Formation and Structure of Radicals from D-Ribose and 2-Deoxy-D-ribose by Reactions with $SO_4^{\cdot-}$ Radicals in Aqueous Solution. An *in-situ* Electron Spin Resonance Study

Janko N. Herak

Faculty of Pharmacy and Biochemistry, The University of Zagreb, Zagreb, Croatia, Yugoslavia

and

Günter Behrens

Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim a.d. Ruhr, Bundesrepublik Deutschland

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ESR spectroscopy has been used to analyse the conformation of the radicals produced by the reaction of $SO_4^{\cdot-}$ with D-ribose (**1**), and 2-deoxy-D-ribose (**6**), at pH 1.3–5. From ribose three different types of radicals formed by H abstraction at C-1, C-2 and C-3 followed by a regioselective α,β-water elimination have been identified: the 2-deoxy-ribonolacton-2-yl (**3**), the 1-deoxy-pentopyranos-2-ulos-1-yl (**4**), and the 4-deoxy-pentopyranos-3-ulos-4-yl (**2**). Using deoxyribose two radicals of similar type, formed by H abstraction at C-3 and C-4 followed by water elimination, have been observed: the 2,4-dideoxy-3-ulos-4-yl (**7**) and the 2,3-dideoxy-4-ulos-3-yl (**8**). In addition, from both sugars an α-hydroxyalkyl radical has been identified based in part on the timing of their conformational motions: the ribos-3-yl (**5**) (the precursor of **2**) and the 2-deoxy-ribos-1-yl (**9**), respectively. For radical **5** the rate constant $k(e)$ for the water elimination and hence transformation into radical **2** was estimated. From the analysis of selective line broadening the frequencies of conformational changes of radicals **2** and **7** have been estimated. For **7** the frequencies of exchange of the two methylene groups were found to differ by more than 3 orders of magnitude.

Introduction

Considerable attention has been payed to the study of radical reactions of carbohydrates [1–7]. Part of the reason for this lies in the importance of such reactions in radiation chemistry of nucleic acids and their constituents [8–10]. In most ESR studies of simple sugars the radicals were produced in the reaction of these compounds with OH, generated from Ti^{III} and H_2O_2 in a three-way mixing system in an ESR cavity [1, 3–5]. In some of these studies it has been shown [3, 5], that the attack of the hydroxyl radicals in the sugars is rather unselective. In the acidic solutions the α,β-dihydroxy substituted radicals originally formed by H-abstraction are transformed into carbonyl-conjugated radicals, $R_2\dot{C}-CO-$, by elimination of water. Although it has been stated that such radical rearrangements take place also in D-ribose and deoxy-D-ribose [1, 5], no detailed spectroscopic analysis of the carbonyl-conjugated radicals, $-\dot{C}H-CO-$, has been reported except for one radical derived from D-ribose [1].

In the present paper we report the ESR analysis of the $-\dot{C}H-CO-$ type radicals produced from D-ribose and 2-deoxy-D-ribose. From the ESR parameters of the spectra we deduced the site of the unpaired electron, from which we can deduce the structure of the precursor radical and the direction of the water elimination reaction. In cases where two different reactions of this type from the same precursor compete, we can conclude from the *type* of the keto-conjugated radical (ulosyl type) observed, which of the two reactions is the preferred one. The regioselectivity of such processes is explained in terms of the stability of the transition states of some of these radicals. From the line width analysis the rates of interconversions of conformation of some radicals have been estimated.

Experimental

The $SO_4^{\cdot-}$ radicals generated by photolysis of peroxodisulfate, $S_2O_8^{2-}$, were used for abstraction of H atoms from the substrates. To an aqueous solution of ca. 10^{-2} mol·dm^{-3} of substrate and 3×10^{-3} mol·dm^{-3} of $K_2S_2O_8$, about 3×10^{-2} mol·dm^{-3} of acetone was added to sensitize the photolytic cleav-

Reprint requests to Dr. G. Behrens.

