Low-Field CIDNP and Protonations of Aromatic Hydrocarbon Radical Anions

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Abstract: Reactions of 0.01-0.1 *M* sodium naphthalene, sodium anthracene, and sodium pyrene in THF or DME with water, methanol, or 2-propanol give CIDNP when carried out in a 60-G magnetic field, but not when carried out in a 5000-G field. This provides a new example in which low-field CIDNP experiments can provide information not available through high-field experiments. CIDNP is consistent with reaction mechanisms in which the radical anion is directly protonated, but not consistent with mechanisms in which radical anions initially disproportionate, reaching equilibrium with the corresponding dianions, which are then protonated. Prior kinetic studies support the latter mechanism for the reaction of sodium perylene with water, and, in agreement with these conclusions, we were unable to detect CIDNP from that reaction even in low fields. Protonation of a disodium arene, formed by the disproportionation of the corresponding sodium arene, could give CIDNP if the disproportionation step were not at equilibrium. In the case of the reaction of sodium anthracene with water in THF, experiments with deuterated materials ruled out this possibility as the sole source of CIDNP. The results require that a significant fraction of the reaction proceeds through direct radical anion protonation.

In 1956 Paul, Lipkin, and Weissman proposed that the reaction of naphthalene radical anion with water could follow Scheme I.[1] More recently there has been a considerable effort to gain insight into the full scope of the mechanisms of reactions of aromatic hydrocarbon radical anions with protonating agents, mainly alcohols and water.[2-4] The principal alternative mechanism to Scheme I has been Scheme II, for which there is substantial kinetic evidence in some systems.

Scheme I

$$\mathrm{Ar}^{-} + \mathrm{HOR} \longrightarrow \mathrm{HAr} + \mathrm{OR}^{-}$$
$$\mathrm{HAr} + \mathrm{Ar}^{-} \longrightarrow \mathrm{HAr}^{-} + \mathrm{Ar}$$
$$\mathrm{HAr}^{-} + \mathrm{HOR} \longrightarrow \mathrm{H_2Ar} + \mathrm{OR}^{-}$$

Ar = aromatic hydrocarbon
$\mathrm{H_2Ar}$ = dihydroaromatic hydrocarbon
HAr^- = anion which would result from loss of H^+ by $\mathrm{H_2Ar}$
HAr = radical which would result from loss of $\mathrm{H}\cdot$ by $\mathrm{H_2Ar}$
Ar^- = radical anion which would result from addition of an electron to Ar

Scheme II

$$2\mathrm{Ar}^{-} \rightleftarrows \mathrm{Ar}^{2-} + \mathrm{Ar}$$
$$\mathrm{Ar}^{2-} + \mathrm{HOR} \longrightarrow \mathrm{HAr}^{-} + \mathrm{OR}^{-}$$
$$\mathrm{HAr}^{-} + \mathrm{HOR} \longrightarrow \mathrm{H_2Ar} + \mathrm{OR}^{-}$$

Ar^{2-} = dianion which would result from addition of two electrons to Ar

Most past mechanistic studies of reactions of aromatic radical anions have relied upon product studies, competition experiments, ESR studies, kinetics (conventional, stopped-flow, pulse radiolysis), etc. It has been shown recently that chemically induced dynamic nuclear polarization (CIDNP) can, under certain circumstances, be used as a mechanistic probe for reactions of radical anions (and presumably, of other stable free radicals).[5] Our purposes here are to demonstrate how CIDNP is applicable to radical-anion protonations and to further verify the mechanisms of some of these reactions.

Experimental Section

NMR spectra were recorded on an Hitachi R20 spectrometer (60 MHz). Low fields in which reactions were run were generated by a set of Helmholtz coils. For high-field reactions, a 5000-G permanent magnet was used.

Naphthalene, anthracene, pyrene, and perylene, purity 99+%, were purchased from a commercial source[6] and used without further purification. Anthracene-d_{10} (98% isotopic purity) was also obtained commercially.[7]

THF and DME were the solvents for the reactions. Their purification and handling has been described previously.[8] THF-d_8[9] was the solvent in experiments in which NMR signals obscured by those of THF were examined; these were the "aliphatic" protons of dihydroarenes.

