Vsevolod Borovkov*, Andrey Taratayko, Alena Bessmertnykh, Victor Bagryansky and Yuriy Molin

Solvent Radical Anions in Irradiated Aliphatic Ketones and Esters as Observed Using Time-Resolved Magnetic Field Effects in the Recombination Fluorescence

Abstract: It has been found that addition of alcohols (~0.1 M) to some liquid ketones and esters results in well-pronounced oscillations in the decay of the delayed fluorescence intensity from irradiated solutions. The analysis of the time-resolved magnetic field effects (TR MFEs) in the recombination fluorescence has shown that these oscillations are a manifestation of singlet-triplet transitions in spin-correlated radical ion pairs (RIPs) created by irradiation. Comparison with literature data indicates that the transitions are due to hyperfine couplings (HFCs) in the solvent radical anion (RA), stabilized due to the presence of alcohol molecules. In acetone, this stabilization effect has been observed for methanol, ethanol, 2- propanol, and, to a smaller extent, for *tert*-butanol. Similar effects have also been observed in diethyl ketone, ethyl acetate, and methyl propionate but not in methyl *tert*-butyl ketone and ethyl trimethylacetate. The results obtained indicate that the interaction between the radical anions (RAs) of carbonyl compounds and alcohol molecules is of importance in pulse radiolysis studies of organic liquids and their mixtures.

*Corresponding author: Vsevolod Borovkov, Voevodsky Institute of Chemical Kinetics and Combustion, Siberian Branch of Russian Academy of Science, 3, Institutskaya st., Novosibirsk 630090, Russia, Fax: +7-383-3307350, E-mail: borovkov@kinetics.nsc.ru; and Novosibirsk State University, 2 Pirogova st., Novosibirsk 630090, Russia
Andrey Taratayko: Novosibirsk State University, 2 Pirogova st., Novosibirsk 630090, Russia; and N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of Russian Academy of Science, 9 Lavrentiev Ave., Novosibirsk 630090, Russia
Alena Bessmertnykh and Victor Bagryansky: Voevodsky Institute of Chemical Kinetics and Combustion, Siberian Branch of Russian Academy of Science, 3, Institutskaya st., Novosibirsk 630090, Russia; and Novosibirsk State University, 2 Pirogova st., Novosibirsk 630090, Russia
Yuriy Molin: Voevodsky Institute of Chemical Kinetics and Combustion, Siberian Branch of Russian Academy of Science, 3, Institutskaya st., Novosibirsk 630090, Russia

1 Introduction

In the liquid-phase radiolysis studies, aliphatic ketones and esters are frequently considered as compounds with good electron accepting properties, which facilitate scavenging of solvated electrons as well as formation of molecular radical anions (RAs). This statement can be supported by data obtained for acetone, which is the most well studied carbonyl compound, used as both a solvent and a solute. By adding acetone to an irradiated solution can quench the infrared wing of the absorption spectrum of the solution; absorption in this spectral range is usually coming from excess electron scavenging [1, 2]. In irradiated acetone solutions, the formation of secondary RAs of aromatic solutes typically lasts on the submicrosecond time scale due to slow electron capture from the solvent RA [3–5]. Data are also available for electron scavenging by ethyl acetate and for electron transfer from the biphenyl RA to ethyl acetate upon radiolysis of the ethanol solutions of these compounds [6].

However, the above view on the interaction of aliphatic ketones and esters with excess electrons raises questions and objections. The anionic states of these compounds with a semi-occupied molecular orbital have not been observed in the gas phase, see, e.g. [7, 8]. A possible way of creating a stable negative charge carrier of an irradiated carbonyl compound is either formation of dimers or clustering. As shown by quantum chemistry calculations for acetone taken as an example, the vertical electron detachment energy for the monomer RA is significant and negative [9], whereas those for dimers and clusters are positive, reaching almost 3 eV for larger clusters [10]. Another possible mechanism for RAs stabilization is given by specific microsolvation effects, as demonstrated in a recent study [11] of the RA of diacetonyl in low temperature matrices.