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age of $S_2O_8^{2-}$ [8, 11]. The radicals were studied *in situ* with ESR spectroscopy at ca. 9.5 GHz and constant temperatures, *e.g.* 4 °C. The arrangement was described elsewhere [11, 12]. The photolysis was conducted at continuous flow using a 1 kW superpressure mercury arc focussed at a flat cell made of fused Suprasil quartz plates. The cell was designed in our laboratory especially for the use with lossy water samples, even those of high conductivity. With this arrangement the production rate of $SO_4^{\cdot}$ radicals was about 1.5×10^{-4} mol·dm^{-3}·s^{-1}. The samples were deaerated by continuously bubbling argon through the solution before flowing it through the cell.

D-Ribose and 2-deoxy-D-ribose (Sigma) and $K_2S_2O_8$ (Merck) were used without further purification.

Results

D-Ribose

Using D-ribose at pH ≈ 4, a complex spectrum, depicted in Fig. 1, was obtained. A closer inspection shows that there are at least four radicals present, each with a different *g* factor. At pH 1.3 three of them were still observable. The two sets of the prominent double doublets together with two similar sets of lines on the low-field side (not shown) belong to a single radical species. The separation between the two sets, one at the low- and the other at the high-field side, is 6.86 mT. Since such separation is too large to be a doublet H-splitting, we conclude that there must be some much broader resonances in the

