Available online at www.sciencedirect.com
SCIENCE DIRECT®
Chemical Physics Letters 385 (2004) 40–44
CHEMICAL PHYSICS LETTERS
www.elsevier.com/locate/cplett

Time-resolved photo-CIDNP of dibenzyl ketone-β-cyclodextrin inclusion complex

S.S. Petrova, A.I. Kruppa *, T.V. Leshina

Institute of Chemical Kinetics and Combustion, Magnetic Phenomena Laboratory, Insitutskaya str. 3, Novosibirsk 630090, Russia

Received 11 November 2003; in final form 11 December 2003
Published online: 14 January 2004

Abstract

This work presents the first observations of time-resolved photo-CIDNP in the dibenzyl-ketone-β-cyclodextrin (DBK–β-CD) inclusion complex. The photo-decay of the DBK–β-CD inclusion complex gives a benzyl radical that is held in the β-CD cavity for a time exceeding the time of its nuclear spin lattice relaxation. By estimating a change in the radical spin-lattice relaxation time in the complex, we determined that the rate constant of dissociation of β-CD complex with the radical is $\leqslant 10^5$ s^{-1}.

1. Introduction

Supramolecular structures of the host–guest type play an important role in a wide range of physicochemical processes: from molecular identification to the development of novel materials. One of the fundamental peculiarities of these systems is the reactivity of guest molecules in the complexes compared to that in solution. A study of the influence of complex formation on radical processes, is of particular interest. Previously, the influence of the inclusion complex on the selectivity of radical processes has been demonstrated using monomolecular photo-processes (ketone decay by Norrish, type I, etc.) [1]. In this case, changes in selectivity are observed both in the solid state and in solutions in which the formation of supramolecular structures can be considered as a model of enzyme-substrate complexes whose existence is assumed to provide a high selectivity of enzymatic processes.

α, β, γ-Cyclodextrins (CDs) are most widely involved in complex formation. These are oligosaccharides consisting of six, seven, and eight α(1–4)-bound glucose residuals that form a cavity of a diameter of ~0.57, ~0.78, and ~0.95 nm, respectively [2]. It is assumed that during complex formation, a guest molecule is partially or completely placed inside this cavity and is held there. If a guest molecule is subjected to chemical transformation, i.e., homolysis of a bond, electron exchange, etc., the active intermediates formed are expected to be initially located also in the CD cavity [3]. The steric difficulties that arise can change the selectivity of the chemical processes, particularly if several potentially reactive intermediates are present [1]. Therefore, one of the factors determining the influence of CD on selectivity is its ability to retain active intermediates. Our recent time-resolved (TR) CIDNP confirmed a fairly long confinement of radicals in a complex [4]. On the other hand, the data obtained by another method of spin chemistry (CIDEP) [5] indicates that radicals cannot be held in the CD cavity for more than several nanoseconds.

To obtain the detail information on the behavior of radicals generated in the CD cavity, we compared the TR photo-CIDNP data for homogeneous solutions with those obtained for complexes with CD. The fact that the time dependence of CIDNP is observed only for the processes occurring in the bulk, whereas the polarization of products formed in geminate processes is time-independent is well-known. The CIDNP time dependence of the reaction products formed in the bulk depends on the recombination rate constant (for radicals,

* Corresponding author. Fax: +7-3832-342350.
E-mail address: kruppa@kinetics.nsc.ru (A.I. Kruppa).

0009-2614/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2003.12.036

it is usually the diffusion encounter constant) and the time of nuclear spin-lattice relaxation in radicals [6]. The complexation of intermediate radicals can affect both parameters. Understanding the influence of complexation on the selectivity of various photo-processes involving radicals with more than one reaction center [7] will necessitate a change in CIDNP mechanism and in the products of geminate recombination. It is expected that the time-resolved photo-CIDNP can be a sensitive method for studying the complexation of short-lived intermediates within CDs. In the present work, we used the TR ^{1}H CIDNP method to study the influence of complexation on the physicochemical characteristics of radical species and, their residence time in a complex using the monomolecular photo-decay of dibenzylketone (DBK). The mechanism of DBK photolysis in solutions has been studied in detail [8]. β-Cyclodextrin (β-CD) was used as the inclusion compound.

2. Experimental

2.1. Chemicals

β-Cyclodextrin was used as received (Aldrich). DBK (Aldrich) was recrystallized from aqueous ethanol. CD_3CN (99.98% D, CIL) was used without additional purification. D_2O (99.9% D) was purchased from Aldrich.

