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THE INFLUENCE OF THE MAGNETIC FIELD AS A TOOL FOR INVESTIGATION OF THE MECHANISM OF REACTIONS OF TRIETHYLGERMYL RADICALS *

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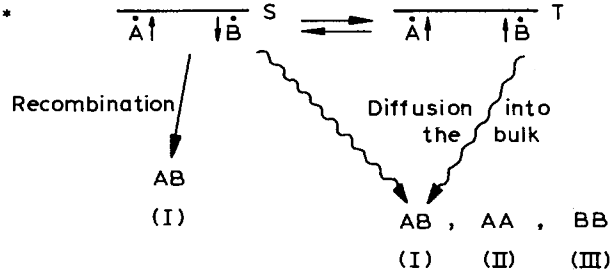
Summary

The influence of the external magnetic field on the product yield in the reaction of Et_3GeM (where M = Na, K) with benzyl chloride was investigated. A mechanism for magnetic effects in this reaction is proposed. To verify the mechanism proposed, theoretical calculations of the recombination probability of triethylgermyl and benzyl singlet radical pairs were carried out. It is proposed that associated state of the organometallic compound in solution affects the cage and the magnetic effects.

Introduction

Radical reaction mechanisms in liquids have been studied successfully by means of magnetic and spin effects during the last few years [2]. It was determined in 1972 [3], that the magnetic field may change the amount of reactive radical pairs (RP), giving rise to variation of the ratio of different reaction products, e.g. products of "cage" recombination and recombination in the bulk (Scheme 1).

SCHEME 1 **



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[*] The main results of this paper were presented on the IIIrd All-Union conference Nuclear and Electron Polarization and Magnetic Effects in Chemical Reactions, Novosibirsk, August 1981 [1].

[**] The vertical arrows characterise the direction of the electron spin of the free radicals $\dot{A}$ and $\dot{B}$; S and T = multiplicity of radical pair (singlet and triplet, respectively).

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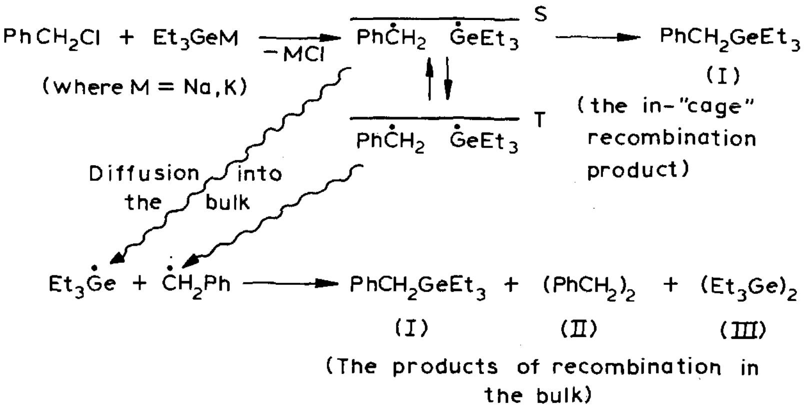
In this case the mechanism of the magnetic effect consists in reorientation of the electron spin which is induced by interaction with magnetic nuclei of free radical (hfi * mechanism) or by difference between g factors of RP (Δg mechanism [2]).

Radical reactions involving elements of Group IV (C, Si, Ge, Sn, Pb) are of particular interest for investigations of magnetic effects in chemical reactions. In organometallic radicals the constants for the hyperfine interaction with heavy atoms are usually very high (hundreds of Øersted) and g factors differ notably from the pure spin value, thus one expects appreciable magnetic effects [2].

The present paper discusses the effect of the external constant magnetic field (MF) on the product yield in the reaction of benzyl chloride with triethylgermylsodium and triethylgermylpotassium in benzene. Recently, it has been shown [4], that a radical pair of benzyl and triethylgermyl free radicals in a singlet state is the precursor of the basic products of this reaction (Scheme 2).

SCHEME 2



The substantial difference in the radical g values ($Ph\dot{C}H_2$: $g = 2.0026$; $Et_3\dot{G}e$: $g = 2.0089$ [5]) and the presence of magnetic nulei in the RP suggests a considerable influence of the MF, and that the radical path of formation of the reaction products will be prevalent [2].

Experimental

Benzyl chloride ("Reanal") was not purified additionally before use. Triethylgermylsodium and triethylgermylpotassium solutions (1 M in benzene) were synthesized as described in ref. 6. The reactions were performed by adding a twofold excess of benzyl chloride to 0.4 ml of 1 M solution of the organo germanium compound in a 5 mm glass tube at room temperature. The reactions are exothermic and take about a minute.

To study the field dependence of the reaction products we used a magnet with tunable MF (from 60 to 7000 G) and a magnet from a Tesla BS 487C NMR spectrometer (18, 800 G).