Therefore, stabilization of negative charge carriers in irradiated liquid aliphatic carbonyl compounds remains an open issue. Note that observation of the EPR spectra of the solvent RAs formed under irradiation could make things clearer, since such spectra are known for many carbonyl compounds. They were observed upon chemical generation of their RA, in particular, in solutions of alcohols (see, e.g. [12]). In these RAs, the spin density is localized at the carbonyl group with dominating hyperfine couplings (HFCs) with the β-protons. Magnetic equivalence of the β-protons is provided by fast conformation transitions as well

as by methyl group rotations in liquid solution. However, under ionizing irradiation, the RAs of many aliphatic carbonyl compounds were observed by EPR technique using low temperature stabilization and matrix isolation [13, 14] only, but never in irradiated liquid solutions.

The aim of the present work is to investigate a series of liquid ketones and esters in order to search for the RAs created in liquids by ionizing irradiation as well as to determine HFC constants in the RAs. To this end, the method of time-resolved magnetic field effect (TR MFE) in the recombination fluorescence of spin-correlated radical ion pairs (RIPs) has been applied. The fluorescent state of a molecule is typically expected to be the result of the recombination of RIP in the singlet spin state. Since high-energy ionization produces RIPs predominantly in the singlet spin state, the coherent evolution of the spin state modulates the recombination fluorescence intensity. This evolution is due to spin interactions of the unpaired electrons in the recombining radical ions. Consequently, the TR MFE method potentially provides the same information as EPR [15, 16]. The advantage of the TR MFE method is the ability to obtain such information on a time scale of 1–100 ns, which is typically inaccessible for conventional magnetic resonance approaches. Previously, this approach has been successfully applied to study the short-lived radical ions of organic molecules in aprotic solvents with low polarity (see, e.g. [17–19]).

2 Experimental and methodological details

2.1 Experimental

We investigate delayed fluorescence from irradiated solutions of $0.3 \div 0.4$ mM of *para*-terphenyl-d_{14} (*p*TP) in the aliphatic carbonyl compounds shown in Figure 1.
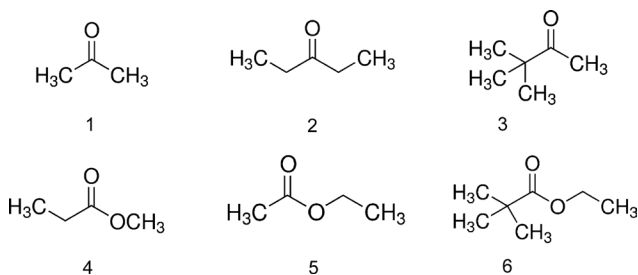

Fig. 1: Molecular structures of the studied solvents: 1 – dimethyl ketone (acetone), 2 – diethyl ketone; 3 – methyl *tert*-butyl ketone; 4 – methyl propionate; 5 – ethyl acetate; 6 – ethyl trimethyl acetate.

The aromatic solute was used, since it has a relatively short fluorescence lifetime, *ca*. 1 ns, at a high fluorescence quantum yield. Besides this, the HFCs in the radical ions of *p*TP are relatively small with a consequence that TR MFE traces are conditioned by a counterion of interest. The fluorescence was excited by X-ray pulses with a duration of about 1 ns and energy of about 20 keV and detected using the time-correlated single photon counting technique as implemented in a homemade X-ray fluorimeter [20]. The light from the samples was collected using an optical bandpass filter (320–410 nm) to select fluorescence of *p*TP. As usual, the time delays between synchronizing pulses were chosen to collect photons, which arrive to detector starting from nearly 100 ns before the prompt luminescence during the exciting X-ray pulse. The earlier portion of the histograms at times < 90 ns before the prompt emission was used to determine the intensity of the background luminescence, which was subtracted from the analyzed delayed fluorescence decay curves.

Experiments were performed at nearly zero (B < 0.05 mT) and relatively strong (B = 0.1 T) magnetic fields. Solutions were degassed by repeated freeze-pump-thaw cycles. All measurements were made at 293 ± 1 K.

Diethyl ketone (99%), methyl *tert*-butyl ketone (99%), methyl propionate (99%) ethyl acetate (99%), methanol (98%), ethanol (98%), 2-propanol (99%), and *tert*-butanol (98%) were distilled before use. Ethyl trimethyl acetate (99%) and *para*-terphenyl-d_{14} (98%) were used as received from Aldrich. Special attention was paid to additional purification of acetone (99.7%, *Reakhim*, *Russia*) from methanol using a combination of standard techniques [21]. To do this, 1 g of potassium permanganate was added to 100 mL of acetone. The resulting solution was left for 1.5 h at room temperature and then acetone was distilled. The first and last 5 mL of the distillate were discarded. Distilled acetone was filled by 4 Å molecular sieves and it was left for 2 days at room temperature. Two days later 25.0 g of anhydrous sodium iodide were dissolved in acetone. The resulting clear solution was placed in a fridge on 1 h. After that the liquid phase was discarded and the solid acetone-sodium iodide complex was placed in a flask. It was heated to melting and distilled discarding the first and the last 5 mL of the distillate. As indicated by a mass-chromatographic analysis, the outlined purification procedures allow one reducing the methanol concentration down to 0.1–0.2 mM. However, we have found out that other impurities remain in the solvent. The impurities of the highest concentrations are acetic acid (< 10 mM) and diacetone alcohol (< 2 mM).

