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Time-resolved CIDNP as a probe of 2,2′-dipyridyl radical anion complexation with β-cyclodextrin

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Abstract

The photochemical reaction of 2,2′-dipyridyl (DP) with 5-sulfosalicylic acid (SSA) was studied using time-resolved CIDNP in homogeneous and β-cyclodextrin (β-CD) aqueous solutions. The degenerate electron exchange rate constant of DP radical anion with diamagnetic precursor was estimated as 1.1×10^8 M^{-1} s^{-1} from CIDNP kinetic in homogeneous solution. It was found that DP-β-CD inclusion complex formation alter the kinetics of DP polarization. For β-CD solution the drastic decreasing of nuclear relaxation time of DP radical anion was found comparing to the homogeneous solution.

1. Introduction

Control of chemical processes by carrying out the reactions in the so called microreactors: micelles, liposomes, lysosomes, host-guest complexes – is one of the most popular trends in modern physical chemistry. However despite the abundance of organized media suggested by organic chemists and numerous data on the effect of these media on chemical processes [1] the details of particular mechanisms of reactions especially in host-guest complexes are still not clear [2,3]. Chemically induced dynamic nuclear polarization (CIDNP) method is known to be the most adequate technique for the study of mechanisms of radical processes [4]. In one experimental series the combination of NMR and CIDNP techniques allows to establish the fact of complex formation and to identify short-lived paramagnetic intermediates formed in both complex and solution, and trace the kinetics of these particles.

We have already reported the complexation behavior of the benzyl radical formed by the process of dibenzyl ketone photodecay in the β-CD solution [5]. We have shown that benzyl radical formed from complexed dibenzyl ketone remains in CD complex and is kept in the β-CD cavity for the time sufficient for relaxation of nuclear polarization. We have estimated the retention time to be not less than 10 μs.

In the present work the complexation behavior of 2,2′-dipyridyl (DP) radical anion was studied. The capture of hydrated electron on DP molecule was used as a source of DP radical anions. Hydrated electrons were generated by two-photon ionization of 5-sulfosalicylic acid (SSA) in water solution. The main photochemical form of SSA in the wide range of pH (4–10) is its dianion ($HSSA^{2-}$). Excitation of the $HSSA^{2-}$ (XeCl laser, 308 nm) under high laser intensity (>40 mJ/cm^2) leads to formation of HSSA radical anion and hydrated electron [6].

2. Experimental section

2.1. Chemicals

2,2′-Dypyridyl (minimum 99.8%, Reanal, Budapest) was recrystallized from petroleum ether. β-Cyclodextrin (minimum 98%, Sigma–Aldrich), 5-Sulfosalicylic acid (Aldrich) and D_2O (99.8% isotopic purity, Aldrich) were used as received.

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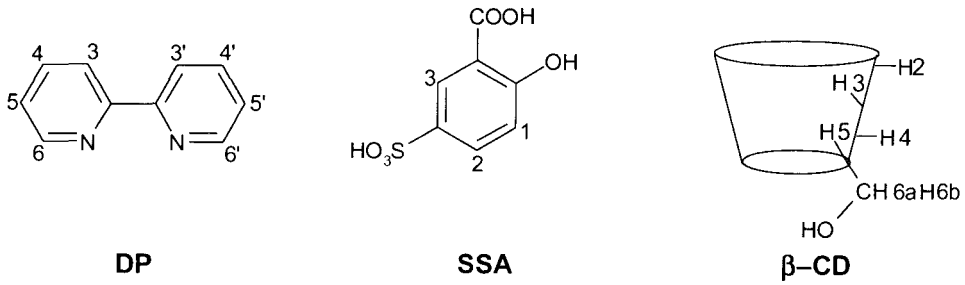


2.2. Equipment

^{1}H NMR spectra were taken on a BRUKER DPX200 NMR spectrometer (200 MHz ^{1}H operating frequency, ($\tau(90°) = 7.2$ μs) at 20 °C. A Lambda Physik EMG 101 MSC eximer laser was used as a light source (308 nm, 100 mJ at output window, 20 mJ/pulse in sample volume, pulse duration of 15 ns) for CIDNP. The samples in standard 5 mm Pyrex NMR tubes were irradiated directly in the probe of NMR spectrometer. The samples were bubbled with argon for 10 min to remove dissolved oxygen just before photolysis.

