the cases of SRS is observed in both directions. The points at which SRS pulses that travel only backwards are produced lie closer to the end of the cell, where the foci of the multifocus structure move with appreciable velocity, whereas the points where SRS propagating in both directions occur correspond to the points where the foci are stopped. These results are in good agreement with the concepts developed above.

We note also that although the SRS pulses are produced at a distance on the order of several centimeters from the ends of the cell, in regions having a transverse dimension on the order of several microns their transverse dimension on emerging from the cell is ~10 μ at a duration $<10^{-10}$ sec (Fig. 2a). This shows that the power of the SRS pulses is more critical and they undergo critical refraction. Consequently, the propagation of the SRS pulses in the medium should be accompanied by formation of a (secondary) multifocus structure inside these pulses [10]. Indeed, the side-view photographs show on the paths of the SRS pulses themselves bright points that correspond apparently to the stopping points of the foci of this secondary multifocus structure [11 - 12].

Thus, the results presented here offer evidence in favor of the nonstationary mechanism of the ultrashort SRS pulses.

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INFLUENCE OF MAGNETIC FIELD ON RADICAL REACTIONS

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The purpose of the present paper is to show that an external magnetic field can exert a noticeable influence on the rates of chemical reactions in which free radicals take part. Such an influence may be due to the fact that the radical-recombination products are usually formed from a radical pair (RP) in the singlet rather than the triplet state. The hyperfine interactions inside the RP cause transitions between the singlet and triplet states, and the probability of such a conversion depends on the magnetic field intensity.

A well-known manifestation of these effects is the influence of the magnetic field on the chemical polarization of nuclei in radical reactions [1].

An influence of the magnetic field on the rates of certain photochemical processes in which triplet states participate was observed earlier by Merrifield

[2] and by Frankevich [3]. We, on the other hand, registered a case where the magnetic field effects reactions of spin-1/2 particles (free radicals), for which the mechanism proposed in [2, 3] and developed in [4], connected with the splitting of the spin states in a zero field, cannot take place.

For a quantitative estimate of the influence of the magnetic field on the probability of the singlet-triplet transition, we consider an RP with two magnetic nuclei with spin I = 1/2. The spin Hamiltonian of such a pair is

$$\hat{H} = \hbar w_e (\hat{S}_{1z} + \hat{S}_{2z}) + \hbar w_I (\hat{I}_{1z} + I_{2z}) + \hbar A S_1 I_1 + \hbar A S_2 I_2, \tag{1}$$

where w_e and w_I are the Zeeman frequencies of the electron and nucleus, respectively, and A is the constant of the isotropic hyperfine interaction (HFI). In strong magnetic fields, when $w_e \gg A$, we can use the secular approximation of the HFA $\hbar A(\hat{S}_{1z}\hat{I}_{1z} + \hat{S}_{2z}\hat{I}_{2z})$, and the HFI mixes the singlet state $|s>$ only with one of the triplet states, the $|T_0>$ state of the zeroth z-projection of the total spin of the pair electrons [1]. The probability P(t) that the RP remains in the initial singlet state at the instant of time t is in this case

$$P_h(t) = 1 - \frac{1}{2} \sin^2 \frac{At}{2}. \tag{2}$$

In weak fields, the nonsecular part of the HFI also becomes significant and the $|s>$ state becomes mixed not only with $|T_0>$, but also with the states $|T_+>$ and $|T_->$ [1]. The corresponding probability P(t) in weak fields is

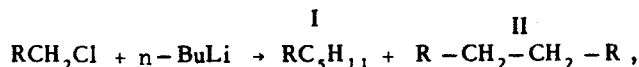$$P_\ell(t) = 1 - \frac{3}{4} \sin^2 \frac{At}{2} - \frac{3}{16} \sin^2 At. \tag{3}$$

Averaging (2) and (3) over the lifetimes of the radical pairs in accord with the diffusion theory of radical recombination [5, 6], we obtain for $A\tau < 1$

$$\bar{P}_h = 0.31 - 0.15\,\epsilon,$$
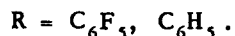$$\bar{P}_\ell = 0.31 - 0.30\,\epsilon, \tag{4}$$

where $\epsilon = \sqrt{A\tau}$.

