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Detection of radical cations of group 14 element organometallics in alkane solutions using the method of time-resolved magnetic field effect

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Radical cations of Group 14 element organometallics R_4E and R_3EER_3 ($E = Si,Ge,Sn$, $R = Me,Et$) were generated in alkane solutions by X-ray irradiation and studied using the time-resolved magnetic field effect technique. Modeling shows that in alkane solutions the *g*-factors of $Me_4E^{+\bullet}$ and $Me_3EEMe_3{}^{+\bullet}$ are close to those measured in low temperature matrices. At concentrations of organometallics of about 0.1 M the fast electron self-exchange between radical cations $Me_4E^{+\bullet}$ ($E = Si,Ge$) and the corresponding neutrals takes place. In the case of R_3EER_3 the electron self-exchange has not been observed. Short times of phase relaxation (~10 ns) are found for all the studied radical cations. Possible contributions to relaxation rates are discussed. For solutions of Me_4E a peculiarity manifested as a positive magnetic field effect in strong magnetic field is observed in spin dynamics at short times. This peculiarity is assigned to the radical cations of olefins arising upon radiolysis of an alkane solvent.

1. Introduction

Relatively low ionization potentials of organosilicon, organogermanium, and organotin compounds allow them to participate in electron transfer reactions with different oxidizing agents.[1] The key intermediates of such processes are the corresponding radical cations of organometallics. Their stability, reactivity and fragmentation pathways define the structure of the final products. Up to now radical cations of Me_4E and Me_3EEMe_3 ($E = Si,Ge,Sn$) were studied by ESR spectroscopy in low temperature matrices.[2,3] These radical cations are characterized by higher isotropic values of the *g*-factors and smaller hyperfine coupling (hfc) constants of an unpaired electron with protons in comparison with their carbon analogs. In many reactions of R_4E and R_3EER_3 in solutions, intermediate formation of the corresponding radical cations has been suggested[1] but these radical cations have never been observed directly because of their extremely short lifetimes. Thus the detection of radical cations of Group 14 element organometallics in solutions is of great importance for understanding their reactivity and reaction mechanisms.

Here we report on the study of radical cations of R_4E and R_3EER_3 in solutions at room temperature using the time-resolved magnetic field effect arising in recombination fluorescence of spin correlated radical ion pairs.[4,5] Previously this method has been used to determine the parameters of ESR spectra of alkane radical cations including those with lifetimes of as short as a few nanoseconds.[6]

Spin correlated radical ion pairs were generated by pulsed X-ray irradiation of alkane solutions of organometallics containing small amounts of *para*-terphenyl-d_{14} (PTP). The irradiation ionizes solvent molecules and primary pairs (radical cation of solvent/electron) are formed mainly in a singlet state. A solvent with ionization potential considerably higher than that of particular organometallic compound was chosen. Under these conditions the rate of the formation of radical cations of the organometallic compound is controlled solely by diffusion and both the capture of a solvent hole by the organometallic compound and an electron by PTP molecule preserves the spin correlation in the radical ion pair. Affecting the dynamics of the spin state of the radical pair the external magnetic field influences on the yield of singlet excited products of geminate recombination of the radical ions and thus on the fluorescence intensity. Analysis shows that the spin dynamics observed in solutions of organometallics occurs in the pairs $(R_4E)^{+\bullet}/(PTP)^{-\bullet}$ or $(R_6E_2)^{+\bullet}/(PTP)^{-\bullet}$ and it allows us to obtain parameters of ESR spectra of short-lived $(R_4E)^{+\bullet}$ and $(R_6E_2)^{+\bullet}$ species at room temperature.

2. Experimental

The fluorescence of alkane solutions of organometallics was detected by the single-photon counting method using a nanosecond X-ray fluorimeter.[7] The light was collected using an optical bandpass filter (260–390 nm) to select fluorescence of PTP. The duration of the ionizing pulse with an energy of 17 keV was 2 ns. The sample cuvette with a solution was situated between the poles of a magnet with a magnetic field induction up to 0.7 T. To decrease the influence of instrumental drift the fluorescence decays were registered for periods of 250 s, alternatively, with and without the magnetic field using computer control. Zero magnetic field was achieved to within ±0.05 mT.

Alkanes were stirred with concentrated sulfuric acid, washed with water, distilled over sodium and passed through a 1 m column of activated alumina. *n*-Hexane was additionally passed through a 1 m column of activated alumina coated by $AgNO_3$. With the gas chromatography we revealed that *n*-hexane available contained 2-methylpentane (0.2%) and 3-methylpentane (0.6%) as the main impurities. These alkane isomers

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could not be removed from *n*-hexane with the purification method used. The concentration of unsaturated hydrocarbon impurities was <10 ppm. The solutions were degassed by repeated freeze–pump–thaw cycles. All measurements were made at 293 ± 0.5 K.

Tetramethylsilane (**1**), hexaethyldisilane (**4**), and *para*-terphenyl-d_{14} were recieved from Aldrich and used without additional purification. Tetramethylgermane (**2**), tetramethylstannane (**3**), hexamethyldigermane (**5**) and hexamethyldistannane (**6**) were synthesized according to known procedures.[8–11]

The time-resolved magnetic field effect was calculated as the ratio $I_B(t)/I_0(t)$ where $I_B(t)$ and $I_0(t)$ were the kinetics of delayed luminescence detected in high and zero magnetic fields, respectively. This ratio is determined by the population of the singlet spin state of geminate radical ion pairs in high and in zero magnetic fields and it is rather independent of the rate of geminate recombination of charges.