2.3. NMR-titration

Stock solutions of 10 mM β-CD and 10 mM DP were prepared in D_2O. To perform the NMR shift titrations host-guest solutions were prepared by mixing given aliquots of both components and D_2O directly in the NMR tubes (5 mm, Pyrex). The concentration of DP was constantly equal to 1 mM. The β-CD concentrations ranged between 1 and 9 mM. The pD of 10 mM DP solution was 7.4 (pH 7.8). For stoichiometry determination by Job's method the samples were prepared by mixing of 10 mM stock solutions of DP and β-CD in different ratio keeping sample volume constant.

2.4. Time-resolved CIDNP

Time-resolved CIDNP experiments [7,8] were performed for mixture containing 2 mM of DP, 4 mM of SSA and 0 or 7 mM of β-CD. The delay time between laser and detection pulses was varied from 0 to 50 μs. The pD of 20 mM SSA solution was brought to 9.4. The pD of probe solution was 8.5.

3. Results and discussion

The complexation efficiencies of SSA and DP with β-CD have to be known before the complexation behavior of the radical anions can be analyzed. NMR spectroscopy demonstrated that SSA does not form inclusion complexes with β-CD. On the contrary, DP forms such complexes. The ^{1}H NMR spectrum exhibits the upfield shift of the H5 β-CD signal and the downfield shift of DP protons. The stoichiometry of DP-β-CD inclusion complex was determined by the Job method to be 1:1. H3, H4 DP protons undergo maximum variations. These protons are the AB part of ABKY system [9] (inset in Fig. 1). Therefore the formation constant K_f of the inclusion complex DP-β-CD was estimated from the change in the central frequency of H3 and H4 DP protons versus increasing of β-CD concentration [10] (Fig. 1). A nonlinear fitting has yielded $K_f = 130 \pm 20\ M^{-1}$.

3.1. The study of SSA photo-ionization in the presence of DP in a homogeneous solution

In our system, the light is absorbed by both components, SSA and DP. In this case, the ratio between the absorption intensities of the substances is equal to the ratio between their optical densities [11]:

$$\frac{I_{HSSA^2}}{I} = \frac{D^{308}_{HSSA^2}}{D^{308}_{HSSA^2} + D^{308}_{DP}},$$

where I is the absorption intensity, and D^{308} is the optical density at 308 nm. The extinction coefficients of components are $\varepsilon^{308}_{HSSA^2} = 1950\ M^{-1}\ cm^{-1}$ and $\varepsilon^{308}_{DP} = 290\ M^{-1}\ cm^{-1}$.

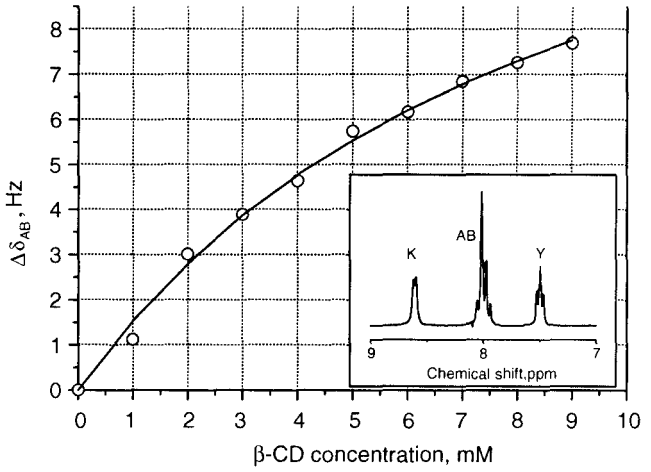


Fig. 1. Nonlinear fit (solid line) of DP chemical shifts variation with the β-CD concentration. [DP] = 2 mM. The inset shows the structure of DP ^{1}H NMR spectrum.

Taking into account the concentrations of the substances (2 mM DP and 4 mM SSA) we get $\frac{I_{HSSA^{2-}}}{I} = 0.93$, i.e., 93% of the light is absorbed by $HSSA^{2-}$ to form the radical pair: HSSA radical anion and hydrated electron. ^1H photo-CIDNP spectrum of the investigated system shows the polarized signals of both SSA and DP (Fig. 2).

Most likely transformations of the primary active intermediates in the investigated system are the recombination of the primary radical ion pair (RIP) resulting in the formation of initial $HSSA^{2-}$ and the capture of the hydrated electron on DP and $HSSA^{2-}$ (Scheme 1).

