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Nuclear Spin Polarization Effects in Systems with Large Hyperfine Couplings. Limitations of Kaptein's Rules

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Abstract: Chemically induced dynamic nuclear polarization (CIDNP) effects are commonly observed in radical pair reactions. Although a rigorous quantitative theory has been formulated, these effects are frequently interpreted in terms of qualitative sign rules originally proposed by Kaptein. We have developed a graphical method based on the exact theory to illustrate the range of magnetic parameters for which the rules are valid. The net effect rule is generally valid if the g factor difference (Δg) of the radicals is large compared to the hyperfine coupling constants (hfc's) of the individual nuclei. The multiplet rule is valid in general, if the hfc's are large compared to the Δg term. Deviations from the rules are observed specifically for multiplets of protons which are coupled to ^{13}C nuclei with large hfc's.

Introduction

Since the first observation of nuclear spin polarization, the CIDNP technique has been applied to a wide variety of thermal[1-4] and photochemical reactions.[5,6] The results of these efforts have provided valuable information about the detailed mechanisms of radical pair reactions and about the magnetic parameters as well as structural details of the intermediate radicals or radical ions. A quantitative theory, the so-called radical pair theory, has been developed,[7-10] which provides accurate descriptions for the large majority of all nuclear spin polarization effects observed to date. However, the success of the CIDNP method is due in no small part to the fact that significant information can be derived from the qualitative aspects of the CIDNP spectrum as well.[3,11]

The general features of a CIDNP spectrum are described as a net effect, if all signals of a multiplet have the same signal direction, or as a multiplet effect, if the signals representing a nucleus or a group of identical nuclei show a combination of absorption and emission. These features are determined by the relative magnitude of the hyperfine coupling constants (hfc's; a) of the magnetic nuclei in the radical pair and of the so-called Δg term, the product of the g-factor difference and the magnetic field strength. Kaptein has formulated two simple sign rules which relate the direction of a net effect (Γ_n) and the "phase" of a multiplet effect (Γ_m) of polarized nuclei i and j to the signs of the magnetic parameters, to the multiplicity, μ, of the precursor, and to the mode of product formation, ϵ.

$$\Gamma_n = \mu \cdot \epsilon \cdot a_i \cdot \Delta g$$

$$\Gamma_m = \mu \cdot \epsilon \cdot a_i \cdot a_j \cdot J_{ij} \cdot \sigma_{ij}$$

The signs of the parameters are assigned according to the following conventions:

μ	+ for triplet precursors − for singlet precursors
ϵ	+ for geminate pair reactions − for chain transfer products
σ_{ij}	+ nuclei i and j are part of the same radical − nuclei i and j are part of different radicals
Γ_n	+ absorption (A) − emission (E)
Γ_m	+ low-field signal(s) E, high-field signal(s) A (E/A) − low-field signal(s) A, high-field signal(s) E (A/E)

The signs of a_{ij}, of the nuclear spin–spin coupling constant, J_{ij}, and of Δg used in these rules coincide with the absolute signs of these parameters. In cases where the Δg term is large relative to the hfc's of the coupled nuclei, net effects are predominant. On the other hand, when the hfc's are large relative to the Δg term and comparable to each other, the spectra of both nuclei exhibit multiplet effects having the same phase. The above rules were derived for pure net and pure multiplet effects; spectra having mixed net and multiplet effects are usually interpreted as superpositions of the two pure effects.

These rules are often used to derive one of the polarization determining parameters, e.g., the precursor multiplicity or the sign of a hyperfine or a spin–spin coupling constant, when the other parameters are known. In cases where spectra exhibit both a

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strong net and a strong multiplet effect, a second parameter is sometimes also determined. These applications require some caution because a number of exceptions to the predictions of the rules have been observed. For example, apparent deviations may occur for products involved in fast exchange reactions, which may cause nuclei without hfc's to acquire polarization via cross-relaxation processes.[12-14] Exceptions have also been reported for reactions involving consecutive radical pairs.[15,16] The exceptions observed in these cases result from processes which are not treated in the simple radical pair theory.

However, the rules also give incorrect predictions for certain spin polarization effects which are adequately described by the exact radical pair theory. Several instances of incorrect predictions have been reported for ^1H CIDNP effects induced in radical pairs with one large ^{13}C hfc.[17] Possible violations of the rules have also been treated theoretically. When Kaptein first proposed these rules, he noted that the predictions of the multiplet rule will be in error when the Δg term is very large relative to the hfc.[11] More recently, Salikhov has analyzed the case of a radical pair in which the hfc of one nucleus is considerably larger than both the hfc's of other nuclei and the Δg term.[18] He concluded that, under these circumstances, the net effect rule may give erroneous results. Although these papers describe possible violations of the rules, the limits for which the rules are valid were not defined. In view of the widespread use of these rules it is important that their limitations be understood.

Polarization Intensities in a Two-Spin System

We have devised a simple formalism which enables us to define the limits for which Kaptein's rules are valid. This method is based on theoretical signal intensities calculated according to the radical pair theory. It allows a quantitative definition of the limits of the rules and provides simple qualitative criteria for their application. We will illustrate the use of this formalism for the simple case of two nuclei of spin $^1/_2$ which are coupled to each other and then discuss its extension to more complex systems.