2.2 Basics of the TR MFE method

Since the fluorescing *p*TP state is a short-lived singlet, the recombination fluorescence intensity is proportional to the RIPs recombination rate, $F(t)$, multiplied by

the probability to find a pair in the singlet spin state, $\rho_{ss}(t)$, at the instant of time when recombination occurs [15, 16]:

$$I(t) \propto F(t) \cdot \rho_{SS}(t). \tag{1}$$

Unfortunately, analysis of the $I(t)$ curve is sophisticated, since the recombination rate depends on unknown factors like the spatial distribution function of the primary RIPs and the radical ion mobilities. On the other hand, it is possible to simulate the evolution of the RIP's spin state by using appropriate EPR parameters of the RIP's partners. That is why two recombination fluorescence decays are usually recorded at different magnetic fields, and their ratio is analyzed. The ratio, $I_B(t)/I_0(t)$, between the fluorescence decay curves recorded in a strong and nearly zero fields, respectively, is referred to as the TR MFE. In particular, the existing theoretical model makes it possible to derive simple formulas for TR MFE curves when each of the recombining radical ions has a group of magnetically equivalent nuclei. The formulas describing this situation, which are used in this work, are presented in Appendix A.

3 Results and discussions

Figure 2a shows the delayed fluorescence decay curve obtained for the 0.3 mM solution of pTP in acetone as well as the decay curve after addition of 0.1 M meth-
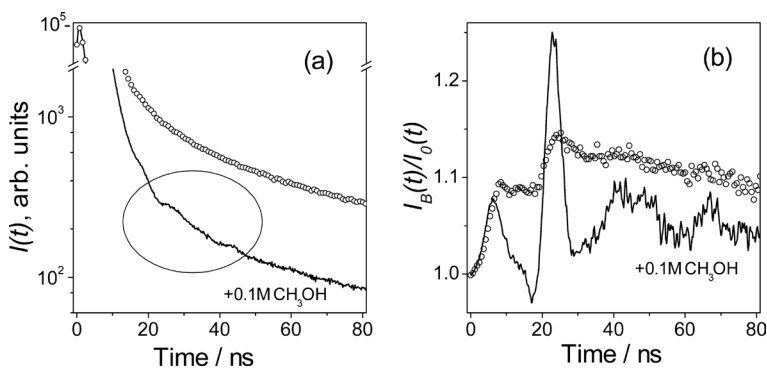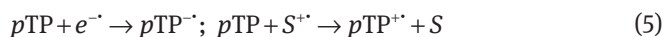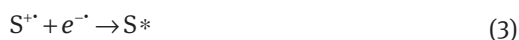

Fig. 2: (a) Recombination fluorescence decays in zero magnetic field as observed from irradiated solutions of 0.3 mM pTP in acetone (circles) and from the same solution after addition of 0.1 M methanol. The curves are normalized at maxima. The ellipse marks the part of the curve where quantum beats appear; (b) Ratios of the fluorescence decay curves, $I_B(t)$ and $I_0(t)$, recorded at B = 0.1 T and zero magnetic field, respectively, for the same solutions as shown in plot (a).

anol to the solution. The radiation induced processes involving radical ions in the solution without methanol are given by the following reactions:

$$S \rightarrow S^{+\bullet} + e^{-\bullet} \tag{2}$$

$$S^{+\bullet} + e^{-\bullet} \rightarrow S* \tag{3}$$

$$S + e^{-\bullet} \rightarrow S^{-\bullet} \tag{4}$$

$$pTP + e^{-\bullet} \rightarrow pTP^{-\bullet}; \ pTP + S^{+\bullet} \rightarrow pTP^{+\bullet} + S \tag{5}$$

$$S^{+\bullet} + pTP^{-\bullet} \rightarrow S + pTP* \tag{6}$$

$$S^{-\bullet} + pTP^{+\bullet} \rightarrow S + pTP* \tag{7}$$

$$pTP^{+\bullet} + pTP^{-\bullet} \rightarrow pTP + pTP* \tag{8}$$

Here, $S^{+\bullet}$ is the radical cation (RC) formed from the solvent molecule after ionization in reaction (2). This RC is the solvent RC itself or the product of its chemical transformations reserving however, both the positive charge and unpaired electron spin on the same particle. $S^{-\bullet}$ is the negative charge carrier, e.g. the solvent RA. Methanol is expected to react predominantly with these primary radical ions.