The rate constants of the capture of hydrated electron for both DP and $HSSA^{2-}$ are available from the literature:

$$e^-_{aq} + 2,2' - DP \xrightarrow{k_1} 2,2' - DP^{\cdot -}$$

$$k_1 = (2.0 \pm 0.2) \times 10^{10} M^{-1} s^{-1} [12], \quad (1)$$

$$e^-_{aq} + HSSA^{2-} \xrightarrow{k_2} HSSA^{\cdot 3-}$$

$$k_2 = (2.7 \pm 0.1) \times 10^{9} M^{-1} s^{-1} [6]. \quad (2)$$

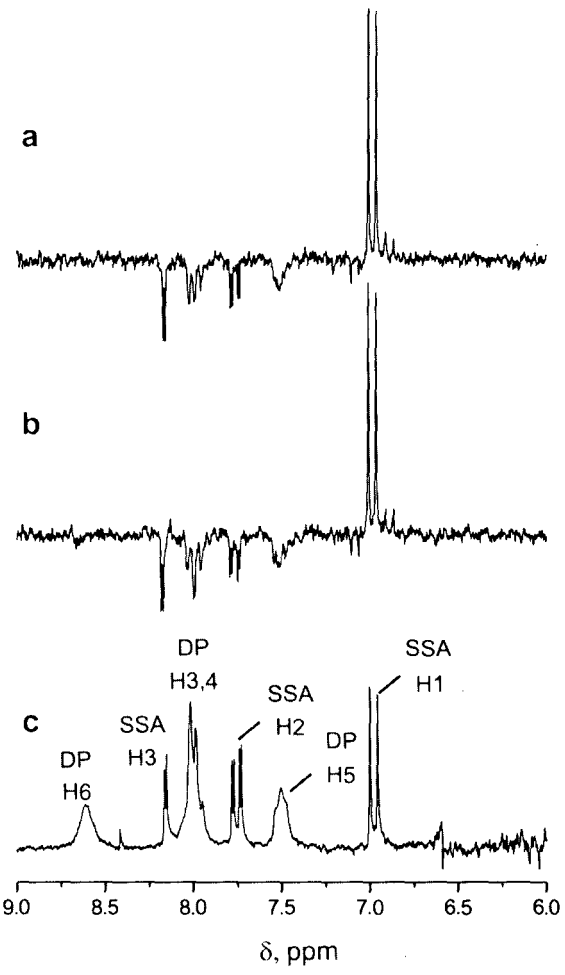


Fig. 2. Partial ^1H photo-CIDNP spectrum of (a) 2 mM DP and 4 mM SSA (at delay time 2 μs, $\tau(90°) = 2\mu s$); (b) 2 mM DP, 4 mM SSA and 6.7 mM β-CD; (c) initial ^1H NMR spectrum of 2 mM DP and 4 mM SSA.

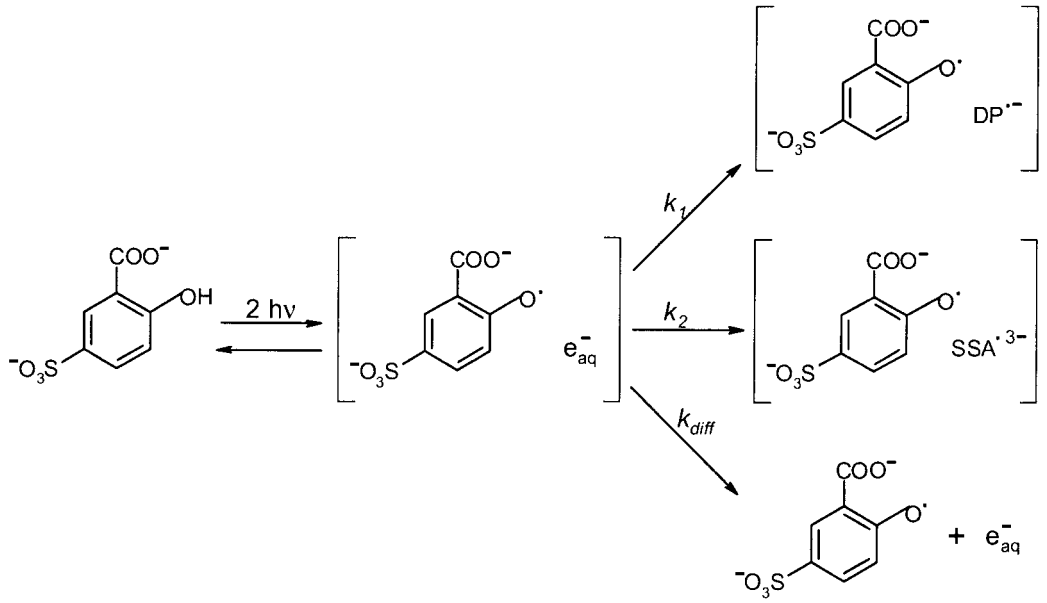
We can estimate the characteristic time of electron capture in these competing reactions: $\tau_1 = 25$ ns, $\tau_2 = 110$ ns. According to these estimates, more than 80% of hydrated electrons are captured by DP molecules to form DP radical anion. The characteristic recombination time of the primary RIP in polar solvents lies in the range of several nanoseconds [13] for oppositely charged radicals. In our case, the radicals are of the same charge. So, the recombination time of the primary RIP is expected to increase due to the repulsive Coulomb interaction between the partners [4]. The characteristic time of the DP electron capture corresponds to a geminate process. Then, RIP $[HSSA^{\cdot -}DP^{\cdot -}]$ formed in this process has to also be geminate. According to [6] the precursor RIP $[HSSA^{\cdot -}e^-_{aq}]$ has singlet multiplicity. Examination of DP polarization sign using the Kaptein rules ($\Gamma = \mu \cdot \varepsilon \cdot a \cdot \Delta g$) [14] gives the same multiplicity for RIP $[HSSA^{\cdot -}\ DP^{\cdot -}]$.

