Simple Rules for Chemically Induced Dynamic Nuclear Polarization

By R. KAPTEIN

(*Department of Theoretical Organic Chemistry, University of Leiden*, P.O. *Box* 75, *Leiden, The Netherlands*)

Summary Qualitative predictions of the radical pair mechanism of CIDNP are summarized in two simple rules.

OBSERVATION of emission (E) and enhanced absorption (A) in the n.m.r. spectra of reacting systems is evidence for the fact that products showing these effects are formed by a radical mechanism. In addition to this simple diagnosis more detailed information on the radical pairs preceding product formation, on the history of the pairs, on their dynamic behaviour, and on the products themselves can be derived from the spectra: *e.g.*, signs of hyperfine coupling constants and g-factor differences (often allowing an identification of the radicals), precursor multiplicities, and signs of nuclear spin coupling constants in the products. This information, however, is present in an indirect way. In order to simplify the analysis of CIDNP spectra we have summarized radical pair theory[1,2] in two rules, by which all qualitative predictions can be made. These rules are valid in the case that reactions are run in high magnetic fields (higher than a few thousand Gauss). Consider a pair of radicals a and b, with g-factors g_a and g_b, $\Delta g = g_a - g_b$; these radicals contain nuclei $i, j, \ldots$ having hyperfine coupling constants A_i, A_j, . . . Let us further assume that nucleus (or group of equivalent nuclei) i belongs to radical a. The CIDNP spectrum of nucleus i, which may be coupled to nucleus j (in the product) with nuclear spin coupling constant J_{ij}, can be described by the signs of two quantities: Γ_{ne} for net effects (A or E) and Γ_{me} for multiplet effects (E/A: low field part E, high field part A in a multiplet; A/E *vice versa*):

net polarization:

$$\Gamma_{ne} = \mu\epsilon\Delta g A_i \qquad \left\{ \begin{array}{l} +:\mathrm{A} \\ -:\mathrm{E} \end{array} \right. \tag{1}$$

multiplet effects:

$$\Gamma_{me} = \mu\epsilon A_i A_j J_{ij}\sigma_{ij} \qquad \left\{ \begin{array}{l} +:\mathrm{E/A} \\ -:\mathrm{A/E} \end{array} \right. \tag{2}$$

where the parameters μ,ϵ, and σ_{ij} enter with the following signs:

$$\begin{array}{ll} \mu \left\{ \begin{array}{ll} + & \text{when the radical pair is formed from a triplet (T) precursor or by encounter of free radicals (F).} \\ - & \text{When the pair is formed from a singlet (S) precursor.} \end{array} \right. \\ \epsilon \left\{ \begin{array}{ll} + & \text{for recombination (or disproportionation) products} \\ - & \text{for products of radicals escaped from the ``cage'' (\textit{e.g.} transfer reaction products).} \end{array} \right. \\ \sigma_{ij} \left\{ \begin{array}{ll} + & \text{if nuclei } i \text{ and } j \text{ belonged to the same radical.} \\ - & \text{if nuclei } i \text{ and } j \text{ belonged to different radicals.} \end{array} \right. \end{array}$$

The use of these convenient rules is illustrated by two examples:

Rule (1). It has been reported previously[3] that methyl acetate formed during thermal decomposition of acetyl peroxide in hexachloroacetone shows E (for the OCH_3

group). This product is a recombination product from the methyl–acetoxy radical pair:

$$\overline{CH_3\cdot + CH_3CO_2\cdot} \longrightarrow CH_3CO_2CH_3^{*}$$

Due to the presence of the oxygen atoms, the acetoxy radical probably has a larger g-value than the methyl radical hence Δg is negative. The methyl radical has a negative A; the pair is formed from S state acetyl peroxide. Thus we have $\Gamma_{ne} = -+--=-$ and we observe E. For methyl chloride (transfer reaction product) one has $\Gamma_{ne} = ----=+$, giving A as has been observed.[3]

Rule (2). The multiplet effect and the role of precursor multiplicity can be demonstrated with the case of photolysis of propionyl peroxide[4] in CCl_4. Ethyl chloride ($J_{ij} > 0$) formed by a transfer reaction after escape from a pair of ethyl radicals, $A(CH_2) = -22$ G, $A(CH_3) = +27$ G, showed A/E multiplet effects both during direct photolysis and during irradiation in the presence of anthracene, in accord with pair formation from an S state: $\Gamma_{me} = --+-++=-$. However, in the presence of acetophenone E/A multiplets were observed[4] for ethyl chloride indicating photosensitized decomposition of the peroxide by T state ketone ($\mu = +$, the other parameters remaining the same, giving $\Gamma_{me} = +$).