2.2. CIDNP

The samples in standard 5 mm Pyrex NMR tubes were irradiated directly in the probe of NMR spectrometer at 50 °C. The samples were bubbled with argon for 10 min to remove dissolved oxygen just before photolysis. The TR CIDNP [9] experiments were performed using a DPX200 BRUKER NMR spectrometer (200 MHz ^{1}H operating frequency, $\tau(90°) = 7.2$ μs). The Lambda Physik EMG 101 MSC excimer laser was used as a light source (308 nm, 15 ns, 100 mJ at output window and 20 mJ per pulse in the sample volume). For TR experiments, the detection radio frequency pulse width was 2 μs for a homogeneous solution DBK in CD_3CN, and 4.2 μs for a DBK–β-CD complex, the delay time between laser and detection pulses was varied from 0 to 1000 μs.

The presaturation of the equilibrium NMR signals of initial compounds [10] in all experiments allows us to observe the polarized signals only in CD_3CN. In D_2O the non-fully saturated signal of residual protons is registered additionally.

The CIDNP time dependences were obtained for 1 mM of DBK solutions in CD_3CN and for 1 mM of DBK in the presence of 1 and 5 mM of β-CD in D_2O.

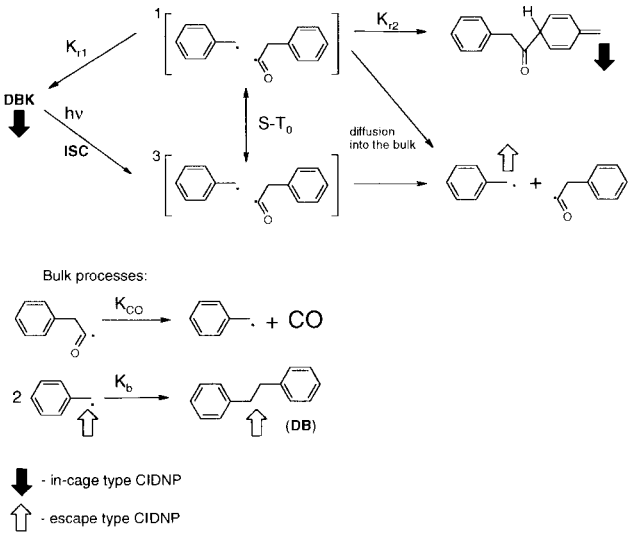
2.3. Preparation of DBK–β-CD complexes

The equimolar amount of DBK dissolved in a small amount of CD_3CN was added to an aqueous (D_2O) solution of β-CD (1 mM), and the reaction mixture was stirred for 10 h. The suspension was then heated up to 50 °C in order to get a transparent solution suitable for NMR studies. For a 1:5 mixture, the same amount of DBK was added to a 5 mM solution of β-CD in D_2O.

3. Results and discussion

To study the peculiarities of TR CIDNP effects during DBK photolysis both in solution and in a complex, we compared their time dependences.

It is established that the DBK photolysis in solution is described by the following scheme [8]:



where K_{r1} and K_{r2} are the rate constants of radicals recombination in primary radical pair resulting in initial DBK and 4-methyl-phenylbenzyl ketone. K_{CO} is decarbonylation rate constant of free phenylacetyl radical and K_b is bimolecular recombination rate constant of benzyl radicals. Assuming the importance of hydrophobic interactions in CD complexation [3], we suggest that the CD cavity mostly contains a more hydrophobic benzyl radical (BR). The changes in CIDNP effects are also possible because it is known that the source of polarization in this reaction is the hyperfine interactions of BR. The HFC constant of BR (~1.6 mT [11]) is greater than that of phenylacetyl radical (< 0.1 mT [12]).

The decarbonylation rate of free nonpolarized phenylacetyl radical is faster (K_{CO} is about 10^7 s^{-1} [13,14]) than the time resolution of our experimental setup. Under these conditions the CIDNP time dependence of dibenzyl

(DB) is fully determined by bimolecular recombination of benzyl radicals (K_b).

