

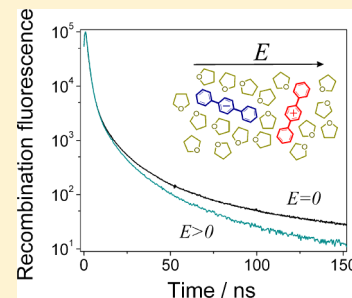
# Measurement of the Relative Mobility of Geminate Ions in Ethereal Solutions of Aromatic Compounds Using the Fluorescence Response of the Solutions to Pulsed Irradiation

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**ABSTRACT:** This work examines the possibility of using the fluorescence response of irradiated solutions of luminophores and the effect of an external electric field on the fluorescence decay to determine the mobility of geminate radical ions when using aliphatic ethers as the solvents. As an example, *p*-terphenyl solutions were studied in a series of ethers (diethyl, dibutyl, methyl *tert*-butyl ether, tetrahydrofuran, 2-methyltetrahydrofuran, 1,4-dioxane, eucalyptol, and 1,2-dimethoxyethane). Verification of the nature of the charge carriers in the irradiated solutions was made by means of the method of the time-resolved magnetic field effect in recombination fluorescence of spin-correlated radical ion pairs. It was found that at a *p*-terphenyl concentration of about 10 mM, the observed fluorescent response from the solutions, in most cases, was due to the recombination of radical ions formed from the aromatic solute. The relative mobility of *p*-terphenyl radical ions in ethers was estimated by using a stochastic computer simulation of the radiation spur composed of 4 primary ion pairs. The ions' mobility was found to be dependent on solvent viscosity in accordance with Walden's rule, with no noticeable effect of solvent polarity.



## INTRODUCTION

The transport of charge carriers in solutions is a phenomenon whose theoretical description is still a challenging problem since it requires taking into account many-particle interactions in molecular media. That is why the main source of information on ion transport is an experiment. However, there is no universal approach that could be applied to measure charge carrier mobility in an arbitrary solvent. As a result, available data on ion transport in liquids are very far from being complete, and many of the widely used solvents have not been studied in this respect.

In particular, the applicability of an experimental approach for such studies is strongly dependent on solvent polarity. Highly polar liquids, like water, are best studied regarding ion transport since the dissolved substance readily dissociates into ions. The mobilities of these ions can be evaluated by measuring solution conductivity at a known concentration of the carrier. In liquids consisting of nonpolar molecules, e.g. alkanes, an appreciable quantity of free charge carriers can only appear after exposure of the medium to external ionizing irradiation. In such a case, ions are generated as partners of geminate radical ion pairs. The low polarity results in a comparatively strong Coulomb interaction between the oppositely charged ions and, consequently, in a high probability of recombination of the ion pairs in a time range of nanoseconds. Due to the interaction with the environment, some fraction of the ion pairs escapes recombination. The appearance of the free ions allows determination of the mobilities of the charged species by time-of-flight techniques<sup>1–3</sup> where the time of ion travel to an electrode is measured. This

time can reach milliseconds, and a major issue in this technique is identifying the charge carriers.

At shorter times, when a considerable number of ion pairs have not yet recombined, the ionic transport in solution can be studied by using time-resolved techniques.<sup>4,5</sup> In this case, any approach is capable of probing the relative motion of geminate ions only since both partners of an ion pair contribute equally to the signal. So, the experiment yields the relative mobility of the ions that is the sum of their individual mobilities.

In 1995,<sup>6</sup> a new approach was suggested to determine the relative mobility of geminate ions: the method of the Time-Resolved Electric Field Effect (TR EFE) in recombination fluorescence. In this approach,<sup>6–8</sup> the response of the decay curve of radiation-induced fluorescence from a solution to an external electric field is analyzed. The external field reduces the probability of recombination of the geminate ion pairs, and, if a recombining ion pair yields an electronically excited fluorescing molecule, the external field leads to a faster decay of the intensity of the recombination fluorescence from the irradiated solution. The higher the mobilities of recombining geminate ions, the faster the field effect rises.