Aromatic hydrocarbon radical anions were prepared following procedures described previously.[8] Concentrations were estimated by quenching aliquots of radical anion solutions with water and titrating the resulting hydroxide solutions with dilute hydrochloric acid.[1]

In each experiment, a radical anion solution (0.5 ml) was injected into an evacuated NMR tube sealed with a serum cap. The NMR tube was placed in the center of the Helmholtz coil arrangement, and a twofold excess of protonating agent (water or alcohol) was injected into the top of the tube. The solutions were mixed by vigorous shaking in a 60-G field until the color of the radical anion disappeared (1-2 sec). Then the NMR tube was quickly transferred to the spectrometer, and an NMR peak was scanned repeatedly if polarization was seen on the initial scan. A stop watch was used to record the time of the first scan. In several instances, the decay of the polarized signal was found to be first order, and apparent relaxation times (T_1) and initial signal enhancement factors (V_0)[10] were calculated.

Results

When the reaction of sodium naphthalene in DME with water was carried out in a field of 5000 G, no CIDNP signals were detected. However, when this and other related reactions were carried out in a field of 60 G, CIDNP was detected in the dihydroarenes which result. Typical signals from polarized reaction products are shown in Figures 1 and 2. In Table I, our CIDNP findings for several radical-anion systems are summarized. In every case, the signals from polarized products were negative peaks (emission).

CIDNP was found from every reaction examined except that of perylene radical anion with water in THF.

Discussion

CIDNP. CIDNP has been reviewed elsewhere.[10] Only those features necessary for our considerations will be set forth here.

In a CIDNP experiment, a reaction is allowed to occur, and the NMR spectra of the products are determined shortly after they are formed. If the intensities of some of the

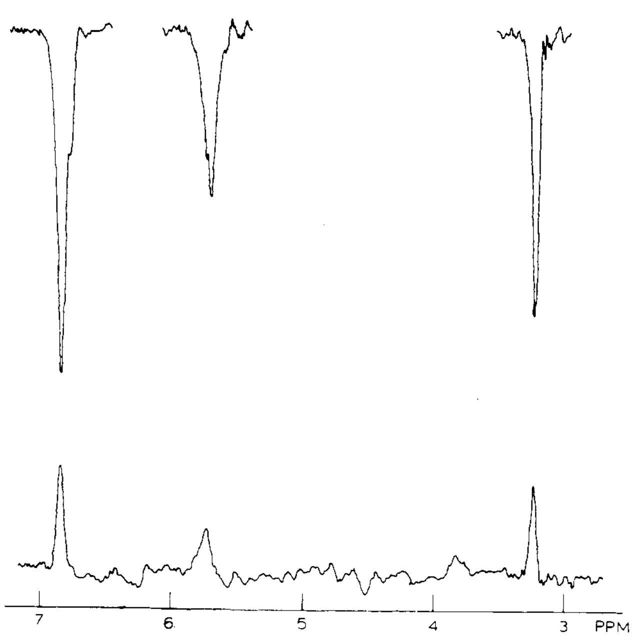

Figure 1. CIDNP spectrum of dihydronaphthalene formed in the reaction of sodium naphthalene in THF-d_8 with water. Each peak (top row) was scanned 5 sec after the reaction was carried out. Bottom peaks are the normal spectrum of aromatic, olefinic, and aliphatic protons of dihydronaphthalene recorded at the same scan rate (0.17 ppm/sec).