3. Theoretical model

The evolution of the singlet state population $\rho_{ss}(t)$ of a singlet-borne radical pair in high and zero magnetic fields may be expressed as:

$$\rho^B_{ss}(t) = \tfrac{1}{4} + \tfrac{1}{4}\exp(-t/T_1) + \tfrac{1}{2}\cos\left(\frac{\Delta g\beta B}{\hbar}t\right) \times \exp(-t/T_2)G^B_c(t)G^B_a(t) \qquad (1)$$

$$\rho^0_{ss}(t) = \tfrac{1}{4} + \tfrac{3}{4}\exp(-t/T_0)G^0_c(t)G^0_a(t) \qquad (2)$$

where $1/T_1 = 1/T_{1a} + 1/T_{1c}$ is the sum of spin–lattice relaxation rates for radical ions composing the radical pair in high magnetic field, $1/T_2 = 1/T_{2a} + 1/T_{2c}$ is that for phase relaxation rates, and $1/T_0$ describes the sum of the phase relaxation rates at zero field. The subscripts a and c refer to the radical anion and the radical cation, respectively. Δg is the difference between the *g*-factors of the radical ions in a pair. $G(t)$ is a function defined by the hfc constants and the *g*-factor of the radical ion.[5,12] The superscripts *B* and 0 correspond to the measurements at high or zero magnetic fields, respectively. The functions $G^{B,0}(t)$ can be calculated analytically when an unpaired electron interacts with a number of equivalent magnetic nuclei or with a rich variety of nuclei having different hfc constants.[12,13]

In the theoretical model used for the description of the experimental curves it was assumed that an ensemble of radical ion pairs could be divided into uncorrelated pairs and spin-correlated singlet born ones whose fraction was denoted as θ. We also assumed that the parameters of ESR spectra of radical ions of a radical ion pair did not change during the time of observation (single pair model). In this case the time-resolved magnetic field effect (TR MFE) $I_B(t)/I_0(t)$ can be described by the equation:

$$\frac{I_B(t)}{I_0(t)} = \frac{\theta\rho^B_{ss}(t) + \frac{1}{4}(1-\theta)}{\theta\rho^0_{ss}(t) + \frac{1}{4}(1-\theta)}, \qquad (3)$$

where $\rho^B_{ss}(t)$ and $\rho^0_{ss}(t)$ are defined by eqns. (1) and (2).

Fig. 1 illustrates the typical features of the TR MFE curves when the hfc and the difference between the *g*-factors of the radicals may make comparable contributions to the spin evolution of the radical pair. The curves were calculated using eqns. (1)–(3) for the value $\Delta g = 0.02$ and the hfc constant $a_c = 0.6$ mT for 12 equivalent protons in the radical cation. In these calculations the half width of the ESR spectrum of the counterion ($\sigma_a = 0.068$ mT) corresponded to the half width of the spectrum of *p*-terphenyl-d_{14} radical anion (calculated using the known hfc constants of the *p*-terphenyl-h_{14} radical anion[14]), the fraction of spin correlated pairs was equal to 0.1, and the spin–lattice relaxation time T_1 was very long.

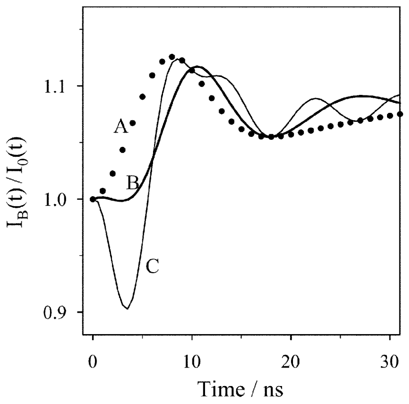

Fig. 1 Calculated time-resolved magnetic field effect curves $I_B(t)/I_0(t)$ in magnetic fields of 0.02, 0.2 and 0.4 T (curves A, B and C, respectively). Calculations were performed for the radical cation with the hfc constant $a_c = 0.6$ mT (12 H), half-width ESR spectrum of radical anion $\sigma_a = 0.07$ mT. Other parameters are $\theta = 0.1$, $\Delta g = 0.02$, $T_2 = T_0 = 20$ ns, $T_1 = 1500$ ns.

The fluorescence time of PTP (1.2 ns) and the width of the response function of the experimental set-up (3 ns) were taken into account upon modeling by convolution of eqns. (1) and (2) with exponential and rectangular time functions.[5]

In a magnetic field of 0.02 T the contribution of the difference in *g*-factors to the spin evolution is unimportant because the frequency of Δg-beats is low. Curve A on Fig. 1 has a maximum whose position is determined by the width of the ESR spectrum of the radical cation. Because of the difference in the *g*-factors of the radical ions the rate of singlet-triplet transitions increases considerably in fields of 0.2 T (curve B) and 0.4 T(curve C) in comparison with zero field. Therefore at the earlier times the ratio $I_B(t)/I_0(t)$ decreases and becomes considerably smaller than unity for a field of 0.4 T. Calculations show that the depth of the minimum increases and its position shifts to earlier times with increasing field intensity.

As will be shown below the experimental curves of TR MFE can be reproduced successfully using the published values of the *g*-factors and hfc constants of radical cations of R_4E and R_3EER_3 stabilized in low temperature matrices.[2,3] Other parameters (relaxation times and a fraction of spin correlated pairs) were fitted to obtain the best agreement between calculated and experimental curves. In a number of the experimental curves there is a peak at $t \sim 5$ ns whose presence cannot be explained in the framework of a model which includes a single radical ion pair. In these cases the simulation has been made for $t > 5$ ns.

4. Results and discussion

The radical cations of compounds **1–6** were generated by X-ray irradiation of 0.03–0.1 M solutions of **1–6** in *n*-hexane in the presence of 3×10^{-5} M PTP. At these concentrations primary radical cations of *n*-hexane were captured by organometallic compounds within ~1 ns since the capture rate constant was expected to be close to the diffusion-controlled one which in this solvent at room temperature was of about 2×10^{10} $M^{-1}s^{-1}$. The probability of the positive charge transfer to PTP was negligible because of the low concentration of this solute. Molecules of PTP served as acceptors of the excess electrons and as luminophore. To check that **1–6** did not capture the electrons the influence of external electric field on the kinetics of the recombination luminescence was studied.[15] The capture of the electrons by the organometallic compounds, except for compound **4**, has not been detected.