The TR EFE technique can be most readily used for luminophores with a high quantum yield and a short fluorescence time. In such cases, the observed fluorescence intensity is directly proportional to the recombination rate of the ion pairs. At a constant mobility of the geminate ions, the TR EFE curve, determined as the ratio of the fluorescence

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intensity decay kinetics in the field,  $I_E(t)$ , to that without the field,  $I_0(t)$ , can be asymptotically approximated by an exponential decay<sup>9</sup>

$$\frac{I_E(t)}{I_0(t)} \approx \exp\left(-\frac{eE^2\mu_s}{4kT}t\right) \quad (1)$$

where  $\mu_s$  is the sum of the mobility values ( $\mu = De/kT$ ) of the recombining ions. Actually, eq 1 is an inexact one but it correctly gives the dependence on the parameters involved. In particular, the quadratic field intensity dependence is closely related to the diffusive nature of the motion of the charge carriers in the solution.<sup>6,8</sup> Importantly, it can be demonstrated with both experimental<sup>10</sup> and theoretical<sup>7,9</sup> results that eq 1 is actually weakly dependent on the initial distribution function and the structure of the radiation spur, which are typically unknown. Thus, the TR EFE method appears to be a suitable approach to estimate the relative mobility of radical cations and anions whose recombination yields a fluorescent state. Coupled with computer simulation<sup>10</sup> of the ion recombination within a radiation spur, the method potentially allows the study of the ionic transport process in more complicated situations where the mobility of charge carriers changes due to chemical transformations.

The TR EFE technique has provided a considerable amount of information on the mobility of radical ions of organic compounds in alkanes,<sup>10,11</sup> which exhibit the highest probability of geminate ion recombination due to their low polarity. In more polar organic solvents, with dielectric constant in the range 3–10, to our knowledge, the transport of organic radical ions, which are charge carriers with an open electronic shell, has not been systematically studied yet.

In this work, we discuss the applicability of the TR EFE method to measuring the mobility of aromatic radical ions in aliphatic ethers. This issue requires careful consideration since the higher solvent polarity in some cases causes one to anticipate a significant reduction in the recombination fluorescence yield. First, the high polarity decreases the probability of geminate ion recombination. Second, this serves to reduce the yield of the fluorescing state of the luminophore upon recombination. Indeed, an electronically excited state can be formed if the following condition is fulfilled:<sup>12</sup>

$$(IP - EA + P^+ + P^- - e^2/\epsilon R) > E_{\text{fl}} \quad (2)$$

where  $E_{\text{fl}}$  is the excited state energy. The left-hand portion is the energy released as a result of the charge recombination: IP is the electron donor's gas phase ionization potential, EA is the gas phase electron affinity of the electron acceptor, and  $P^+$ ,  $P^- < 0$  are the solvation energies of the recombining ions. The term  $(-e^2/\epsilon R)$  estimates the Coulombic interaction of ions separated by a distance  $R$  in a medium with dielectric constant  $\epsilon$ .

The solvation energy can be estimated by using the well-known Born equation,  $P = -e^2/2r(1 - 1/\epsilon)$ , where  $r$  is the characteristic ionic radius. If instead of alkanes, solvents with  $\epsilon \approx 10$  are used, the solvation energy grows considerably, by 1–2 eV for not-too-large organic ions. Since  $r < R$ , especially for a distance electron transfer, which looks to be a very probable pathway for the exothermic recombination reaction, the energy yield of the recombination should be reduced in more polar liquids.

Besides limitations due to their higher polarity, in liquid ethers there could be an additional factor that potentially

hinders use of the TR EFE technique. It is the deprotonation of primary radical cations in the ether, which is generally assumed to occur within picoseconds, forming independent particles, neutral radicals, and cations.<sup>13–15</sup> In this case, the IP value in eq 2 corresponds to the ionization energy of an open shell species that is much lower compared to molecules of similar structure. This significantly reduces the energy yield upon ion recombination. Additionally, such deprotonation reactions must exclude both spin correlation within ion pairs formed as the result of the deprotonation and magnetic field effects<sup>16</sup> upon recombination fluorescence.