Indeed, Γ is negative for negative net CIDNP on DP protons. The g-factors of radicals are available from the literature and correspond to $g_{DP^{\cdot}} = 2.0030$ [15], $g_{HSSA^{\cdot}} = 2.00476$ [6], so Δg is also negative. The hfi constants for the DP radical anion correspond to H3 = H3′:0.120 mT; H4 = H4′:0.105 mT; H5 = H5′:0.458 mT; H6 = H6′:0.054 mT [16] (numeration corresponds to the structural formulas given in the Experimental section). In compliance with mechanism of spin density infiltration into the even alternant hydrocarbon protons the hfi constants for the DP radical anion protons are negative ($a < 0$). Since the polarized DP is initially the product of back electron transfer in RIP, then $\varepsilon > 0$. Therefore, $\mu < 0$, i.e., the primary RIP $[HSSA^{\cdot -}e^-_{aq}]$ in the singlet state is the precursor of the RIP $[HSSA^{\cdot -}DP^{\cdot -}]$. Thus, the analysis of polarization on DP confirms the assumption of the preservation of spin correlation in the RIP $[HSSA^{\cdot -}DP^{\cdot -}]$.

Let us consider now the polarization kinetics observed in a given reaction. The SSA polarization intensity is almost time-independent which is likely to be due to either a short time of nuclear relaxation in the HSSA radical anion or a slow (slower than nuclear relaxation) process of degenerate electron exchange between radical ion and $HSSA^{2-}$. The time dependence of DP polarization is shown in Fig. 3b. The substantial polarization is observed only for the small delays between a laser and detection pulses; further the polarization decreases rapidly to zero. Fig. 3b shows also the best approximation of the time dependence of DP polarization according to the first-order kinetics. The process which annihilated polarization by the first-order process rate can be the degenerate electron exchange between the DP radical anion and its diamagnetic precursor [17]:

$$\downarrow DP^{\cdot -} + DP \overset{k_{ex}}{\rightleftarrows} DP^{\cdot -} + \downarrow DP, \quad (3)$$

where k_{ex} is an electron exchange constant. In addition, owing to the high protonation rate of the DP radical anion [18], the observed polarization compensation with time can be related to proton exchange:



Scheme 1.

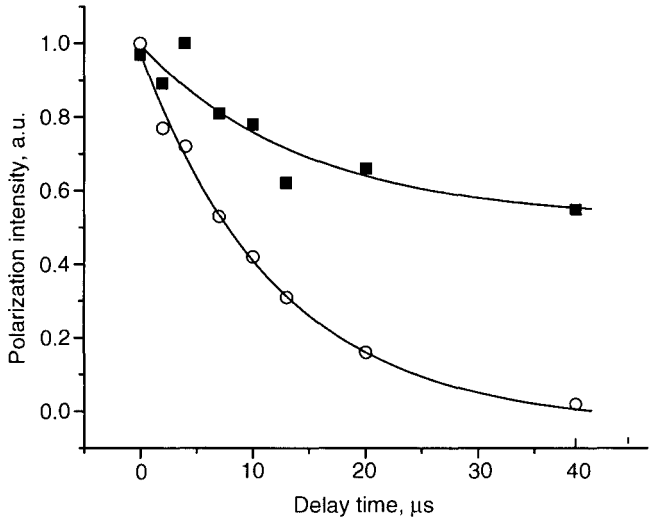


Fig. 3. Dependence of polarization intensity on H3, H4 DP on the delay between the laser and recording pulses (normalized to polarization intensity on H1 SSA): (○): in homogeneous solution; (■): in β-CD solution.