Fig. 1a shows the photo-CIDNP spectrum recorded during the DBK photo-decay in acetonitrile. By the end of the bulk processes (200 μs), the polarization of the major escape product (DB) is equal to the polarization of in-cage DBK but with an opposite sign. Fig. 1b shows the time dependence of DBK and DB polarizations. The DBK polarization is time independent and the characteristic time of DB formation (~10 μs) is shorter than the time of the nuclear relaxation in BR (~350 μs [15]). Taking this into account, the CIDNP spectrum for a delay time of 200 μs is in a good agreement with the CIDNP theory for high magnetic fields [6]. Fig. 2a shows a similar photo-CIDNP spectrum for photolysis of the 1:1 mixture of DBK and β-CD in D_2O. Fig. 2b presents the time dependence of polarized signals. The ratio between the DBK and DB polarizations observed is changed substantially. For a delay time of 200 μs the DB polarization is about 40% of the DBK one. A change in the DB polarization intensity compared to that of DBK can be due to a change in the ratio between the rates of bimolecular recombination and nuclear

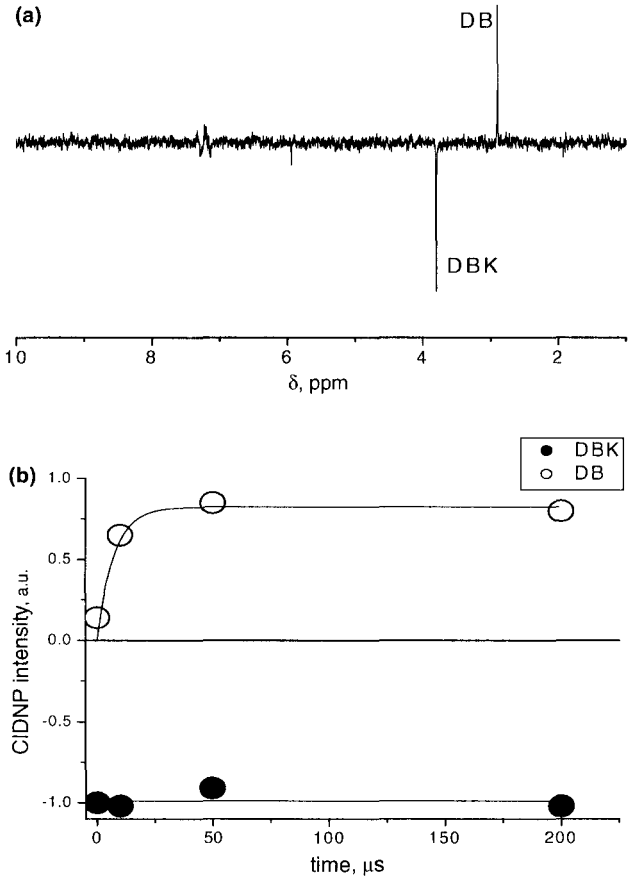


Fig. 1. (a) ^{1}H photo-CIDNP spectrum of DBK photolysis in CD_3CD at delay time 200 μs, 16 scans, $B_0 = 1$ mM, $A = 0$. (b) Photo-CIDNP time dependence in CD_3CN.

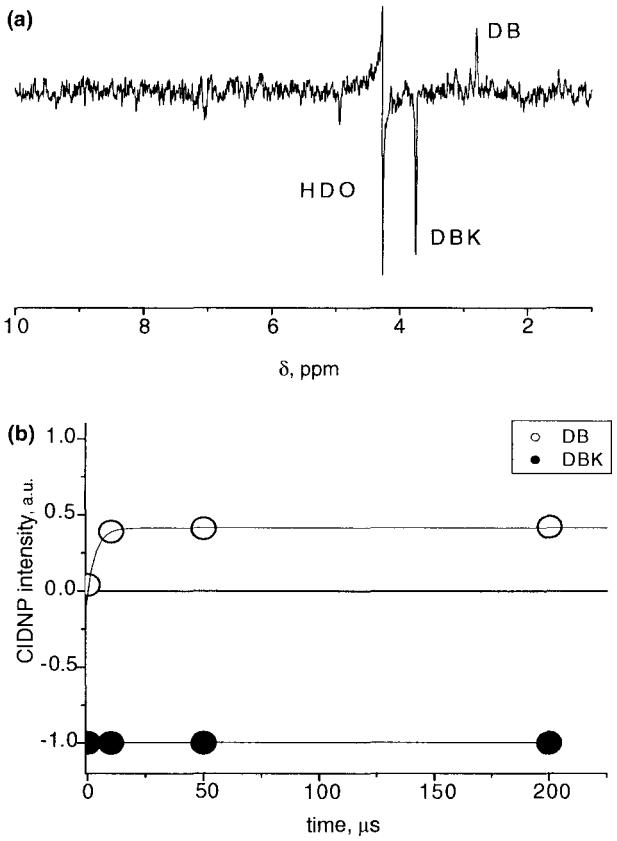


Fig. 2. (a) ^{1}H photo-CIDNP spectrum of DBK–β-CD complex photolysis in D_2O at delay time 200 μs, 32 scans, $B_0 = 1$ mM, $A = 1$, HDO is the signal of residual protons in D_2O (see Section 2). (b) Photo-CIDNP time dependence in D_2O, $A = 1$.