On the other hand, it is known<sup>17</sup> that the magnetic resonance spectra of radical ions of some aromatic solutes in liquid ethers can be detected by using the recombination fluorescence. This indicates unequivocally that, one way or another, at least a portion of the delayed fluorescence from an irradiated ethereal solution of aromatic compounds originates from the recombination of spin-correlated radical ions of solute molecules. Therefore, using the TR EFE method to study radical ion transport in liquid ethers is certainly not a universal approach, but does not seem to be a fruitless task either.

## EXPERIMENTAL SECTION

The radiation-induced fluorescence of irradiated ethereal solutions of *p*-terphenyl (*p*TP), which is a good luminophore with a short fluorescence lifetime, was registered by using a nanosecond X-ray fluorimeter working in single photon counting mode.<sup>18</sup> A solution was placed between the electrodes of a nonmagnetic material in a cuvette similar to that described in ref 8. The cuvette was positioned between the poles of an electromagnet. The strength of the electric field created between the electrodes in the solution was up to 40 kV/cm. Through the thin wall of one of the electrodes, the solution was irradiated with X-ray pulses with a quantum energy of about 20 keV and duration about 2 ns. The cuvette temperature was stabilized to within  $\pm 1$  K by an encircling gas flow in the range 233–333 K.

As solvents, we used diethyl ether (DEE, 99%), dibutyl ether (DBE, 98%), methyl *tert*-butyl ether (MTBE, 99%), tetrahydrofuran (THF, 99%), 2-methyltetrahydrofuran (MTHF, 99%), 1,4-dioxane (DO, 99%), eucalyptol (1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane, EUC, 99%), and 1,2-dimethoxyethane (monoglyme, MG, 99%). All the solvents, except for EUC, were additionally purified by distillation and passage through a column with activated alumina. The solvents were then stored over sodium. In the case of monoglyme, thorough purification is particularly important to reduce the residual conductivity of the solvent. As charge acceptors, we used *p*-terphenyl (98%) and *p*-terphenyl-*d*<sub>14</sub> (98% D atoms) as received from Aldrich. Since the ion mobility values obtained in this work for THF were clearly lower as compared to MTHF, which has a very similar viscosity, we checked the viscosities of the solvents available using a capillary viscometer (VPG-3). Within an accuracy of about  $\pm 3\%$ , the measured viscosities gave nearly the same value, 0.48 cP at 298 K, in agreement with literature data (see Table 1).

Before the delayed fluorescence was measured, oxygen was removed from the solution by several freeze–pump–thaw cycles in a special compartment of the cuvette. The concentration of *p*TP was typically about 10 mM but in some experiments it was varied from 0.3 to 30 mM as permitted by the solubility of the *p*-terphenyl.

## COMPUTER SIMULATION

As mentioned above, eq 1 is an approximation. Results obtained in both ref 9 and this work demonstrate that when eq 1 is used in a straightforward manner, the value of the relative ion mobility is underestimated by about 10%, if the mobility may be considered constant.

In particular, the TR EFE curves are affected by the finite fluorescence time of the luminophore and, to a small extent, the initial structure of the radiation spur. In solutions with a solute concentration of  $\sim 1$  mM, the effect of the typically more mobile primary charge carriers should be taken into account.<sup>9</sup> At higher concentrations,  $\sim 10$  mM, TR EFE curves can be distorted due to various factors such as the annihilation of triplet molecules arising, e.g., from the recombination of triplet ion pairs within the radiation spur.<sup>19</sup> In concentrated solutions, the charge carrier mobility can also be slowed down due to the formation of complexes between a radical ion and a solute molecule.<sup>10</sup> To consider these factors thoroughly, a detailed computer simulation of nonhomogeneous ion recombination at various electric field strengths and solute concentrations is necessary. The details of the computer simulation model used in this work are described in Appendix A.

