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Special Features of Stable Free Radical Formation on Plasma-irradiated α-D-Glucose Studied by ESR Spin-Trapping Technique

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The structure of the stable free radicals produced in argon plasma-irradiated α-D-glucose was characterized by the ESR spectral measurements of the spin adducts obtained from the reactions with 2,4,6-tri-t-butylnitrosobenzene (BNB) with the aid of computer simulations.

A number of ESR studies of stable free radicals generated in powdered (polycrystalline) saccharides through various sources such as γ-, X-, and UV-ray irradiation have been reported.[1-8] Effect of plasma irradiation on polysaccharides has also been studied, but it has not been attempted to elucidate the chemical structure of the resulting stable free radicals except for occurring of the glycosidic bond cleavage in polysaccharides, since the purpose of plasma-irradiation was focused mainly on altering the surface physical properties and/or enhancing the surface reactivities.[9,10] The powder ESR spectra thus obtained are poorly resolved and often uninterpretable due to the superposition of more than one radical. Moreover, the peak height of the differential ESR spectrum for a mixture of radicals does not simply represent the amount of radical species. Thus, studies of these ESR spectra yield only few quantitative information about the nature of the stable free radicals produced, and often contain some contradictions as pointed out by Kochetkov et al.[11]

In order to evaluate a specific effect of plasma-irradiation on the free radical formation of monosaccharides distinguished from that by the other irradiation methods, we have carried out plasma-irradiation on fine powdered α-D-glucose(<100 mesh) at ambient temperature and report here the special features for the stable free radical formation studied by the ESR spectral measurement and its spin trapping reactions.[12]

One of nitroso spin traps, 2,4,6-tri-t-butylnitrosobenzene (BNB), is known to give two types of spin adducts, nitroxide and N-alkoxyanilino radical, depending on the nature of the trapped radical and the spin adduct shows a large hyperfine splitting constants of β-hydrogens derived from only the trapped radicals to make the structure of the trapped radicals firmly assignable.[14] High solubility of α-D-glucose in aqueous media may induce rapid quenching and/or rearrangements of the original radical produced due to destroying the crystalline structure and deformation of the pyranose ring.

Thus, although several water-soluble spin traps are available, the spin trapping reactions were carried out in suspension of α-D-glucose in benzene solution containing 10% BNB spin trap where the α-D-glucose-derived radicals are sufficiently long-lived.

Powdered anhydrous α-D-glucose (100 mg) dried in vacuo for 1 day was placed in a specially-designed ampule (30 mm i.d., 100 mm long) connected with capillary tube (2 mm i.d.) at the upmost part of the ampule and argon gas was impregnated (0.5 Torr) and sealed. Then the plasma states was sustained by a radio frequency discharge of inductive coupling with 50 W at 13.56 MHz, which is essentially the same procedure as that reported ealier.[15] Figure 1 shows the ESR spectra of the free radicals induced by plasma irradiation for five minutes (Fig. 1a) and thirty seconds (Fig. 1b). The spectral feature appears different from those obtained from various sources previously reported, and a shorter plasma irradiation gave a more defined spectrum. The spectral intensity was proportional to the plasma power and duration, but the spectral shape remained unchanged for longer plasma irradiation.

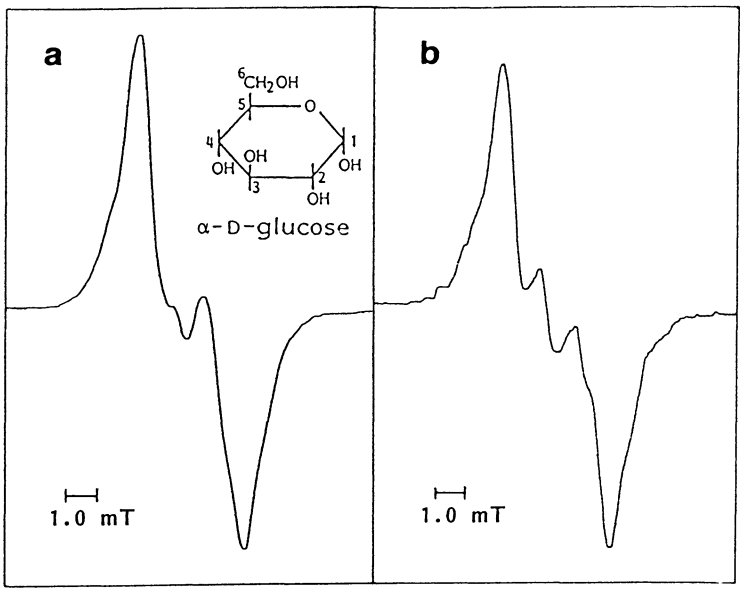

Fig. 1. ESR spectra of argon plasma-irradiated α-D-glucose, (a) for 5 min irradiation and (b) for 30 s irradiation.