The polarization intensities induced in a radical pair are essentially determined by the difference in the electron precession frequencies, ω, of the two radicals. For a two-spin AX system the intensities of the doublet of nucleus A are given by[3]

$$I_1 \propto \pm[\omega_{1+}^{1/2} - \omega_{1-}^{1/2}] \tag{1}$$

and

$$I_2 \propto \pm[\omega_{2+}^{1/2} - \omega_{2-}^{1/2}] \tag{2}$$

The frequency difference depends on the difference in the Zeeman energies of the two radicals and on the hfc's of the two nuclei,

$$\omega_{1\pm} = {}^1\!/_2 g\beta\hbar^{-1}[(\Delta g H_0/g \pm {}^1\!/_2 a_A + {}^1\!/_2 a_X)] \tag{3}$$

and

$$\omega_{2\pm} = {}^1\!/_2 g\beta\hbar^{-1}[(\Delta g H_0/g \pm {}^1\!/_2 a_A - {}^1\!/_2 a_X)] \tag{4}$$

The proper sign for eq 1 and 2 is dictated by the precursor spin multiplicity and by the mechanism of product formation. It is important that *the same sign* be used in both equations. The diagrams used in the following discussion were calculated for products formed by coupling of radical pairs generated from triplet precursors (μ, $\epsilon > 0$). In this case, positive signs are appropriate.

The relative intensities of the two lines can be displayed as a function of $\Delta g H_0$ for particular values of a_A and a_X using the formalism suggested by Müller for the graphical analysis of CIDNP spectra.[19] More general results, i.e., graphs that are independent of a particular value of a_A, are obtained when the resulting intensities are plotted as a function of the parameter $G = \Delta g H_0/a_A$, for given ratios of a_X to a_A.

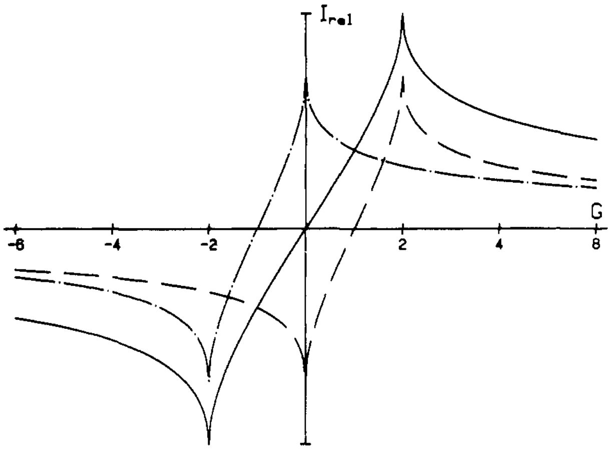

Figure 1. Relative polarization calculated for the doublets of a two-spin AX system with identical hyperfine coupling constants. The intensities of the individual signals (dashed lines) and of the calculated net polarization (solid line) are plotted as a function of the parameter $G = \Delta g H_0/a_A$.

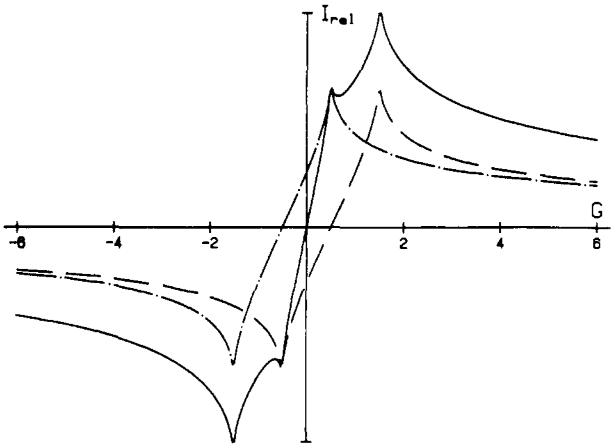

Figure 2. Relative polarization calculated for the A doublet of a two-spin AX system with $a_X = 0.5a_A$ as a function of G. The intensities of the individual signals are shown as dashed lines; the calculated net polarization is shown by the solid line.

Limitations of the Net Effect Rule

We consider first the simplest case of two different nuclei with identical hfc's. For this case, the relative intensities predicted for the two nuclei are identical for all values of G. Figure 1 shows the intensities I_1 and I_2 of the individual signals (dashed lines) as well as the net polarization, the sum of I_1 and I_2 (solid line). The *intensity* of the net effect varies throughout the graph but its *sign* changes only at the origin when the sign of G changes. In this simple case, Kaptein's net effect rule is valid for all values of G.

The second, more general case considered here is that of two nuclei with different hfc's. In this case, the relative intensities of the two transitions show an analogous dependence on G, but the maxima of the curves are shifted in a direction determined by the relative magnitude of the hfc's. When the *nucleus under consideration* (A) *has the larger of the two hfc's* ($|a_X/a_A| < 1$), the two intensity curves are shifted toward the origin as illustrated in Figure 2 for hfc's of the ratio $a_X/a_A = 0.5$. This renders the net effect curve somewhat more complex than that in Figure 1. Nevertheless, this curve changes sign only at the origin, indicating once again, that the net effect rule is valid for all values of G.

When *the nucleus A has the smaller of the two hfc's*, the intensity curves of the individual signals are shifted further apart (Figure 3; $a_X/a_A = 2$). This causes the resulting net effect curve

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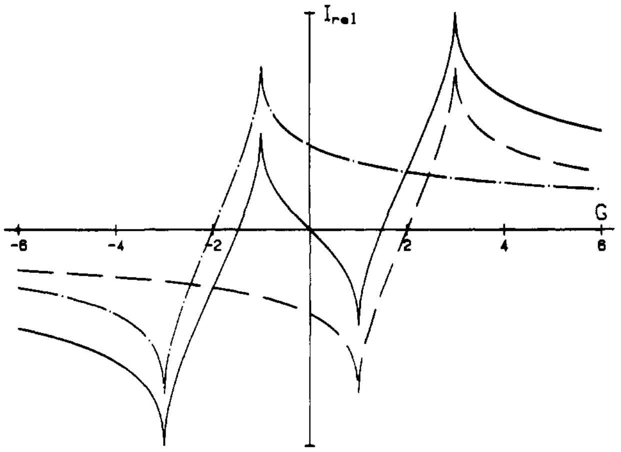