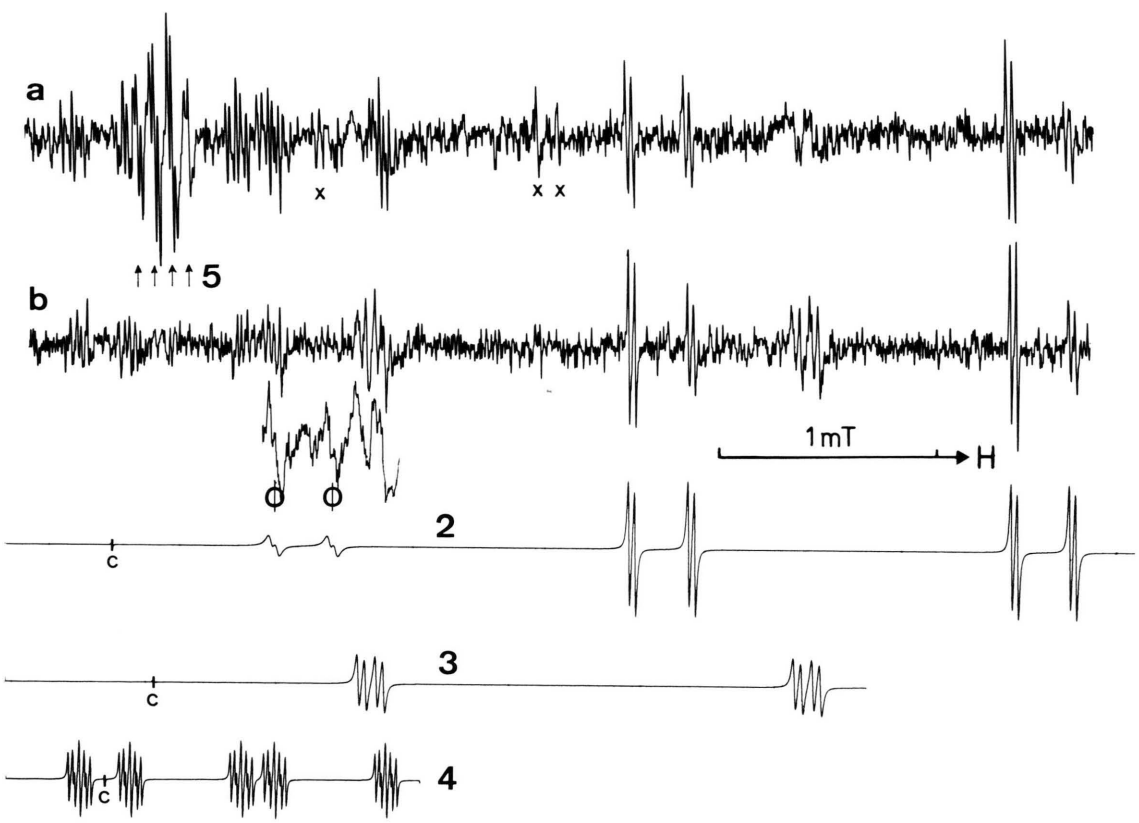


Fig. 1. High-field part of ESR spectra of D-ribose at pH 4.0 (a), and at pH 1.3 (b). Below are the simulated spectra of radicals **2**, **3** and **4**, respectively. For simulations the line widths of 0.010, 0.014 and 0.006 mT were used, respectively. For the two inner groups of lines of radical **2** the width of 0.028 mT is used. The centres of the spectra are marked by c. The four arrows indicate the lines corresponding to radical **5**. The insert depicts the broadened lines (Φ) of radical **2** measured at three-fold modulation amplitude and microwave power, and pH adjusted to 1.7. Some extra lines (×) have not been assigned.

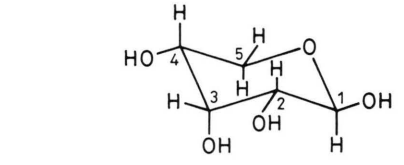
middle part of the spectrum, hardly to observe under the high resolution conditions applied. The situation is very similar to that first observed for the vinyl radical [13] or even more similar to the 1,4-dioxan-2-yl radical [14]. It is reasonable to assume that the separation of 6.86 mT corresponds to the sum of two β-proton splittings, the average being 3.43 mT. The other parameters are 1.762, 0.272 and 0.029 mT and $g = 2.0044$. The simulated spectrum, calculated with these parameters is also shown in Fig. 1. For simulation the width of 0.010 mT for the lines belonging to the outer four groups, and 0.028 mT for the inner groups of lines are used. The simulated spectrum fits the measured one nicely. The broader inner lines are too broad to be clearly observed at moderate resolution used in Fig. 1a and 1b. However, they are seen better when higher microwave power and larger modulation amplitude were applied (see lines marked ϕ in Fig. 1b). The broadening of these lines is brought about by the exchange of two non-equivalent protons at "intermediate rates", see Discussion.

In aqueous solution D-ribose is known to be predominantly in the pyranose form. Of the four different conformers in equilibrium in water conformer **1** is the most abundant one [15]. The above spectroscopic parameters are assigned to radical **2** because of the similarity with the ESR parameters of the analogous radical derived from xylose [5].

The couplings of the γ-H at C-2 (0.272 mT) and of the δ-proton at C-1 (0.029 mT) on the other side of the carbonyl group are slightly larger than the related couplings in similar open-chain radicals, *e.g.*: $\dot{C}H_2-CO-CH_2-CH_2-CH_2-OH$ [8].

The second spectrum consisting of broad doublets at pH 4, further split in smaller doublets (0.035 mT) at pH 1.3 is characterized by $a(\alpha H) = 2.020$ mT, $a(\beta H) = 4.040$ mT, $a(\gamma H) = 0.085$, $a(\delta H) = 0.035$ mT and $g = 2.0034$. The spectrum is assigned to radical **3**, mainly on the basis of its *g* factor, which is typical for the ester type radicals (*viz.* $R'-\dot{C}H-CO-O-R''$) [16]. The lines are sharper at pH 1.3 than at pH 4, because the frequency of the protonation – deprotonation exchange at a β-hydroxyl group (*e.g.* at C-3) is faster at lower pH [12]. The large splitting of the β-proton indicates this proton to be axial. Radical **3** is formed by H abstraction at C-1 and followed by water elimination. This radical has already been observed and identified [1]. In the present study we obtain much higher resolution and more precise spectroscopic parameters.