Table I. CIDNP in Dihydroaromatic Hydrocarbons from Reactions of Aromatic Hydrocarbon Radical Anions with Protonating Agents[a]

Parent hydrocarbon	Solvent	Proton source	CIDNP signals[b]
Naphthalene	DME	H_2O	Arom,[c] olef
Naphthalene	DME	D_2O	Arom,[d] olef
Naphthalene	THF-d_8	D_2O, H_2O	Arom, olef, aliph
Naphthalene	DME	CH_3OH	Arom, olef
Anthracene	DME	H_2O	Arom
Anthracene	DME	$(CH_3)_2CHOH$	Arom
Anthracene-d_{10}	THF-d_8	H_2O	Aliph[e]
Pyrene	DME	H_2O	Arom
Perylene	THF	H_2O	None detected

[a] In every case, the counterion was sodium, and the experiment was conducted at room temperature. The concentrations of radical anions were in the range 0.01–0.1 *M*. The reactions were carried out in a field of 60 G. [b] All signals were emissive. Each proton in a dihydroaromatic hydrocarbon is aromatic (arom), olefinic (olef), or aliphatic (aliph). [c] T_1 = 9.5 sec; V_0 = 11.5. [d] T_1 = 7.8 sec; V_0 = 9. We consider these values to be experimentally indistinguishable from those in footnote *c*. [e] T_1 = 14.7 sec; V_0 = 5.

NMR transitions are unusual (abnormally large or small, negative), then the reaction gives CIDNP, and the reaction products are said to be polarized. Polarization, in this sense, exists if the populations of the nuclear-spin states are not the equilibrium populations. No polarization exists at equilibrium.

The current theory for thermal reactions is the radical-pair theory, the essential feature of which is that CIDNP results from radical–radical reactions of appropriately constituted free radicals.

Absence of CIDNP from High-Field Reactions. One of the special cases in which no CIDNP may be generated, even though seemingly appropriate radical–radical reactions are involved, is that of reactions of stable free radicals in high fields (greater than a few hundred gauss). Many such reactions probably follow the general mechanism of eq 1, where Z· is a stable free radical, X is a diamagnetic reactant, R· is an intermediate reactive free radical, and P is a product. The mechanisms of reactions of the naphthalene radical anion with alkyl halides are of this type, and these reactions give no CIDNP when carried out in high magnetic fields, but they do give CIDNP when carried out in low fields (ca. 100 G).[5] A detailed explanation has been given previously. It is sufficient here to observe that if reaction 1b is very fast, then *all* the radicals R· may be scavenged by Z· in a time that is short compared with nuclear spin–lattice relaxation in R·. Since radical-pair processes do not involve changes in nuclear-spin states in high fields,[10] all the initially formed radicals R· proceed to product with their original nuclear-spin states intact, and no polarization is possible. In low fields, the radical-pair processes involve a component of nuclear-spin "flips"[10] so that the rapid trapping of all the radicals R· does not suppress CIDNP.

$$\mathrm{Z}\cdot + \mathrm{X} \longrightarrow \mathrm{R}\cdot \qquad (1a)$$

$$\mathrm{Z}\cdot + \mathrm{R}\cdot \longrightarrow \mathrm{P} \qquad (1b)$$

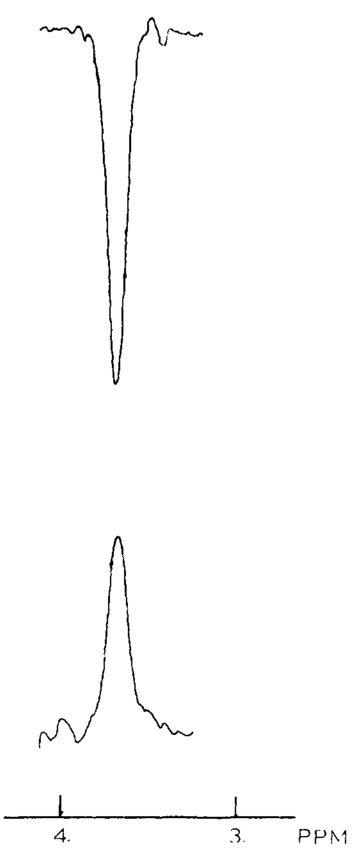

Figure 2. Polarized and normal methylene peaks of dihydroanthracene from the reaction of sodium anthracene-d_{10} in THF-d_8 with water.