relaxation in a radical. Thus, a part of polarized radicals have time to be subjected to relaxation prior to their recombination. It is also possible that the existence of DB polarization in a 1:1 mixture is caused by photolysis of noncomplexed DBK molecules. Let us consider this in more detail.

Denoting the initial DBK concentration by B_0 and the ratio between the initial concentrations of β-CD and DBK as A, from the equation for a complex dissociation constant:

$$K = \frac{[\beta\text{-CD}][\text{DBK}]}{[\text{DBK}\text{–}\beta\text{-CD}]},$$

one can find the concentration of nonassociated DBK molecules as:

$$[\text{DBK}] = \frac{B_0(A-1)+K}{2}\left[\sqrt{1+\frac{4KB_0}{[B_0(A-1)]^2}}-1\right].$$

The dissociation constant K of the DBK–β-CD complex is known and according to [7] amounts to 8.6×10^{-4} M. For the relations $A = 1$ and 5 and the initial DBK concentration of 1 mM, the concentration of nonassociated DBK molecules will be 0.6 and 0.16 mM,

respectively. Thus, for $A = 1$ most of the DBK molecules are in the free state and otherwise for $A = 5$ they are mostly in the complexed state. Indeed, Fig. 3 shows that for $A = 5$ no DB polarization was observed for only the polarization of DBK formed as a primary pair product is recorded. We concluded that the source of DB polarization for $A = 1$ is photolysis of noncomplexed DBK molecules whereas the photolysis of the DBK–β-CD complex leads to the polarization of DBK only (compare Fig. 2a with Fig. 3a). The two following conclusions can be drawn. First, the assumption that the β-CD cavity contains just the benzyl and not the phenylacetyl fragment is considered true. Second, it may be deduced that $K_{\text{diss}} < T_{1N}^{-1}$, where K_{diss} is the dissociation rate of BR-β-CD complex, because the nuclear polarization in benzyl radicals vanishes before their escape into the bulk.

Now let us ascertain how complexation can affect the time of nuclear relaxation in the system studied. According to the literature, there are the data on the influence of complexation on the spin–spin relaxation time of stable radicals complexed with β-CD [16,17]. In β-CD complexes, the anisotropies of both g-tensor and HFI contribute to electron relaxation. It is known that the HFI anisotropy also contributes to the nuclear spin-lattice relaxation in radicals [18], this contribution is assumed to change for BR in the β-CD cavity.

To understand how the T_{1N}^{-1} value depends on the surroundings, let us first estimate it for BR in solution. According to the literature [11], the components of HFI tensor for the BR CH_2-protons are: 1.436, 0.725 and 2.511 mT and the isotropic constant is 1.557 mT. Since the trace of the anisotropic part of the tensor tends to zero, the nuclear relaxation rate in a radical obeys the equation [19]:

$$T_{1N}^{-1} = \frac{1}{12}(\Delta a^2)\frac{\tau_c}{1+\omega^2\tau_c^2},$$

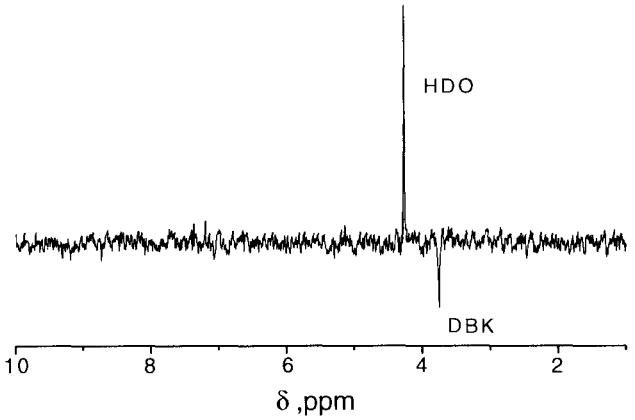


Fig. 3. ^{1}H photo-CIDNP spectrum of DBK–β-CD complex photolysis in D_2O at delay time 200 μs, 32 scans, $B_0 = 1$ mM, $A = 5$. HDO is the signal of residual protons in D_2O (see Section 2).

