

CHEMICALLY INDUCED NUCLEAR POLARIZATION (II):⁺ DEPENDENCE ON LANDÉ FACTORS
IN RADICAL RECOMBINATION REACTIONS

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(Received in UK 10 November 1969; accepted for publication 18 November, 1969)

The theoretical treatment of CINEP has been confined so far to dynamic(longitudinal) polarization in radical transfer (1) and transversal polarization in radical recombination (2) and transfer reactions (3). These theories, however, cannot explain why both transfer and recombination may give rise to longitudinal and transversal polarization as well; an explanation for the fact that the type of polarization may vary with the intensity of the magnetic field (4) is also lacking. A simple theory explaining these effects is presented here; a quantitative treatment will be published elsewhere (5).

A radical pair $[R_1 \cdot \cdot R_2]$ with g-values⁺⁺ g_1 and g_2 may exist in each of the four electron Zeeman states $\psi_1 = ++$, $\psi_2 = b(-+) + a(+ -)$, $\psi_3 = a(-+) - b(+ -)$ and $\psi_4 = --$ (energy decreasing), whereby a and b are given by eq. 1 and $a^2 + b^2 = 1$.

$$a/b = \frac{1}{J} \left[\sqrt{(\Delta E)^2 + J^2} + \Delta E \right] \quad (1)$$

(J = electron coupling constant, $\Delta E = \mu_B H(g_1 - g_2)$)

To explain CINEP in this system, the following postulates have to be made:

1. CINEP arises from transitions $\psi_3 \rightarrow \psi_2$ (or $\psi_2 \rightarrow \psi_3$).
2. These transitions involve simultaneous spin inversions of two nuclei, which may either be in the same ("Y-type", $\Delta m_{jz} = \pm 2$) or in the opposite direction ("X-type", $\Delta m_{jz} = 0$).

⁺) Part I of this series: F. Gerhart and G. Ostermann, Tetrahedron Letters, in press.

⁺⁺) These g-values refer to the radicals in the radical pair and may thus differ from those of the free radicals.

3. The initial population of states ψ_2 and ψ_3 , n_2 and n_3 respectively, is proportional to the "singlet" character" of the respective state if the precursor is a singlet ($n_3 > n_2$), whereas the reverse is true if the precursor is a triplet molecule ($n_2 > n_3$).

Let us first consider the case of large inequivalence, i.e. $\Delta E/J \gg 1$. If such radical pairs are generated from a singlet precursor, n_2 and n_3 will not differ greatly (since $n_2 = n_3$ for $\Delta E/J \rightarrow \infty$), but $n_3 > n_2$ will still hold. The "allowed" transitions $\psi_3 \rightarrow \psi_2$ for a particularly simple system of this type (only one proton in both R_1 and R_2) are indicated as arrows in fig. 1 a.

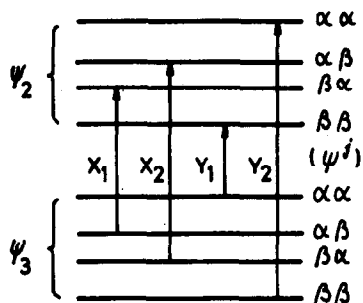


Fig. 1 a

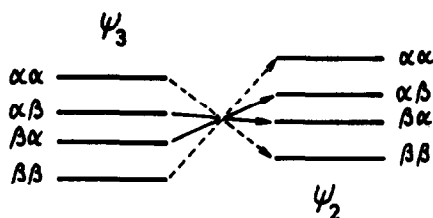


Fig. 1 b

The rates of the two X transitions $X_1^{+)}$ and $X_2^{+)}$ will usually not be identical since $g_1 \neq g_2$; the same will be true for $Y_1^{+)}$ and $Y_2^{+)}$. Furthermore, the electron spin change may be described by $-+ \rightarrow +-;$ thus the transitions have $S_0 \rightarrow S_0$ character and will not give rise to dissociation of the radical pair.

Two main differences arise in the case $\Delta E/J = 0$. First, the transitions $\psi_3 \rightarrow \psi_2$ have $S_0 \rightarrow T_0$ character and therefore will be followed by dissociation (2). Second, we may no longer distinguish between transitions X_1 and X_2 (or Y_1 , Y_2); thus, their rates must be identical. These "degenerate" transitions, X_a and Y_a , are shown as solid and dashed arrows, respectively, in fig. 1 b.

⁺) Index 1 indicates that the spin inversions of electron and nucleus of radical R_1 (greater g value) are in the same direction, whereas they are in opposite direction if the index is 2.