The samples were analyzed for the product as described in ref. 4. The experimental product ratio II/I was determined from the ratio of integral intensities of PMR signals of dibenzyl (II) and phenyltriethylgermylmethane (I) α-CH_2 groups. The

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* hfi = hyperfine interaction.

PMR spectra were taken on a Tesla BS 487C spectrometer at 80MHz operating frequency. Numerical calculations were performed on a BESM-6 computer. Each point of the field curve is an average over not less than three series of experiments. The plots shows arithmetic mean errors.

Results and discussion

In the present work we measured the ratio of the yields of escape product dibenzyl (II) and in cage product phenyltriethylgermylmethane (I) in the reaction of benzyl chloride with Et_3GeNa and Et_3GeK at various MF strengths. Figure 1 shows the dependence of II/I ratio on MF strength for the reaction of Et_3GeNa with benzyl chloride. A similar field dependence was obtained for the reaction of benzyl chloride with triethylgermylpotassium.

As follows from previously mentioned reaction scheme, MF may influence the geminal recombination probability of the singlet RP (P_s) which causes changes in the probability of exit of the benzyl and triethylgermyl radicals into the bulk P_e (since $P_e = 1 - P_s$) and in the rate constant of radical recombination in the bulk. Reactions of benzyl chloride with triethylgermylsodium and triethylgermylpotassium are characterized by large cage effects: 0.7 and 0.8 for Et_3GeNa and Et_3GeK, respectively [4]. Thus, one should expect the greatest relative changes in the probability of exit of the radicals from cage at higher MF.

The experimentally measured products ratio II/I is expressed through rates of formation of the products I and II as follows (see Scheme 1):

$$II/I = V(II)/(V(I) + V(I)_b),$$

where $V(I)$ = formation rate of the product I in the cage, that is equal to $P_s v$, where v = generation rate of free radicals A and B in the cage;

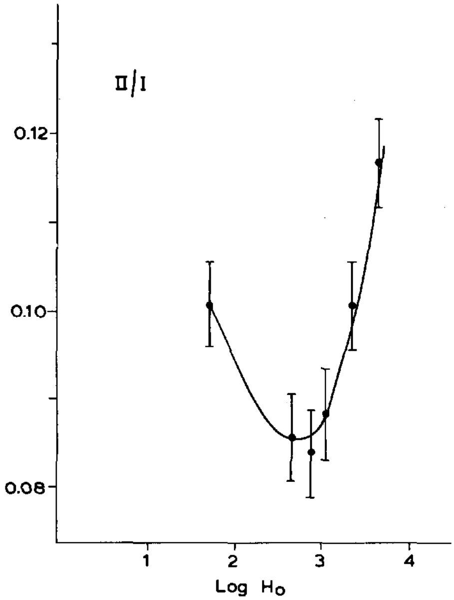

Fig. 1. The ratio of products II and I (II/I) in the reaction of Et_3GeNa with $PhCH_2Cl$ in benzene vs. magnetic field strength.

$V(\mathrm{I})_\mathrm{b}$ = formation rate of product I in the bulk, $V(\mathrm{I})_\mathrm{b} = K_\mathrm{r}[\mathrm{A}][\mathrm{B}]$;
$V(\mathrm{II})$ = formation rate of the symmetrical product II, equal to $K_\mathrm{r}'[\mathrm{A}]^2/2$.

Hence the product ratio:

$$\mathrm{II}/\mathrm{I} = K_\mathrm{r}'[\mathrm{A}]^2/2(P_\mathrm{s}v + K_\mathrm{r}[\mathrm{A}][\mathrm{B}])$$

The concentration changes of A and B radicals with time are described by following expressions:

$$\mathrm{d}[\mathrm{A}]/\mathrm{d}t = P_\mathrm{e}v - K_\mathrm{r}'[\mathrm{A}]^2/2 - K_\mathrm{r}[\mathrm{A}][\mathrm{B}]$$

$$\mathrm{d}[\mathrm{B}]/\mathrm{d}t = P_\mathrm{e}v - K_\mathrm{r}''[\mathrm{B}]^2/2 - K_\mathrm{r}[\mathrm{A}][\mathrm{B}]$$

The concentrations of radicals A and B are equal (because $K_\mathrm{r}' = K_\mathrm{r}''$ [11]). Hence, under stationary conditions:

$[\mathrm{A}]^2 = P_\mathrm{e}v/(K_\mathrm{r}'/2 + K_\mathrm{r})$, and for the experimentally measured product ratio:

$$\mathrm{II}/\mathrm{I} = K_\mathrm{r}'P_\mathrm{e}/(K_\mathrm{r}'P_\mathrm{s} + 2K_\mathrm{r})$$

Rate recombination constants of radicals involved are practically equal [11], thus one may assume that:

$K_\mathrm{r} \approx K_\mathrm{r}'$, hence

$$\mathrm{II}/\mathrm{I} = P_\mathrm{e}/(2 + P_\mathrm{s}) = (1 - P_\mathrm{s})/(2 + P_\mathrm{s}).$$

This result means that the escape of radicals from the cage into the bulk will be the stage of greatest sensitivity to MF influence. Thus, the values of experimentally measured product ratio II/I (ordinates on Fig. 1) reflect the variations of theoretically calculated values of $(1 - P_\mathrm{s})/(2 + P_\mathrm{s})$.

