THE LOW FIELD CIDNP IN THE REACTION OF PHENYLDIAZONIUM

TETRAFLUOROBORATE WITH NATRIUM METHOXIDE AND ALKALI

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At present the CIDNP method is a useful tool for investigation of organic reaction mechanisms. Usually the CIDNP effects are studied for the reactions proceeding in the magnetic field of a standard NMR spectrometer ($14-23 \times 10^3$ Oe). In this communication we will show that significant information on a reaction mechanism may be obtained by the low magnetic field CIDNP method. We have studied the reactions of phenyldiazonium tetrafluoroborate with sodium methoxide and alkali. There is no common viewpoint on the free radical formation mechanism in these reactions.[1] Some authors suppose that the CIDNP effects in these reactions appear in those radical pairs (RP) containing $\cdot OCH_3$ and $\cdot OH$ radicals. An alternative viewpoint is that the CIDNP effects arise during the homolytical decomposition of the intermediate product, diazooxide $Ar-N = N-O-N = = N-Ar$.[2] On the other hand, the last mechanism takes place during the thermal decomposition of N-nitrozoacetanilide (N NA).[1] In this connection we have also studied a field dependence of CIDNP during NNA thermolysis as a possible model process.

We investigated the low field ^{1}H CIDNP by two methods: a) a standard technique with the sample "transfer",[1] b) a direct observation of the low magnetic field CIDNP.[3] In the latter case we used a pulse NMR spectrometer for low magnetic fields developed in our Laboratory. The NNA thermolysis reaction (0.3 ml of 0.5M NNA solution in CH_3CN, t = $+60^{\circ}C$) was studied by the sample "transfer" technique. The low field CIDNP in the reaction of phenyldiazonium tetrafluoroborate could be observed only by a direct method. For that purpose $C_6H_5N_2^+BF_4^-$

solution in CH_3CN (30 ml, 0.5M) was placed in the probe of a spectrometer, then the solution of CH_3ONa or NaOH in dry CH_3OH (10 ml, 2.0M) was added. The reaction was carried out at room temperature in a polarizing magnetic field, H_p, induced by Helmholtz coils. The H_p field intensity varied in the range of 0.6-120 Oe; the spin echo signal was registered in the earth magnetic field (0.6 Oe), the field switching time being 4 msec. The ^{1}H CIDNP of the main reaction product (benzene) was observed during 1-1.5 min after a nucleophilic reagent solution had been added. That enabled us to perform 5-6 measurements of the polarized signal intensity on the same sample at various H_p values.

Fig.1 shows the ^{1}H CIDNP enhancement for benzene plotted as a function of the magnetic field intensity for the reaction of $C_6H_5N_2^+BF_4^-$ with CH_3ONa and NaOH (curve a). A similar field dependence of CIDNP for benzene as a product of NNA thermolysis was observed. A unique phenomenon of the low field CIDNP sign alternation was observed in these systems.
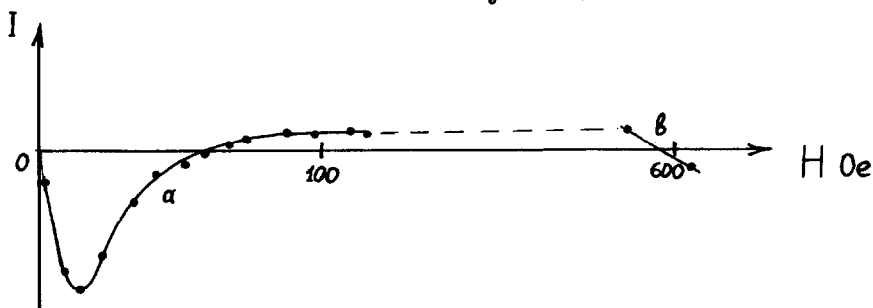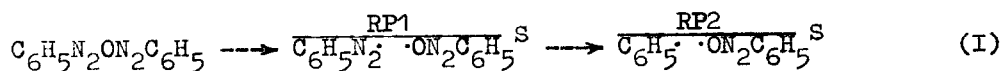

Fig.1

The published theoretical interpretation of the low magnetic field mechanism enabled us to identify the partners of those radical pairs which were precursors of the reaction products. A convenient relationship between the low field net polarization sign and the RP parameters was obtained by the technique of projection operators.[4] Thus, we may conclude that the polarization sign alternation in low magnetic fields (i.e. a double change in the field CIDNP dependence, see Fig.1, curve b) is observed when

$$JA_1 \approx \frac{1}{4}(\sum_j A_j^2 - A_1^2),[5] \tag{1}$$

where A_1 is the hfi constant of the nucleus under study, $\sum_j A_j^2$ is a sum of the hfi constants squared (in a radical-partner), J is the exchange integral of the radical spin-spin interaction in RP. The published computations of the low field CIDNP effects for a one-proton RP[6,7] are consistent with relation (1).

The polarization sign alternation may take place only within a narrow range of values of J, A_1, $\sum_j A_j^2$.[8]

Thus, the field dependence of benzene CIDNP effects in the reaction of $C_6H_5N_2^+BF_4^-$ with CH_3ONa and NaOH and in the NNA thermolysis allows us to choose a scheme where CIDNP appears in identical radical pairs,

$$C_6H_5N_2ON_2C_6H_5 \longrightarrow \overline{C_6H_5N_2 \cdot \ \cdot ON_2C_6H_5}^S \xrightarrow{RP1} \overline{C_6H_5 \cdot \ \cdot ON_2C_6H_5}^S \quad (I)$$

So the analysis of the field dependence of CIDNP enables us to conclude that the CIDNP effects appear in those RP containing no $\cdot OH$ and $\cdot OCH_3$ radicals.

In scheme (I) CIDNP may arise in RP1 and RP2. Evaluations of the exchange integrals by (1) are as follows:

for RP1 $A_1 = 1.6$ Oe,[1] $A_j^2 = 2527$,[9] $J = -395$ Oe

for RP2 $A_1 = 19.5$ Oe,[11] $A_j^2 = 2527$, $J = -27.5$ Oe

The data obtained on CIDNP[1] show that usually J does not exceed 10^2 Oe, except for RP involving π-radicals with a high degree of unpaired electron delocalization (e.g. benzyl radicals).[12] Hence, it is doubtful that $J=-395$ Oe for RP1 where partners are σ-radicals with a small degree of unpaired electron delocalization. Consequently, we consider that $J=-27.5$ Oe is more probable, and therefore the low magnetic field ^1H CIDNP arises mainly in RP2. On the other hand, RP1 prevails in high fields.[1] The change in the relative contributions of consequent radical pairs to a total CIDNP is attributed to the fact that there appear some new channels of $S - T$ conversion ($S-T_+$) in low magnetic fields. This CIDNP mechanism is known to be more sensitive to hfi constants ($A_{C_6H_5N_2} = 1.6$ Oe, $A_{C_6H_5} = 19.5$ Oe) in low fields, and therefore the RP2 contribution becomes predominant.

Summarizing, it can be said that the low field CIDNP method is useful for

studying the mechanisms of organic radical reactions.

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3. We have recently shown that both methods give qualitatively similar results for thermolysis reactions.

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5. The expression was obtained for RP escape products (benzene in the reaction under study).

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8. According to our calculations for a one-proton RP, the CIDNP sign alternation is not observed even if J and A deviations are about 20%.

9. $A_J^2 = 8/3(A_{N_1}^2 + A_{N_2}^2)$, $A_{N_1} = 30.7$ Oe, $A_{N_2} = 2.3$ Oe.[10]

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