

ENHANCEMENT OR SUPPRESSION OF CIDNP INTENSITIES BY A SECOND MAGNETIC NUCLEUS: INTERPLAY BETWEEN g FACTOR DIFFERENCE, EXTERNAL MAGNETIC FIELD, AND HYPERFINE COUPLING CONSTANTS

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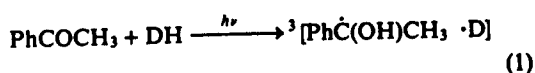
The enhancement factors of the ^1H polarization induced in radical pairs generated by α -cleavage of $^{12}\text{C}=\text{O}$ - and $^{13}\text{C}=\text{O}$ -labelled ketones deviate from the ratios expected on the basis of the relative abundances of the respective carbon isotopomers. For dibenzyl ketone, the ratio of absolute CIDNP intensities of the $^1\text{H}(^{12}\text{C})$ doublet (90% $^{12}\text{C}=\text{O}$) to the $^1\text{H}(^{13}\text{C})$ singlet (10% $^{13}\text{C}=\text{O}$) was found to be $>9:1$ at 58.3 kG and $<9:1$ at 21 kG. Similar deviations were observed for other ^{12}C labelled ketones, viz. deoxybenzoin ($^{12}\text{C}=\text{O}$) and acetophenone ($^{12}\text{C}=\text{O}$ or $^{13}\text{CH}_3$). This novel enhancement or suppression effect on the CIDNP enhancement can be ascribed to the presence of a second hyperfine coupled nucleus in the intermediate radical pair. The individual contributions of the g factor difference (Δg), the external magnetic field strength (H_0), and the hfc constants of the observed (a_A) and the interacting nucleus (a_X) in the enhancement-suppression are exemplified. The experimental results are consistent with theoretical calculations of the mutual effect of Δg , H_0 , a_A and a_X on the CIDNP enhancement factor of the observed nucleus.

INTRODUCTION

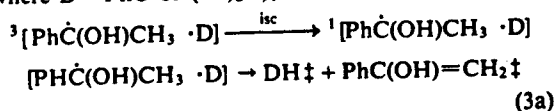
Since its discovery¹ in 1967, the phenomenon of chemically induced dynamic nuclear polarization (CIDNP) has been intensively studied.^{2,3} It has been amply demonstrated that this technique is a very powerful tool for investigating organic reaction mechanisms.^{3,4} In 1971, Kaptein⁵ formulated two simple qualitative sign rules to account for the polarization phases of nuclei, and these rules have been widely used to assign the magnetic parameters of the intermediate radical (ion) pairs. Most reported CIDNP studies were focused on the polarization of a single type of nucleus, typically ^1H . Only a limited number of studies exist that probe the effect of a second magnetic nucleus with an appreciable hyperfine coupling constant (hfc) on the CIDNP pattern and enhancement factor of the 'primary' nucleus.

Several years ago, Roth and co-workers^{6a,b} and others^{6c,d} drew attention to the CIDNP patterns in systems containing a second nucleus with a sizable hfc constant. The CIDNP spectra of such systems often deviate from those predicted by Kaptein's rules. We also observed that the CIDNP enhancement factor of nuclei could be suppressed by the presence of a second nucleus.⁷ More pronounced suppression effects could be observed if the second nucleus has a larger hfc constant than the nucleus under consideration. In this paper we report a novel phenomenon: CIDNP intensities can be either reduced or enhanced owing to interaction with a second magnetic nucleus. The degree of enhancement or suppression depends on the external magnetic field strength (H_0), the electron g factor difference (Δg) and the ratio of the hfc constants. The observed phenomena can be reproduced accurately by the 'exact radical pair' theory of CIDNP.

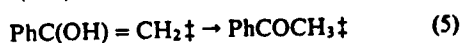
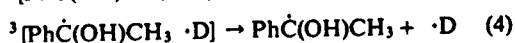
by hydrogen abstraction, generating α -phenylhydroxymethyl radicals paired with either a phenoxy or an *N,N*-diphenylaminyl radical [equation (1)]. These radical pairs, initially of triplet multiplicity, can either undergo intersystem crossing [equation (2)] or diffuse apart ('escape') to generate free radicals [equation (4)]. Intersystem crossing can be followed by reverse hydrogen transfer ('disproportionation'), either regenerating the ketone or generating an enol [equations (3a) and (3b)]. Enol-to-ketone tautomerization also regenerates acetophenone [equation (5)]. As a result of this reaction sequence, the methylene protons of the enol and the methyl protons of the regenerated acetophenone are overpopulated in the β nuclear state (emissive nuclear polarization).



