marked which quite clearly indicates that the radicals are accommodated within voids. The coupling constant observed for the seven equivalent protons, a_H 0.38 mT, is in good agreement with that previously reported for the irradiated solid[39a,b] (a_H 0.935 and 0.39 mT) and liquid[40] (a_H 0.395 mT) cycloheptatriene.

TABLE 3

E.s.r. data for the cycloheptatrienyl radical established in cycloheptatriene–cycloamylose complexes at 77 K

		a_H/mT		Line width (mT)	
Matrix	T/K	77 K	293 K	77 K	293 K
α-CA	77—293	0.415	0.38	0.19	0.18
β-CA	77—293	0.395	0.38	0.175	0.135
γ-CA	77—293	0.38	0.38	0.17	0.075

The smallest line width observed for the γ-CA complex is also smaller than for the cyclohexadienyl radical in benzene–γ-CA complexes, supporting the idea presented in the previous discussion regarding the influence of the guest molecules in the different complexes. However, it is possible that the cycloheptatrienyl radical will exhibit less broadening than the cyclohexadienyl radical for a particular tumbling rate.

(iv) *Radical Anions.*—(a) *Hexafluorobenzene.* For monohalogenobenzenes, *e.g.* fluorobenzene, it is difficult to stabilise either hydrogen or electron adduct radicals in CA matrices. The hydrogen adducts of halogenobenzenes up to and including hexafluorobenzene have been prepared and characterised by Yim and Wood.[16] As with these other matrices, it appears to be far easier to stabilise hydrogen adducts or hydrogen removal radicals than electron adducts. We therefore sought a guest whose electron affinic properties were extremely high.[41,42] Hexafluorobenzene appeared to be tailor-made for this study and our early attempts to prepare the electron adduct were unsuccessful.[43] As Wood and his co-workers[38,44] have pointed out it is necessary to dope the adamantane matrix with an electron donor, trimethylamine–borane, in addition to fluorobenzene in order to stabilise the electron adduct of the latter. We have since managed to observe the electron adduct $C_6F_6^-$ from hexafluorobenzene in β- and β-CA complexes and without a stabiliser present but only between 77 and 128 K. The adduct rapidly disappears above this temperature (Yim and Wood[38] give the observation temperature 90 K higher for this adduct in adamantane). The coupling constant to six equivalent fluorines (spin $\frac{1}{2}$), a_F 13.67 $\pm$ 0.05 mT (g 2.0015), is in good agreement with that reported by Wood and his co-workers[44] (a_F 13.7 mT). It was possible to calibrate the fluorine coupling constant using the hyperfine separation of the hydrogen atom doublet (a_H 50.8 mT) also observed in the spectrum, which gives a probable error of *ca.* $\pm$0.05 mT for a_F. The second-order splittings of the M_I $\pm$1 components (1,5,9) are most easily observed[44,45] (Figure 2F). The centre line is complicated by the anisotropically broadened hydrogen adduct radical ($C_6F_6H\cdot$) spectrum[16] (observed up to 200 K). No assignment of coupling constants was possible due to inadequate resolution.

In view of the large fluorine coupling the radical anion is considered to be a σ rather than a π radical.[38,44] Yim and Wood[38] have demonstrated that in the series of fluorobenzenes the π–σ crossover occurs somewhat between difluorobenzene anion and 1,2,4,5-tetrafluoro-

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[38] M. B. Yim and D. E. Wood, *J. Amer. Chem. Soc.*, 1976, **98**, 2053.

[39] (*a*) D. E. Wood and H. M. McConnell, *J. Chem. Phys.*, 1962, **37**, 1150; (*b*) S. Azai, S. Shida, K. Yamaguchi, and Z. Kuri, *ibid.*, p. 1885.

[40] R. W. Fessenden and S. Ogawa, *J. Amer. Chem. Soc.*, 1964, **86**, 3591.

[41] R. N. Compton and R. H. Huebner in *Adv. Radiation Chem.*, 1970, **2**, 281.

[42] R. Koster and K. D. Asmus, *J. Phys. Chem.*, 1973, **77**, 749.

[43] J. Bardsley, Ph.D. Thesis, University of Salford, 1974.

[44] L. F. Williams, M. B. Yim, and D. E. Wood, *J. Amer. Chem. Soc.*, 1973, **95**, 6475.

[45] R. W. Fessenden, *J. Chem. Phys.*, 1962, **37**, 747; R. W. Fessenden and R. H. Schuler, *ibid.*, 1965, **43**, 2704.