The eight distinct groups of well resolved lines (in Fig. 1, only five groups are depicted) belong to radical **4**. The splittings and *g* factor (see Table I) are similar to the values assigned to an analogous radical in D-glucose [3]. Our spectrum of **4** is better resolved;



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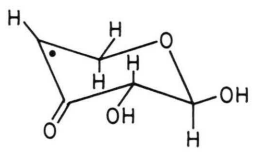

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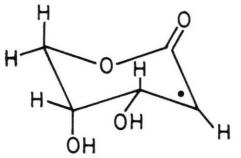

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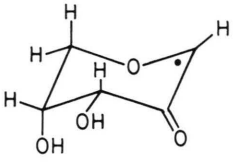

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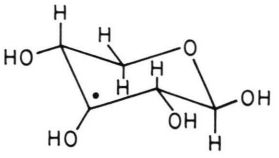

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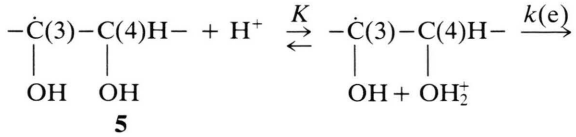
Table I. ESR parameters of radicals obtained from D-ribose and D-deoxyribose.

Radical	Hyperfine splittings (mT) $a(\alpha H)$	$a(\beta H)$	$a(\gamma H)$	a (other)	g factor
2	1.762	3.430*	0.272	0.029	2.0044
3	2.020	4.040	0.085	0.035	2.0034
			0.670		
4	1.420		0.518	0.028	2.0049
			0.052	0.020	
5					2.0031
7	1.788	3.43*	0.186		
			0.130	0.012	2.0043
			0.076		
8	1.798	3.175*	0.064		2.0043
			0.040		
9					2.0031

* Averaged splittings of two non-equivalent protons.

the couplings of all protons, except one, are observed. This radical is derived from the α-hydroxy radical formed by H-abstraction from ribose at C-2. The unpaired electron at the C-1 site is conjugated with a carbonyl group at one side and the ether group on the other side. From that fact we expect radical **4** to have the largest g factor of all radicals we have obtained from D-ribose after H-abstraction (see Table I).

The remaining strong signals (marked by arrows) in the middle of the spectrum at pH 4 have been noticed earlier [5]. They look like a quartet (a = 0.075 mT), further split into triplets, and are characterized by g = 2.0031. Gilbert and coworkers [5] assigned the lines to radical **5**. The in-phase flipping of the radical between two conformers (one designated by **5** and the other one with the hydrogens on C-2 and C-4 in the equatorial position) at rates in the intermediate exchange region causes the wings of the outer lines of the spectra of two *equivalent* β-protons to be broadened and therefore not observed. The central line of the 1:2:1 triplet is further split by additional protons. From the existing experimental data it is not possible to conclude which of the four pyranose conformers is responsible for radical **5**. At lower pH the signals of this radical disappear at the expense of radical **2** (which is observed with increased intensity) as seen in Fig. 1b, according to the following equation:



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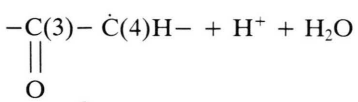

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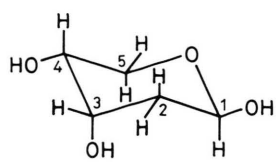
At pH 5.5 radical **5** reaches its maximum concentration while radical **2** is hardly observed. The stationary concentration of radical R_o, which can be transformed by water elimination, is reduced to 70% of the maximum concentration when the bimolecular termination rate is equal to the rate of water elimination [17]:

$$k(\mathrm{e}) = 2k(\mathrm{term}) \cdot K \cdot [\mathrm{R}]/[\mathrm{H}^+].$$

[R] stands for the stationary concentration of all radicals derived from the substrate. Half of the amount of radical **5** is transformed into radical **2** at pH 3.3, which corresponds to the proton concentration $[H^+] = 5 \times 10^{-4}$ mol·dm^{-3}. From the production rate (see Experimental) [R] = 4×10^{-7} mol·dm^{-3}. By assuming $2k$(term) = 10^9 mol·dm^{-3}·s^{-1} and K (K = k(dissociation)/k(protonation)) to be similar to that found for 1,2-dihydroxyethyl radical by Bansal *et al.* [18], K = 0.18 mol·dm^{-3}, we get k(e) = 1.4×10^5 s^{-1} for radical **5**, which is also the rate constant of formation of radical **2**.

