Tetrahedron Letters No.53, pp. 4705-4710, 1969. Pergamon Press. Printed in Great Britain.

A THEORY EXPLAINING CHEMICALLY INDUCED NUCLEAR SPIN POLARIZATION IN RADICAL TRANSFER AND DISPROPORTIONATION REACTIONS

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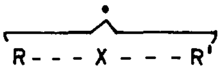
(Received in UK 6th October 1969; accepted for publication 16th October 1969)

Nuclear spin polarization in free radical transfer reactions may be explained, in some cases, by dynamic nuclear polarization (CIDNP) occurring in the free radical (1). This mechanism, however, cannot account for the "multiplet-effects" frequently observed in radical transfer (2,3), disproportionation (2), and recombination reactions (4). For the latter, the multiplet-effect (ME) has been explained as a "transversal Overhauser effect" involving singlet-triplet-transitions of radical pairs (5). We wish to propose somewhat similar mechanisms for radical transfer and disproportionation reactions.

Radical transfer reactions

The transition state of a transfer reaction (I) may formally be regarded as an array of three radicals (II),



$\overbrace{R---\overset{\bullet}{X}---R'}$ (I) $\left[R\bullet \quad X\bullet \quad R'\bullet\right]$ (II)

which may be treated as a loosely coupled radical pair $[R\cdot \ \cdot R']$ interacting with the spin of the radical X.

As a first approximation R and R' are assumed to be identical (as far as the electron g values are concerned) and spin-spin-interactions are neglected. We then obtain the Zeeman-states of a $[R\cdot \ \cdot R]$ radical pair split into two sets by the spin of X (fig. 1).

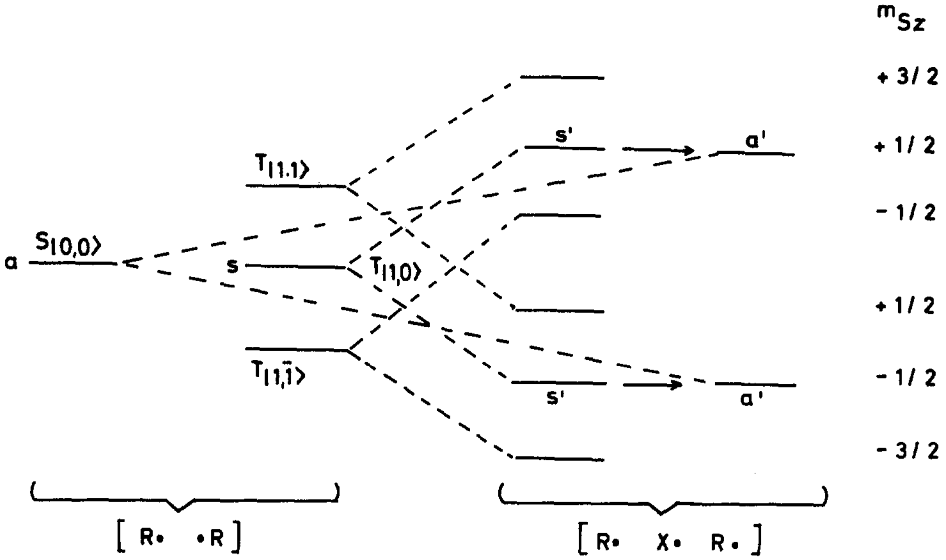


Figure 1. Zeeman levels of three-radical-array [R• X• R•] deduced from those of a radical pair [R• •R]

In the transition state X must be bonded equally to both radicals R; the electron spin function must therefore be symmetric. As a consequence, in the formation of the transition state all Zeeman levels with $m_{Sz} = \pm 1/2$ (sign dependent on the spin of the attacking radical) will become populated with the exception of those designated as "antisymmetric" (a') in fig. 1. As in radical pairs (5), we postulate transitions between s' and a' states (indicated by an arrow in fig. 1) to occur most rapidly if the nuclear states are $m_{jz(s')} = m_{jz(a')} = 0$ (or ± 1/2, if states with $m_{jz} = 0$ do not exist). The a' states should therefore be populated predominantly with $m_{jz} = 0$ or $m_{jz} = \pm 1/2$. The consequence of such a s'→ a' transition (demonstrated in a very simplified manner by III) is that "bonding" now only occurs between one of the R-radicals and X, an effect which may be interpreted as the product-forming step.

$$R\uparrow X\downarrow R\uparrow \xrightarrow{s'\to a'} R\uparrow X\downarrow R\downarrow \qquad (\mathrm{III})$$

It may further be shown that the radical R and the molecule RX resulting from an a' state with $m_{jz} = 0$ will both be predominantly in nuclear state $m_{jz} = 0$ (more exactly speaking, the population should decrease with increasing $|m_{jz}|$).