In the studies of organogermanium and organotin compounds, having relatively low ionization potentials,

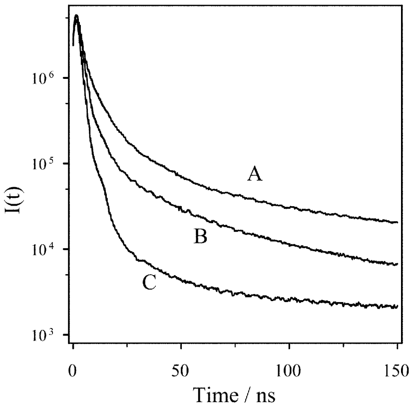

Fig. 2 The delayed luminescence decay curves for 0.1 M solutions of Me_4Si (curve A), Me_4Ge (curve B), Me_4Sn (curve C) in *n*-hexane in the presence of 3×10^{-5} M *p*-terphenyl-d_{14} in the zero field. The curves are normalized to their maximum.

n-dodecane was also used as a solvent. The TR MFE curves obtained for *n*-hexane and for *n*-dodecane were similar, but in the latter solvent they were more pronounced because of higher fraction of spin-correlated pairs.

4.1 Kinetics of luminescence decay

Fig. 2 shows the luminescence decay curves for 0.1 M solutions of **1**, **2** and **3** in *n*-hexane normalized to the maximum of their intensity. Since the fluorescence time of PTP is very short (~1 ns), the delayed fluorescence decay is proportional to the recombination rate of radical ion pairs. The decay for solution of **1** is shown with curve A whose shape is typical for the case when the fluorescence is caused by geminate recombination of radical ions that do not fragment during the time of observation. One can assume that the reason of a faster luminescence decay in the cases of **2** and **3** (curves B and C, respectively) is a fragmentation of their radical cations with a formation of species, none of which is a radical ion. Radical cations $(R_4E)^{+\bullet}$ (E = Si,Ge,Sn) are known to fragment readily according to the scheme:[1,2]

$$(R_4E)^{+\bullet} \rightarrow R_3E^{+} + R^{\bullet}$$

One may expect that upon the recombination of the cation Me_3E^+ with the radical anion of PTP an excited state of the luminophor will be formed with a lower probability as compared to $Me_4E^{+\bullet}$. It is also possible that the excited molecule formed in such a case is effectively quenched by the closely situated neutral radical.

For the solution of **3** the luminescence decay is so fast that a spurious response from the photomultiplier becomes noticeable at $t = 14$ ns (curve C). Note that the luminescence decays for compounds **5** and **6** are even faster than for **2** and **3**, respectively.

4.2 Time-resolved magnetic field effects (TR MFE)

We already mentioned that for all compounds studied except for **4** at low concentration of *p*-terphenyl-d_{14} the detected fluorescence appeared as a result of recombination of the geminate radical ion pairs $(Me_4E)^{+\bullet}/(PTP)^{-\bullet}$ or $(Me_6E_2)^{+\bullet}/(PTP)^{-\bullet}$. Hence the influence of external magnetic field was determined by spin dynamics in these pairs.

To determine the parameters of the ESR spectra of the radical cations the experimental TR MFE curves were simulated using the model described in Section 3. In the radical cations we took into account the hfc with protons only. Because of the small hfc constants in the radical anion of PTP its contribution to the spin dynamics was small and this contribution was taken into consideration in the framework of a quasi-classical approach[13] with $\sigma_a = 0.068$ mT and $g = 2.0028$.[14] The experimental curves for various magnetic fields are presented for compounds **1** and **5** only. For other compounds we show the curves for which the effect of the difference between the *g*-factors of the radical ions is best pronounced.

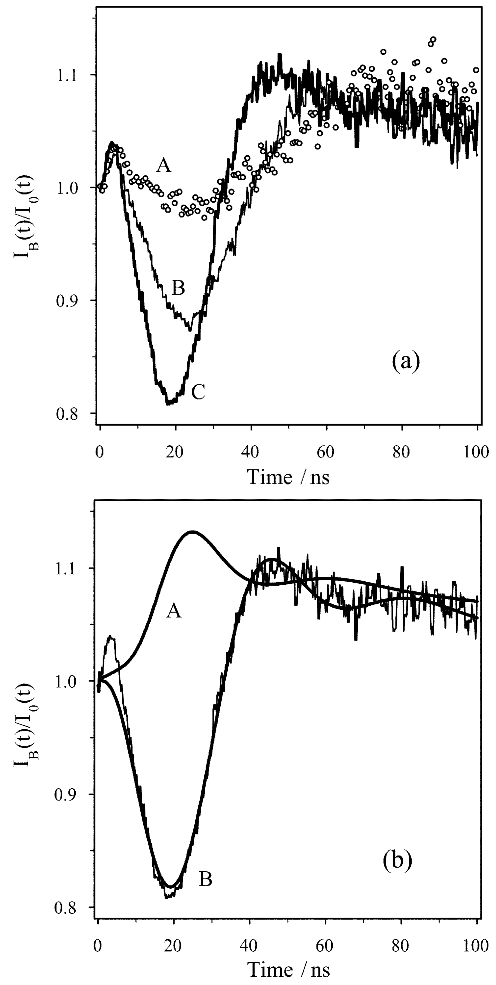

Fig. 3 (a) Time-resolved magnetic field effect curves for 0.1 M solutions of Me_4Si in the presence of 3×10^{-5} M *p*-terphenyl-d_{14} in *n*-hexane in the magnetic fields of 0.3 T (curve A), 0.5 T (curve B), 0.7 T (curve C) (b) experimental (noisy curve) and calculated (A,B) curves of time-resolved magnetic field effect for 0.1 M solutions of Me_4Si in the presence of 3×10^{-5} M *p*-terphenyl-d_{14} in *n*-hexane in the magnetic field of 0.7 T. Curve A: $a_c = 0.245$ mT. Curve B: $a_c = 0$. For both curves $g_c = 2.0050$. Other simulation parameters corresponding to each a_c values are given in Table 1.

