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Note

Enolate semiquinones formed during the alkaline oxidative degradation of 2-deoxy sugars

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Mixtures of semiquinone anion-radicals are formed from sugars with free hemiacetal groups or from α-hydroxycarbonyl compounds[1,2] by heating aqueous alkaline solutions in the presence of oxygen. The supposed mechanism involves the formation of α-hydroxycarbonyl intermediates by retro-aldol reactions and their subsequent aldol condensation to give phenolates. The conversion of phenolates into semiquinones and then into quinones is believed to be caused by the abstraction of electrons by oxygen. We now report on the formation of enolate semiquinones from 2-deoxy sugars.

The sugars studied were 2-deoxy-D-*arabino*-hexose, 2-deoxy-D-*ribo*-hexose, 2-deoxy-D-*erythro*-pentose, and 3-deoxy-D-*ribo*-hexose[3]. Under the standard conditions[1,2] (see Experimental), the 2-deoxyhexoses gave e.s.r. spectra (Fig. 1) that consisted of one component characterised by the hyperfine splitting of five non-equivalent protons: a_1 0.195, a_2 0.157, a_3 0.027, a_4 0.014, a_5 0.008 mT, and g 2.0043. This result was confirmed by the spectral simulation. The splitting constants were evaluated by the autocorrelation method[4] and by proton-coupling-constant extraction (PCCE)[5,6], and then used for the spectral simulation. The result of the simulation was good, but a small degree of asymmetry in the experimental spectrum was caused probably by motional restriction. The proposed structure of the enolate semiquinone was confirmed by quantum chemical calculations in order to obtain the theoretical values of the splitting constants. The calculation was performed by the semiempirical AM1[7] method, which involves the NDDO Hamiltonian[8] and the AMPAC program[7]. A suitable parameterisation of this method was obtained by an appropriate consideration of the hydrogen-bond effect. The calculations involved the UHF approximation[9].

All of the possible configurations of the proposed enolate semiquinone, which contained three hydrogen atoms on the aromatic ring and two on the enolate group,

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Fig. 1. The experimental (upper trace) and simulated e.s.r. (lower trace) spectra of radicals formed from a 0.5M solution of 2-deoxy-D-*arabino*-hexose in 6M NaOH kept for 5 min at 100°.

were studied. Because these structures are dianion-radicals in aqueous alkaline solutions, the influence of the sodium counter-ions was also taken into account. The semiquinones with oxygen atoms in the *meta*-position were not considered because the counter-ion could not be incorporated into these structures. The AMPAC package takes into account the counter-ion "sparkles" with an integral number of charges (*i.e.*, +1). The counter-ions do not contribute to the wave function of the system, but they exert polarising effects that influence the wave function and the physical characteristics of the system. For each of the model systems studied, the influence of two "sparkles" was taken into account, one on the aromatic ring and the other on the enolate ion, both within a distance of 0.2 nm.

The criterion for the optimum conformation was the upper enthalpy of the system. From the 24 systems studied, three were chosen as the most suitable and they are shown in Fig. 2 in the form of slightly occupied molecular orbitals (SOMO). It is clear that these orbitals are π-symmetric. The measured values of the splitting constants of the hydrogen atoms reflect considerable spin–spin interaction. The experimental splitting constants were correlated with the calculated spin densities (ρ_H^{UHF}) and their mutual proportionality was utilised. Thus, $a_H^{exp} = Q\rho_H^{UHF}$, where ρ_H^{UHF} is the spin density on the appropriate hydrogen atom and Q is the proportionality constant obtained by the least squares method for the available set of ρ_H^{UHF} values. The correlation coefficient was 0.999311 and the R factor was 0.0266 [$R = \Sigma(a_i^{exp} - a_i^{calc})^2/\Sigma(a_i^{exp})^2$; the value of Q obtained was 240.6 $\pm$ 1.71]. The results of the calculations are summarised in Table I.

On the basis of quantum chemical calculations (energy criterion; Table I), the most probable structure appears to be **1**. However, because of the limited accuracy of

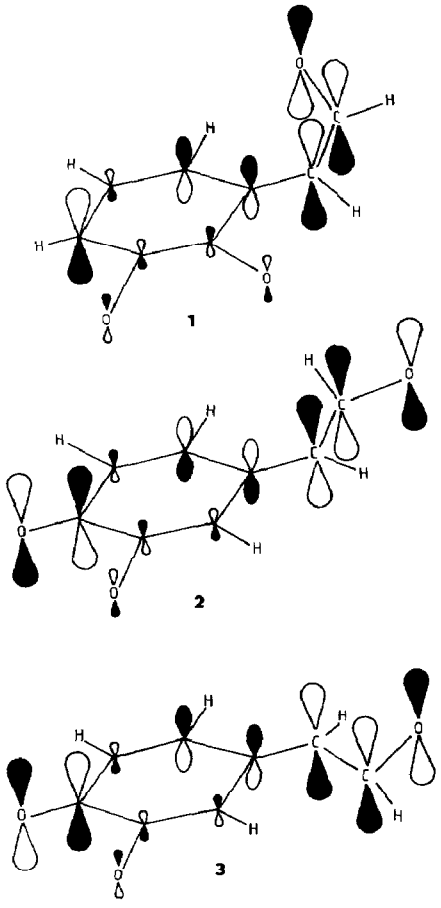

Fig. 2. The SOMO drawings of the structures **1**–**3** with π-symmetry.

the semiempirical AM1 method, structures **2** and **3** could not be eliminated. This conclusion is supported also by the good agreement between experimental and calculated splitting constants for all three structures. The importance of counter-ions must be emphasised, because they not only increase the stability of dianion-radicals but also cause dramatic changes in the distribution of their spins.

All three structures proposed indicate that the enolate structure can be stabilised and incorporated into a semiquinone structure when there is no hydroxyl group in the position α to the anomeric carbon. This conclusion was confirmed by the fact that 3-deoxy-D-*ribo*-hexose gave semiquinones without the involvement of stabilisation. These structures were identical with those obtained from D-glucose and common sugars with a free hemiacetal group, and which have been characterised[1,2].

TABLE I

Calculated characteristics of the dianion-radicals 1–3

Structure	a_H^{exp} (*mT*)	a_H^{calc} (*mT*)	*ΔH* (*kJ/mol*)	*Ionisation potential* (*eV*)
1	0.014	0.016	−856.94	6.31
	0.008	0.010		
	0.157	0.152		
	0.027	0.029		
	0.195	0.200		
2	0.014	0.016	−786.14	6.34
	0.008	0.010		
	0.157	0.159		
	0.027	0.034		
	0.195	0.199		
3	0.014	0.016	−786.48	6.31
	0.008	0.010		
	0.157	0.165		
	0.027	0.031		
	0.195	0.202		

EXPERIMENTAL

General methods. — The e.s.r. spectrum was obtained with a Bruker ER-200D-SRC spectrometer equipped with the data system ER140 based on an ASPEC computer.

Formation of radicals. — Solutions (M) of substrate in 6M sodium hydroxide were prepared in the presence of air and immediately poured into the cell, which was kept at 100°. After cooling the solution to room temperature, the e.s.r. signals were measured.

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