Predictive power

1. A transfer reaction $R\cdot + X\text{-}R' \longrightarrow R\text{-}X + R'\cdot$ should result in an overpopulation of levels $m_{jz} = 0$ (or $\pm 1/2$) for R-X. Unreacted R'-X, on the other hand, should have underpopulation of states $m_{jz} = 0$ (e.g.those closest to zero), because the molecules with $m_{jz} = 0$ undergo transfer most rapidly.

For coupling patterns of the type A_nX_m with all J_{AX} equal and $J_{AX} > 0$ overpopulation of the $m_{jz} = 0$ (or $\pm 1/2$) state gives rise to absorption of the low field part of the multiplets and emission of the high field part (which we define as "positive ME"), whereas in the case of underpopulation the reverse effect ought to be observed ("negative ME").
In accord with our theory, the reaction of n-butyllithium with isopropyliodide (R = butyl, R' = isopropyl) yields both polarized n-butyliodide and isopropyliodide (2b,2d), the former showing positive (multiplet A), the latter negative ME (multiplet E)(fig.2)[+].

2. If R = R', the ME's should cancel each other, so that no net polarization ought to be observed. Indeed, the reaction of n-butyllithium with n-butyliodide shows no RASER effects (2d).(Slight distortions indicate a very small ME perhaps due to side reactions; in this case positive and negative ME's obviously should not cancel completely).

[+] Reproduced from A.R.Lepley, (2b).

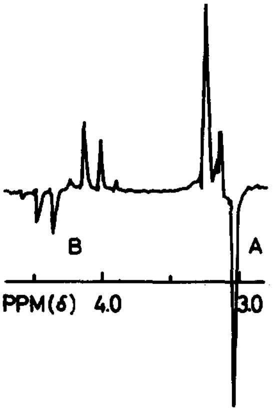


Figure 2^{+}

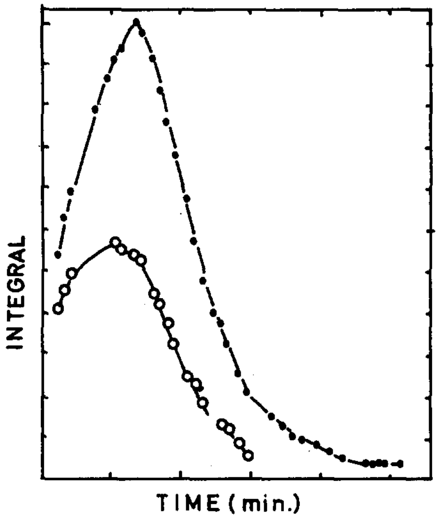


Figure 3^{+}

3. Polarization of R-X and R'-X should occur with identical rates. If the relaxation times T_{RX} and $T_{R'X}$ are also equal, stationary concentrations should always be equal and their maxima be reached simultaneously. A plot (fig 3)$^{+}$ of the integrals (positive parts only) of the iodomethylene (●) and iodomethine (○) proton signals of n-butyliodide and isopropyliodide, respectively, versus time for the reaction of n-butyllithium with isopropyliodide (2b) shows this prediction to be in rather good agreement with theory.

4. For R-X and R'-X obtained from the transfer reactions $R\cdot + R'\text{-}X \rightarrow R\text{-}X + R'\cdot$ and $R'\cdot + R\text{-}X \rightarrow R'X + R\cdot$, respectively, reverse ME's ought to be observed, i.e. absorption and emission lines should be interchanged. This prediction remains to be confirmed by experiment.

Radical disproportionation reactions

Polarization effects as have been observed in radical dispropotionation reactions (2a,2d) may easily be explained by extension of the radical pair model proposed by Closs (5) for recombination reactions.

Consider a solution containing free radicals R with electron and nuclear spins in thermoequilibrium. Singlet and triplet encounters of these radicals will occur giving rise to a uniform population of singlet and triplet states of radical pairs $\left[R\cdot\ \ \cdot R\right]$. Disproportionation, however, is likely to occur only via singlet pairs, since a triplet pair would yield an alkane and an energetically unfavorable triplet-alkene. We assume both of the following mechanisms for disproportionation to be operating:

1. singlet encounters and disproportionation of singlet radical pairs
2. triplet-singlet-transitions in radical pairs.

Mechanism 1 would not give rise to polarization, but mechanism 2 should. According to the theory of Closs (5), such triplet-singlet-transitions should be favored by states with $m_{jz}= 0$ (or ± 1/2). Therefore, both alkane and alkene should be generated with overpopulated $m_{jz}= 0$ (or ± 1/2) levels.

It should be noted that radical pairs generated in the singlet state should undergo "cage-disproportionation" without polarization.
however, if part of the radicals escape from the cage by a singlet-triplet-transition-mechanism whereby depopulation of the radical pair levels with $m_{jz}= 0$ (or ± 1/2) occurs, polarization ought to be observed. In this case the signs of the ME's of alkane and alkene are predicted to be opposite to those of the products obtained in a free radical reaction (as discussed above).

The authors would like to thank Prof. Dr. U. Schöllkopf for helpful and stimulating discussions.

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