Figure 3. Relative polarization calculated for the A doublet of a two-spin AX system with $a_X = 2a_A$ as a function of G. The intensities of the individual signals are shown as dashed lines; the calculated net polarization is shown by the solid line.

to change sign not only at the origin, but also at two finite values of G. Accordingly, the exact radical pair theory predicts net effects of opposite directions for systems with different magnitudes but identical signs of G. An examination of this and similar cases shows that Kaptein's rule is valid for large values of G, *i.e.*, for the range

$$|G| \geq |a_X/a_A|$$

On the other hand, the rule is invalid for

$$|G| < |a_X/a_A|$$

and the maximum net intensity in violation of the rule is found for

$$|G| = |a_X/a_A| - 1$$

These considerations confirm a conclusion reached by Salikhov, but they provide a more precise definition of the limits inherent in this qualitative rule. Of course, these rigorous definitions for the validity of the net effect rule can be applied only if both hfc's are known. In practice, a qualitative criterion is desirable for the many cases where the available hfc data are incomplete. An examination of graphs of the type shown above leads us to suggest that *the net effect rule can be applied safely only when both signals of the doublet have the same direction* or when one of the signals has zero intensity.

Attempts to identify Kaptein parameters on the basis of net effects, which are the sum of signals with opposite directions, may lead to erroneous assignments. We illustrate this uncertainty by simulating the A doublet of an AX system with $a_X/a_A = 2$. The product containing these nuclei is assumed to be formed by recombination of a radical pair initially of triplet multiplicity. The simulated spectra for $G = 1$ $(a_X/a_A - 1)$ and for $G = 1.7$ $(a_X/a_A - 0.3)$ show net effects of opposite direction despite an an identical set of Kaptein parameters (Figure 4). Clearly, net effects which are the sum of signals having opposite directions cannot be used without a quantitative simulation of the spectrum.

Limitations of the Multiplet Rule

Up to this point we have illustrated the limitations of the net effect rule. Kaptein's rule governing multiplet effects has complementary limitations which, once again, are conveniently defined using graphs of the type shown in Figures 1–3. In these graphs as well as in others we have examined, the lines representing the relative intensities of the two peaks intersect near $|G| = |a_X/a_A|$. At this point, the multiplet effect changes phase. In general, the multiplet rule will be valid in the range $|G| < |a_X/a_A|$ and will be violated for $|G| > |a_X/a_A|$. The deviations are most pronounced for $|G| \approx |a_X/a_A| + 1$ and become smaller as $|G|$ increases. In contrast to the net effect rule, which may be valid for all values of G (vide supra), violations of the multiplet effect rule occur at sufficiently high values of G regardless of the ratio a_X/a_A.

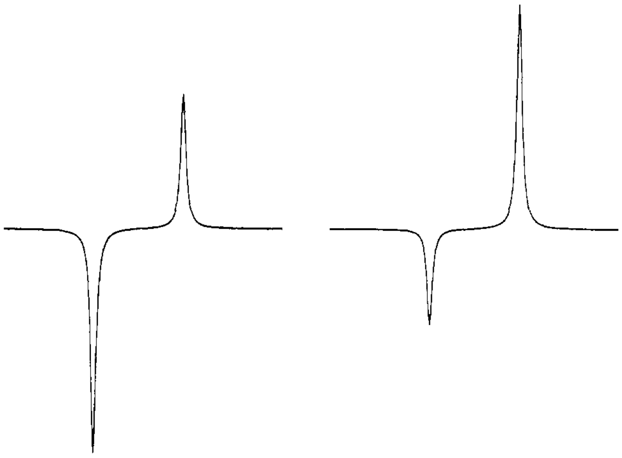


Figure 4. Simulated CIDNP spectra of the A doublet of a two-spin system with $a_X = 2a_A$ for values of $G = a_X/a_A - 1$ (left) and $G = a_X/a_A - 0.3$ (right). The two spectra have the same multiplet phase but opposite net effects; they are normalized to the same overall intensity.

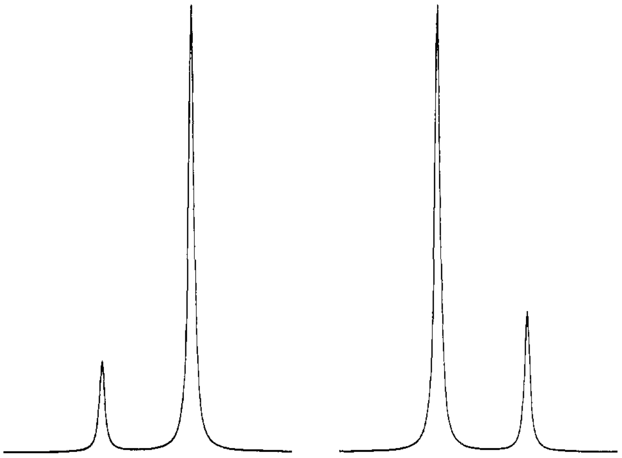


Figure 5. Simulated CIDNP spectra of the A doublet of a two-spin system with $a_X = 2a_A$ for values of $G = a_X/a_A + 0.1$ (left) and $G = a_X/a_A + 1$ (right). The two spectra have the same net polarization but they show multiplet effects of opposite phase; they are normalized to the same overall intensity.