2-Deoxy-D-ribose

Using 2-deoxy-D-ribose (**6**) as substrate two prominent spectra are observed; both comprise four groups of lines (Fig. 2). Like for radical **2** in D-ribose, the separation between the two symmetrically positioned groups of about 6 mT is far too large to account for any proton splitting. Here we also conclude that the complete spectra for each of the two radical species comprise two more groups of lines, located closer to the center of the spectrum. These lines are much broader than the outer lines for the same reasons as stated for radical **2**. The positions of these lines are barely observable under our experimental conditions (see Fig. 2). The prominent four groups of lines compose a spectrum that can be described by g = 2.0043 and the following proton couplings: a(αH) = 1.788 mT, a(β2H) = 3.43 mT, a(γ1H) = 0.186, a(γ2H) = 0.130 mT and a(δH) = 0.012 mT (see Table I). These parameters are assigned to radical **7**. The simulated spectrum for this radical is also shown in Fig. 2. All the protons, except the one of the hydroxyl group give rise to resolved splittings. The fact that the two inner lines in each of the line groups are broader than the outer ones suggests the flipping of the γ-positioned meth-



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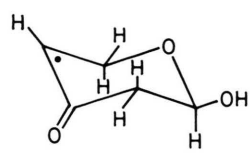

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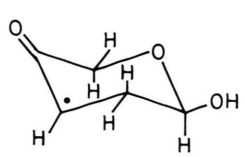

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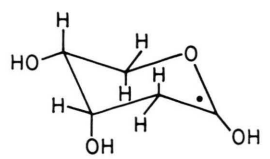

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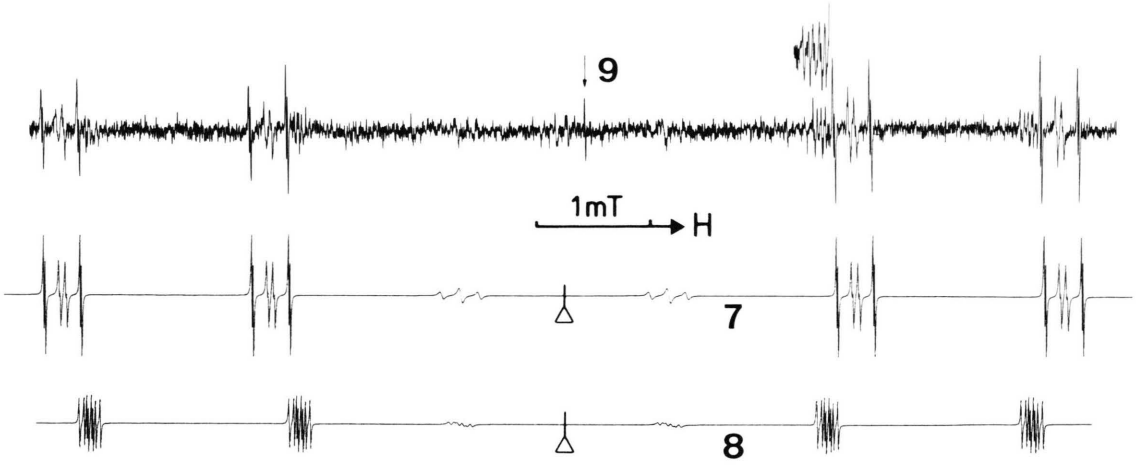

Fig. 2. ESR spectra of 2-deoxy-D-ribose at pH 3.0. The insert (**8**) is recorded at slower rate and higher resolution, presented at extended scale (1.4 ×). The simulated spectra for radicals **7** and **8** are shown below. For the simulation the line width of 0.007 mT was used. Different line widths were used for the inner two groups of the spectra of radicals **7** and **8** (0.025 mT) (the two β proton couplings are assumed to be equal), and the inner lines of the side groups in radical **7** (0.010 mT) (the two γ proton couplings assumed equal). The centres of the spectra are marked by triangles. The arrow indicates the line assigned to radical **9**. Some weak lines shown in the record have not been assigned.

ylene group. The kinetics of the proton "exchange" will be discussed later.