When both net polarization and multiplet effects are present, the CIDNP spectrum can usually be accounted for by a superposition of the effects predicted by rules (1) and (2). However, when $\Delta g \beta H_0$ is very large compared to A_i, rule (2) can give erroneous results, because the apparent multiplet effect can be reversed as compared to the effect predicted by (2); in this case and also in the case of strongly coupled spectra, where apparent net effects may arise from second order effects ("intensity borrowing"), it is better to make use of computer simulation techniques.

The rules break down also when reactions are run in low magnetic fields. This is due to the fact that mixing of the S state with all three T states becomes important in low fields, whereas in the high field case only S–T_0 mixing need to be considered. In zero field, however, we can again use rule (2), although it should be interpreted differently. A single nucleus cannot be polarized in zero field because in solution there is no preferred direction of quantization; polarization can only arise when at least two coupled nuclei are present, due to unequal population of the zero field levels of the product. This case was first treated by Glarum.[5] When, after carrying out the reaction in zero field, the sample is transferred adiabatically to the high spectrometer field (*i.e.* populations of the zero field levels are transferred to the high field levels according to the correlation diagram) rule (2) can be applied with E/A and A/E having the following meaning: E/A: E for group of nuclei (say i) appearing at low field in the n.m.r. spectrum and A for the high field group (j); A/E *vice versa*. Glarum[5] showed that for a group of n_i (spin-$\frac{1}{2}$) nuclei i coupled to a group of n_j nuclei j the pattern is a multiplet of n_j lines [instead of the normal ($n_j + 1$) lines], with the high field line absent. For the j nuclei (appearing at high field): n_i lines with the low field line absent. Thus E/A means E and A "$n - 1$ multiplets" with the inner lines being absent.

Few studies have yet been made in zero field (or in the earth's field of 0·5 G). An example is provided by the work of Ward *et al.*[6] They observed zero field polarization in 2-iodopropane present during decomposition of benzoyl peroxide. The methine proton of 2-iodopropane showed an E sextet with the high field line absent (when reaction was carried out in high field E/A multiplets were observed). This is in accord with polarization originating from escape from F-pairs (encounters of free isopropyl radicals) and subsequent symmetric iodine atom transfer reaction:

$$\begin{tikzcd}
\overline{2R}\cdot \arrow[r] \arrow[d] & 2R^{*}\cdot;\ R^{*}\cdot + RI \arrow[r] & R^{*}I + R\cdot \\
R{-}R^{*}
\end{tikzcd}$$

$\Gamma_{me} = +-+-++=+$. The methyl group would be expected to show a single A line (upfield); the low field line of the doublet is however, present (E line) although it has a lower intensity than the A line. This might be due to deviation from pure adiabatic transfer of the sample, but is more likely to be due to the fact that the field was not exactly zero. Computer calculations indicate[7] that this system is sensitive to residual magnetic fields. The observed pattern[6] is simulated almost exactly,[7] taking a value of the field of 0·5 G.

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[1] R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Letters*, 1969, **4**, 195, 214.

[2] G. L. Closs, *J. Amer. Chem. Soc.*, 1969, **91**, 4552; G. L. Closs and A. D. Trifunac, *ibid.*, 1970, **92**, 2183.

[3] R. Kaptein, *Chem. Phys. Letters*, 1968, **2**, 261.

[4] R. Kaptein, J. A. den Hollander, D. Antheunis, and L. J. Oosterhoff, *Chem. Comm.*, 1970, 1687.

[5] S. H. Glarum, presented at the CIDNP Symposium, Houston, U.S.A., Feb. 1970; S. H. Glarum, personal communication.

[6] H. R. Ward, R. G. Lawler, H. Y. Loken, and R. A. Cooper, *J. Amer. Chem. Soc.*, 1969, **91**, 4928.

[7] R. Kaptein and J. A. den Hollander, *J. Amer. Chem. Soc.*, to be published.