Note that the luminescence in the solutions studied can be observed only due to the fast emissive deactivation of the singlet-excited pTP molecules. Thus, independent of the methanol concentration, the fluorescence appears as the result of recombination of RIPs comprising either the pTP RA (reaction 6) or the pTP radical cation (reaction 7), or, quite probably *a priori*, both of them (reaction 8).

Importantly, both $S^{+\bullet}$ and $S^{-\bullet}$ are radical ions. This immediately follows from Figure 2b, since the nonzero effect of external magnetic field on the recombination fluorescence can appear only for recombination of RIPs, in which the spin coherence between the partners does exist.

As can be seen from Figure 2a, addition of methanol results in a significant quenching of the delayed fluorescence intensity as well as in the appearance of visible oscillations in the decay curve. Such oscillations originate from the coherent singlet-triplet mixing in the spin-correlated RIPs generated by irradiation; these oscillations are most clearly visible in the TR MFE curve, $I_B(t)/I_0(t)$, as shown in Figure 2b.

Let us discuss now on the shape of the TR MFE curve obtained for the solution with methanol, which exhibits very characteristic features that allow us to draw several qualitative conclusions. First, the singlet-triplet transitions are governed by HFC in the recombining radical ions since the transitions due to either the paramagnetic relaxation or the difference in the g-values of the RIP's partners result in different quantum beats patterns [15, 16]. The comparatively large amplitude of the oscillations in the TR MFE curve, which are comparable to those in

alkane solutions, suggests that the observed fluorescence is due to recombination of RIPs, which are (i) of a single kind; and (ii) almost instantaneously formed by ionization pulse. Otherwise, the oscillations from different pairs having different frequencies would partly cancel each other.

As it was considered in detail previously [15, 22], the peaks in the TR MFE curve in Figure 2b and their sequence are typical for a RIP, composed of radical ions, with one radical having a group of magnetically equivalent protons with an appreciable HFC constant, whereas the partner radical has negligible HFCs. The former cannot be the pTP radical ion, since its HFC is too small to contribute to the spin evolution of RIPs on the time scale of 0−80 ns. Thus, we reject reaction (8) as the channel resulting in the fluorescence in our experiments. Besides this, reaction (6) cannot involve the RC of acetone with negligible HFC [23, 24].

In solutions in diethyl ketone, methyl propionate and ethyl acetate (Figure 3), addition of methanol, as well as in the acetone case, results in the appearance
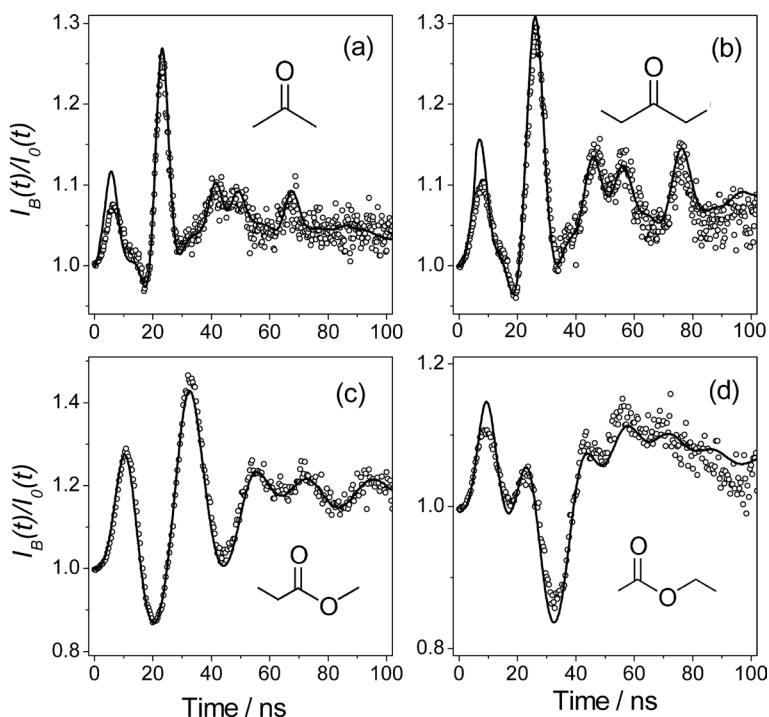