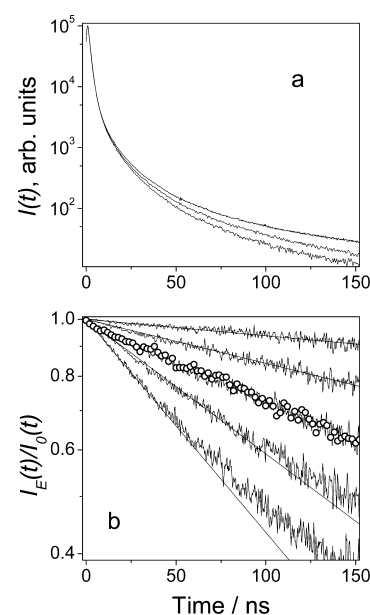
To determine the mobility of the geminate ions from the experiment, a set of TR EFE curves obtained from the computer simulations performed for a variety of mobility values at different temperatures, field intensities and dielectric constant of the media was used. These calculated curves were approximated by an exponential dependence to determine their decay rate (inverse time) within the time range where the secondary charge carriers were formed. Further, the rates were compared to the decay rates of the experimental TR EFE curves, which were also approximated by an exponential dependence (see below). It was assumed that the relative mobility of geminate ions in a studied ethereal solution was equal to the value of the relative mobility used in the corresponding simulation multiplied by the ratio of the decay rates and corrected, if necessary, for other field strengths or temperatures in accord with eq 1. The difference between the evaluated mobility values obtained by using different reference TR EFE curves was within 3–4% which was primarily determined by the accuracy of the stochastic modeling.

## RESULTS AND DISCUSSIONS

### Fluorescent Response of Irradiated Ether Solution.

Figure 1a shows kinetic curves  $I(t)$  of the fluorescence response of a 10 mM *p*TP solution in THF at different electric fields after an irradiation pulse. In both THF and other studied ethers, the response curves were nonexponential ones similar to that observed from the concentrated luminophore solutions in alkanes (see, e.g. refs 8 and 19) but the fluorescence intensity of the ethereal solution was lower as compared to hydrocarbon solvents. The decrease in the intensity amounted to from about 1 order of magnitude for monoglyme and more viscous ethers to about 2 orders of magnitude for THF and diethyl ether. The possible reasons for such a decrease could be the absence of the electronic excitation energy transfer from the solvent excited state to luminophore, which takes place in normal alkanes,<sup>19</sup> or the above-mentioned deprotonation process, which results in the instant decay of a portion of primary solvent radical cations.

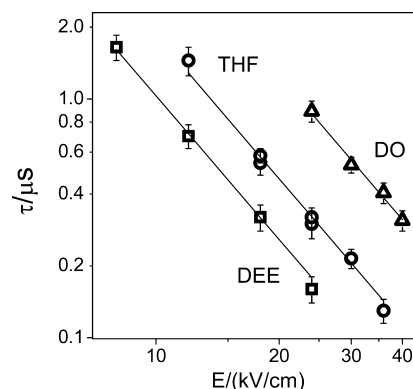
As in the case of alkanes,<sup>10</sup> an increasing electric field strength,  $E$ , leads to a faster decay of fluorescence intensity. Figure 1b shows TR EFE curves at different values of  $E$ . In