As in the case of the net effects, the relative direction of the two signals provides a convenient criterion for the multiplet rule when the available hfc data are incomplete. We suggest that *the multiplet rule can be used safely only for cases where the two peaks have opposite directions.*

Once again, we illustrate an existing range of ambiguity by two simulated spectra representing the A doublet of an AX system with an hfc ratio, $a_X/a_A = 2$ and $\mu, \epsilon, \sigma, J > 0$. The spectra are simulated for values $G = 2.1$ (Figure 5, left) and for $G = 3.0$ (Figure 5, right). These simulated spectra show pronounced effects of opposite phase even though they have an identical set of Kaptein parameters.

Systems with More Than Two Nuclei

The preceding discussion has been limited to simple, but comparatively rare, two-spin systems whereas in practice more complex multiplets are encountered much more frequently. However, the interpretation of higher order multiplets does not require any new concepts; it is quite analogous to the interpretation of doublets. In systems where a nucleus (A) is coupled to several identical nuclei (X), it is useful to consider separately multiplets containing an even number of signals and those with an odd number of lines.

For a multiplet having an even number of lines, the rules are applied to pairs of lines equidistant from the center of the multiplet. The dependence of the relative intensity of these pairs upon G (Figure 6) parallels that of a simple AX doublet. Consequently,

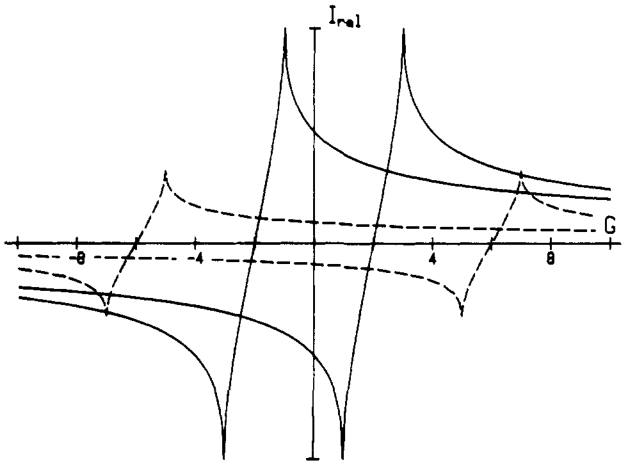


Figure 6. Relative polarization calculated for the A quartet of an AX_3 spin system with $a_X = 2a_A$ as a function of *G*.

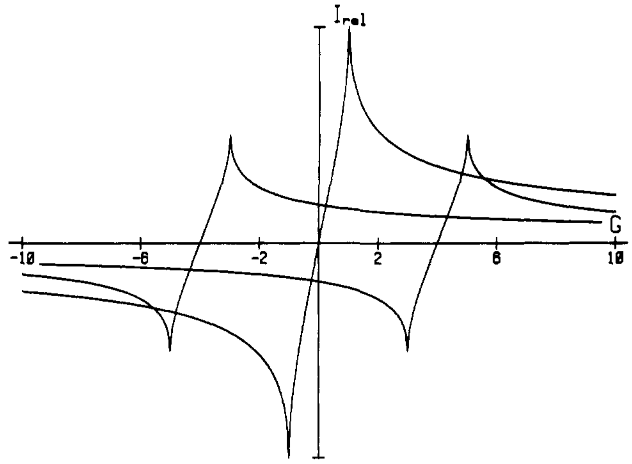


Figure 7. Relative polarization calculated for the A triplet of an AX_2 spin system with $a_X = 2a_A$ as a function of *G*.

the net effect rule may be applied safely to any pair of signals when both signals have the same direction. In practice, it is preferable to use the innermost lines because they have greater intensities and because the net effect rule will be valid over a larger range of *G*.

In a multiplet containing an odd number of lines the situation is different because of the presence of the central line. As illustrated by the graph of the intensities predicted for an AX_2 triplet (Figure 7), the intensity of the center line changes sign only at the origin. This behavior is independent of the ratio of the hfc's of the coupled nuclei. Consequently, the net effect rule can be applied safely to the center line in all odd multiplets.

For these more complex systems the multiplet phase may be determined independently for each pair of signals equidistant from the center. As illustrated in Figures 6 and 7, the intensity curves for each pair of lines intersect. As in the case of the two-spin system, this indicates a reversal of the multiplet phase. Once again the multiplet effect rule can be used safely only when the signals have opposite directions. In higher order multiplets the phase of the outermost lines will be in agreement with the rule for a greater range of *G* values. However, these are the weakest lines and also the ones for which the intensity is most likely to be distorted by relaxation effects.

Experimental Examples

The conditions for observing CIDNP effects contrary to the predictions of Kaptein's rules have seldom been realized experimentally. This is due largely to the fact that most CIDNP effects have been observed for ^1H nuclei, which have a limited range of hfc's. However, the conditions may be met for protons coupled to either ^{13}C or ^{19}F nuclei, which have a range of hfc's significantly larger than that of protons. We have selected several photoreactions of ^{13}C-labeled carbonyl compounds because the ^{13}C acyl hfc's are among the largest known in organic radicals and because the chemistry of the carbonyl moiety appears to be well understood. Specifically, we discuss effects observed during the photohomolysis of benzoin and during the irradation of benzaldehyde in cyclohexane solutions.

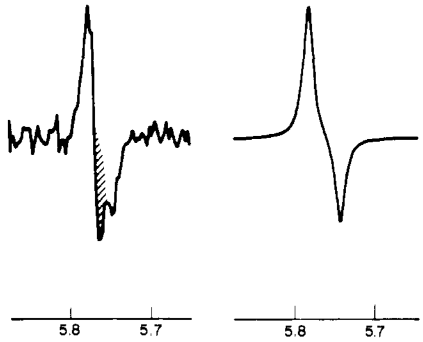
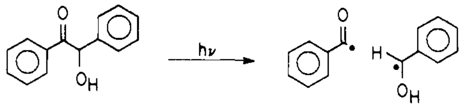


Figure 8. Left: ^1H polarization (90 MHz) observed for the benzylic proton of benzoin-^{13}CO during irradiation in benzene-d_6. The shaded area indicates the polarization of the residual benzoin-^{12}CO ($\sim$10%). Right: Simulated ^1H CIDNP spectrum of the benzylic proton of benzoin-^{13}CO for $\Delta g = 0.0025$, $a_C = 130$ G, $a_H = -14.9$ G.