Tetramethylsilane (1). Fig. 3a shows the TR MFE curves for 0.1 M solution of **1** in *n*-hexane in magnetic fields of 0.3, 0.5, and 0.7 T (curves A, B and C, respectively). The decrease of magnetic field effect to a value less than unity and the strong dependence of the curve shape on the intensity of magnetic field reveal directly the difference in the *g*-factors of radical ions in the geminate pair. This conclusion is in accordance with the published value 2.0050 ± 10^{-4} for the isotropic *g*-factor of radical cation $(Me_4Si)^{+\bullet}$ at temperatures below 180 K,[3] which differs considerably from the value of the *g*-factor of PTP radical anion. According to[3] the unpaired electron of $(Me_4Si)^{+\bullet}$ at $T < 115$ K couples with two groups of six equivalent protons with the hfc constants of 0.465 and 0.93 mT being opposite in sign. At $T > 170$ K the hyperfine structure of the ESR spectrum corresponds to the coupling with 12 equivalent protons with hfc constants of 0.245 mT. Such behavior is

Table 1 Parameters used in the simulation of time-resolved magnetic field effect

Radical cation	Solvent	*g*-factor	Hyperfine coupling constants with protons/mT	Magnetic field/T	T_2 (T_0)^b/ns	T_1/ns	θ
$\mathbf{1}^{+\bullet}$ ($(CH_3)_4Si^{+\bullet}$)	*n*-hexane	2.0050[a]	0.245 (12 H)[a]	0.7	22.6	144	0.22
			0	0.7	22.6	144	0.22
$\mathbf{2}^{+\bullet}$ ($(CH_3)_4Ge^{+\bullet}$)	*n*-dodecane	2.0165[a]	0.4 (12 H)[c]	0.3	16	1500	0.15
			0	0.3	8	1500	0.16
$\mathbf{3}^{+\bullet}$ ($(CH_3)_4Sn^{+\bullet}$)	*n*-dodecane	2.0194[a]	0.66 (12 H)[c]	0.3	7	1500	0.03
			0	0.3	4	1500	0.03
$\mathbf{5}^{+\bullet}$ ($(CH_3)_6Ge_2^{+\bullet}$)	*n*-hexane	2.0302[a]	0.52 (18 H)[a]	0.03	10	10	0.15
			0.52 (18 H)[a]	0.3	10(5)	10	0.22
$\mathbf{6}^{+\bullet}$ ($(CH_3)_6Sn_2^{+\bullet}$)	*n*-hexane	2.074[c]	0.34 (18 H)[a]	0.1	5	5	0.03

[a] published value for ESR spectrum in low temperature matrices.[2,3] [b] in the parenthesis is T_0 value, where it is not equal to T_2. [c] estimation obtained from published values[2,3] (see text for explanations).

explained by a fast spectral exchange between the two sets of protons at elevated temperatures.

Fig. 3b shows simulations of the experimental TR MFE curve obtained for 0.7 T magnetic field using eqns. (1–3) under the assumption that the *g*-factor of $(Me_4Si)^{+\bullet}$ is equal to 2.0050. Curve A was obtained for the case when the hfc constant with 12 equivalent protons was equal to the published value of 0.245 mT. Curve B was obtained under the assumption that the hfc constants in $(Me_4Si)^{+\bullet}$ equaled zero. Other parameters of simulation are shown in Table 1. Curve B fits the experiment well with the exception of a small maximum at early times. An inconsistency of calculated curve A and the experimental one results from the nonzero value of the hfc constants for $(Me_4Si)^{+\bullet}$ and it can not be eliminated by any variations of other simulation parameters. The lack of the hfc of unpaired electron in $(Me_4Si)^{+\bullet}$ for 0.1 M solution of **1** may be ascribed to the fast electron self-exchange between the radical cation and molecules of **1**. If we assume the rate constant of such exchange to be close to the diffusion-controlled one ($k \sim 10^{10}$ $M^{-1}s^{-1}$) then the condition of fast exchange ($k\cdot[\mathbf{1}]) \gg \gamma\sigma_c \approx 7.5 \times 10^7$ s^{-1} is really met at $[\mathbf{1}] =$ 0.1 M. Although the above experiments do not provide the information about the hfc in radical cation $(Me_4Si)^{+\bullet}$, the successful simulation of the magnetic field effect, using the published value of the *g*-factor, leaves no doubt that the observed spin dynamics occurs in the pairs $(Me_4Si)^{+\bullet}/(PTP)^{-\bullet}$.

The pronounced experimental TR MFE curve obtained for solution of **1** gives the possibility for a more accurate determination of the relaxation parameters T_0 and T_2 as compared to other organometallics compounds. However, independent variation of these phase relaxation parameters also leads to their approximate equality.

Preliminary experiments showed that the peculiarity manifested as a positive effect at $t \sim 5$ ns depends only weakly on the concentration of **1** and temperature. Such a peculiarity could appear due to a lower rate of the phase relaxation in a high magnetic field as compared to that in zero field but, in the framework of the single-pair model, the observed local maximum of magnetic field effect cannot be quantitatively described. It is possible that at $t < 10$ ns the recombination of another radical ion pair contributes to the observed fluorescence. Olefin radical cations are known to appear upon alkane radiolysis[16] and the characteristic values of the hfc constants in these radical cations are of about 1–3 mT, which should result in a drastic increase in magnetic field effect at 5–10 ns when the influence of magnetic field on spin dynamics in pairs $(Me_4Si)^{+\bullet}/(PTP)^{-\bullet}$ is not yet large. The ionization potentials of olefins are lower than that of **1**, therefore a positive charge cannot be transferred from olefin radical cation to **1**.[17] The presence of olefin radical cations should result not only in the peak at early times, but in some decrease in the amplitude of quantum beats at longer times. However, the latter effect is not significant because its contribution evaluated from the peak amplitude is of about 10–20%.