Fig. 3: Ratios, $I_B(t)/I_0(t)$, of the delayed fluorescence decays at B = 0.1 T and in zero magnetic field, respectively obtained for solutions of 0.3 ÷ 0.4 mM of pTP + 0.1 M of methanol in acetone (a), diethylketone (b), methyl propionate (c), ethyl acetate (d). Smooth lines are simulation results calculated using the parameters given in Table 1.

of sharp features in the TR MFE. On the other hand, adding methanol gives no noticeable effect on both the fluorescence intensity and the TR MFE curves in the cases of the methyl *tert*-butyl ketone and ethyl trimethylacetate solutions.

We have succeeded to simulate the experimental curves (Figure 3) by assuming that (i) the RIP's partners are formed immediately after the irradiation pulse; (ii) one of the RIP partners is the solvent RA with the number of equivalent β-protons corresponding to spin density localization on the carbonyl group; (iii) its partner is the RC of *p*TP with the second moment of the spectrum $\sigma^2 = (0.074$ mT$)^2$ as calculated using the data for the *p*TP-h_{14} RC [25]. The calculated curves shown in Figure 3 were obtained using equations (A2)-(A8) with the parameters given in Table 1.

The HFC constants are determined from the instants of time where the oscillations have maxima and minima with an accuracy better than 10%. They are very close to the constants available for the individual RAs of the corresponding carbonyl compounds, especially to the values obtained in liquid alcohol solutions (see Table 1). Therefore, the good coincidence between the experimental and calculated TR MFE curves indicates that the observed fluorescence from the solutions with methanol results from recombination of spin-correlated RIPs of a single kind. The RIP consists of the RA of a solvent molecule and the RC of *p*TP.

Note that addition of methanol results also in a significant quenching of the recombination fluorescence intensity (Figure 2a). This can be explained by a concurrence of methanol with aromatic solutes for scavenging solvent RCs; such RCs are believed to react readily with alcohols via proton transfer [3, 27]. The following recombination of ion pairs involving the charged product of such a deprotonation reaction cannot lead to the magnetosensitive fluorescence. On the other hand, one of the recombining particles is the radical ion of the aromatic solute:

Tab. 1: Parameters used to calculate the curves, which fit the experimental data shown in Figure 3.

Radical anion[a] of	HFC constant/ mT, ±0.02	HFC constant/mT (literature data)	Phase relaxation time[e], T_2/ns
Acetone	$a(6H) = 1.62$	$a(6H) = 1.69$[b]	35
Diethylketone	$a(4H) = 1.42$	$a(4H) = 1.43$[b]	80
Ethyl acetate	$a(3H) = 1.12$	$a(3H) \approx 1.36$[c]	45
Methyl propionate	$a(2H) = 1.13$	$a(2H) \approx 1.35$[d]	55

[a]As observed after the addition of 0.1M methanol; [b]ref [12]; [c]as observed at comparatively rapid rotation of methyl group in aqueous glass at 143 K [26]; [d]as estimated using data on methyl acetate RA, which exhibits the same HFC constant with the β-protons at low temperature [26]; [e]for spin-lattice relaxation time only the lower estimate, $T_1 > 100$ ns, can be obtained.

otherwise, observation of the recombination fluorescence is improbable. Therefore, our data suggest that the chemical decay of the primary solvent RCs in the reaction with alcohol, in the cases presented in Figure 3, is not too fast to exclude the formation of pTP RCs even when the methanol concentration is very high as compared to that of pTP.

The phase relaxation time, T_2, that is introduced in the modeling (Table 1), allows us to estimate the residence time of the unpaired electron spin on a particular solvent molecule at our experimental conditions; this time is as long as more than tens nanoseconds.

It is likely that stabilization of the excess electron on a particular solvent molecule occurs due to the formation of hydrogen bonds between the solvent RA and the hydroxyl groups of the alcohol molecules. This assumption is supported by the results of Ref [28]. In the cited work, it was found that the formation of a hydrogen-bonded complex between the acetophenone RA and one or several methanol molecules in the gas phase provides a significant energy gain up to 1 eV and essentially changes the electronic RA structure.