The four groups of sharp lines adjacent to and partly overlapping the lines belonging to radical **7** compose a second spectrum with $g = 2.0043$. A closer inspection of the parameters (see Table I) shows that the radical in question must be very similar to radical **7**. We assign these parameters to radical **8**. Strictly speaking, it is not possible to distinguish the structures of radicals **7** and **8** solely on the basis of their couplings and g factors. Our assignment is based on the similarity of the α- and β-proton splittings between radicals **2** and **7**.

At pH 4 a strong single line at $g = 2.0031$ is observed which is still present at pH 1.8. We believe that line represents radical **9**. The g factor of 2.0031 is characteristic for α-OH radicals [3, 5]. Radical **9** is the only α-OH radical derived from 2-deoxy-D-ribose which cannot get transformed by elimination since it has no β leaving group. Like in radical **5**, the flipping of the two groups of methylene protons at intermediate rates causes the outer lines to be broadened beyond detection, see Discussion.

Discussion

It has been found that $SO_4^{\cdot}$ radicals readily abstract hydrogen atoms from both D-ribose and 2-deoxy-D-ribose in aqueous solutions. The initially formed radicals are mostly not observed due to the elimination processes. Most of the radicals observed are produced from the initial ones by water elimination:

$$R'-\dot{C}(OH)-C(OH)H-R'' \xrightarrow{H^+} R'-CO-\dot{C}H-R'' + H_2O.$$

In both D-ribose and 2-deoxy-D-ribose not all possible radicals of this kind are observed. In D-ribose the product radicals derived from the radicals formed after H-abstraction at C-1 (radical **3**), C-2 (radical **4**), and C-3 (radical **2**), are detected. In addition, the precursor radical formed by H abstraction at C-3 (radical **5**) is observed. In contrast, no radicals that would indicate H-abstraction at C-4 or C-5 were observed. In 2-deoxy-D-ribose, the observed radicals **7** and **8** are the reaction products of the radicals formed by H abstraction from C-3 and C-4, respectively. Radical **9** is formed by H-abstraction at C-1. No indication for the H-abstraction by the $SO_4^{\cdot}$ radical at the two methylene groups (C-2 and C-5) has been observed, probably due to the intramolecular competition.

It is obvious that the formation of the $-\dot{C}H-CO-$ radicals by water elimination is a selective process. It has been noticed [2, 3] that the α,β-water elimination process is favoured for a conformation with a leaving β-hydroxy group in the direction of p-orbital of the

unpaired electron, *viz.* axial OH groups. The absence of carbonyl-conjugated radicals derived from $\dot{C}(4)-OH$ in D-ribose cannot be understood solely on the basis of lower reactivity of the equatorial β-hydroxy groups. The D-ribose conformer **1** with a β-OH in axial position at C-3, abundant in solution, would give rise to radicals $-\dot{C}(3)H-C(4)O-$, which were not observed. It is possible that the axial H atom at C-4 in conformer **1** is less likely to be abstracted. It is also worth mentioning that from the first-formed 2-yl radical only radical **4** is formed. The water elimination from radical C(2) shifting the radical site toward C(3) (2→3 water elimination) seems to be slower than the 2→1-water elimination: radical $-\dot{C}(3)H-C(2)O-$ is not observed. Likewise, from the 3-yl radical only the 3→4-water elimination is observed (radical **2**). The $-\dot{C}(2)H-C(3)-O-$ radical was not formed, indicating that the 3→2-water elimination cannot compete with the 3→4 elimination. We do not see convincing arguments that the steric factors could account for the observed differences in reactivities. However, different stability of the transition states involved could explain these differences.