where ω is the resonance frequency of the NMR spectrometer, $(\Delta a^2) = (a_{xx} - a_{\text{iso}})^2 + (a_{yy} - a_{\text{iso}})^2 + (a_{zz} - a_{\text{iso}})^2$, and τ_c is the time of rotational radical correlation. It is shown [8] that the BR diffusion in solutions is well described by a hydrodynamic Stokes–Einstein model. In this case, we observe a satisfactory linear dependence of the translation diffusion coefficient on the T/η ratio, where T is the temperature and η is the solvent viscosity. The experimental value $D_{\text{trans}}(BR) = 0.91 \times 10^{-9}$ m^2 s^{-1} ($T = 298$ K and $\eta = 0.01$ P) [8]. From the Stokes–Einstein relationship, $D_{\text{trans}} = kT/(6\pi r_A \eta)$ we can determine a BR hydrodynamic radius (r_A), which can be used to estimate the time of rotational correlation [18]:

$$\tau_c = \frac{4\pi r_A^3 \eta}{3kT}.$$

For a viscosity of 0.01 P and a temperature range of 298–323 K, we get the value $\omega^2\tau_c^2 \ll 1$. Therefore, the resonance frequency of the NMR spectrometer has no noticeable effect on the times of nuclear relaxation in a radical. The time of spin-lattice relaxation of the BR CH_2-protons is estimated to be ~200 μs. Since we do not know any specific interactions between a BR and solvents (hydrogen bonding, complexing), the value estimated should be compared with the known value of 350 μs [15] determined in chloroform ($\eta = 0.006$ P). Taking into account the difference in the viscosities of the solvents, the estimate obtained is in fair agreement with the literature value. This indicates HFI anisotropy is a main component of nuclear relaxation of a free BR.

When the radical is in the inclusion complex, its relaxation can change significantly as compared to that of a free radical. Since the HFC tensor anisotropy is weakly dependent on whether BR is in solution or in an inclusion complex; of major importance is the influence of complexation on the rotational correlation time. As has been shown, for the radicals whose volume is comparable with or smaller than that of the inner CD cavity, there are two types of rotational correlation times: $\tau_\parallel$ – for the rotation along the axis of the CD cavity and $\tau_\perp$ [16,19]. It was found that $\tau_\perp$ is well approximated by the Stokes–Einstein relationship for the entire CD molecule and radical rotation along the CD cavity axis ($\tau_\parallel$) can occur 10–40 times faster. On the other hand, no rotation anisotropy is observed for compounds of larger volume and without free rotation in a cavity (e.g., adamanthylmethylamine) [20]. The maximum change in relaxation times can be expected for the case where the radical is rigidly fixed in the CD cavity. In this limiting case, the ratio between the relaxation times of the free radical and the radical in the complex, with respect to the above relationships, can be found from:

$$\frac{T_{1N}(\text{BR})}{T_{1N}(\text{BR–β-CD})} = \frac{r_A^3(\text{BR–β-CD})}{r_A^3(\text{BR})} \approx \frac{D_{\text{trans}}^3(\text{BR})}{D_{\text{trans}}^3(\text{BR–β-CD})}.$$

We think that the estimate obtained from the experimental values of translational diffusion coefficients is most correct because it takes into account the influence of the complex and radical nonsphericity. It is shown [20] that even for fairly large guest molecules the coefficient of inclusion complex diffusion is almost equal to the CD molecule diffusion coefficient. Thus, the diffusion coefficients of adamanthyl-methylamine and β-CD in the complex are 0.42×10^{-9} and $\sim 0.40 \times 10^{-9}$ m^2 s^{-1}, respectively whereas their diffusion coefficients for the free state are 0.84×10^{-9} and 0.32×10^{-9} m^2 s^{-1} (D_2O, 298 K). In this case, the diffusion coefficient is also linearly dependent on the T/η ratio [21]. The diffusion motion of inclusion complexes is also well described by the Stokes–Einstein model. Assuming that BR is firmly held in the β-CD cavity, D_{trans}(BR-β-CD) is taken to correspond to $\sim 0.4 \times 10^{-9}$ m^2 s^{-1}. Thus, the above estimates indicate that when BR is in the β-CD cavity, the relaxation time of CH_2-protons decreases to about 10 μs. The estimated nuclear relaxation time is minimal because a rapid rotation of BR along the axis of the β-CD cavity results in the loss of a contribution from HFC tensor components to the relaxation rate.