The present experiments provide another example of the successful observation of CIDNP from low-field reactions even when corresponding high-field reactions give no CIDNP. Scheme I is of the form of eq 1 so the explanation outlined above can also apply here.

CIDNP as a Discriminator between Schemes I and II. If a radical–radical reaction is at equilibrium, then it cannot induce CIDNP. Polarization is a nonequilibrium condition; at equilibrium, any polarization introduced by the forward reaction must be removed by the reverse reaction.

The most likely form of Scheme II which might be operative is one in which the initial step, $2\mathrm{Ar}^- \rightleftarrows \mathrm{Ar}^{2-} + \mathrm{Ar}$, is a rapidly established equilibrium. The products of this reaction are thermodynamically unfavored for the cases considered here. Consequently, the reverse reactions are thermodynamically favored, and such electron-transfer reactions among hydrocarbons and their anions are frequently nearly diffusion controlled. The proton transfers of the second step of Scheme II are likely to be slower. In such cases, Scheme II would be inconsistent with an observation of CIDNP.

Since Scheme I predicts CIDNP, but the "prior equilibrium" form of Scheme II does not, an observation of CIDNP discriminates between the two mechanisms. Further discrimination is possible through experiments involving deuterated materials (see later sections).

Mechanisms of Reactions of Aromatic Hydrocarbon Radical Anions with Proton Sources. The data of Table I show that CIDNP was found from most of the reactions we examined. This includes reactions of sodium naphthalene in DME with water and methanol, reactions of sodium naphthalene in THF with water, reactions of sodium anthracene in DME and THF with water and in DME with 2-propanol, and reactions of sodium pyrene in THF with water. No CIDNP was found from the reaction of sodium perylene in THF with water.

These findings support Scheme I for all these reactions except that of sodium perylene in THF with water. Since CIDNP was detected easily in the other cases, the absence of CIDNP from the latter reaction is support for Scheme II.

Test for Scheme III in the Reaction of Sodium Naphthalene with Water. One mechanism not usually considered for these reactions is Scheme III. Intuition might suggest that proton transfer from HOR to Ar^- should be so fast that the dissociative electron-transfer initial step of Scheme III could not compete. However reasonable or unreasonable this argument may be, it does not rule out Scheme III. We felt that a special characteristic of the radical-radical reaction of Scheme III, $H + Ar^- \rightarrow HAr^-$, might provide a striking CIDNP result in appropriate experiments.

Scheme III

$$\mathrm{Ar^{-} + HOR \longrightarrow Ar + H + OR^{-}}$$
$$\mathrm{H + Ar^{-} \longrightarrow HAr^{-}}$$
$$\mathrm{HAr^{-} + HOR \longrightarrow H_2Ar + OR^{-}}$$

CIDNP intensities depend, among other things, on the magnitudes of the coupling constants between the magnetic nucleii and the unpaired electrons of the radicals involved in the radical-radical step. The proton-electron coupling constant for a hydrogen atom H is huge compared with those for protons in ordinary organic free radicals and radical anions. According to Scheme III, the hydrogen atom originates in the proton source HOR. Consequently, if Scheme III were operative, a dramatic change in the resulting CIDNP intensity of the aliphatic protons of dihydronaphthalene might have been anticipated on changing from a proton source to a deuteron source. Since NMR signals from THF and DME obscure those of the aliphatic protons of dihydronaphthalene, THF-d_8 was employed as the solvent. The findings were that regardless of whether H_2O or D_2O was the reactant, the observed enhancements of the aliphatic protons were similar. This seems inconsistent with Scheme III but quite consistent with Scheme I.

Test for Scheme II with a Nonequilibrium Initial Step in the Reaction of Sodium Anthracene in THF with Water. If the second step of Scheme II were significantly competitive with the reverse reaction of the first step, then CIDNP could be induced by the first step of the scheme. By using deuterated reactants, we were able to rule out this possibility as the only source of CIDNP in reactions of sodium anthracene in THF with water.