From the product analysis a number of different radical species is expected to be formed in irradiated aqueous solutions of D-ribose [19] and 2-deoxy-D-ribose [20]. In the present study only some of these have been observed. The difference can be explained by the fact that in the two studies the initial radicals are different. The OH radicals, the major reactive species in ^{60}Co-irradiated aqueous solutions in the presence of N_2O [19, 20], are essentially unselective in their chemical reaction with sugars as substrates [2, 3, 5, 20, 21]. In contrast, the $SO_4^{\cdot-}$ radical used in the present study, is much more selective in the reaction with the type of substrates as used in the present work [22–24].

A very interesting feature of some of the radicals in these systems is the appearance of selectively broadened lines in the spectra. It is well known that the broadening is associated with the rate of the radical conformation change. In radicals **2**, **7**, and **8** the two non-equivalent methylene protons in β-position give rise to a triplet structure with a broader central line (instead of four discrete lines), see the Figures. In this case the exchange rate is close to the fast-exchange limit [25, 26], characterized by the correlation time $\tau_c < 1/(a_1 + a_2) \cdot \gamma_e$, where a_1 and a_2 are the coupling constants and γ_e is the gyromagnetic ratio ($\nu/B = g_e \cdot \mu_B/h = 2.8025 \times 10^7$ Hz/mT). The sum $a_1 + a_2 \approx 6.8$ mT and hence the fast exchange limit is $\tau_c < 5 \times 10^{-9}$ s. The fast exchange broadens the inner lines according to the relation

$$\Delta a = \frac{1}{8\pi} \cdot \gamma_e \cdot (a_1 - a_2)^2 (M_{I_1} - M_{I_2})^2 \tau_c,$$

where I_1 and I_2 are the spins of the coupling nuclei and M_{I_1} and M_{I_2} are the exchanging spin states [25]. (The outer components do not change the sign of M, and $M_{I_1} = M_{I_2}$ and hence broadening does not occur.) For radicals **2** and **7**, the exchange-broadening of the inner lines, Δa, was estimated to be 0.018 mT. If the exchange takes place between an equatorial and an axial proton in the methylene group at the β-position, it is reasonable to assume that $a_1 - a_2 \approx 4$ mT. That gives $\tau_c \approx 10^{-9}$ s and consequently the rate of conformational change is $\approx 10^9$ s^{-1}.

The exchange rate of the γ-methylene protons of radical **7** is not so fast. The four lines due to two different couplings are clearly resolved. In this case the flipping rate is close to the slow exchange limit, $\tau_c > 1/(a_1 + a_2)\gamma_e$. Since $a_1 + a_2 \approx 0.3$ mT, τ_c is expected to be $\tau_c > 1.2 \times 10^{-7}$ s. In such cases the broadening. Δa, is related to the correlation time as [25]:

$$\Delta a = 1/(2\pi\tau_c\gamma_e).$$

The inner two lines are broadened by about 0.003 mT and the correlation time for the flipping γ-methylene protons, $-C(5)H_2-$, is $\tau_c \approx 2 \times 10^{-6}$ s, corresponding to the rate of conformational change of $\approx 5 \times 10^5$ s^{-1}.

The absence of all but the central lines in radicals **5** and **9** is explained in a similar way. In radical **5** the unpaired spin, located on C-3, is surrounded by symmetrically arranged groups. In such a case the flipping of equally-coupling protons bound to C-2 and C-4 may be considered to modulate the splitting *in-phase*. If the flipping rate is in the intermediate range, the outer two lines of the quasi-triplet are smeared out and not observed. The line width of the center line is not affected by this type of exchange. In D-ribose the middle line is further split by the interaction of the unpaired electron probably with the adjacent OH and with other not assigned protons. In deoxy-D-ribose, the situation with the 1-yl radical **9** is somewhat different. In this radical the *in-phase* modulation of the $-C(2)H_2-$ and of the γ′-methylene proton splittings may be responsible for a similar

broadening of the outer lines and for the observation of only one line, the center line.

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