As seen from (4), in weak fields the probability $\bar{P}$ is noticeably decreased (by ~7%) already at $A\tau \sim 0.01$. This can lead in turn to a change in the ratio of the intracell recombination products and the products of the reactions of the radicals in the volume when the reactions occur in different magnetic fields.

We have succeeded in experimentally observing an appreciable influence of a magnetic field on the ratio of the products in the reaction of substituted benzylchlorides with n–BuLi:

$$\overset{\text{I}}{} \qquad \overset{\text{II}}{}$$
$$RCH_2Cl + n-BuLi \rightarrow RC_5H_{11} + R-CH_2-CH_2-R,$$

where

$$R = C_6F_5, \ C_6H_5.$$

As shown in [7], the main reaction products (I and II) are produced from a pair of benzyl and butyl radicals in the singlet state. It is known, in addition, that the asymmetrical product I is produced predominantly in intracell recombination of the radicals, whereas the symmetrical product II is the result of recombination of the radicals in the solution.

Solutions (~1.0 m) of benzylchlorides with n-BueLi reacted for 15 minutes in a 15 mm cell in the earth's magnetic field and in fields of 15000 and 25000 Oe, at the temperature of boiling n-hexane. The reaction products were analyzed by the NMR of F^{19} and H^1. The NMR spectra were recorded with the spectrometers JNM-4H-100 ("JIOL") and Varian A-56/60A at working frequencies 100 and 60 MHz for H^1 and 94.6 and 56.4 for F^{19}, respectively.

Reaction	Magnetic field	Ratio of products in reaction (I and II)
Pentafluorobenzylchloride + n–BuLi	$H \sim 15000$ Oe H_{earth}	6.2 ± 0.3 4.5 ± 0.5
Benzylchloride + n–BuLi	$H \sim 25000$ Oe H_{earth}	5.6 ± 0.5 4.7 ± 0.3

The table lists the measured ratios of products I and II, obtained by comparing the integrated line intensities in the NMR spectra of H^1 and F^{19}. As seen from the table, on going from the earth's field to strong magnetic fields the ratio of the products I and II increases[1]). The largest effect (~30%) is observed for the reaction of pentafluorobenzylchloride with n-BuLi. Our theoretical model describes quite well the experimental results obtained in the investigated reactions. Thus, substituting in (4) the values of the HFI constants for the pentafluorobenzyl radical [8] ($|a_0^F| = 9.5$ Oe, $|a_M^F| = 4.9$ Oe, $|a_n^F| = 17.1$ Oe; $|a_\alpha^n| = 16.8$ Oe, $A = \Sigma|a_i| = 80$ Oe $= 1.4 \times 10^{-9}$ sec^{-1}) and a time $\tau \sim 2 \times 10^{-11}$ sec [9] we obtain $\overline{P}_\ell \sim 0.26$ and $\overline{P}_h \sim 0.29$ for the reaction of pentafluorobenzylchloride with n-BuLi. The lesser influence of the magnetic field on the benzylchloride reaction is apparently due to the smaller HFI constants in the benzyl radical than in the pentafluorobenzyl radical (for the benzyl radical we have $A = \Sigma|a_i| = 0.9 \times 10^9$ sec^{-1}).

Thus, the foregoing estimates and experimental results show that the singlet-triplet radical-pair conversion due to the hyderfine interaction with the magnetic nuclei decreases the ratio of the products of the intracell radical recombination reaction and of the radical recombination in solution on going from strong to weak magnetic fields. The effect of the magnetic field on the yield of the radical-recombination products increases with increasing HFI constant.

We note in conclusion that inasmuch as the free radicals contain as a rule magnetic nuclei, the magnetic-field effect observed by us should appear in principle in many chemical reactions.

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