Complexation between the ketone or ester RAs and the methanol molecules in liquid solutions, found by the TR MFE method, allows one to take a new look at the results of the pulse radiolysis studies on the ketone/alcohol mixtures. For example, Rodgers [3] reported the disappearance of the absorption band, assigned to the acetone RA, after addition of ethanol. It was suggested that the RAs decayed via the proton transfer reaction with ethanol. However, it looks plausible that the formation of a hydrogen-bonded complex, involving RA and several alcohol molecules, can also significantly change the electronic structure of the RA excited states thus shifting the absorption band.

We have also studied the methanol concentration dependence of the quantum beats pattern in acetone solutions as demonstrated in Figure 4a. A decrease in concentration leads to the diminishing the quantum beats amplitude; this effect is most clearly seen for the second peak at nearly 23 ns. On the other hand, in the absence of methanol, this peak does not disappear completely though it is expected that in pure acetone, the HFCs of solvent RAs would averaged out to give a narrow unresolved EPR signal due to the fast degenerate electron exchange with adjacent solvent molecules.

It is probable that at the lowest methanol concentration the TR MFE curve is strongly affected by impurities (see Experimental section) that encounter a negative charge carrier within a few nanoseconds (as estimated from the content of impurities in acetone). However, at higher methanol concentration, this impurities' effect most likely becomes insignificant.

If the quantum beats amplitude is used as a measure of the solvent RA "stabilization efficiency" then the different alcohols can be compared. At a
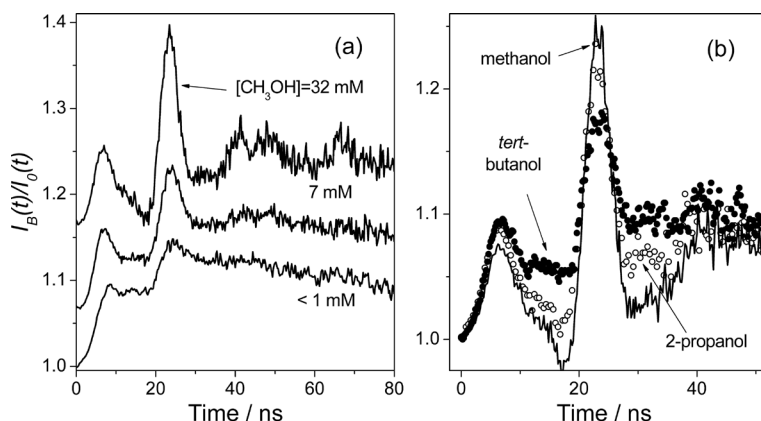
Fig. 4: (a) Ratios, $I_B(t)/I_0(t)$, of the delayed fluorescence decays at B = 0.1 T and zero magnetic field, respectively, obtained for acetone solutions of ~0.4 mM of pTP-d_{14} in the presence of methanol; the methanol concentration is given in the plot. The bottom curve was obtained without addition of methanol; (b) the same dataset obtained for acetone solutions after addition of 0.1 M methanol (line), 2-propanol (open circle), and *tert*-butanol (solid circle).

concentration of 0.1 M, the effect of ethanol addition is indistinguishable from that for methanol, while the conditional efficiency decreases slightly on going to 2-propanol and, to a greater extent, to *tert*-butanol as shown in Figure 4b.

The role of alkyl substituents in the interaction between the RAs of aliphatic carbonyl compounds and alcohols remains unclear on this stage. For example, the *tert*-butyl fragment in the carbonyl compound prevents the stabilization by added alcohol molecules while the same fragment in the alcohol molecule decreases the stabilization efficiency but does not exclude this process completely.

4 Conclusions

Irradiation of solutions of luminophore in aliphatic ketones and esters gives rise to the delayed fluorescence, which originates from recombination of spin-correlated RIPs. By analyzing the time-resolved magnetic field effects (TR MFEs) in the recombination fluorescence it has been found that addition of alcohols to the solutions in some cases resulted in the appearance of the well-pronounced quantum beats in the singlet spin state population of the RIPs on the nanosecond time scale. These beats are caused by HFCs that are characteristic for the individual RAs of the carbonyl compounds used as the solvents. The absence of averaging out of HFCs by degenerate charge transfer is explained by a compara-

tively strong localization of excess electron on a particular carbonyl molecule due to the formation of a hydrogen bond between the solvent RA and one or, probably, several molecules of the added alcohol.