$$\downarrow \mathrm{DPH}^{\cdot} + \mathrm{DP} \overset{k'_{ex}}{\Longleftrightarrow} \mathrm{DPH}^{\cdot} + \downarrow \mathrm{DP}, \tag{4}$$

where k'_{ex} is a proton exchange constant. However the kinetics study of polarization of the DP formed from the DPH shows that the process (4) is slower than nuclear relaxation in DPH ($O_{1DPH} = 44$ μs) [18].

The total compensation of geminate polarization holds for slow relaxation:

$$k_{ex}([\mathrm{DP}] + [\mathrm{DP}^{\cdot -}]) \gg \frac{1}{T_{1R}},$$

where T_{1R} is the time of nuclear spin-lattice relaxation of $DP^{\cdot -}$. When there is a substantial difference in the concentrations of DP and intermediates, which corresponds to our experimental conditions, the time dependence of polarization intensity is of the form [19]:

$$I_{DP}(t) = I_{DP}(0) \times e^{-k_{ex}[DP]t},$$

where I_{DP} is the DP polarization intensity. The polarization destruction follows the first order with the rate constant k_{ex}[DP] which can be estimated from experimental kinetics as $(9 \pm 0.3) \times 10^4\ s^{-1}$. Allowing for the concentration used $k_{ex} = (5.5 \pm .015) \times 10^7\ M^{-1}\ s^{-1}$. Studying the polarization kinetics one can observe only half the exchange processes related to the exchange of the polarized radical and non-polarized molecule [13]. Therefore, the total exchange constant is $2 \times k_{ex}$, i.e. $(1.1 \pm 0.3) \times 10^8\ M^{-1}\ s^{-1}$.

3.2. The study of photoreaction between DP and SSA in the β-CD aqueous solution

As mentioned above, β-CD can form inclusion complexes with DP whereas no stable complexes with $HSSA^{2-}$ are detected. So in β-CD aqueous solutions the reaction between complexed (DP) and uncomplexed ($HSSA^{2-}$) reagent is expected. The photoreaction has been studied using the following concentrations of reagents: 2 mM DP, 4 mM SSA, and 6.7 mM β-CD. In this case, at any moment, a molar fraction of DP is about 0.6 in the free state (P_{DP}) and about 0.4 in the complex ($P_{DP:CD}$). The observed CIDNP effects are the same as in a homogeneous solution. But, the kinetics of DP polarization changes in the presence of β-CD. The DP CIDNP intensity decrease to 60% as regards to initial value.

The observed kinetics of DP polarization can be explained in terms of some assumption. First, the rate con-

stants of the capture of activated electron by DP in both free state and the complex are almost the same. Since the rate constant of the capture of activated electron is close to the diffusion limit and is determined mainly by the diffusion of the activated electron, we consider this assumption justified. For example, the rate constant of the capture of activated electron for the pyrene-1-sulfonate ion (1.7×10^{10} M^{-1} s^{-1} [20]) is comparable with that for DP in homogeneous solution. At the same time, the rate constant for its complex with β-CD is 9.1×10^{9} M^{-1} s^{-1} [20]. Thus, the molar fractions of successive radical pairs ([HSSA$^{\bullet}$ $^{-}$DP$^{\bullet-}$]and[HSSA$^{\bullet}$ $^{-}$DP$^{\bullet-}$:CD]) should be close to those of P_{DP} and $P_{DP:CD}$. Assuming also that the probabilities of recombination for these pairs have close values we can estimate the ratio between the concentrations of radical ions that escaped the geminate recombination: $\chi_{DP}/\chi_{DP:CD}\sim P_{DP}/P_{DP:CD}$, where χ_{DP} and $\chi_{DP:CD}$ are the molar fractions of radical anions in a solution and in the complex with β-CD, respectively.

