



## STUDY OF A FRACTION OF SPIN-CORRELATED PAIRS IN RADIATION SPURS BY THE METHODS OF TIME-RESOLVED MAGNETIC FIELD EFFECTS AND QUANTUM BEATS

S. V. ANISHCHIK, O. M. USOV, O. A. ANISIMOV and YU. N. MOLIN

Institute of Chemical Kinetics and Combustion, 630090, Novosibirsk, Russia

(Received for publication 6 May 1997)

**Abstract**—The fractions  $\Theta^{\beta}$  and  $\Theta^{\gamma}$  of spin-correlated singlet radical-ion pairs in alkane solutions irradiated by  $\beta$ -particles and X-rays were got from experiments on magnetic field effect and quantum beats in recombination fluorescence. The ratio  $\Theta^{\beta}/\Theta^{\gamma}$  values of 1.3–2.8 for the solvent series studied were found both from magnetic effect and quantum beats. The Monte Carlo calculations were made to explain the variations of  $\Theta^{\beta}/\Theta^{\gamma}$  in different solvents. The high value of  $\Theta^{\beta}/\Theta^{\gamma} = 2.8$  for isooctane is probably due both to large separation between ions in pair and to high concentration of neutral radical in the spur.  
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### 1. INTRODUCTION

Experimental (Klein and Voltz, 1979; Baker *et al.*, 1987; Brocklehurst, 1993; LaVerne and Brocklehurst, 1996a, 1996b) and theoretical (Lozovoy *et al.*, 1990; Brocklehurst, 1992; Bartczak and Hummel, 1993) studies have been made of the dependence of magnetic field effect in recombination fluorescence on the ionization density in a track (or on the number of particles in multiparticle spurs). The experimental data have been summed up by LaVerne and Brocklehurst (1996b) giving the dependences of magnetic field effect on the value of linear energy transfer in hydrocarbons irradiated by various ionizing particles:  $\beta$ -particles, X-rays, protons and helium nuclei. In this series a considerable decrease in magnetic field effect has been related to decrease in the fraction of spin-correlated radical-ion pairs among the recombining pairs. This is caused by the increasing probability of cross-recombination in dense spurs which does not show any magnetic field effect because there is no spin correlation in this case. Thus the magnitude of magnetic field effect bears information on either the fraction of spin-correlated geminate pairs which recombine in a spur or a related fraction of singlet pairs (Baker *et al.*, 1987; Brocklehurst, 1993; LaVerne and Brocklehurst, 1996a, 1996b). A quantitative determination of the fraction of spin-correlated pairs using magnetic field effects involves, however, some difficulties. The magnitude of magnetic field effect depends on spin correlation loss in a pair upon recombination in zero and high magnetic fields. In high magnetic field the spin evolution of a singlet pair leads to the equal population of *S* and *T*<sub>0</sub> pair states at long delay times after ionization event (Brocklehurst, 1985). In zero field an adequate theoretical consideration of spin

correlation loss is possible only if all stages of spin evolution are known up to the recombination of a secondary pair which results from the capture of free electrons and solvent holes by acceptor molecules. It is difficult to calculate this evolution in zero magnetic field as there is no sufficient information on both the reaction rates of the radical ion partners and the their ESR parameters.

Recently, another approach to the determination of the fraction of spin-correlated pairs has been proposed (Usov *et al.*, 1997) based on the measurement of the amplitude of quantum beats in recombination fluorescence. Since quantum beats take place only if recombining radical-ion pairs are spin-correlated one can determine the fraction of spin-correlated pairs by measuring the amplitude of the beats. This method has been applied (Usov *et al.*, 1997) to a series of hydrocarbon solutions irradiated by  $\beta$ -particles emitted by a <sup>90</sup>Sr–<sup>90</sup>Y radioactive source.

The goal of this paper is to determine the fraction of spin-correlated radical-ion pairs using both the methods for alkane solutions irradiated by the sources that give different ionization densities: fast electrons and X-rays.

### 2. EXPERIMENTAL

Single photon counting was used to observe recombination fluorescence. In experiments on  $\beta$ -particle irradiation we used a <sup>90</sup>Sr–<sup>90</sup>Y isotope with activity of about 5  $\mu$ Ci and maximum energies of 0.54 and 2.25 MeV, respectively, in combination with a nanosecond fluorimeter to perform experiments in magnetic field. The fluorimeter described earlier (Anisimov *et al.*, 1983) was improved (Grigoryants

*et al.*, 1995) to increase the time resolution. X-ray experiments were performed on the setup described by Anishchik *et al.* (1989). The X-ray pulses of about 2 ns were emitted by a molybdenum target under the action of the 40 keV electron beam. The radiation spectrum of such a target has characteristic lines with energies of 17 and 20 keV as well as a wide band of bremsstrahlung with a maximum energy of 40 keV.