For the spin trapping reactions of the radicals thus formed by plasma irradiation for thirty seconds by use of BNB, rather complicated ESR spectra were observed as shown in Figs. 2a and 2b. Effort of the computer simulation disclosed that, as shown in Figs. 2c and 2d, the spectra consisted of a mixture of three nitroxide spin adducts, A, B and C trapped by carbon-centered radicals, and N-alkoxyanilino radical, D (stick plots). The spectral feature of A-type spin adduct is typical for that trapped by a primary alkyl radical. Since α-D-glucose possesses only one conceivable carbon at C_6 which could yield a primary alkyl radical by elimination of hydroxyl group, the structure of the trapped radical to give a spin adduct, A, may be safely assigned to the C_6-centered methylene radical ($—\dot{C}H_2$). This is, we believe, the first evidence for the

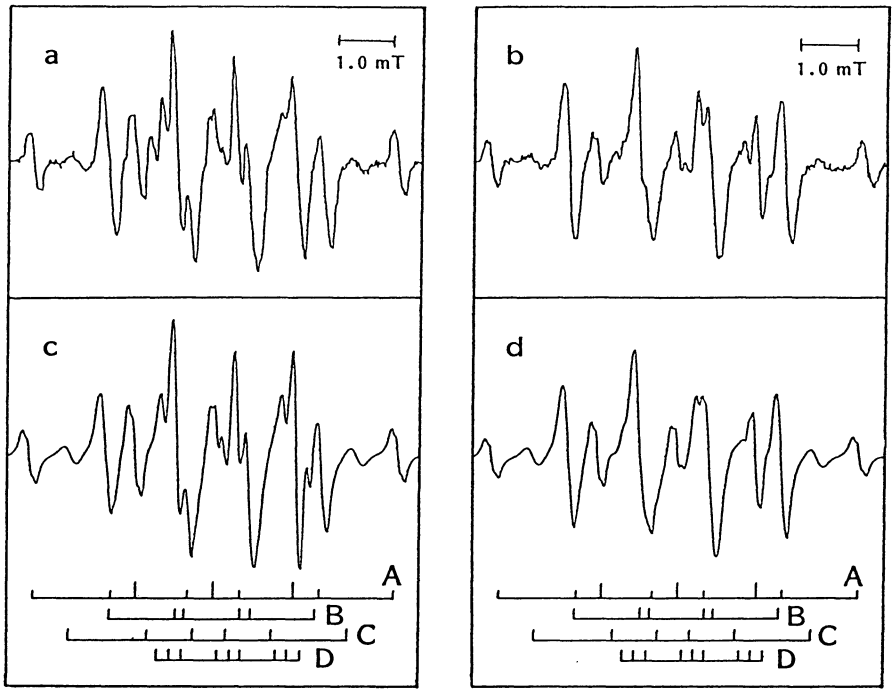

Fig. 2. ESR spectra of BNB spin adducts in benzene solution, (a) for 3 h standing and (b) for 30 h standing, and the corresponding simulated spectra, (c) and (d). The stick plots below the spectra show resonance position of the spin adducts. The major spectral parameters are as follows: For A; g=2.0063, a_N=1.35, a_H=1.79 mT. For B; g=2.0064, a_N=1.19, a_H= 1.30 mT. For C; g=2.0063, a_N=1.36, a_H=2.14 mT. For D; g=2.0041, a_N= 1.02, a_H=0.20 mT. The ratio of A,B,C and D was ca.3:3:1:4 for (c) and ca.2:4:1:1 for (d).

formation of such a radical from saccharides since the speculative assignment made by Collins.[1)]

The spectral features of the nitroxide spin adducts, B and C, are typical for those trapped by carbon-centered radical having one hydrogen atom attached to its own carbon atom.[14)] Many pathways for the formation of such radicals can be envisaged in α-D-glucose, i.e. C_6 carbon by elimination of hydrogen atom to give a primary hydroxylalkyl radical, and all pyranose ring carbons of C_1-C_5 by elimination of hydroxyl group to give a secondary alkyl radical. However, comparison of the values of the hyperfine splitting constants, A_N=1.18, A_H=1.30 mT for B and A_N=1.36, A_H=2.14 mT for C with those of reported values for a variety of BNB spin adducts clearly indicated that the trapped radical should be a primary hydroxyalkyl radical for B and a secondary alkyl radical for C, respectively.[14)] Thus, we are inclined to consider that although the similar type of radical formation due to the C-C bond cleavage in the pyranose ring can not be completely ruled out, the structure to give a spin adduct, B, is best assignable to C_6-radical(—$\dot{C}$HOH), the facile formation of which has also been reported.[6)]

Assignment of a spin adduct, D, to N-alkoxyanilino radical can easily be made based on the spectral shape, the lower g-value. Furthermore, the spectral comparison of Figs. 2a and 2b clearly indicated that the spin adduct, D, was rather short lived. This is also consistent with the result reported by Terabe et al.[14)] Thus, it was found that a tertiary alkyl and/or a secondary hydroxyl-

alkyl radical by elimination of a hydrogen atom from the pyranose ring carbon was also formed. However, the precise structures of the radicals to give spin adducts, C and D, with respect to the pyranose ring carbons are not yet known at present.

For the spin trapping reactions of the radicals of α-D-glucose induced by plasma irradiation for five minutes, N-alkoxyanilino radical, D, was not formed under otherwise identical conditions. Thus, the spectral difference between Fig. 1a and Fig. 1b can be ascribed to the absence and presence of the tertiary alkyl radical and/or a secondary hydroxylalkyl radical. It should be noted here that all amounts of radicals in plasma-irradiated α-D-glucose did not react with BNB spin trap even for a prolonged standing under the present heterogeneous conditions so that the simulation spectra represent neither the ratio nor the intensity of the radicals of α-D-glucose produced by argon plasma irradiation.

It is hoped that more insight into nature of radical formation of various saccharides by plasma-irradiation will be gained in the course of attempts now in progress to define the scope and limitations.

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