In the first step of Scheme II, the only protons which are coupled with the unpaired electrons in the radicals are those which originate with the aromatic hydrocarbon from which the radical anion is prepared. At no stage of the scheme are protons originating in the proton source coupled with an unpaired electron. Consequently, protons originating in the proton source could not become polarized through the mechanism of Scheme II. By using anthracene-d_{10} in THF-d_8, we were able to examine the possible polarization of the protons originating in the water. The result was that CIDNP of approximately the same intensity as for the reaction of ordinary anthracene radical anion was observed. Thus, Scheme II as the sole source of CIDNP is ruled out. Scheme I remains consistent with the observations since in that scheme, protons from the proton source are incorporated into a free radical in a step preceding the radical-radical step.

Comparisons with Other Results. Levin, Sutphen, and Szwarc have concluded from stopped-flow kinetic studies that the reaction of sodium perylene in THF with water proceeds via Scheme II.[3b] This is consistent with our finding no CIDNP from this reaction. This finding was especially pleasing in that it is evidence that CIDNP is not so sensitive a tool in these reactions that it gives a response because of negligible reaction pathways.

Bank and Bockrath found kinetics supporting Scheme I for reactions of sodium naphthalene in THF and DME with water.[2b] This is consistent with our finding CIDNP from these reactions.

The reactions of anthracene radical anion with water and alcohols show complex and variable kinetics, depending on metal ion, solvent, protonating agent, and concentration.[2c,3c,4] For reactions of sodium anthracene in DME with water (and with several alcohols other than *tert*-butyl alcohol), the kinetics support Scheme I. Our findings in DME are also consistent with Scheme I.

For reactions in THF, the picture from kinetics is confused by irreproducibilities and disparate results. It does not seem worthwhile to repeat these details here; we will simply state the conclusions that can be drawn from our data. Our experiments with deuterated material, described earlier, are not consistent with any reaction mechanism in which a proton from the protonating agent is never incorporated into a free radical undergoing a radical-radical reaction. This specifically rules out the *sole* operation of Scheme II and any variant of it such as the following

$$\mathrm{2MAr \rightleftharpoons (MAr)_2 \rightleftharpoons [M_2Ar;\ Ar] \xrightarrow{H_2O} MArH + Ar + MOR \longrightarrow etc.}$$

which has been proposed by Rainis, Tung, and Szwarc[3c] to account for kinetic terms second order in alkali anthracene and zero order in anthracene. Such processes could still be significant in our reactions, but significance must also be attached to processes in which protons from water *are* incorporated into free radicals which then undergo radical-radical reactions, as in Scheme I or a variant of it such as the following.

$$\mathrm{2MAr \rightleftharpoons (MAr)_2 \xrightarrow{H_2O} ArH\cdot + MAr + MOH \longrightarrow etc.\ as\ in\ Scheme\ I}$$

Do our data provide indications of the *level* of significance of Scheme I or related processes in the reaction of sodium anthracene with water in THF? Yes, but not with great force. The enhancement factor for the methylene protons of dihydroanthracene formed in this reaction is 7. For the related reaction of sodium naphthalene with water, a process which is generally agreed to proceed by Scheme I exclusively, the signal enhancement factor of the methylene protons of dihydronaphthalene is 17. We cannot regard these as being very precise values. It is noteworthy that the latter corresponds approximately to those (ca. 20) observed in reactions of alkyl halides with sodium naphthalene, the mechanisms of which are analogous with Scheme I.[5] Seven is a substantial fraction of 17; therefore it would appear that a substantial portion of the sodium anthracene reaction proceeds by Scheme I or a variant of it.[11]

Finally, we note that the reactions of pyrene radical anion with protonating agents do not seem to have been previously investigated. The simplest interpretation of our results is that they proceed by Scheme I, although they could proceed only partially by Scheme I or its variants.