The solvents used (Aldrich) were purified by passing through a chromatographic column filled with 10% silver nitrate on alumina. The presence of unsaturated hydrocarbons was monitored by UV spectrophotometry. The absorption cut-off (optical density 1 at 1 cm layer) was at the wavelengths between 195 and 215 nm. *p*-Terphenyl-*d*<sub>14</sub> (Aldrich, 99%) was used as received. Diphenylsulfide-*d*<sub>10</sub> was prepared as described by Usov *et al.* (1997). Samples were degassed by repeated freeze-pump-thaw cycle and sealed in thin-walled quartz cuvettes. All experiments were carried out at room temperature.

### 3. RESULTS

Figure 1 shows the curves of time-resolved magnetic field effects in the recombination fluorescence of a  $10^{-3}$  M *p*-terphenyl-*d*<sub>14</sub> (PTP-*d*<sub>14</sub>) solution in isooctane under  $\beta$ - and X-ray irradiation. The magnetic field effect  $(I_H - I_0)/I_0$  was determined as a ratio of the difference between intensities of recombination fluorescence in high and zero magnetic fields to the intensity in the zero field. In both cases the magnetic field effect first increases then passes through the maximum and after a decrease increases again and flattens out. Note that in solvents other than isooctane a region of a steep rise is much less pronounced or even absent. At short delay times, the maximum is due to coherent evolution of the spin wavefunction as a result of the hyperfine interaction

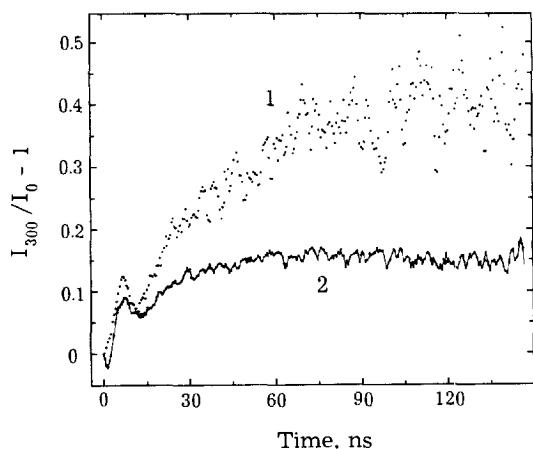


Fig. 1. Time dependence of magnetic effect of recombination fluorescence from  $10^{-3}$  M *p*-terphenyl-*d*<sub>14</sub> in isooctane under irradiation with  $\beta$ -particles (1) and X-rays (2). Magnetic field is 300 mT.

of electron and nuclear spins. According to the theory (Brocklehurst, 1985), in most systems, due to a large set of *hfi* constants, the populations of spin sublevels are rapidly equalized. This causes the first peak to be followed by a horizontal plateau. However if the process of recombination involves radical ion pairs of several types (e.g. a pair with a solvent hole and that with a solute radical cation) the latter can yield peaks at different times. Thus the first peak before flattening out may be followed by a new rise (see Fig. 1). A characteristic time of the increase in magnetic field effect is inversely proportional to

$$a_{\text{eff}} = (\sum_i a_i^2 + \sum_j a_j^2)^{1/2} \quad (1)$$

where  $a_i$  and  $a_j$  are the hyperfine coupling constants in radical cations and anions, respectively. The lower are the values of the *hfi* constants, the slower is the growth in magnetic field effect with time. The rate of the second rise in the curves of magnetic field effect depends on the hyperfine interactions in (PTP-*d*<sub>14</sub>)<sup>+</sup> / (PTP-*d*<sub>14</sub>)<sup>-</sup> pairs. A considerably steeper rise in the first region is likely to correspond to the hyperfine interactions in either solvent radical cations or the products of their monomolecular dissociation, e.g. in olefin radical cations. The value  $\chi$  for magnetic field effect in all systems studied was determined at the steady-state level, i.e. at times of 100–150 ns.