Based on the DB CIDNP dependence on the β-CD concentration, we concluded that the residence time of BR in a complex exceeds nuclear spin-lattice relaxation time. Therefore, the rate constant of the BR-β-CD complex dissociation should not exceed 10^5 s^{-1}. For nitrophenol, comparable in its size and structure with BR, the rate constant of the dissociation of its complex with α-CD was determined to be 10^5 s^{-1} [22]. On the other hand, it is known that the dissociation constants of the complexes of 4-nitrophenol with α- and β-CD are close to each other. This allows us to assume that the dissociation rate constants of the complexes are also close to each other. In these assumptions, our estimate for the dissociation rate constant of the BR complex with β-CD is in agreement with the data on molecules similar in size to BR.

It should be noted that the results obtained for benzoin photolysis in CD solutions confirmed the confinement of hydroxybenzyl radicals in the β-CD cavity. These results are in disagreement with conclusions based on the studies of this process by CIDEP methods [5]. They reported fast ejection of the fragment radicals from the β-CD cavity. Work on the elucidation of the reasons for the differences in the results of the two spin chemical methods is in progress.

Acknowledgements

The authors are grateful to the Russian Foundation for Fundamental Research (RFBR, Grant 03-03-32403) for financial support of this study.

References

[1] V. Ramamurthy, Tetrahedron 42 (1986) 5753.
[2] J. Szejtli, Chem. Rev. 98 (1998) 1743.
[3] K. Takahashi, Chem. Rev. 98 (1998) 2013.
[4] S.S. Petrova, A.I. Kruppa, T.V. Leshina, Book of Abstracts VI Voevodsky Conference, Novosibirsk, 2002, p. 193.
[5] Y. Kitahama, H. Murai, Chem. Phys. Lett. 261 (1996) 160.
[6] K.M. Salikhov, Yu.N. Molin, R.Z. Sagdeev, A.L. Buchachenko, in: Yu.N. Molin (Ed.), Spin Polarization and Magnetic Effects in Radical Reactions, Akamemiai Kiado, Budapest, 1984, p. 419.
[7] B.R. Rao, M.S. Syamala, N.J. Turro, V. Ramamurthy, J. Org. Chem. 52 (1987) 5517.
[8] K. Okamoto, N. Hirota, M. Terazima, J. Phys. Chem. A 101 (1997) 5269, and references therein.
[9] G.L. Closs, R.J. Miller, J. Am. Chem. Soc. 101 (1979) 1639; G.L. Closs, R.J. Miller, J. Am. Chem. Soc. 103 (1981) 3586.
[10] S. Schablin, A. Wokaun, R.R. Ernst, J. Magn. Reson. 27 (1977) 273.
[11] J.M. Park, C.A. McDowell, Mol. Phys. 32 (1976) 1511.
[12] H. Fisher, K.-H. Hellwege (Eds.), Landolt–Bornstein New Series, Numerical Data and Functional Relationship in Science and Technology: Magnetic Properties of Free Radicals, Group II, Part C, vol. 9, Springer, Berlin, 1977–1979.
[13] M.J. Perkins, P.B. Roberts, J. Chem. Soc. Perk. Trans. II (1974) 297.
[14] G.F. Lehr, N.J. Turro, Tetrahedron 37 (1981) 3411.
[15] G.L. Closs, A. Trifunac, J. Am. Chem. Soc. 92 (1970) 7227.
[16] M. Okazaki, K. Kuwata, J.Phys. Chem. 88 (1984) 4181.
[17] M. Okazaki, K. Kuwata, J. Phys. Chem. 88 (1984) 3163.
[18] C.P. Poole, H.A. Farrah, Relaxation in Magnetic Resonance, Academic Press, New York, 1971, p. 392.
[19] N. Balabai, B. Linton, A. Napper, S. Priyadarshy, A.P. Sukharevsky, H.D. Waldeck, J. Phys. Chem. 120 (1998) 9617.
[20] M. Sanchez, T. Pamella, E. Cervello, C. Jaime, A. Virgili, Magn. Res. Chem. 38 (2000) 925.
[21] M.P. Eastman, B. Freiha, C.C. Hsu, K.C. Lum, C.A. Chang, J. Phys. Chem. 91 (1987) 1953.
[22] F. Cramer, W. Saenger, H.Ch. Spatz, J. Am. Chem. Soc. 89 (1967) 14.