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Determination of Anisotropy of Molecular Motion with ^{13}C Spin–Lattice Relaxation Times[1a]

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Abstract: A computer program has been written to calculate the rotation diffusion tensor for anisotropic motion from ^{13}C spin–lattice relaxation-time data. Application of this program to ^{13}C spin–lattice relaxation-time measurements of methyl-substituted cycloalkanes is shown. The degree of anisotropic motion within this series of compounds becomes smaller with increasing ring size. The lower limits of the barriers of rotation for the methyl groups are estimated.

Introduction

Although the basic theory for the evaluation of anisotropy of molecular motion by measuring spin–lattice relaxation times has been given by Woessner[2] more than 10 years ago, there is, to our knowledge, up to now, no extensive application of Woessner's formalism for ^{13}C relaxation times in the literature. Most of the current, steadily increasing literature on ^{13}C relaxation times[3,4] deals, at most, with an interpretation of these data in terms of isotropic overall motion of a given molecule. This approximation can result in misinterpretation of data and, more seriously, in a considerable loss of information given by ^{13}C spin–lattice relaxation times. The first application of the theory of anisotropic motion toward ^{13}C relaxation times was given by Grant and coworkers,[5] wherein they studied molecules containing only three T_1's with three rotational diffusion constants. A similar approach, using quadrupole relaxation of the ^{14}N and ^{2}H nuclei, was recently given by Lehn.[6]

In this work, we add a least-squares treatment which allows us to secure the best three rotational diffusion constants when an overdetermined (more than three) set of T_1 values is available. As an extension of our work on unsubstituted cycloalkanes,[7] we have measured the ^{13}C relaxation times of the asymmetric tops, methylcyclopropane through methylcyclooctane, and present here an interpretation of these data within the concept of anisotropic motion in the liquid phase.

Computational Method. The original equation of Woessner[3] for dipolar relaxation in a molecule undergoing anisotropic motion has the following general form

$$\frac{1}{T_{1(j)}} = \mathrm{f}(R_1, R_2, R_3, \lambda_{ij}, \mu_{ij}, \nu_{ij}) \tag{1}$$

where R_1, R_2, and R_3 are the diagonal components of the rotational diffusion tensor in the principal axis system, and λ_{ij}, μ_{ij}, and ν_{ij} are directional cosines relative to this coordinate system for the appropriate ij proton-carbon-13 interactions. To obtain all three Rs, the T_1's and directional cosines of at least three (j = 1, 3) different carbons must be determined. When $j > 3$ for a rigid molecule, the T_1 data set is overdetermined, and a nonlinear least-squares approach is used by minimization of the sum of squared deviations, S, in experimental and calculated relaxation rates, $1/T_1$.

$$S = \sum_{j=1}^{m} \left\{ \frac{1}{T_{ij(\mathrm{exp})}} - \sum_{i=1}^{n} \mathrm{f}(R_1, R_2, R_3, \lambda_{ij}, \mu_{ij}, \nu_{ij}) \right\}^2 \tag{2}$$

Here, m is the number of carbon atoms for which experimental data are used in the analysis and n is the total number of hydrogens in the molecule. This search for the best R_1, R_2, and R_3 parameters is achieved using the "simplex method" for function minimization of Nelder and Mead.[8] The procedure only requires that m be at least equal to the number of different R values to be determined. Use of $m > 3$, of course, improves the statistical estimate of these rotational diffusion constants. The explicit form of the Woessner equation,[3] including resonance frequency, is

$$\mathrm{f}(R_1, R_2, R_3, \lambda, \mu, \nu) = \frac{C_+ b_+}{{b_+}^2 + \omega^2} + \frac{C_- b_-}{{b_-}^2 + \omega^2} + \frac{C_1 b_1}{{b_1}^2 + \omega^2} + \frac{C_2 b_2}{{b_2}^2 + \omega^2} + \frac{C_3 b_3}{{b_3}^2 + \omega^2} \tag{3}$$

where the five b variables are linear combinations of the rotational diffusion constants

Roberts et al. / Determination of Anisotropy of Molecular Motion