Table 1 summarizes the values of  $\chi^\beta$  and  $\chi^X$  for  $\beta$ - and X-ray irradiation, respectively, in  $10^{-3}$  M PTP-*d*<sub>14</sub> solutions for various solvents. The values obtained in experiments with  $\beta$ -irradiation are close to those obtained earlier in the same solvents (Appleton and Brocklehurst, 1987; Appleton *et al.*, 1986; Brocklehurst, 1976, 1977). Although in the recent works (LaVerne and Brocklehurst, 1996a, 1996b) the larger values of magnetic field effect were obtained in cyclohexane solutions this is probably due to the fact that PPO was used as an additive instead of *p*-terphenyl. Table 1 also gives the  $\Theta^\beta$  and  $\Theta^X$  fractions of spin-correlated pairs calculated from  $\chi^\beta$  and  $\chi^X$ , respectively, for the most typical  $\rho_0$ , where  $\rho_0$  is the equilibrium population of singlet states in zero magnetic field (see Discussion for details).

Figure 2 shows quantum beats in the recombination fluorescence of the solution containing 0.12 M diphenylsulfide-*d*<sub>10</sub> and  $10^{-3}$  M PTP-*d*<sub>14</sub> in *cis*-decalin under X-ray and  $\beta$ -irradiation. The curves of quantum beats were extracted from experimental data as described by Usov *et al.* (1997). Figure 3 shows the values for the amplitudes of quantum beats given in Fig. 2 for various half-periods of oscillating curves. The decrease of the amplitudes with time is linear within experimental error ( $\pm 0.05$ ). The linearity extends over a considerably greater range than would be expected for a pure exponential decay. This is because in our experiments  $T_2$  values are close to  $1/a$ , where  $T_2$  is the phase relaxation time in diphenylsulfide-*d*<sub>10</sub><sup>+</sup> cation and  $a^2$  is the second moment of the ESR spectrum line for the PTP-*d*<sub>14</sub>



magnetic fields, the populations of the singlet  $S$  and triplet  $T_0$  states level off and the  $T_+$  and  $T_-$  levels remain unpopulated due to large Zeeman splitting (Brocklehurst, 1985). Thus for spin-correlated pairs the population of the singlet state  $S$  that leads to fluorescence is  $1/2$  at long times in high magnetic field. The case of zero field is more complex. The stationary population in zero field depends on details of the mixing of singlet and triplet states (Appleton and Brocklehurst, 1987). If this mixing results only from hyperfine interactions in the same pair  $\rho_0$  is equal to  $1/3$  (Knapp and Schulten, 1979). When the pair recombination is accompanied by the processes of ion-molecular charge transfer the value of  $\rho_0$  gets smaller. In particular, for single charge transfer event when the  $S^+/A^-$  pair is substituted by the  $D^+/A^-$  pair due to the capture of a solvent  $S^+$  radical-cation by acceptor molecule  $D$  (the lifetime of both pairs exceeding  $\hbar/a$  where  $a$  is the  $hfi$  constant in the corresponding pair) the value of  $\rho_0$  is  $5/18$  (Appleton and Brocklehurst, 1987). The multiple charge transfer leads to a complete mixing of all four system sublevels. Hence in this case we have  $\rho_0 = 1/4$ . The same result is valid for fast spin relaxation of radical ions in zero field. Taking this into account and using the formula for magnetic field effect given by LaVerne and Brocklehurst (1996b) one derives the relation between the fraction of spin correlated pairs  $\Theta$  and the magnitude of the magnetic field effect

$$\Theta = \chi / \{1 - (4\rho_0 - 1)(\chi + 1)\} \quad (2)$$

This relation shows that  $\Theta$  becomes independent of  $\rho_0$  only for  $\rho_0 = 1/4$ . In this case we get  $\Theta = \chi$ . In other cases the dependence of  $\Theta$  *vs.*  $\chi$  is more complex; to calculate  $\Theta$  it is necessary to know not only  $\chi$  but also  $\rho_0$ . Unfortunately for most systems  $\rho_0$  is not known. Therefore to calculate  $\Theta$  (or the fraction of singlet pairs  $f_s$ ) using experimental data on  $\chi$  it is necessary to make a plausible assumption on the value of  $\rho_0$ .

Table 1 summarizes  $\Theta$  calculated using expression (2) for several most typical values of  $\rho_0$ . As follows from the Table, when  $\rho_0$  is varied between  $1/3$  and  $1/4$  the values of  $\Theta$  vary greatly.

It has been shown (Usov *et al.*, 1997) that the beat amplitude  $A(0)$  extrapolated to  $t = 0$  is related to the fraction of spin correlated pairs  $\Theta$  *via* the expression:

$$\Theta = A(0)/(4 - 3A(0)) \quad (3)$$

The values of  $\Theta$  calculated using this formula are given in Table 1.