The observed kinetics of DP polarization in β-CD solution corresponds to the situation when the life-time of the DP radical anion is of the same order of magnitude as the relaxation time T_{1R}, so the polarization is destroyed incompletely and the stationary polarization is observed due to competition between the reactions of exchange (3) and relaxation.

When $t\rightarrow\infty$ the expression for the stationary polarization of DP is of the form:

$$I_{DP}(\infty)=I_{DP}(0)\left(1-\frac{W_3}{W_4+W_3}\right)=I_{DP}(0)\frac{1/T_{1R}}{k_{ex}[DP]+1/T_{1R}},$$

where $I_{DP}(0)$ is the geminate polarization corresponding to the experimental one at the initial moment, and W_3 and W_4 are the rates of exchange and nuclear relaxation, respectively.

The complete evolution of DP polarization in β-CD solution can be illustrated by the following set of processes:

$$DP_{|}^{\bullet-}+DP\overset{k_{ex}(5)}{\Longleftrightarrow}DP^{\bullet-}+DP_{|} \quad (5)$$

$$DP_{|}^{\bullet-}:CD+DP\overset{k_{ex}(6)}{\Longleftrightarrow}DP^{\bullet-}+DP_{|}:CD \quad (6)$$

$$DP_{|}^{\bullet-}+DP:CD\overset{k_{ex}(7)}{\Longleftrightarrow}DP^{\bullet-}:CD+DP_{|} \quad (7)$$

$$DP_{|}^{\bullet-}:CD+DP:CD\overset{k_{ex}(8)}{\Longleftrightarrow}DP^{\bullet-}:CD+DP_{|}:CD \quad (8)$$

$$DP_{|}^{\bullet-}\xrightarrow{1/T_{1R}(9)}DP \quad (9)$$

$$DP_{|}^{\bullet-}:CD\xrightarrow{1/T_{1R}(10)}DP:CD \quad (10)$$

$$DP_{|}^{\bullet-}:CD\underset{k(11.2)}{\overset{k(11.1)}{\rightleftharpoons}}DP_{|}^{\bullet-}+CD \quad (11)$$

In general the rate constants of processes (5)–(7) correspond to the following ratio: $k_{ex}(5)\neq k_{ex}(6)=k_{ex}(7)\neq k_{ex}(8)$ and $1/T_{1R}(9)\ll 1/T_{1R}(10)$ [5]. Let us consider the limiting cases.

(1) The escape o the DP radical anion from the complex with β-CD is faster than nuclear relaxation in the complex, i.e. $k(11.1)\gg 1/T_{1R}$ (10). The polarization kinetics will be described mainly by processes (5), (7) and (9). The situation, in this case, should be close to a homogeneous solution, i.e., polarization should tend to zero with time.

(2) The escape o the DP radical anion from the complex with β-CD is slower than nuclear relaxation in the complex, i.e., $k(11.1)\ll 1/T_{1R}$ (10). In this case, the part of escape polarization corresponding to a molar fraction of DP radical anions in the complex with β-CD relaxes rapidly to the equilibrium value which prevents it from penetrating into DP due to exchange. This is close to the case observed, i.e., $I_{DP}(\infty)/I_{DP}(0)=0.6$.

Moreover, if the rate constant of complex formation, $k(11.2)$, is close to the diffusion one (more than 10^{8} M^{-1} s^{-1}), then for the employed β-CD concentrations we can rapidly (faster than the degenerate electron exchange) reach equilibrium, and the nuclear relaxation in the DP radical anion will be described by the effective rate of to processes (9) and (10) [21]:

$$1/T_{1R,eff}=\chi_{DP}1/T_{1R}\ (9)\ +\chi_{DP:CD}1/T_{1R}\ (10).$$

This effective relaxation time is estimated as 7 μs, whereas for a homogeneous solution this time corresponds to T_{1R} (9) and its value substantially exceeds the characteristic time of the CIDNP kinetics decay (10 μs).

We have already shown that the nuclear relaxation time in the radical located in the complex with β-CD can decrease by more than the order of magnitude as compared with the free radical [5]. Therefore, a substantial decrease in the effective time of nuclear spin-lattice relaxation in a cyclodextrin solution as compared with the homogeneous one, indicates that the radical anion is kept in the β-CD cavity for the time sufficient for the relaxation of nuclear polarization.

So this is a second example illustrating the influence of host-guest complex formation on the chemical polarization of short-lived intermediates.

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