Tetramethylgermane (2). Fig. 4 shows the experimental and calculated TR MFE curves for 0.1 M solution of **2** in *n*-dodecane in magnetic field of 0.3 T. In the simulations we used the published value 2.0165 as the isotropic value of the *g*-factor of $(Me_4Ge)^{+\bullet}$.[2] Curve A was calculated for the case when an unpaired electron interacts with 12 equivalent protons with the hfc constants being equal to 0.4 mT. This value was obtained using the assumption that the reported hfc constants for $(Me_4Ge)^{+\bullet}$ (1.2 and 0.4 mT[2]) for two groups of equivalent protons was opposite in their signs as in the case of $(Me_4Si)^{+\bullet}$. Curve B was obtained using the hfc constants equal to zero. Other modeling parameters are given in Table 1. The value of spin–lattice relaxation time was assumed to be much longer than the time of observation and it was not varied. Because of a rather poor agreement between the experimental and calculated TR MFE curves we failed to determine separately the phase relaxation times in different fields and for the performed simulations it was assumed that $T_0 = T_2$.

As in the case of $(Me_4Si)^{+\bullet}$, the inconsistency between curve A and experimental one is a result of the contribution of the hfc in $(Me_4Ge)^{+\bullet}$ to the spin dynamics whereas zero hfc in the radical cation leads to a better agreement with the experiment. If the signs of the hfc constants in the radical cation of **2** observed in low temperature matrices were the

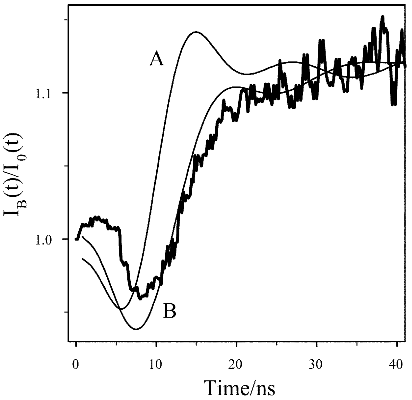

Fig. 4 Experimental (noisy curve) and calculated (A, B) curves of time-resolved magnetic field effect for 0.1 M solutions of Me_4Ge in the presence of 3×10^{-5} M *p*-terphenyl-d_{14} in *n*-dodecane in the magnetic field of 0.3 T. Curve A: $a_c = 0.4$ mT. Curve B: $a_c = 0$. For both curves $g_c = 2.0165$. Other simulation parameters corresponding to each a_c values are given in Table 1.

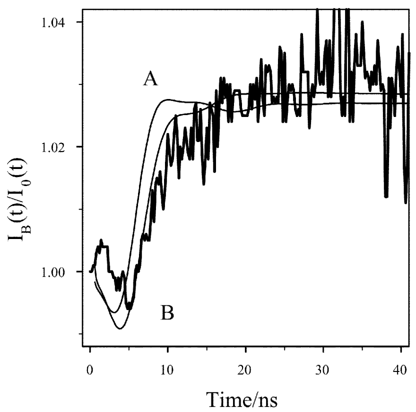

Fig. 5 Experimental (noisy curve) and calculated (A, B) curves of time-resolved magnetic field effect for 0.1 M solutions of Me_4Sn in the presence of 3×10^{-5} M *p*-terphenyl-d_{14} in *n*-dodecane in the magnetic field of 0.3 T. Curve A: $a_c = 0.66$ mT. Curve B: $a_c = 0$. For both curves $g_c = 2.029$. Other simulation parameters corresponding to each a_c values are given in Table 1.

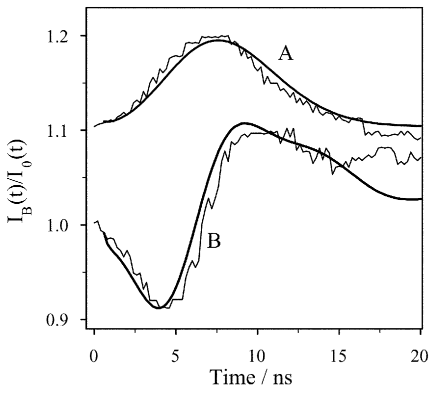

Fig. 6 Experimental (noisy) and calculated (smooth) curves of time-resolved magnetic field effect for 0.06 M solutions of Me_6Ge_2 in the presence of 3×10^{-5} M *p*-terphenyl-d_{14} in n-hexane in the magnetic fields of 0.03 T (curves A) and 0.3 T (curves B). Simulation parameters are given in Table 1. Curves A are shifted vertically by 0.1.

same, then the inconsistency mentioned above just increased because of the increase in ESR spectrum width and corresponding shift of the maximum towards earlier times. The inconsistency also increases if one uses a higher value of the *g*-factor (2.0196) also reported in ref. 2.

The main reason of the lack of clearly pronounced quantum Δg-beats for the solutions of **2** is likely to be the short phase relaxation of electron spin of $(Me_4Ge)^{+\bullet}$. The values of simulation parameters $T_0 = T_2$ are ~10 ns (Table 1). The increase in field intensity to shorten the period of beats to value less than 5–10 ns does not help because of smoothing of the beats pattern caused by the apparatus response function and finite fluorescence lifetime of luminophor. Possible reasons of short phase relaxation time will be discussed in the last subsection.

As in the case of **1**, the TR MFE curve for **2** in both *n*-dodecane and *n*-hexane has a peculiarity at $t \leq 5$ ns, which cannot be described by the single pair model. As in the previous case, fast formation of radical cations of olefins upon radiolysis of alkane solvent may be a possible reason. However, because of the considerable difference between the *g*-factors of the radical cation and PTP radical anion one can conclude that main contribution to the spin dynamics observed in solutions of **2** at t > 5 ns comes from $(Me_4Ge)^{+\bullet}$. Similar to $(Me_4Si)^{+\bullet}$, the ESR spectrum of $(Me_4Ge)^{+\bullet}$ seems to be narrowed due to fast electron self-exchange involving the radical cation.