The experimental curve with a minimum (Fig. 1) is typical of the two basic mechanisms of MF influence: hfi and Δg [2]. The left-hand side of the curve is associated with a decrease in the probability of the escape of radicals due to reduction of the efficiency of the hfi-induced singlet-triplet mixing with increasing MF strength. The right-hand side pertains to an increase in P_e due to acceleration of the S–T_0 transitions by the Δg mechanism. To verify the reliability of the above interpretation of the field dependence, we computed $(1 - P_\mathrm{s})/(2 + P_\mathrm{s})$ values for a singlet pair of triethylgermyl and benzyl radicals. The so-called semiclassical theory proposed by Schulten and Wolynes [7] and improved in ref. 8 was the basic algorithm of the computation program. This theory allowed us to compute the S–T mixing dynamics in the case of an arbitrary number of magnetic nuclei in RP in any magnetic field [8]. The computation was based on the following parameters:

1) effective hfi constants of radicals:
   $A(\mathrm{Ph\dot{C}H_2}) = (\frac{1}{3}\sum_i I_\mathrm{i}(I_\mathrm{i} + 1)a_\mathrm{i}^2)^{1/2} = 1.25$ mT;
   a_i constants: $H(\alpha) = -1.628$ mT, $2H(\mathrm{o}) = -0.515$ mT,
   $2H(\mathrm{m}) = 0.179$ mT, $H(\mathrm{p}) = -0.617$ mT [5]
   $A(\mathrm{Et_3\dot{G}e}) = (\frac{1}{3}\sum_k I_\mathrm{k}(I_\mathrm{k} + 1)a_\mathrm{k}^2)^{1/2} =$
   24.1 mT (for $^{73}\mathrm{Ge}$); 0.612 mT (for nonmagnetic isotopes of Ge)
   a_k constants: $H(\mathrm{CH_2}) = 0.475$ mT, $H(\mathrm{CH_3}) = 0.056$ mT,
   $^{73}\mathrm{Ge} = 8.47$ mT ($I = 9/2$) [5]
2) the difference between g values of RP: $g(\mathrm{Ph\dot{C}H_2}) = 2.0026$, $g(\mathrm{Et_3Ge}) = 2.0089$ [5];
3) the in-cage lifetime of RP: τ_D;

4) the in-cage recombination probability (λ) neglecting the S–T evolution, $\lambda = K\tau_r/(1 + K\tau_r)$, here K = rate recombination constant of radical pair in contact, and τ_r = total time of the contacts on recombination radius.

The whole RP ensemble is divided into subensembles with definite local hfi fields at the location of the unpaired electrons. Then P_s is averaged over all the RP subensembles by the Monte-Carlo method. The procedure of recombination probability computations is described in details in ref. 8. The value of $(1 - P_s)/(2 + P_s)$ is calculated separately for a hypothetic pair of triethylgermyl and benzyl radicals containing either nonmagnetic isotopes of germanium (Fig. 2a), or 100% of a magnetic one (Fig. 2b). The curve for the RP involving naturally abundant germanium (7.76% ^{73}Ge) was obtained by addition of the two previous curves and shown in Fig. 2c.

As seen from comparison of Figs. 1 and 2c,d, the trend of the calculated curve for natural germanium coincides with experiment. It must, however, be noted that the