[46] (*a*) T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, 1960, **32**, 1873; (*b*) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, 1963, **85**, 2360.

benzene anion (the anion from trifluorobenzene was not observed).

Experimental and theoretical data for fluorine coupling are generally difficult to correlate because the parameters used in theoretical calculations are not definitive enough for fluorine. The theoretical a_F values determined by Yim and Wood,[38] although in the right order relatively speaking, are far removed in absolute terms from the experimental values. Thus it appears at present not worthwhile performing such calculations until improved equations and theory are available.

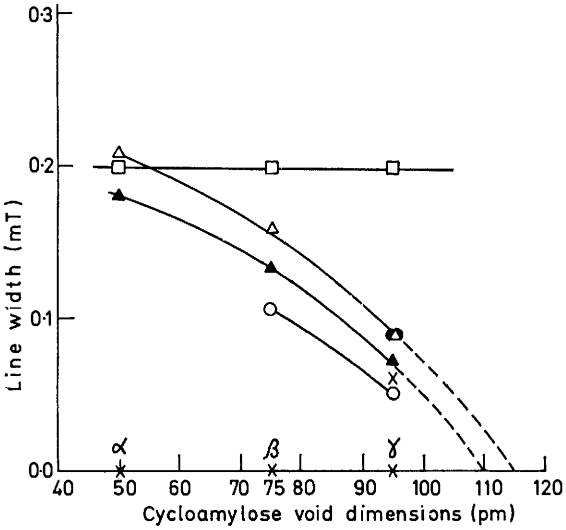

FIGURE 3 Radical line width variations with cycloamylose void dimensions: △, cyclohexadienyl in benzene–CA; ×, cyclohexadienyl in cyclohexa-1,4-diene–CA; □, 1-hydroxy-1-methylethyl in acetone–CA; ○, benzyl in toluene–CA; ●, *m*-fluorobenzyl in *m*-fluorotoluene–CA; ▲, cycloheptatrienyl in cycloheptatriene–CA

(b) *Cyclo-octa*-1,3,5,7-*tetraene*. For this guest in γ-CA a nine line (approximately binomial intensity distribution) e.s.r. spectrum indicative of the radical anion ($C_8H_8^-$) and the coupling constant, a_H 0.321 mT, is in good agreement with those previously observed in solution [46a] and in adamantane.[47] In the latter instance the hydrogen adduct, $C_8H_9^{\bullet}$, was also observed at reduced microwave power but we have thus far found no evidence for this adduct in γ-CA. The radical anion is planar [46b] and may be preferentially stabilised in the γ-CA void.

(v) *Line Width Variations*.—The theory of e.s.r. line widths is extremely complex and different radicals in similar environments as studied here may exhibit different line widths for a variety of reasons. The main reasons for changes in line width of an identical radical when the void dimensions vary are the increase or decrease in tumbling rate. The line width variations with void dimensions for a number of the radicals studied are illustrated in Figure 3. It is fairly clear that although the limiting line width (observed for the largest void–γ-CA) is different for each radical the incremental change in line width with void dimensions is almost identical and can be explained in terms of solid to liquid line narrowing. The fact that a different limiting line width is observed can be explained in a number of ways, differences in tumbling rate, residual anisotropy, radical relaxation, or radical–guest interaction along channels. For example, the cycloheptratrienyl and benzyl radicals exhibit smaller limiting line widths than the cyclohexadienyl radical. In γ-CA these radicals can be easily accommodated and since the γ-CA core is hydrophobic interaction with the void would be minimal. Thus the tumbling rate may be identical in all instances.

It is difficult to choose between the other possible causes. However, in these systems radical–guest interaction may be minimised due to the torus-shaped γ-CA molecules causing a slight blocking effect on motion along channels. In this case the effect results from differences in residual anisotropy or relaxation.

It has been possible to observe line width variations for an identical radical, the cyclohexadienyl (CHDyl) radical, generated by hydrogen addition to and hydrogen removal from different guests, benzene and cyclohexa-1,4-diene (CHD), in complexes with γ-CA. The environments of these radicals should be identical removing differences in radical anisotropy and relaxation. However, the line width decreases by *ca.* 33% for the CHDyl radical in a CHD–γ-CA complex. It is evident here that either the organic guests to some extent control the tightness of the conformation of the channel forming CA hosts or organic guest–radical interactions along channels is important. However, it is difficult to discriminate between these two possibilities. Line width variations resulting from different preparations of the same complex having slight structural differences cannot be totally ruled out.

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[47] A. R. McIntosh, D. R. Gee, and J. K. S. Wan, *Spectroscopy Letters*, 1971, **4**, 217.