where $\text{D} = \text{PhO}$ or $(\text{Ph})_2\text{N}$;



where \ddagger represents a polarized nucleus;



We have studied these reactions with acetophenone labelled in either the carbonyl or methyl position. The

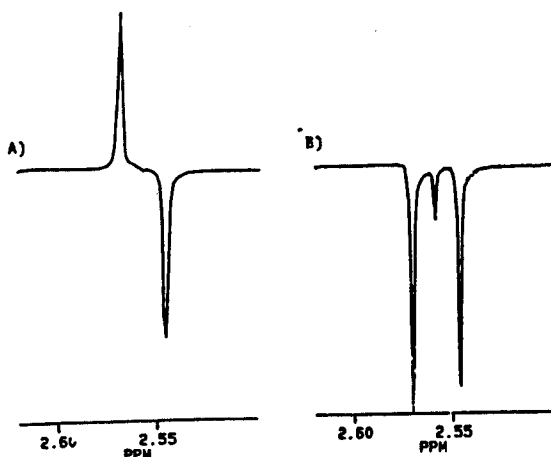


Figure 2. ${}^1\text{H}$ CIDNP of the methyl protons of 10 mM acetophenone (90% ${}^{13}\text{C}=\text{O}$) in acetonitrile- d_3 in the presence of (A) 20 mM diphenylamine or (B) 20 mM phenol at a field of 58.3 kG

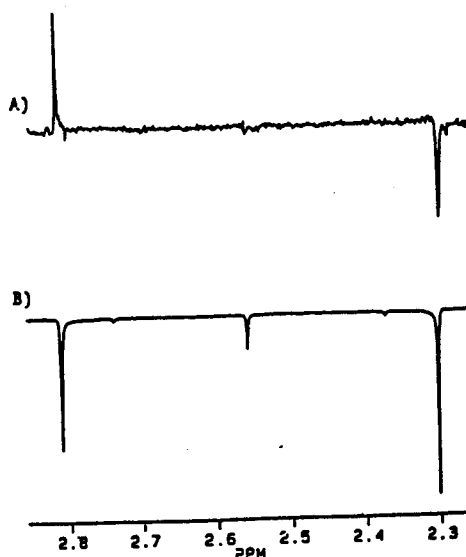


Figure 3. ${}^1\text{H}$ CIDNP of the methyl protons of 10 mM acetophenone (91.3% ${}^{13}\text{CH}_3$) in acetonitrile- d_3 in the presence of (A) 20 mM diphenylamine or (B) 20 mM phenol at a field of 58.3 kG

polarization patterns observed for the CH_3 signal of [${}^{13}\text{C}=\text{O}$]acetophenone during the photoreaction with diphenylamine and phenol as hydrogen donor, respectively, are shown in Figures 2(A) and (B). Once again, the outer doublets represent the methyl protons coupled to ${}^{13}\text{C}=\text{O}$ (90% ${}^{13}\text{C}$), whereas the central peaks are due to methyl groups adjacent to ${}^{12}\text{C}=\text{O}$ (10% ${}^{12}\text{C}$). The ratio of the doublet intensity (i.e. the sum of absolute intensities) to the singlet intensity is $>30:1$ for the reaction with diphenylamine [Figure 2(A)] and $9:2:1$ for the reaction with phenol [Figure 2(B)].

With ${}^{13}\text{CH}_3$ -labelled acetophenone (91.3% ${}^{13}\text{CH}_3$), the magnitude of the second hfc changes from 6.68 G^{11} (of ${}^{13}\text{COH}$) to 5.5 G^{11} (of ${}^{13}\text{CH}_3$), which causes slightly different CIDNP patterns for the methyl protons of the regenerated acetophenone [Figures 3(A) and (B) with diphenylamine and phenol as hydrogen donor, respectively]. The data in Figures 2(A) and 3(A) are remarkable, since they show pronounced multiplet effects with the polarization of the central singlet near zero. The CIDNP intensity ratio of doublet (coupled to ${}^{13}\text{CH}_3$) to singlet (attached to ${}^{12}\text{CH}_3$) in the reaction with phenol is $9:1$, smaller than the ratio of ${}^{13}\text{C}(\text{H}_3)$ to ${}^{12}\text{C}(\text{H}_3)$ in the reagent acetophenone.