If the net number of transitions $\psi_3 \rightarrow \psi_2$ (X type assumed) is d_1 for X_1 , d_2 for X_2 , and d_a for X_a transitions, the final population of the nuclear levels of R_1-R_2 will be $n(\alpha\alpha)$, $n - d_1 + d_2(\alpha\beta)$, $n - d_2 + d_1(\beta\alpha)$, $n(\beta\beta)$ for the case $\Delta E/J \gg 1$, and $n(\alpha\alpha)$, $n - d_a(\alpha\beta)$, $n - d_a(\beta\alpha)$, $n(\beta\beta)$, for $\Delta E/J = 0$ ($n = 1/4(n_2 + n_3)$). The former partition is apparently characteristic for a longitudinal, the latter for transversal polarization.

The influence of $\Delta E/J$ on the observed spectra may be conveniently demonstrated for the case of an AMX coupling pattern in R_1-R_2 (A, M in R_2 , X in R_1). The "allowed" transitions" (X type, singlet precursor assumed) are shown in fig. 2⁺ ($X_1: \rightarrow$; $X_2: \dashrightarrow$; symbols indicate which nuclei are flipping).

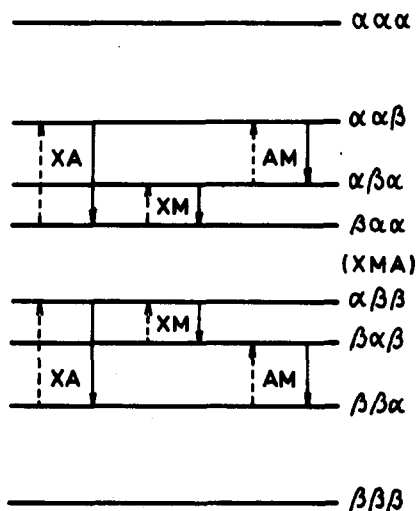


Fig. 2

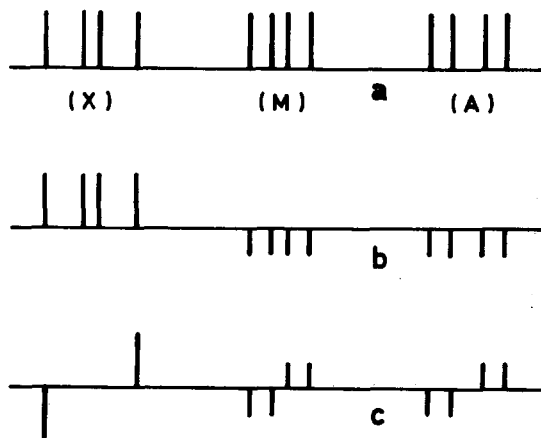


Fig. 3

The resulting theoretical spectra are shown in fig. 3 ($J_{AX} > J_{MX} > 0 > J_{AM}$); a) unpolarized R_1-R_2 , b) $\Delta E/J \gg 1$ ("X₁ type", i.e. rate of X₁ greater than that of X₂),

⁺ The partition generated by $\psi_3 \rightarrow \psi_2$ and subsequent recombination is the same as if the nuclear transitions associated with X_1 , X_2 , and X_a had occurred in the recombination product; consequently, the transitions may be represented by arrows in the level scheme of R_1-R_2 .

c) $\Delta E/J = 0$ (X_a type). (In fig. 3 the rates of transitions "AX" and "BX" are assumed to be equal; transitions "AB" are neglected).

It should be pointed out that for longitudinal polarization, absorption and emission do not alternate within the line group resulting from transitions of a given nucleus (fig. 3b). Such alternation may only occur if transversal relaxation is operating (fig. 3c), a general feature of all $A_n X_m$ (or $A_n B_m$) spectra.

The theoretical dependence of longitudinal (—) and transversal (-----) polarization on $\Delta E/J$ is shown in fig. 4 (5). This graph may also be interpreted as representing the field dependence of the two polarization types since $\Delta E/J$ is (in a given system) proportional to H.