Deviations from Kaptein's Net Effect Rule

A CIDNP result contrary to Kaptein's net effect rule was observed during the photolysis of benzoin (**1**) labeled with ^{13}C in the carbonyl position.[20] The photochemistry of this system is well understood.[21,22] Irradiation of **1** populates a short-lived excited singlet state, which undergoes rapid intersystem crossing to the triplet state. In this state, the molecule suffers an α cleavage resulting in the formation of benzoyl and hydroxybenzyl radicals (pair A). These radicals may recombine to regenerate the starting material ($\epsilon > 0$). Alternatively, the hydroxybenzyl radicals which diffuse away from their geminate partner ($\epsilon < 0$) may transfer a hydrogen atom to a suitable acceptor to form benzaldehyde (**2**). During the photoreaction, CIDNP effects are observed for all proton signals of the reactant and of the product, benzaldehyde. For a sample of **1** containing ^{13}C at natural abundance, the benzylic proton of **1** (emission) and the aldehydic proton of **2** (enhanced absorption) show particularly strong net effects.[21,22] These results are fully compatible with the predictions of Kaptein's rule provided that the products are formed by the pathways discussed above.



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PAIR A

The photolysis of the ^{13}C-labeled compound gives rise to a significantly different result: the benzylic ^1H doublet shows a pronounced multiplet effect with a slight excess of absorption (Figure 8, left). The observation of a multiplet effect for a proton coupled to a ^{13}C nucleus with a large hfc is unexceptional; the ^{13}C satellites of strong net CIDNP signals frequently show multiplet effects.[23] However, the net effect is unusual because it is opposite to the effect predicted (μ, ϵ, $\Delta g > 0 > a_H$; $\Gamma_n < 0$) and observed for the unlabeled compound, a small but unmistakable violation of Kaptein's rule for net effects. On the other hand, a simulation of the ^1H effects (Figure 8) on the basis of the radical pair theory,[8] shows excellent agreement with the experiment. The relative polarizations calculated for this pair are shown in Figure 9. They confirm the above prediction that for

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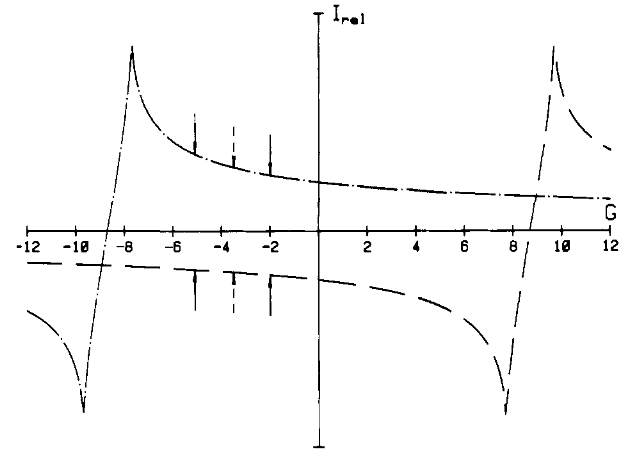


Figure 9. Relative polarization of the proton lines of a ^{1}H–^{13}C spin system calculated according to the radical pair theory with $|a_C/a_H| = 8.7$ as a function of the parameter $G = \Delta g H_0/a_H$. The dashed arrows are placed at $G = -3.5$, the value of G at 21 kG for pair A containing a benzoyl-^{13}*CO* radical. The solid arrows are placed at $G = -2.0$ and -5.1 indicating the values of G' at 21 kG for pair A containing both benzoyl-^{13}*CO* and hydroxybenzyl-^{13}*COH* radicals.

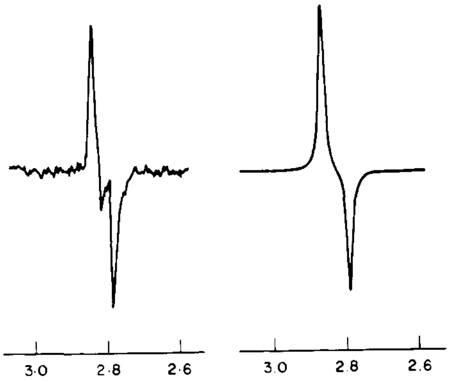
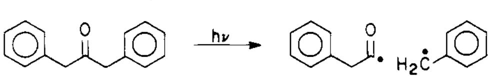


Figure 10. Left: ^{1}H polarization (90 MHz) observed for the benzylic protons of diphenylacetone-^{13}*CO* during irradiation in cyclohexane-d_{12}. Right: Simulated CIDNP spectrum of these protons for $\Delta g = 0.0020$, $a_C = 123.8$ G, $a_H = -16.4$ G.

cases of substantially different hfc's ($a_C = 130$ G,[24] $a_H = 14.9$ G;[25] $a_C/a_H = 8.7$) the net effect rule would be violated up to relatively high values of G.

Another example of a net effect in violation of Kaptein's rule is observed during the photolysis of 1,3-diphenylacetone-^{13}*CO* (**3**). The triplet state of this ketone undergoes α-cleavage generating phenylacetyl radicals paired with benzyl radicals (pair B).[26-28]



3 PAIR B

In this system the hyperfine coupling constants ($a_C = 124$ G,[29] $a_H = -16.4$ G[30]) are also substantially different. The photolysis results in strong polarization for the benzylic protons of the recombination product. As in the previous example, the unlabeled compound shows emission[31-33] whereas the ^{13}C-labeled ketone shows an A/E multiplet effect in which the absorption component is slightly larger (Figure 10). Again, this effect is opposite to that predicted by Kaptein's rule (μ, ϵ $\Delta g > 0 > a_H$; $\Gamma_n < 0$) but in agreement with the exact theory.