Therefore, by utilizing the TR MFE method, which provides the magnetic resonance parameters of short-lived radical ions generated in liquid ketones and esters, proves the formation of solvent RAs at the presence of alcohol molecules. This is, perhaps, not surprising, since these conditions are similar to those previously used in EPR studies of chemically generated RAs of these compounds [12]. However, the considerable stabilization effect due to impurities containing hydroxyl group does not allow one at this stage to make definite conclusions on the nature of the RAs formed in a pure solvent. In any case, the first application of the TR MFE method shows that the technique is promising for further investigations of primary radiation-induced processes in liquids, forming hydrogen bonds.

Appendix A

When the fluorescence time is short, the intensity of recombination fluorescence in nonpolar solutions is proportional to the recombination rate of the RIPs, $F(t)$, multiplied by the singlet state population of RIPs ensemble [15, 16]:

$$I(t) \propto F(t) \cdot [\theta \rho_{SS}(t) + (1-\theta)/4], \tag{A1}$$

where $\rho_{ss}(t)$ is the time dependence of the singlet state population of the initially singlet-correlated RIPs. θ is a semiempirical parameter to take into account the fact that in a multiparticle radiation spur only a fraction of recombining RIPs is spin-correlated, whereas some of them are composed of radical ions originating from different primary ionization events. The second term in the brackets takes account of such spin-uncorrelated RIPs.

In this approximation, the TR MFE curve,

$$\frac{I_B(t)}{I_0(t)} = \frac{\theta \cdot \rho_{SS}^B(t) + (1-\theta)/4}{\theta \cdot \rho_{SS}^0(t) + (1-\theta)/4}, \tag{A2}$$

depends only on the singlet state populations of the spin-correlated RIPs, $\rho_{ss}(t)$, in non-zero and zero external magnetic fields as indicated by superscripts B and 0, respectively. The $\rho_{ss}(t)$ dependence can be evaluated taking the paramagnetic relaxation into account as previously suggested [15]:

$$\rho_{ss}^{B}(t) = \frac{1}{4} + \frac{1}{4}\exp\left(-\frac{t}{T_1}\right) + \frac{1}{2}\exp\left(-\frac{t}{T_2}\right) G_c^{B}(t) G_a^{B}(t), \tag{A3}$$

$$\rho_{ss}^{0}(t) = \frac{1}{4} + \frac{3}{4}\exp\left(-\frac{t}{T_0}\right) G_c^{0}(t) G_a^{0}(t), \tag{A4}$$

where $1/T_{1,2} = 1/T_{(a)1,2} + 1/T_{(c)1,2}$ are the sums of the longitudinal or phase relaxation rates of the RIP partners, and T_0 is the parameter to describe phase relaxation of the RIP in a zero magnetic field in the same manner. Subscripts "a" and "c" point to the parameters of RA and RC, respectively.

The analytical solutions to $G^{0,B}(t)$ are known only for some particular cases: the case of groups of equivalent magnetic nuclei and the case of a large number of nonequivalent magnetic nuclei. For a large of magnetic nuclei having different HFC constants that is the case of radical ions of *para*-terphenyl, in the framework of the semi-classical approximation, the functions $G(t)$ are (in magnetic field units for σ and a) [29],

$$G^{0}(t) = \frac{1}{3} \cdot [1 + 2 \cdot (1 - (\gamma\sigma t)^2) \cdot \exp(-(\gamma\sigma t)^2/2)], \tag{A5}$$

$$G^{B}(t) = \exp[-(\gamma\sigma t)^2/2], \tag{A6}$$

where σ^2 is the second momentum of the radical ion EPR spectrum, γ is the electron gyromagnetic ratio.

For n magneto-equivalent protons with the HFC constant a [22],

$$G^{0}(t) = \frac{1}{3}\left[\frac{n+3}{n+1} + \frac{2n(n+2)}{n+1} \cdot \left(\cos\left(\frac{a\gamma t}{2}\right)\right)^{n+1} - 2n \cdot \left(\cos\left(\frac{a\gamma t}{2}\right)\right)^{n-1}\right], \tag{A7}$$

$$G^{B}(t) = \left(\cos\left(\frac{a\gamma t}{2}\right)\right)^{n}. \tag{A8}$$

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