DISCUSSION

Under the influence of an external magnetic field, the electron spin will precess along the axis of the field at

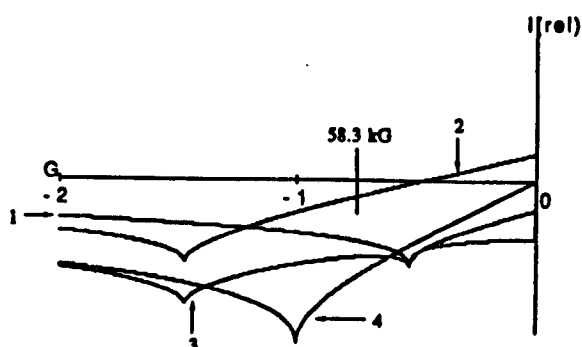


Figure 5. Calculated CIDNP intensities for a system of $a_A = 14.1$ G, $a_X = 6.68$ G, $g_1 = 2.00302$ and $g_2 = 2.0032$. Curves 1 and 2 represent, respectively, the low- and high-field signals of nucleus A; curve 3 is the sum of the absolute intensities of the doublet signals; curve 4 is the polarization intensity of the nucleus A in the absence of nucleus X

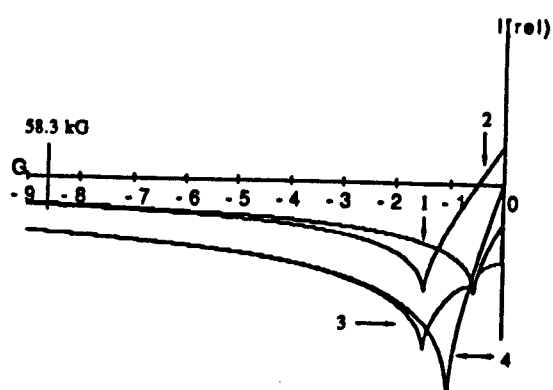


Figure 6. Calculated CIDNP intensities for a two-spin system of $a_A = 14.1$ G, $a_X = 6.68$ G, $g_1 = 2.00302$ and $g_2 = 2.0051$. Curves 1 and 2 represent the signals of nucleus A; curve 3 is the sum of the absolute intensities of the doublet; curve 4 is the polarization intensity of the nucleus A in the absence of nucleus X

fits the theoretically predicted one value fairly well. This particular example shows an 'unexceptional' effect of the second nucleus on the CIDNP enhancement factor of the observed nucleus.

Changing the acetophenone ^{13}C label from the carbonyl to methyl position slightly reduces the magnitude of the second hfc. This is not expected to affect the polarization induced in the α -phenylhydroxymethyl-phenoxy radical pair, since the ΔgH_0 term strongly dominates the hyperfine term. Indeed, the CIDNP patterns of Figures 2(B) and 3(B) are very similar; the intensity ratios of the ^{13}C -H doublet to the ^{12}C -H singlet are close to the respective isotopomer ratio. For

the α -phenylhydroxymethyl-diphenylaminy radical pair, on the other hand, reducing the magnitude of the second hfc does not change the CIDNP patterns [see Figures 2(A) and 3(A)]. This can be ascribed to a much smaller contribution to the ΔgH_0 term (i.e. $\Delta gH_0 \approx 0$) to the overall intersystem crossing of the intermediate radical pair.

The experimental and calculated CIDNP intensity ratios of the systems studied are summarized in Table 1. Most of the experimentally observed CIDNP intensity ratios are in acceptable agreement with those calculated, with the notable exceptions of the results observed during the photolysis of DBK at 21 kG. The reason for this discrepancy is not obvious, insufficient resolution being one possible explanation. The noticeable overlap of the ^{12}C with the lower field ^{13}C signal may distort the assigned ratio. This effect may be amplified by the subtraction yielding the CIDNP spectra.*

The above examples demonstrate that Δg , H_0 and the magnitude of the second hfc all affect the CIDNP enhancement of the nucleus under study. The interdependence of the individual parameters is illustrated by Figure 7, where the relative CIDNP intensities of nucleus A (z axis) are plotted as a function of a_X (x axis) and the parameter G (y axis). Figure 7(a) and (b) show the CIDNP intensities of the doublet, whereas Figure 7(c) and (d) show the sum of the doublet intensities and the sum of the absolute intensities, respectively.