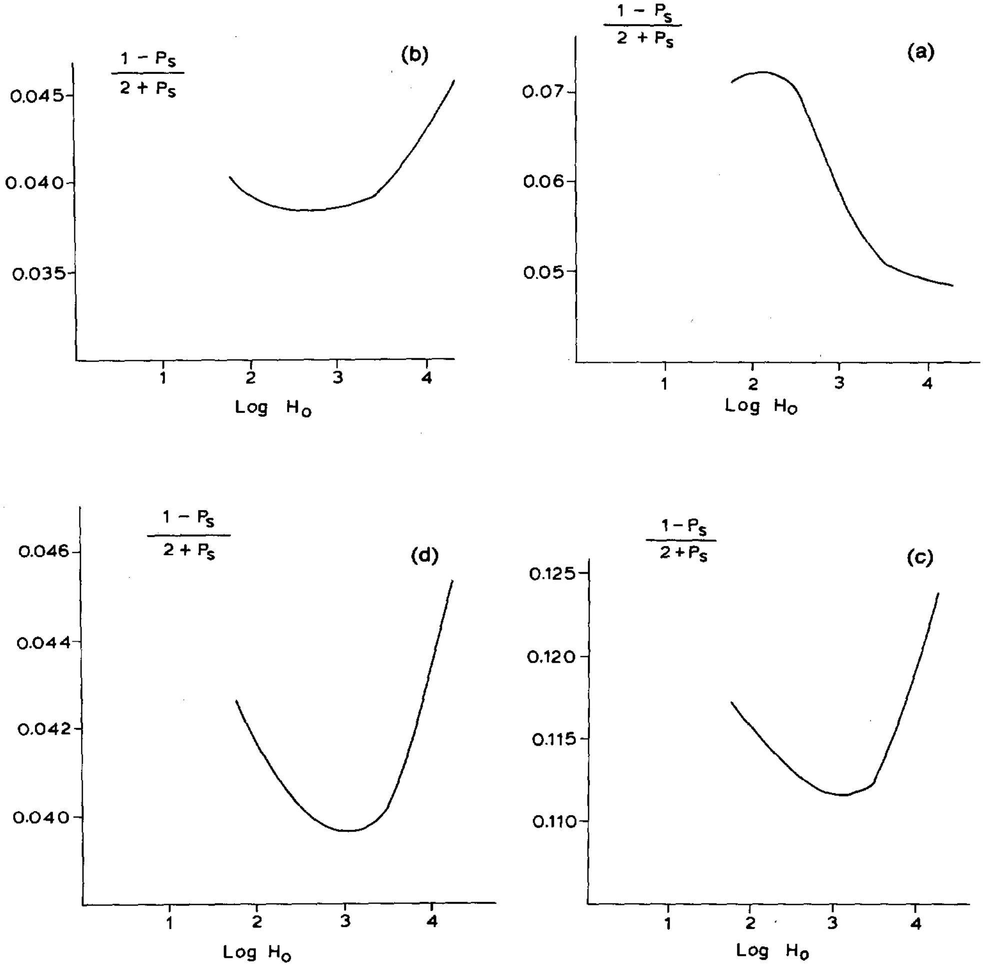

Fig. 2. Plots of $(1 - P_s)/(2 + P_s)$ vs. magnetic field strength for a singlet pair of triethylgermyl and benzyl free radicals: a) neglecting ^{73}Ge ($\lambda = 0.908$, $\tau_D = 10^{-9}$s); b) 100% ^{73}Ge ($\lambda = 0.908$, $\tau_D = 10^{-9}$ sec); c) 7.76% ^{73}Ge ($\lambda = 0.908$, $\tau_D = 10^{-9}$ sec); d) 7.76% ^{73}Ge ($\lambda = 0.699$, $\tau_D = 10^{-9}$ sec).

scale of experimental effects exceeds calculations substantially. The largest difference in values of the product ratio II/I at various MF strengths compared to the smallest value (percentage) was taken as a measure of the magnetic effect:

$$\frac{\mathrm{II/I(high\ field)} - \mathrm{II/I(low\ field)}}{\mathrm{II/I(low\ field)}} \times 100\% \qquad \text{(see Fig. 1)}$$

The calculations were carried out for RP with particles size 5 Å in a nonviscous liquid (benzene, $\eta = 0.602$ cp), where the diffusion coefficient (D), was 10^{-5} cm^2/sec. This was correlated to the RP lifetime $\tau_D = b^2/D = 10^{-9}$ sec (b = radius of the reactive zone: ca 10 Å).

Possibly, disregarding the associated state of the organogermanium compound in the computations is the reason for the discrepancy between the experimental and calculated curves. The existence of triethylgermyllithium associates in benzene (12–14 Å in size) is shown by X-ray diffraction spectra [9]. One may presume, similarly to the previously studied reaction of benzyl halides with n-butyllithium, that the triethylgermyl radical, like the n-butyl one, reacts as a complex with the organo germanium compound [3,10]. The associated state of the triethylgermyl radical may explain the large magnitude of the cage effects, which are not specific for three radical recombination in nonviscous liquids. In this case steric hindrance may appear in the recombination reaction of the associated triethylgermyl radical with the free benzyl radical, which may cause changes in λ. It must be noted that the hexameric trimethylsilyllithium described in the literature [12] has only two faces which are accessible during the reaction.
Indeed, use of $\lambda = 0.699$ instead of $\lambda = 0.908$ (compare Figs. 2c and 2d) allows the calculated $(1 - P_s)/(2 + P_s)$ value to approach the experimental ratio of products.

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