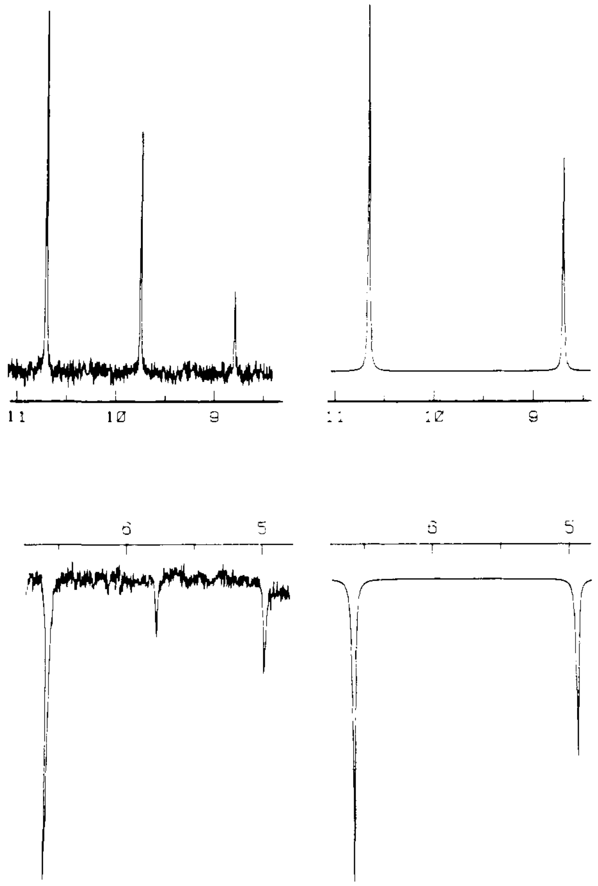


Figure 11. Left: ^{1}H polarization (90 MHz) observed for benzaldehyde-^{13}*CO* (top) and for the benzylic proton of benzoin-^{13}*COH* (bottom) during the irradiation of benzoin (90% ^{13}COH) in C_6D_6. The center peak in each case represents the polarization of the unlabeled material. Right: Simulated ^{1}H CIDNP spectra for the benzaldehyde-^{13}*C* (top) and benzoin-^{13}*COH* (bottom) calculated according to the radical pair theory for $\Delta g = 0.0025$, $a_C = 23.4$ G, $a_H = -14.9$ G.

Deviations from Kaptein's Multiplet Rule

As expected on the basis of our earlier discussion, deviations from Kaptein's rules are not limited to violations of the net effect rule. In appropriate systems the multiplet effect rule may be invalid as well. An example is found in the ^{1}H CIDNP effects observed during the photolysis of benzoin (**1**) labeled with ^{13}C in the hydroxybenzyl position.[20] We focus our discussion on the pronounced E/A multiplet effect observed for the benzylic doublet ($^1J_{CH} = +145$ Hz)[34] of the labeled benzoin and on the equally pronounced A/E multiplet effect observed for the doublet ($^1J_{CH} = +173$ Hz)[34] of benzaldehyde-^{13}*CO* (Figure 11, left). These multiplet effects are opposite to those predicted by Kaptein's rule for a system with μ, a_c, σ, $J > 0 > a_H$, in which benzoin is regenerated by recombination ($\epsilon > 0$) and benzaldehyde is formed from hydroxybenzyl radicals after separation from their geminate partner ($\epsilon < 0$). In contrast to the qualitative rule, the exact radical pair theory can reproduce the observed multiplet phase (Figure 11, right).

The relative signal intensities calculated for pair A explain the failure of the rule. The ^{13}C hfc of the hydroxybenzyl radical ($a_C = +23$ G)[36] is less than twice as large as the ^{1}H hfc ($a_H = -14.9$

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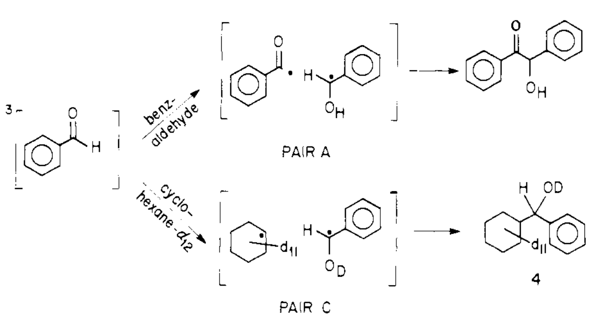
G).[25] For hfc's of this ratio, the multiplet rule is valid within the range $-2 < G < +2$ (cf. Figure 3), whereas at 21 kG this pair has a value of $G = -3.5$—hence the failure of the rule. On the other hand, the net effects are in agreement with Kaptein's rule as well as with the exact theory, as expected for this G value.

Photoreactions of Benzaldehyde in Cyclohexane

In the systems discussed so far, only two principal nuclei were considered and nuclei with marginal hfc's were neglected. The nuclear spin polarization effects observed during the photoreactions of benzaldehyde (**2**) in cyclohexane solution provide an insight into the effects of additional nuclei with a range of hfc's.

