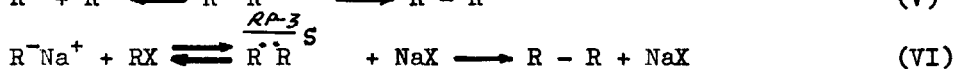
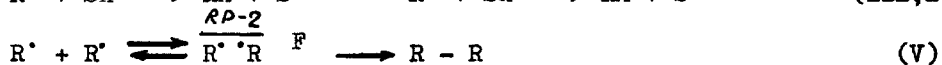
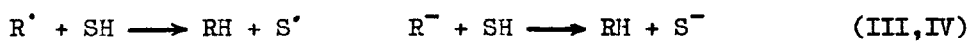
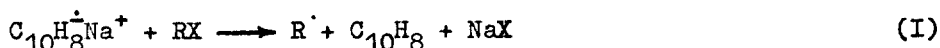


CIDNP IN REACTIONS OF SODIUM NAPHTHALENE WITH ALKYL  
HALIDES IN VARIOUS MAGNETIC FIELDS  
(from 0.5 to 23000 Oe)

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Studies of the reaction of sodium naphthalene ( $C_{10}H_8^{\dot{-}}$ ) with alkyl halides by chemical methods show participation of free radicals in generation of the alkylation, coupling and reduction products.<sup>1-3</sup>




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Here SH is a solvent, RP is a radical pair, \*) is a polarized radical.

Garst et al.<sup>3</sup> employed the CIDNP method to choose among the possible radical stages of the above reaction (see the scheme). They obtained an unexpected result: CIDNP was observed only in low magnetic fields (20-300 Oe) on the coupling (R-R) and reduction (RH) products. The above fact made Garst reject the way of R-R dimer generation (V), most probable according to the chemical data, and suppose that the reaction provided no conditions for the nuclear spin selection resulting in the high field CIDNP.<sup>3</sup> The latter is, however, doubtful as the absence of selection may be expected only in the reaction with the cage recombination and cage escape products being the same. Garst

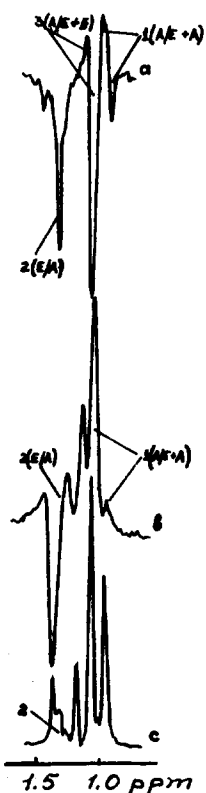


Fig.1

$^1\text{H}$  CIDNP in reaction of  $\text{C}_{10}\text{H}_{18}$  with isobutyl iodide. (1) -  $\text{CH}_3$  in 2,5-dimethylhexane, (2) -  $\text{CH}_2$  in 2,5-dimethylhexane, (3) -  $\text{CH}_3$  in isobutyl iodide: a) in 0.5 Oe\*) b) in 14000 Oe field, c) NMR spectrum of the reaction products.

concludes that the R-R dimers appear in (VI). It remains incomprehensible, however, why there is no CIDNP in high fields. It is well known<sup>4,5</sup> that in the reaction of alkyl halides with alkyl lithium (the reaction is similar to (VI)<sup>3</sup>) CIDNP is observed in various magnetic fields (0.5-23000 Oe).

This work gives a number of experimental data which, we think, remove the above contradictions. The  $^1\text{H}$  CIDNP effects have been observed (in contrast to Garst<sup>3</sup>) in various magnetic fields from 0.5 to 23000 Oe on the products of alkyl radical and hydrocarbon recombinations in the reactions with  $\text{C}_2\text{H}_5\text{Br}$ ,  $(\text{CH}_3)_2\text{CHCl}$ ,  $(\text{CH}_3)_2\text{CHBr}$ ,  $(\text{CH}_3)_2\text{CHCH}_2\text{I}$ .

The CIDNP effects observed in the reaction of  $\text{C}_{10}\text{H}_{18}$  with isobutyl iodide are given in Fig.1. CIDNP in high fields is described by the CKO theory.<sup>6</sup> Supposing that the multiplet effects appear in RP-2,3, but the net polarization only in RP-1, CIDNP is then well consistent with the above scheme. We analyzed the CIDNP effects in low fields by the method proposed by Salikhov et al.<sup>7</sup> Analysis of all the net effects observed by us and earlier by Garst et al.<sup>3</sup> and Rakchys<sup>8</sup> shows a small magnitude of exchange interaction energy (J) in the radical pairs (see the table). It is an attractive fit to the J magnitudes we have estimated for the alkyl radical pairs in the reaction of BuLi with the substituted benzylchlorides. The multiplet effects do not change the sign in transition from a high magnetic field to that of the earth which is consistent with the results

\*) A maximum CIDNP was observed in fields of about 20-50 Oe.

of Salikhov et al.<sup>7</sup>

Thus, the CIDNP effect analysis corroborates the existence of radical stages I, II, V, VI and VII in reaction of sodium naphthalene with alkyl halides.

The reaction was performed in a 0.5 mm tube by pouring together 0.3–0.6 M solution of sodium naphthalene<sup>3</sup> in DME and THF with an equivalent amounts of alkyl halide at room temperature. The tube was placed either between the poles of an electromagnet (interval magnetic field 5–2000 Oe) or in the probe of a NMR spectrometer Varian A 56/60 A where NMR spectra were detected.

TABLE

Estimations of exchange integrals for the radical pair in the reaction of  $C_{10}H_8^{\dot{}}$  with alkyl halides

RX		RP, product precursor	CIDNP, product	J, Oe
$(CH_3)_2CHCH_2I$		cage product RP-3	octane, $CH_3(A)$ $CH_2(E)$	> -320 > -9
$(CH_3)_2CHCl$	[3]	escape product RP-1	propane $CH_3(E)$	< +8
--"---		cage product RP-1	propane $CH_3(E)$	< -7
$I(CH_2)I$	[3]	cage product RP-1	cyclobutane $CH_2(E)$	< 4
$pFC_6H_4CH_2Cl$	[8]	cage product RP-1	dibenzyl pF(A)	< -1
$pFC_6H_4CH_2Cl$	[5]	cage product of F-pair of two benzyl radicals	dibenzyl pF(E)	< -10

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