Although the goal of this paper is not to analyze the most justified choice of  $\rho_0$ , it is noteworthy that the data obtained with  $\rho_0 = 5/18$  or  $\rho_0 = 1/4$  better correlate with the ones obtained by the quantum beats methods. Obviously, spin evolution in solvent radical-cations (holes) must be taken into account to interpret the results on magnetic field effects.

Let us discuss the changes in the  $\Theta$  upon transition from  $\beta$ - to X-ray irradiation. One can expect that  $\Theta^X$

is lower than  $\Theta^\beta$  because the probability of cross recombination is greater in X-ray track which is formed by secondary electrons. This probability is known to depend on linear energy transfer (LET). According to LaVerne and Brocklehurst (1996b) LET in hydrocarbons for  $^{90}\text{Sr}$ – $^{90}\text{Y}$   $\beta$ -particles and 15 keV X-rays is about 0.15 and 5 eV/nm correspondingly. About 20 eV is necessarily to create one ion pair in hydrocarbons (Van den Ende *et al.*, 1980). So, average separation between ion pairs for the above cases is about 130 and 4 nm, correspondingly. Therefore for X-rays the pair separation is comparable with electron thermalization distance  $r_0$  that gives a big probability of cross recombination. The experiments with saturated solutions of p-terphenyl in squalane irradiated by 15 keV X-rays (Brocklehurst, 1993) give for  $\Theta^\beta/\Theta^X$  the value about 2.6. Close value was got from computer calculations (Bartczak and Hummel, 1993).

Table 1 shows the  $\Theta^\beta/\Theta^X$  values for various hydrocarbons which were calculated using the data on both the beats and magnetic field effects (for various values of  $\rho_0$ ). Within the variations of  $\rho_0$  values (from  $1/3$  to  $1/4$ ) the differences between the  $\Theta^\beta/\Theta^X$  values are observed to be not greater than 10% for each solvent. Thus at least to within this accuracy (comparable with that of performed experiments) we may compare the data on  $\Theta^\beta/\Theta^X$  obtained in experiments on magnetic field effects and quantum beats.

Table 1 shows that except for *cis*-decalin the difference between the  $\Theta^\beta/\Theta^X$  values for two methods does not exceed 10%. Thus, there is quantitative agreement between the experimental data obtained using the time-resolved magnetic field effects and the quantum beats method.

Table 1 also demonstrates that a decrease in the fraction of spin-correlated pairs upon transition from  $\beta$ - to X-ray radiation in isooctane is more pronounced than in cyclohexane and decalin. A similar result has been obtained by LaVerne and Brocklehurst (1996b) who compared the magnitudes of magnetic field effects in cyclohexane and isooctane solutions irradiated by  $\beta$ -particles, protons and helium nuclei. LaVerne and Brocklehurst attributed this to a substantially larger electron thermalization distance  $r_0$  in isooctane. A large initial distance between electron and cation must lead to an increase in the probability of cross recombination in dense spurs. Electron thermalization distance  $r_0$  weakly affects on  $\Theta^\beta$  because average separation between pairs is significantly larger than  $r_0$  but in X-ray track and other dense tracks a big  $r_0$  must lead to an increase in the probability of cross recombination. This causes a stronger decrease in the fraction of spin-correlated pairs.

We have studied the dependence of the probability of geminate recombination  $P_g$  in multiparticle spurs on the parameter  $r_0$  of spatial distribution in pairs under ionization. To this end we have performed the