Tetramethylstannane (3). The experimental and the calculated TR MFE curves for solution of 0.1 M **3** in *n*-dodecane in a magnetic field of 0.3 T are shown in Fig. 5. In the simulations we used the published value of *g*-factor 2.0194 for $(Me_4Sn)^{+\bullet}$.[2] As in the previous cases, the calculations were made under two different assumptions about the values of the hfc for $(Me_4Sn)^{+\bullet}$. The hfc constant 1.32 mT for only 6 equivalent protons was reported,[2] the other constants are evidently small. For curve A the hfc constants with 12 protons were chosen as large as 0.66 mT. Curve B was obtained using hfc constants equal to zero. Other modeling parameters are given in Table 1. Due to relatively small contribution of the hfc the calculated curves A and B do not differ markedly. Therefore, unlike the previous cases, the simulations do not allow one to conclude unambiguously whether a fast electron exchange occurs for the radical cations of **3**.

As in the two previous cases, the TR MFE curve for **3** in both *n*-dodecane and *n*-hexane also exhibits a peculiarity at $t \leq 5$ ns, which cannot be described by the single pair model. Nevertheless, the evident dip in TR MFE curve at 5 ns indicates that the radical cation $(Me_4Sn)^{+\bullet}$, with a considerable shift in the *g*-factor, contributes to the spin dynamics of radical pair at early times.

Hexaethyldisilane (4). Experiments with compound **4** have not demonstrated a shift between the *g*-factors of recombining radical ions. As has already been mentioned (Section 4), using the time-resolved *electric* field effect method,[15] we have found that in solutions of **4** excess electrons were captured not only by PTP molecules, but by hexaethyldisilane ones as well. In this case the pairs $(Et_6Si_2)^{-\bullet}/(Et_6Si_2)^{+\bullet}$ are formed at first because concentration of **4** is much higher than that of PTP. Later both the radical cation and the radical anion of **4** may transfer their charges to PTP molecules. Under these conditions spin dynamics seems to be rather complicated and we failed to determine the parameters of ESR spectrum of $(Et_6Si_2)^{+\bullet}$.

Hexamethyldigermane (5). The experimental and the calculated TR MFE curves obtained for 0.06 M solution of **5** in *n*-hexane in magnetic fields of 0.03 T (curves A) and of 0.3 T (curves B) are shown in Fig. 6. In the simulations the published values 2.0302 for the *g*-factor and 0.52 mT for the hfc constant with 18 equivalent protons[2] were used for $(Me_6Ge_2)^{+\bullet}$ and no spectral exchange was assumed for the radical cation $(Me_6Ge_2)^{+\bullet}$. Fig. 6 demonstrates that the calculated magnetic field effect curves shown as smooth lines are in a good agreement with the experimental ones. The agreement allows to conclude one that spin dynamics observed is determined by the radical cation $(Me_6Ge_2)^{+\bullet}$.

There is no agreement with the experiment under the assumption that the hfc constants in the radical cation are negligibly small. It means that unlike Me_4E compounds there is no fast electron self-exchange involving the radical cation in 0.06 M solution of **5**. The absence of the peculiarity in the magnetic field effect at early times is the other difference. It does not contradict to the suggestion mentioned above concerning the instantaneous formation of alkene radical cations under alkane solution irradiation since the ionization potential of **5** is considerably lower than those of alkenes.[17,18] At an organometallic concentration of 0.06 M the positive charge transfer from the olefin radical cations should occur within 3 ns.

Hexamethyldistannane (6). A characteristic feature of solutions of **6** (like solutions of **3**) was a low fraction of fluorescence sensitive to magnetic field. The magnetic field effect in solution of **6** was observed for $t \leq 8$ ns (Fig. 7). The isotropic component of the *g*-tensor for $(Me_6Sn_2)^{+\bullet}$ has not been published while the perpendicular component of that was reported

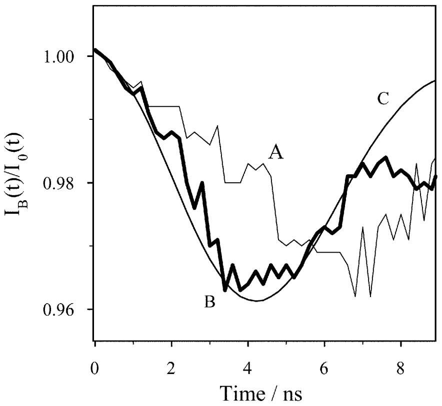

Fig. 7 Experimental curves of time-resolved magnetic field effect for 0.06 M solution of Me_6Sn_2 in the presence of 3×10^{-5} M *p*-terphenyl-d_{14} in *n*-hexane in the magnetic fields of 0.1 T (curve A) and 0.2 T (curve B). Curve C is calculated with the parameters: $a_c = 0.34$ mT, $g_c = 2.074$. Other simulation parameters are given in Table 1.

to be 2.11.[2] One can assume that the parallel component of the *g*-tensor is close to the *g*-factor of a free electron, as in the case of $(Me_6Ge_2)^{+\bullet}$ and thus the isotropic component can be estimated as 2.074. For low temperature matrices the value of 0.34 mT for the hfc constants was reported for $(Me_6Sn_2)^{+\bullet}$.[2]

Fig. 7 shows the experimental TR MFE curves for 0.06 M solution of **6** in *n*-hexane in magnetic fields of 0.1 T (curve A) and 0.2 T (curve B) along with the calculated one for a magnetic field of 0.1 T. The accordance between the experimental curve A and the calculated one could be some better with the use of a lower *g*-factor value. However, the small fraction of magnetic sensitive fluorescence and very fast fluorescence decay result in a high uncertainty of determination of simulation parameters in this case. Nevertheless, the evident dip in TR MFE curve at time about 4 ns indicates that the radical cation $(Me_6Sn_2)^{+\bullet}$ with a considerable shift in the *g*-factor contributes to the spin dynamics of radical pair at early time.

4.3 Spin relaxation

According to the data presented in Table 1, the best agreement between the simulated and the experimental curves takes place under the assumption that the times of phase relaxation T_0 and T_2 are approximately equal and rather short, of about 10 ns. For the radical cations that we have studied several mechanisms seem to be able to contribute to the phase relaxation.