One of the signals [Figure 7(a)] always has the polarization predicted by Kaptein's net effect rule.⁵ The magnetic field strength, $H_{0,\text{max}}$, at which this signal reaches maximum intensity decreases with increasing

* A referee raised the question of how changes in radical pair lifetimes (due to a chemical process, e.g. decarbonylation) affect the CIDNP enhancement factor and whether the large discrepancy between the observed and calculated CIDNP ratios for DBK could be ascribed to a breakdown of equation (8). Our previous study¹⁶ has shown that the most efficient spin sorting is achieved when the competing process(es) (e.g. diffusional separation, decarbonylation or chemical transformation reactions) are compatible with the intersystem crossing rate of radical pairs. A mismatch between the competing rates leads to less efficient spin sorting and, therefore, smaller CIDNP enhancement. For a given intersystem crossing rate, a change of radical pair lifetime (due to decarbonylation) will change the absolute CIDNP enhancement. Similarly, for a given competing process, the variation of the intersystem crossing of radical pairs, due to the incorporation of additional magnetic nuclei (α and β), will change the absolute CIDNP enhancement. In the case of DBK, the competing chemical process is the same for all radical pairs, regardless of the presence of a ^{13}C nucleus and, therefore, does not show any net effect on the relative CIDNP enhancement factor. We are not aware of any conditions which cause a breakdown of equation (8).

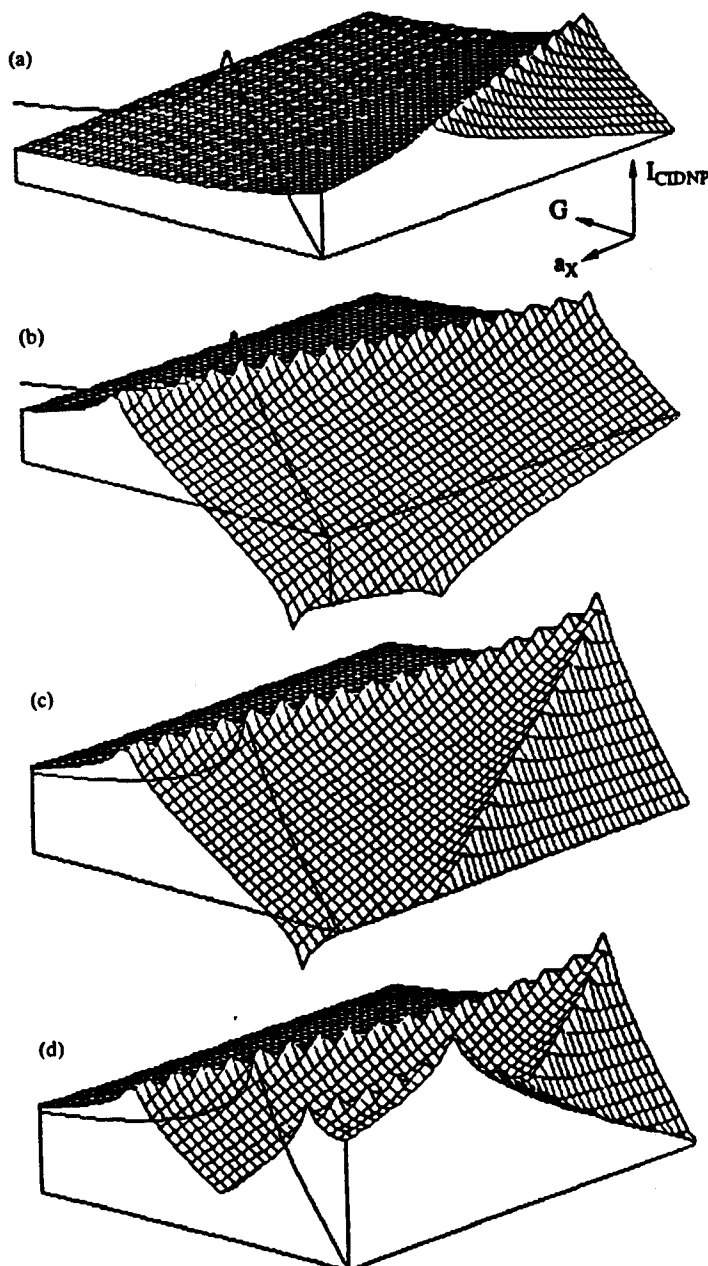


Figure 7. Computer simulation of relative CIDNP intensities (I) for a doublet of a nucleus A as a function of the hfc of a second nucleus X (a_X) and of the parameter G ($= \Delta g H_0 / a_A$). The graph contains I vs G plots for values of $0 < a_X < 70$ G at increments of 1.4 G. For ease of comparison, curve 1 for $a_X = 0$ G is plotted also at the value $a_X = 70$ G. The parameters used in the simulation are $a_A = 50$ G, $\Delta g = 0.0016$ and $G = 0$ to -3.5 . (a) and (b) show the intensities of the individual signals; (c) shows the sum of (a) and (b); (d) shows the sum of the absolute intensities of (a) and (b)

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