Radical Pair Substitution in CIDNP

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Summary CIDNP in recombination products of radical pairs which undergo rapid transformations is interpreted by a 'co-operative effect.'

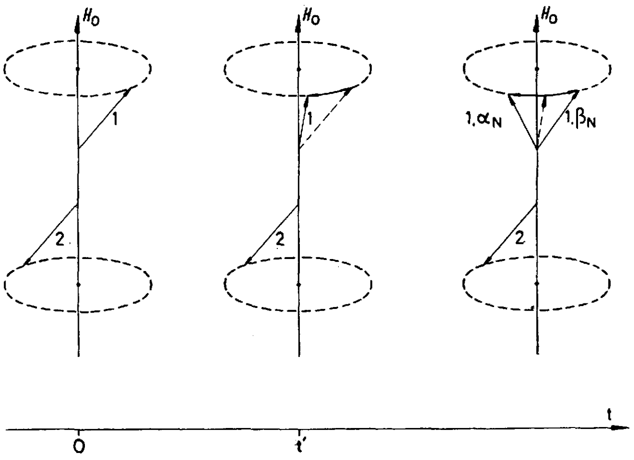
THE radical pair theory[1] has been very successful for the interpretation of CIDNP in many systems. However, the polarizations of the phenyl protons of methylbenzoate and toluene formed during the decomposition of acetylbenzoylperoxide seem to be paradoxical.[2] The decomposition of aroylperoxides is illustrative of radical pair substitution, *i.e.* the radicals undergo rapid transformations, which lead to subsequent geminate radical pairs, each forming recombination products. The CIDNP effects of the products of the secondary pairs have up to now been interpreted by the 'memory effect.' This concept is based on the assumption that the effects of the S-T_0 mixing in the primary pair, appear in the products of the secondary pair.[3]

Although in many systems this readily accounts for the observed effects it fails especially in cases where both the S-T_0 mixing in the primary and in the secondary pair would hardly give a CIDNP effect. This failure arises from the separation of the effects of the subsequent pairs. If, on the other hand, the S-T_0 evolution is described in a continuous fashion, then the CIDNP effects of the products of the secondary pairs result from the 'co-operative effect' of both primary and secondary pair. Considering the hypothetical case of a radical pair with only one proton, pair 1 has different *g*-factors and the hyperfine interaction is zero, but pair 2 has equal *g*-factors and non-zero hyperfine interaction.

$$\overline{R_1H\cdot\quad R_2^{\cdot}} \longrightarrow \overline{R_1'H\cdot\quad R_2^{\cdot}}$$

$$\Delta g \neq 0;\ A = 0 \qquad\qquad \Delta g = 0;\ A \neq 0$$

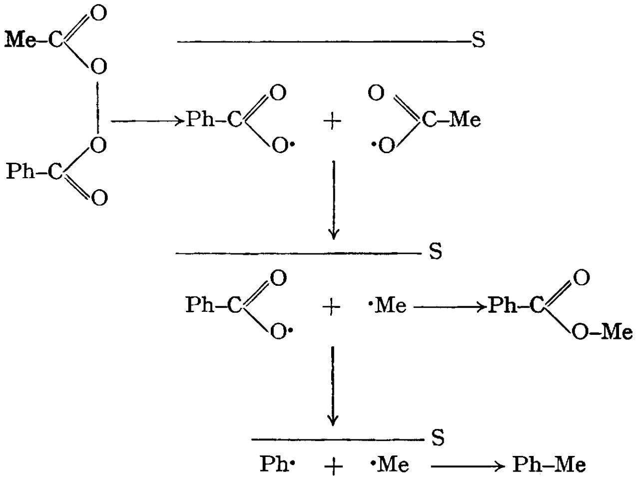
For the recombination product of the pair 2, the 'memory effect' predicts a zero polarization, neither pair 1 nor pair 2 gives a net CIDNP, (this follows simply from Kaptein's rule, ${}^4\Gamma_{ne} = \mu\epsilon\Delta g\, A_i$, the product being zero, since either Δg or A_i is zero).



FIGURE

However, the continuous model leads to a different result, one expects CIDNP effects in the recombination product of pair 2. This can be understood qualitatively by considering the effective field picture.[5] Suppose pair 1 is generated at time $t = 0$ in the electronic singlet state as visualized in the Figure by oppositely oriented electron spin vectors. As there is no interaction between the electron spins, they will undergo a free Larmor precession. Different *g*-factors enhance different Larmor-frequencies and the two spin vectors dephase; triplet character is mixed in, irrespective of the nuclear spin state. At a certain time $t = t'$ the reaction takes place, and the motion of the spin vectors proceeds in a way determined by pair 2. Dependent on the nuclear spin state electron spin vector 1 will precess faster or slower than vector 2. As a result the pairs with *e.g.* β nuclear spin will attain more singlet character than the α nuclear spin pairs. Consequently the β nuclear spin pairs have the larger probability of recombination, leading to an emission signal in the n.m.r. spectrum. This result is closely analogous to the case with a pair having both a *g*-factor difference and a non-zero hyperfine interaction. In the given example the CIDNP effect arises as a 'co-operative effect' of pairs 1 and 2, since each individual pair cannot produce any net CIDNP effect.

The sign (emission or absorption) of this 'co-operative effect' can be obtained by adding the values for the e.s.r. parameters of the two pairs and inserting these into Kaptein's rules.[6] In the case of one substitution reaction we can qualitatively predict the polarization of the recombination product of pair 2 by taking into account two contributions, one for pair 2 and one for the 'co-operative effect' of the two pairs. The latter contribution vanishes when the lifetime of pair 1 is very short ($<10^{-10}$ s). At longer lifetimes of pair 1 ($>10^{-7}$ s) the probability of formation of the recombination product of pair 2 becomes too small to allow observation of CIDNP of this product.



SCHEME

The thermal decomposition of acetylbenzoyl peroxide[7] can be used as an example (Scheme). The explanation of the observed polarizations in the recombination product methylbenzoate is straightforward, the methyl group shows emission [$\Gamma_{ne} = - + - -$; $g_{PhCO_2^{\cdot}} > g_{Me^{\cdot}}$; $A_H(Me^{\cdot}) < 0$], the effects of the phenyl protons being unimportant [$A_H(PhCO_2^{\cdot})$ very small].

The difference between the *g*-factors of the methyl and the phenyl radicals is very small and hence the phenyl– methyl radical pair cannot be responsible for the observed net effects of both the methyl and phenyl protons of toluene. The CIDNP signals of toluene are however readily explained by the 'co-operative effect' concept. As the *g*-factor difference of the benzoyloxy–methyl radical pair overshadows that of the phenyl–methyl pair and the hyperfine interactions are positive and large for the phenylradical the 'co-operative effect' predicts emission for the protons of the phenylgroup of toluene ($\Gamma_{ne} = - + + +$). Similarly the emission for the methylgroup of toluene is predicted ($\Gamma_{ne} = - + - -$). It is easily verified that in this case inclusion of the first pair (benzoyloxy–acetoxy) will not affect these qualitative predictions [$A_H(PhCO_2^{\cdot})$ and $A_H(MeCO_2^{\cdot})$ very small, $g_{PhCO_2^{\cdot}} > g_{MeCO_2^{\cdot}}$].[2,3]

A computer programme which allows simulation of CIDNP spectra in the case of radical pair substitution was developed.

The derivation of the formulae pertaining to the quantitative description of the problem under consideration will be presented elsewhere.[6]

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