For radical cations $(Me_4E)^{+\bullet}$ it is necessary to take into account the modulation of the hfc with protons as a result of fast electron self-exchange:

$$Me_4E + Me_4E^{+\bullet} \rightarrow Me_4E^{+\bullet} + Me_4E$$

For the fast exchange limit $\gamma^2{\sigma_c}^2{\tau_c}^2 \ll 1$ the corresponding contribution to the phase relaxation rate is approximately equal to $\gamma^2{\sigma_c}^2\tau_c$, where ${\tau_c}^{-1}$ is the frequency of electron transfer, γ is the magnetogyric ratio. If the rate of electron exchange is defined by the frequency of diffusional collisions, then ${\tau_c}^{-1} = (k[\mathbf{1}])/2$. For a 0.1 M solution of **1** in *n*-hexane ($k \sim 2 \times 10^{10}$ s^{-1}) such estimation gives $T_2 \sim 180$ ns. For 0.06 M solutions of **2** and **3** in *n*-dodecane ($k \sim 4 \times 10^9$ s^{-1}) the intermediate exchange rate, $\gamma^2{\sigma_c}^2{\tau_c}^2 \sim 1$, takes place and the use of fast exchange expression gives the understated estimates for the phase relaxation times of about 10 ns. Thus the modulation of hfc with protons allows us to explain the observed relaxation rate in *n*-dodecane solutions of **2** and **3**, but it does not seem to be effective enough for the solutions of **1** in *n*-hexane.

One more contribution to the phase relaxation may be related with participation in the electron self-exchange of the molecules containing not only protons, but also other magnetic nuclei. The natural abundance of magnetic isotopes ^{29}Si (4.7%), ^{73}Ge (7.8%), and $^{117}Sn + {}^{119}Sn$ (16%) is high enough and the hfc constants with these nuclei are about 10 mT, *i.e.* they are considerably higher as compared to the hfc constants with protons. When unpaired electron in a radical cation couples with these magnetic nuclei the rate of singlet–triplet transitions increases dramatically and the fast exchange limit $\gamma^2{\sigma_c}^2{\tau_c}^2 \ll 1$ is no longer met due to a larger value of the hfc constant for the magnetic isotope. The slow spectral exchange limit is expected to be more appropriate for such case. Under these conditions the electron self-exchange results in the phase relaxation with $T_2 \sim 1/(PkC)$ where P is the probability of meeting a molecule containing at least one magnetic nucleus with a large hfc constant. Estimations show that the magnetic isotope ^{29}Si can decrease time T_2 for 0.1 M solution of **1** in *n*-hexane to a value of about 20 ns which is close to that obtained in simulation. Contributions of the magnetic isotopes of Ge and Sn to the time of phase relaxation of radical cations $Me_4Ge^{+\bullet}$ and $Me_4Sn^{+\bullet}$ in *n*-dodecane are of about 60 and 30 ns, respectively. It should be noted that involving such mechanisms of "slow magnetic isotope exchange" for phase relaxation for a 0.1 M solution of **1** in *n*-hexane explains the above-mentioned approximate equality of phase relaxation rates in strong and zero magnetic fields. Also note that the amount of ^{13}C nuclei in Me_4E compounds is comparable to other magnetic isotopes of Group 14 elements but the hfc constants with ^{13}C are considerably lower (about 1 mT)[2,3] and the estimated contribution of ^{13}C to the phase relaxation is of no importance.

Thus the degenerate electron exchange allows us to explain the fast phase relaxation of radical cations $(Me_4E)^{+\bullet}$ if the contributions from both protons and magnetic isotopes of Group 14 elements are taken into account. A weak dependence of magnetic field effects on the concentration of Me_4E (E = Si,Ge,Sn) and the viscosity of the solutions may be explained by opposite dependencies of these two mechanisms on the rate of electron exchange. One should note that under our experimental conditions the electron exchange does not contribute essentially to the rate of spin–lattice relaxation, because the Larmor frequencies considerably exceed the exchange frequencies and the hfc constants are not big in comparison with the external magnetic field. Simulations support this conclusion: the best accord with experiment is for $Me_4E^{+\bullet}$ when $T_1 \gg T_2$.

In the case of radical cations $(Me_4Ge)^{+\bullet}$ and $(Me_4Sn)^{+\bullet}$ whose *g*-factors differ considerably from the value 2.0023, spin–rotational interaction and modulation of *g*-tensor anisotropy by rotation should be considered as possible contributors to the relaxation as well. According to ref. 19, the rate of phase relaxation caused by spin–rotational interaction in low magnetic fields is described by:

$$1/T_2 = (kT/12\pi r^3\eta) \times [(g_{zz} - 2.0023)^2 + 2((g_{xx} + g_{yy})/2 - 2.0023)^2], \qquad (6)$$

where r is the radius of the radical, η is the solution viscosity, kT is the Boltzmann factor, g_{xx}, g_{yy}, g_{zz} are the main components of the *g*-tensor. Using the approach of work[20] one can estimate that the volume of radical cation $(Me_4Sn)^{+\bullet}$ is equal to 1.4×10^{-22} cm^3. With the use of the published *g*-value we obtain $T_2 \approx 120$ ns for the solutions of **3** in *n*-dodecane at room temperature. For the radical cation $(Me_4Ge)^{+\bullet}$ the estimation gives $T_2 \approx 450$ ns. Thus one can believe that the contribution of spin–rotational interaction to the observed relaxation is negligible. The estimations show that in a magnetic field of 0.3 T the contribution of modulation of the *g*-tensor anisotropy by rotation can be ignored as well.

In the case of radical cations $(Me_6\ Ge_2)^{+\bullet}$ and $(Me_6\ Sn_2)^{+\bullet}$ when the electron exchange is not observed and the anisotropy of the *g*-tensor is high, the contribution of the spin–rotational mechanism to spin relaxation may prevail. The correlation time of spin-rotational interaction under our conditions is short and phase and spin–lattice relaxation times are expected to be equal, *i.e.* $T_2 \approx T_1$, which is in agreement with the results of simulations. The estimation of relaxation times using eqn. (6) for radical cations $(Me_6Ge_2)^{+\bullet}$ and $(Me_6Sn_2)^{+\bullet}$ in *n*-hexane ($\eta = 0.3$ cP) gives the values $T_2 \approx T_1$ of about 40 ns and 6 ns, respectively, with the use of the published data on *g*-values. Modulation of the *g*-factor anisotropy by rotation contributes to the phase and the spin–lattice relaxation as well, but for field intensities of 0.1–0.2 T this contribution may be ignored even for $(Me_6Sn_2)^{+\bullet}$ that has the largest *g*-factor anisotropy.