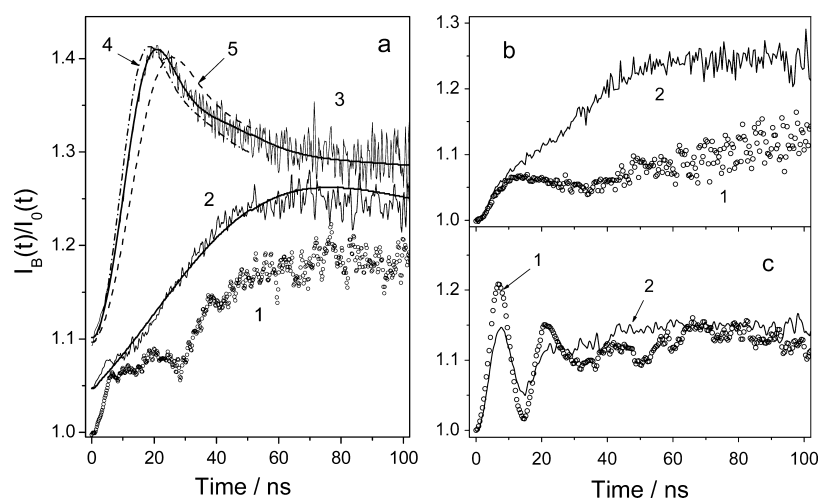
**Figure 1.** (a) Fluorescence intensity decay curves for a solution of 10 mM *p*TP in THF in zero electric field (the upper curve) and at a field strength of 24 and 36 kV/cm (top to bottom),  $T = 298$  K. (b) Ratios  $I_E(t)/I_0(t)$  of (top to bottom) 12, 18, 24, 30, and 36 kV/cm (noisy lines),  $T = 298$  K. Circles show the calculated TR EFE curve at a relative mobility of secondary charge carriers equal to  $6.3 \times 10^{-8}$  m<sup>2</sup>/Vs,  $E = 24$  kV/cm. Straight lines show an exponential approximation of the experimental TR EFE curves within the range where the ratios exceed 0.6.

accord with eq 1, they look very similar to exponential decays. Deviations are observed when the fluorescence is quenched by the electric field to such an extent that other channels of fluorescent state formation become significant. One such channel in a concentrated solution can be the annihilation of electrically neutral triplet-excited molecules moving independently of the electric field.

To visualize the electric field dependence of the TR EFE curves in Figure 2, the time constants of exponential decay, which approximate experimental curves like that shown in Figure 1b, were compared to the field strengths for a number of solvents. The inverse quadratic dependence of  $\tau$  on  $E$  well describes the experimental data, thus indicating the observed



**Figure 2.** Dependencies of the characteristic times of decay in TR EFE curves vs field strength  $E$  for DEE (squares), THF (circles), and DO (triangles). Lines show an approximation for a  $\tau \propto E^{-2}$  type of dependence.

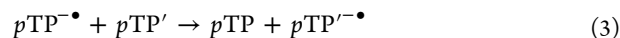


**Figure 3.** (a) Experimental TR MFE curves for the  $p\text{TP-}d_{14}$  solution in THF at concentrations of 0.3 mM (curve 1, circles) and 10 mM (noisy curve 2), as well as for the  $p\text{TP-}h_{14}$  solution at a concentration of 10 mM (noisy curve 3). Calculated TR MFE curves, corresponding to the geminate ions formed from  $p\text{TP-}d_{14}$  and  $p\text{TP-}h_{14}$ , assuming that radical cations of  $p\text{TP}$  undergo fast dimerization, are shown by smooth curves 2 and 3, respectively. Dashed curve 4 is obtained by assuming no dimerization of any of the  $p\text{TP-}h_{14}$  radical ions, while curve 5 shows effects of dimerization of both the ions. Specific modeling parameters can be found in the text and Appendix B. (b, c) Experimental TR MFE curves for  $p\text{TP-}d_{14}$  solutions in EUC (b) and MG (c) at concentrations of 0.3 mM (circles) and 0.01 M (noisy lines).

fluorescence to be a result of the recombination of radical ion pairs that is controlled by the ions' diffusion and drift in electric fields created by other ions and external sources.

**Identification of Charge Carriers.** One of the important issues related to measuring the mobility of short-lived species is identification of the latter. To resolve the problem, in this work we have used the method of Time-Resolved Magnetic Field Effect (TR MFE) in recombination fluorescence of spin-correlated radical ion pairs.<sup>16</sup> The method refers to the ratio of the fluorescence decay curves measured in a magnetic field and without the field,  $I_B(t)/I_0(t)$ . The B and 0 indexes show that the irradiated solution was in an external nonzero (0.1 T in this work) and zero (<0.05 mT) magnetic field, respectively.