The photoreactions of benzaldehyde and several of its derivatives were among the early photoinduced reactions to be studied with the help of the CIDNP technique.[21,22] Triplet **2** reacts with a ground-state molecule of **2** to produce the same pair which is generated by the α-cleavage of benzoin. Alternatively, triplet **2** may abstract a hydrogen (or deuterium) atom from an appropriate solvent (cyclohexane), generating hydroxybenzyl radicals paired with cyclohexyl radicals (pair C).[37] This pair may couple ($\epsilon > 0$) to produce α-phenylcyclohexylmethanol (**4**).



The benzoin generated during the irradiation of benzaldehyde-^{13}C contains two ^{13}C nuclei. Accordingly, the benzylic proton appears as a doublet of doublets ($^1J_{CH} = +145.3$ Hz; $^2J_{CH} = -3.1$ Hz).[34] Overall, these signals show weak net absorption but, in addition, each pair shows a multiplet effect. The pairs of lines split by the $^2J_{CH}$ coupling show a strong A/E effect whereas the pairs of lines split by the $^1J_{CH}$ coupling show a weaker effect of opposite sign (E/A). The weak net absorption and the weak E/A multiplet effect violate the Kaptein rules whereas the strong A/E multiplet effect is in agreement with the multiplet rule.

The multiplet effects are readily understood if one considers that the benzyl hfc ($a_C = +130$ G)[24] is over eight times as large as the hydroxybenzyl hfc ($a_H = -14.9$ g),[25] whereas the Δg term is less than four times as large as the ^{1}H hfc. Hence, Kaptein's rule is applicable. On the other hand, the hydroxybenzyl ^{13}C hfc ($a_C = +23$ G) is comparable in magnitude to the ^{1}H hfc but the Δg term is substantially larger. Accordingly, Kaptein's rule is violated.

Although we are dealing with a three-spin system, the observed effects can still be derived from the calculated signal intensities as illustrated in Figure 9. This diagram was calculated for pair A with $a_C/aH = 8.7$. Because of the presence of the additional sizable ^{13}C hfc, the above definition of G is modified to include the additional hfc

$$G' = G \pm a_{C(OH)}/a_H$$

For values of $G'_1 = -2.0$ and $G'_2 = -5.1$, the observed effects are reproduced quite adequately.

When product **4** is generated from ^{13}C-labeled **2**, its benzylic proton appears as a doublet ($^1J_{CH} = +140$ Hz) having a strong A/E multiplet superimposed on an emissive net effect (Figure 12). Both the net and multiplet effects are in agreement with Kaptein's rules. However, the relative values of Δg, a_C, and a_H of pair C suggest that the net effect should be opposite to the rule. Indeed, a simulation of the polarization on the basis of the magnetic parameters for the principal nuclei in pair C, $\Delta g = 0.0006$, $a_C = +23$ G, $a_H = -14.9$ G, predicts a slight net absorption for this multiplet. The explanation for this apparent discrepancy lies in the coupling of the protons on the aromatic ring and, more importantly, the deuterons of the cyclohexyl radical with the electrons of the radical pair. When the hfc's of these nuclei are included in the simulation, the observed spectrum is reproduced quite accurately (Figure 12). This result illustrates the importance of including all nuclei in such a simulation.

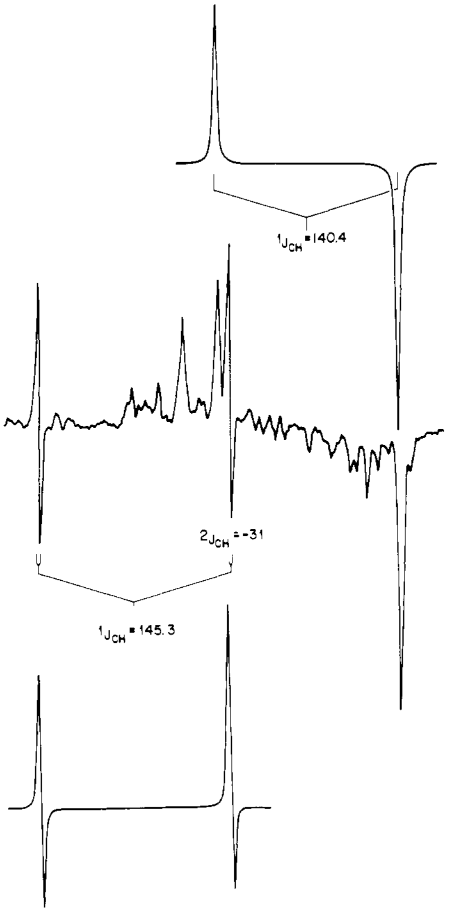


Figure 12. Top: Simulated ^{1}H CIDNP spectrum for the benzyl proton of α-phenylcyclohexylmethanol-d_{11},^{13}COH, for $\Delta g = 0.0006$, $a_C = 23.4$ G, $a_H = 14.9$ G. Center: ^{1}H polarization (90 MHz) observed during the irradiation of benzaldehyde-^{13}C in C_6D_{12}. Bottom: Simulated ^{1}H CIDNP spectrum of benzoin-^{13}CO,^{13}COH for $\Delta g = 0.0025$, $a_{CO} = 130$ G, $a_{COH} = 23$ G, $a_H = -14.9$ G.

Variations

The diagrams discussed in this paper are calculated for a fixed ratio of hfc's and for a variable Δg term. It is interesting to examine how the effects observed in the above systems could be varied experimentally. The simplest experimental change is a variation of magnetic field. For example, the experiments could be carried out in fields of 14 or 46 kG, corresponding to proton frequencies of 60 and 200 MHz, respectively. Considering pair A derived from benzoin-^{13}C, the anomalous net absorption character would be very weak at the lower field (Figure 9, $G = -2.3$) but quite pronounced at the higher field ($G = -7.7$). In the photoreaction of benzoin labeled with ^{13}C in the hydroxybenzyl position, the CIDNP spectrum at 14 kG would show a more dramatic violation of the multiplet effect rule (cf. Figure 3) whereas the spectrum at 46 kG would show less pronounced deviations.