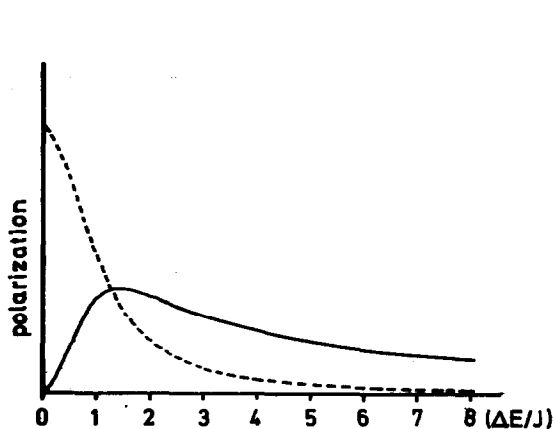
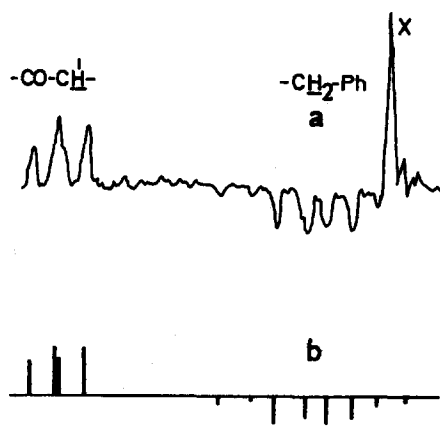


Fig. 4

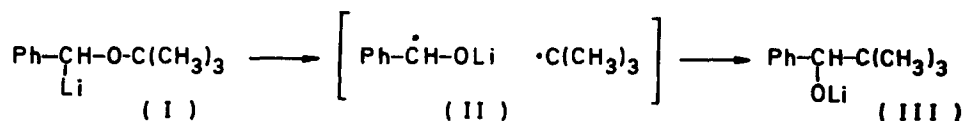
Fig. 5⁺

Reactions occurring via radical pairs with different g values of the components should give rise to transversal polarization if the reaction is run in a weak magnetic field; however, the polarization becomes longitudinal ("dynamic") with increasing magnetic field. The field intensity at which this change in polarization type occurs will vary inversely with the "inequivalence" ($g_1 - g_2$). The same ought to be true for radical transfer reactions (6).

⁺) The signal marked x is due to dibenzyl (enhanced absorption).

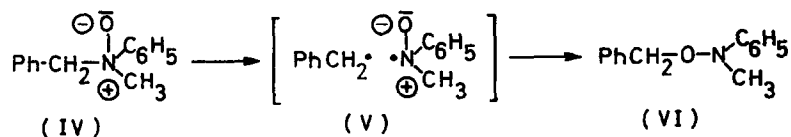
Predictive power

1. 1,1,2-triphenyl-ethane, prepared by thermal decomposition of benzyl-azodiphenylmethane, shows transversal polarization (7) (X_a type). This is in agreement with theory since benzyl and benzhydryl radical should not differ appreciably in their g values; both are "carbon" radicals. Transversal polarization is also observed for III obtained from rearrangement of I (8), which proceeds via the radical pair II. Again the g values of the ketyl and the *t*-butyl radical are obviously not sufficiently different to give rise to longitudinal polarization.



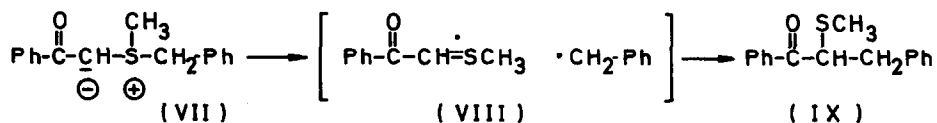
This rearrangement seems to be an example of Y_a type relaxation which results in an overpopulation of the levels at or near zero. According to the theory of Cross (2) an underpopulation should be expected.

2. In VI obtained from the Meisenheimer rearrangement of IV both the benzyl and methyl protons are emitting (9).



The polarization is thus longitudinal (Y_2 type). In this system the nitroxide and the benzyl radical are known to differ in their g values by about 10^{-3} . If J is assumed to be $10^6 - 10^7 \text{ sec}^{-1}$ (as in radical anion pairs (10)) the condition $\Delta E/J \gg 1$ seems to be met.

The thermal rearrangement of VII yields IX, the spectrum of which is shown in fig 5 a (11). Apparently this is a case of longitudinal (X type) polarization as may be seen from comparison with a calculated spectrum (fig. 5 b).



If signs are neglected, the integral over the X lines (fig. 5 a) is nearly equal to that over the AB part (1 : 1.08), whereas in unpolarized IX this ratio is 1 : 2. This is in excellent agreement with the theory presented here, which predicts a ratio of 1 : 1 for polarized IX. It may be shown that this is a general phenomenon common to all cases of coupling patterns $A_n X_m$ (or $A_n B_m$) in R_1-R_2 .

The author wishes to thank Prof. Dr. U. Schöllkopf for stimulating discussions and support of this work.

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