Figure 3 shows experimental and calculated TR MFE curves for deuterated and protonated  $p$ -terphenyl in a number of ethers at different solute concentrations. The shape of the TR MFE curves is closely related to singlet–triplet transitions within spin sublevels of the spin-correlated radical pairs.<sup>16</sup> These transitions are driven by Zeeman and hyperfine interactions in the radicals as well as their paramagnetic relaxation. The calculation procedure for the TR MFE curves, taking into account the reaction of the degenerate electron exchange



is described in Appendix B. Reaction 3 is of importance since it results in both additional phase relaxation and narrowing of the ESR spectrum width for a radical involved in self-exchange.

In panels a–c in Figure 3, the curves numbered 1 were obtained at a comparatively low  $p\text{TP}$  concentration of 0.3 mM. At this concentration, in a solvent with THF's viscosity, the average time between binary encounters of molecular species is about 150 ns. In all cases, an increase in the solute concentration to 10 mM considerably changes the TR MFE curves, thus suggesting at least one of the primary charge carriers is scavenged by  $p\text{TP}$  molecules. This is also strongly supported by the effect of deuterating the solute (Figure 3a, curves 2 and 3).

The steepness of the TR MFE curve grows with the width of the EPR spectrum of the geminate radical ions.<sup>16</sup> The shallow steepness of the TR MFE curve in the experiment with deuterated  $p\text{TP}$  (Figure 3a, curve 2) demonstrates that both recombining species have a comparatively small hyperfine coupling, roughly less than 0.1 mT. Note that both  $p\text{TP}$  radical anions and solvated electrons in THF should exhibit negligible coupling because in both cases interactions of the unpaired electron spin with surrounding magnetic nuclei are weak. Therefore, the effect of increasing the  $p\text{TP-}d_{14}$  concentration indicates that  $p\text{TP}$  radical cations are formed in the ethereal solutions under study.

Discussing the nature of positive charge carriers before they are captured by  $p\text{TP}$  molecules is beyond the scope of this work. Here, the most important is the fact that the positive charge carriers that are formed after solvent ionization transfer their charges to aromatic solutes with a sufficiently high probability. These primary carriers affect the TR MFE curves in the initial parts of the curves, as is well seen in the case of the deuterated compound. However, in calculating TR MFE curves in concentrated solutions it was assumed that at longer times than the scavenging time,  $\sim 5$  ns at concentration of 10 mM and the viscosity of THF, this influence can be considered insignificant.

The calculation of TR MFE curves performed for solutions of protonated  $p\text{TP}$  in THF at concentrations from 6 to 30 mM using eqs B1–B7 from Appendix B showed that the best match with the experiment was achieved (see Figure 3a, curve 3) under the following assumptions:

(1) The positive charge carriers in the  $p\text{TP}$  solutions are finally transformed into a dimer complex between  $p\text{TP}$  radical cation and neutral molecule in which spin density is, on average, distributed equally between the particles. It is highly probable that this complex is formed at the first encounter of the particles. From the point of view of magnetic field effect calculations, the rapid radical cation dimerization results in a decrease in the second moment of the radical's ESR spectrum width,  $\sigma_c^2$ , by a factor of 2 compared to the spectrum width of the monomer  $p\text{TP}$  radical cation (see Appendix B). To



demonstrate the effect of the radical ion dimerization, in Figure 3a two TR MFE curves are calculated by assuming either no dimerization of radical ions (curve 4) or the dimerization of both radical cations and anions of *p*TP (curve 5).

(2) *p*TP radical anions are involved in degenerate electron exchanges (reaction 3), with a rate constant of about  $1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . In THF, such a value of the rate constant is an order of magnitude less than that for binary encounters of molecular species in the solution. For a higher exchange rate constant, the maximum in the TR MFE curve shifts toward longer times, and the TR MFE curves cannot be consistently described at different *p*TP concentrations within the range from 6 mM to 30 mM.