Other variations of the Δg term can be achieved by chemically changing the substrate. For example, the introduction of a heavy atom substituent into a position of high spin density is known to increase the g factor via spin–orbit coupling. At the same time, the hfc's are affected to a much lesser extent. Even greater

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changes in Δg may be achieved by substituting an appropriate radical in a given pair. We consider the case of a benzoyl-^{13}CO radical paired with hydroxybenzyl (pair A), with *p*-bromobenzyl ($g = 2.0047$),[38] and finally with dichloromethyl ($g = 2.0080$, $a_H = -17$ G).[39] The anti-Kaptein net effect discussed for pair A would be even more pronounced for the pair containing the *p*-bromobenzyl radical ($\Delta g = 0.0041$; $G = -5.8$). With dichloromethyl as the second radical, the *g*-factor difference ($\Delta g = 0.0074$; $G = -9.1$) has reached the range where Kaptein's net effect would be obeyed. However, now the multiplet rule would be substantially violated.

Conclusion

The quantitative radical pair theory has been used to define the limits of the qualitative rules introduced by Kaptein for the analysis of CIDNP spectra. The rules are generally valid for net effects if the Δg term is large compared to the hfc's and for multiplet effects if the hfc's are large compared to the Δg term. Deviations from the rules are predicted specifically for multiplets of nuclei A, which are coupled to nuclei X, with larger hfc's. In systems with one large hfc, the ^{13}C CIDNP spectra usually exhibit unexceptional net effects whereas the ^1H CIDNP spectra show at least partial multiplet character. The net signal direction or the multiplet phase of these signals deviate from the qualitative sign rules, but they are in good agreement with the quantitative predictions of the radical pair theory. The definition of the range of validity restricts the applications of the rules to some extent but, in exchange, allows them to be used with greater confidence. It is recommended that quantitative simulations be used whenever a radical pair with at least one relatively large hfc is discussed.

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Registry No. 1, 119-53-9; ,1-^{13}CO, 76124-72-6; **1**-^{13}CO,^{13}COH, 53290-42-9; **3**-^{13}CO, 68120-92-3; benzaldehyde, 100-52-7; cyclohexane, 110-82-7; benzaldehyde-^{13}C, 10383-90-1; α-phenylcyclohexylmethanol-d_{11},^{13}COH, 86885-10-1.

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Automerization of Gaseous Phenylium Ions. Direct Evidence from the Phenylation of Methyl Halides

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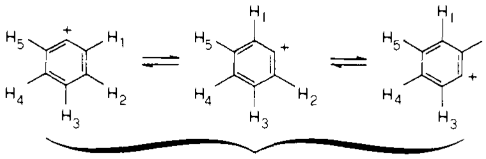
Abstract: The reaction of free [^3H]phenylium ion, generated from nuclear decay of [*p*-$^3H_2$]benzene in the presence of gaseous methyl halide (CH_3X: X = F, Cl, or Br; partial pressure 30–760 torr), yields the corresponding labeled halobenzenes (F, 32–65%; Cl, 80–90%; Br, 84–91%), together with minor amounts of toluene, halotoluenes, benzyl halides, and fragmentation products. The resulting tritiated halobenzenes are characterized by a significant ^3H scrambling over the ring (ortho < meta < para), whose extent increases appreciably when the reaction is carried out at low CH_3X pressures. These results are consistent with related experiments involving the decay of [1,4-$^3H_2$]benzene in gaseous CH_3OH (*J. Am. Chem. Soc.* **1982**, *104*, 4773–4780), and are interpreted in terms of a general mechanism involving a relatively fast ($k \simeq 10^7$ s^{-1}) automerization sequence in the [^3H]phenylium ion via consecutive 1,2-hydrogen shifts. An alternative interpretation of the CH_3OH data (*J. Am. Chem. Soc.* **1982**, *104*, 3244–3246) can therefore be excluded.

Introduction

The techniques currently available for the production of unsolvated ions of defined structure in both gaseous and condensed phases[1] contribute to the understanding of the *intrinsic* properties of highly reactive species, such as the phenylium ion (**1**),[2] involved as elusive transients in solvolytic reactions.[3] The aptitude of phenylium ion (**1**) to undergo isomerization, in particular, the automerization process (eq 1), has recently received special attention.[2]



(1)

(1)

Observation of the automerization (eq 1) is in contradiction with theoretical predictions of high-energy barriers for process 1, irrespective of the nature of the intermediate species involved ($\Delta E^* = 44–77$ kcal mol^{-1}).[4] Nevertheless, two independent experimental studies[2,5] have been reported recently, whose results are consistent with a relatively fast automerization of phenylium ion (**1**) via consecutive 1,2 hydrogen shifts (eq 1). This conclusion is based essentially upon the fact that, when [*p*-^3H]phenylium ion, $(\mathbf{1})_p$, is generated in gaseous methanol (5–65 torr) by the decay of one of the tritium nuclei of [*p*-$^3H_2$]benzene (**2**), the formed tritiated anisole (**4**) exhibits partial ^3H reshuffling over the ring positions, in the following order: ortho < meta < para (eq 2).[2]

Occurence of the phenylium ion automerization sequence $(\mathbf{1})_p \rightleftharpoons (\mathbf{1})$ in eq 2 has been recently questioned by Dewar and Reynolds,[6] who attribute the label scrambling, observed in tritiated anisole (4), to consecutive hydrogen shifts within the ring-protonated anisoles (**5**) (eq 3). This process supposedly involves multiple crossings over energy barriers whose height is calculated as low as 26–28 kcal mol^{-1}.[6] In this view, the significant isotopic

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