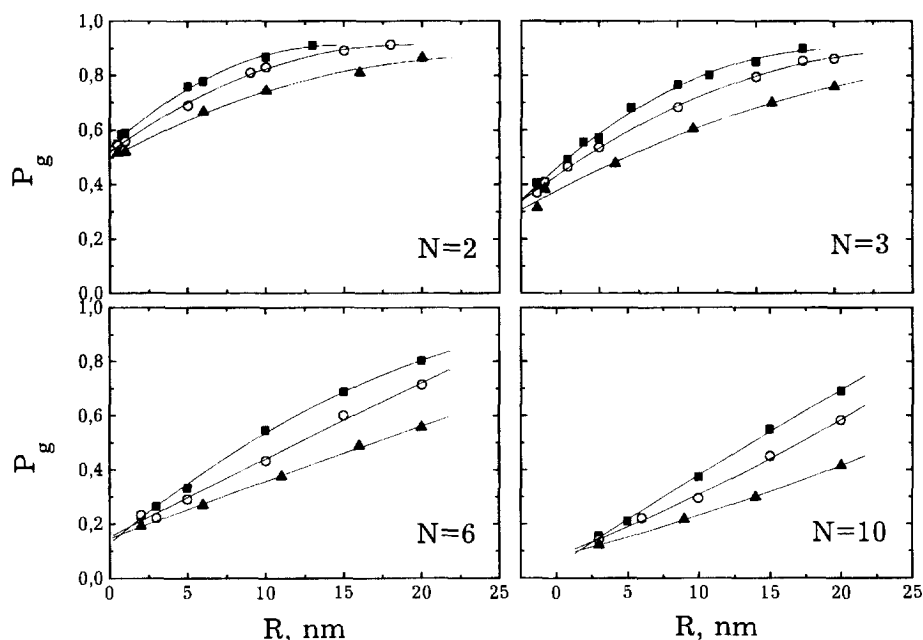


Fig. 4. The geminate recombination probability  $P_g$  in multi-particle clusters vs cluster radius  $R$  at different parameters  $r_0$  of spatial distribution in pairs at  $r_0 = 6$  nm (■),  $r_0 = 9$  nm (○),  $r_0 = 20$  nm (▲), for different numbers of pairs  $N$  in a cluster.

Monte-Carlo calculations (Lozovoy *et al.*, 1990). In the starting configurations the cations were placed with equal probability in a ball with radius  $R$ . For every cation, its geminate electron was placed at a random distance  $r$  from the cation with an exponential probability density

$$F(r) = r_0^{-1} \exp(-r/r_0). \quad (4)$$

For all solvents except isooctane  $r_0 = 6$ –7 nm, for isooctane  $r_0 = 9.5$  nm (Cserep *et al.*, 1981; Schmidt and Allen, 1970). Step by step calculations were performed to obtain time dependence of recombination rate of geminate and cross recombination. The ratio of the geminate recombination rate to the overall charge recombination rate proceeds rapidly to plateau (Lozovoy *et al.*, 1990; Bartczak and Hummel, 1992). The value  $P_g$  was determined as the ratio at steady-state level. The cluster size  $R$  and the number of pairs were varied.

The calculated results are given in Fig. 4. As follows from Fig. 4, an increase in  $r_0$  from 6 to 9 nm leads (as was expected) to a decrease in probability  $P_g$  in multi-particle spurs. This decrease, however, is insufficient to explain the experimental data (Table 1). The model of spherical clusters is expected to be the most sensitive to the influence of  $r_0$  on  $P_g$ . For realistic X-ray track structure one can expect even weaker dependence  $P_g$  on  $r_0$ . So, one can conclude that explanation of LaVerne and Brocklehurst (1996b) is valid only partly.

Another possible cause of the relatively high values of  $\Theta^\beta/\Theta^\alpha$  in isooctane compared to cyclic and linear hydrocarbons may be a high rate “instantaneous”

paramagnetic relaxation of radical ions in dense spurs. In a cluster this rate strongly depends on the density of paramagnetic particles due to their electron dipole-dipole interactions and quickly decreases with time because of reduction of the density. Thus, upon transition from  $\beta$ - to X-ray, the fraction of recombining spin-correlated pairs may decrease not only due to an increase in the probability of cross recombination but also due to an increase in the concentration of paramagnetic particles in dense spurs, in particular, that of neutral radicals. According to numerous observation (Cserep *et al.*, 1981), the radiation yields of neutral radicals in liquid alkanes of sundry structure are almost the same. However, the spatial distribution of radicals in a spur may be quite different for various alkanes. The main fraction of neutral radicals forms in the spur due to the decay of triplet excited solvent molecules that form mainly via ISC conversion of singlet excited molecules. The lifetimes prior to decay differ greatly. In branched aliphatic hydrocarbons such as isooctane the decomposition rate of singlet-excited molecules is very high (Rothman *et al.*, 1973; Hermann *et al.*, 1984). On the contrary the  $S_1$  states in cyclic and linear hydrocarbons are relatively long-lived and their lifetimes vary from one to several nanoseconds (Hermann *et al.*, 1984). During these times the diffusion and migration of excitations from the spur may cause a noticeable decrease in the local concentration of radicals in the vicinity of a recombining spin-correlated radical-ion pair. Thus a substantial increase in the  $\Theta^\beta/\Theta^\alpha$  ratio in isooctane is likely to be related to a higher local density of radicals

in multi-particle spurs compared to other alkanes. It was shown by Holroyd (1969), that isooctane molecule can form two neutral radicals directly via disintegrating of  $S_1$  state.

*Acknowledgements*—This work was supported by INTAS (grant 93-1626) and the Russian Foundation for Basic Research (grant 96-03-33694).

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