Relaxation times T_2, T_1 obtained for $(Me_6Ge_2)^{+\bullet}$ and $(Me_6Sn_2)^{+\bullet}$ from simulations coincide with those estimated from eqn. (6) only in order of magnitude. One should however take into account that the accuracy of both the theoretical estimations and the evaluation of T_2 and T_1 by simulation is not high. Besides, the single-pair model used may be too simplified since it ignores possible chemical transformation of the radical cations or fluorescence arising from recombination of other pairs. An especially large ambiguity arises in the case of organotin compounds whose radical cations fragment very rapidly. It is possible that this is the reason for unrealistically low values of the parameter θ obtained in simulations.

Conclusions

The study of time-resolved magnetic field effect shows that the fluorescence from the irradiated alkane solutions of Me_4E and Me_6E_2 (E = Si,Ge,Sn) on addition of *p*-terphenyl-d_{14} appears to be a result of recombination of radical ion pairs $(Me_4E)^{+\bullet}/(p\text{-terphenyl-}d_{14})^{-\bullet}$ or $(Me_6E_2)^{+\bullet}/(p\text{-terphenyl-}d_{14})^{-\bullet}$. Thus, due to the high sensitivity and resolution of the TR MFE method, Group 14 element organometallics radical cations $(Me_4\ E)^{+\bullet}$ and $(Me_6E_2)^{+\bullet}$ have been detected in solutions at room temperature for the first time.

The simulation of the effects of magnetic fields allows us to find that in alkane solutions the *g*-factors of radical cations $(Me_4E)^{+\bullet}$ and $(Me_6E_2)^{+\bullet}$ are close to those in low temperature matrices. The hfc constants obtained for $(Me_6Ge_2)^{+\bullet}$ is close to that for low temperature matrices, too.

The rate of the electron self-exchange between radical cations $(Me_4E)^{+\bullet}$ (E = Si,Ge) and corresponding neutrals in alkane solutions is found to be close to that of the diffusion-controlled reaction, whereas it is not observed for $(Me_6Si_2)^{+\bullet}$. At the concentration of Me_4E compounds of about 0.1 M the electron self-exchange results in a noticeable narrowing of ESR spectrum and fast phase relaxation of $(Me_4Si)^{+\bullet}$ due to modulation of the hfc constants with protons and magnetic isotopes of Group 14 elements. In the case of radical cations $(Me_6E_2)^{+\bullet}$ which have a bigger *g*-tensor anisotropy, the spin-rotational interaction brings the main contribution to the observed phase and spin–lattice relaxation in magnetic fields of about 0.1 T.

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References

1 J. K. Kochi, *Organometallic Mechanisms and Catalysis*, Academic Press, New York, London, 1978.

2 J. Iley, in *The Chemistry of Organic Germanium, Tin and Lead Compounds*, ed. S. Patai, John Wiley & Sons Ltd, 1995, p. 267.

3 L. Bonazzola, J. P. Michaut and J. Roncin, *J. Phys. Chem.*, 1991, **95**, 3132.

4 B. Brocklehurst, *Radiat. Phys. Chem.*, 1997, **50**, 213.

5 V. A. Bagryansky, O. M. Usov, V. I. Borovkov, T. V. Kobzeva and Yu. N. Molin, *Chem. Phys.*, 2000, **255**, 237.

6 V. I. Borovkov, V. A. Bagryansky, I. V. Yeletskikh and Yu. N. Molin, *Mol. Phys.*, 2002, **100**, 1379.

7 S. V. Anishchik, V. M. Grigoryantz, I. V. Shebolaev, Yu. D. Chernousov, O. A. Anisimov and Yu. N. Molin, *Prib. Tekh. Eksp.*, 1989, **4**, 74 (in Russian).

8 D. F. van de Vondel, *J. Organometal. Chem.*, 1965, **3**, 400.

9 W. F. Edgell and C. H. Ward, *J. Am. Chem. Soc.*, 1954, **76**, 1169.

10 V. F. Mironov and A. L. Kravchenko, *Izv. Akad. Nauk SSSR*, 1965, 1026 (in Russian).

11 M. P. Brown and G. W. A. Fowles, *J. Chem. Soc.*, 1958, 2811.

12 *Spin polarization and magnetic field effects in radical reactions*, ed. Yu. N. Molin., Elsevier, Amsterdam, 1984.

13 K. Schulten and P. G. Wolynes, *J. Chem. Phys.*, 1978, **68**, 3292.

14 Landolt-Börnstein: A. Berndt, M. T. Jones, M. Lehnig, L. Lunazzi, G. Placucci, H. B. Stegmann and K. B. Ulmschneider, in *Numerical Data and Functional Relationship in Science and Technology, Group II. Atomic and Molecular Physics. V.1: Magnetic Properties of Free Radicals. Part d1*. eds. H. Fischer and K.-H. Hellwege, Springer-Ferlag, Berlin, Heidelberg, New York, 1980.

15 V. I. Borovkov, S. V. Anishchik and O. A. Anisimov, *Chem. Phys. Lett.*, 1997, **270**, 327.

16 D. W. Werst, M. F. Desrosiers and A. D. Trifunac, *Chem. Phys. Lett.*, 1987, **133**, 201.

17 *Energy of Chemical Bonds, Ionization Potentials and Electron Affinities*, ed. V. N. Kondratyev, Nauka, Moscow, 1974, (in Russian).

18 C. G. Pitt, M. M. Bursey and P. F. Rogerson, *J. Am. Chem. Soc.*, 1970, **92**, 519.

19 P. W. Atkins and D. Kivelson, *J. Chem. Phys.*, 1966, **44**, 169.

20 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.