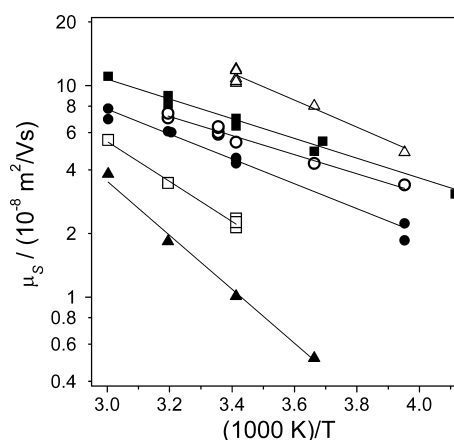
Though the self-exchange reaction 3 leads to the spin state dephasing rate, its contribution is not large enough to fit the experimental TR MFE curves. Better agreement was achieved when an additional dephasing rate corresponding to  $T_2 \approx 50$  and 120 ns for deuterated and protiated compounds, respectively, was introduced. Most probably, the difference can be explained by a dephasing effect of the primary positive charge carrier, whose contribution to spin dynamics is more prominent for the deuterated compound.

Note, the values for the second moment in the ESR spectrum for the width of the radical cation and the radical anion of *p*TP differ by only 15%. That is why the assumption that radical cations participate in the dimerization reaction instead of their counterions is not well justified by the achieved agreement between the experimental and calculated TR MFE curves shown in Figure 3a (curve 3). On the other hand, in liquid ethers, namely MG and MTHF, the EPR spectrum of monomer radical anions of *p*TP is observed,<sup>20,21</sup> while dimerization is a typical reaction of radical cations of aromatic compounds.<sup>17</sup>

In high-viscosity solvents like dioxane and eucalyptol (Figure 3b), the rate of scavenging of primary charge carriers becomes less so the TR MFE curves are markedly affected by hyperfine interactions with the precursors of *p*TP radical cations. Interestingly, in monoglyme, which has a viscosity very close to that of THF, the rate of formation of *p*TP radical cations is an order of magnitude less than in THF. This can probably be explained by the properties of the precursor, which yet remain unidentified.

In solvents with a low rate of *p*TP radical ion formation, we failed to verify via the TR MFE technique that in these solvents *p*TP radical cations dimerize quickly, as well as the assumption that radical anions participate in degenerate electron exchange. Nevertheless, it was assumed that dimerization occurred upon encounters of radical cations with other molecules with a high probability in all the solvents under study. The mobility of the charge carriers was determined in the time range when *p*TP radical ions or the corresponding dimers were to have formed.

**Temperature Dependence.** Figure 4 shows the dependencies of the relative mobilities of secondary charge carriers in concentrated *p*TP solutions, which are believed to be solute radical anions and complexes of solute radical cation and neutral molecule, in a number of ethers on reciprocal temperature. Except for solutions in DBE, these dependencies are described well enough by the Arrhenius law. For dibutyl ether, the best approximation was achieved when a dependence of the  $\sim \exp(B/(T - T_0))$  type was used at  $T_0 = 140 \text{ K}$ . Note, in the slightly more viscous MTHF the mobility of the radical ions was found to be higher than in THF across the studied temperature range.



**Figure 4.** The dependence of the relative mobilities of secondary charge carriers in *p*TP solutions in DEE (triangle,  $\Delta$ ), MTHF (solid square,  $\blacksquare$ ), THF (open circle,  $\circ$ ), DBE (solid circle,  $\bullet$ ), DO (open square,  $\square$ ), and EUC (solid triangle,  $\blacktriangle$ ) vs reciprocal temperature  $T$ . Lines are the result of the Arrhenius approximation,  $\mu_s \propto \exp(-E_a/RT)$ .

Table 1 shows the relative mobilities and their apparent activation energies obtained at 293 K from the Arrhenius approximation; also shown are the values of the effective activation energy for the reciprocal viscosity of the solvents under study. Note that even a cursory examination of literature data showed that the scatter in the reported viscosity values is high, sometimes exceeding 10%. So these effective values as evaluated from the Arrhenius approximation of the viscosity at different temperatures are rather approximate and typically are known with accuracy of  $\sim 20\%$ .

As for the experimental points, the lowest accuracy was achieved for solutions in DEE. In this solvent, the decay in fluorescence intensity is comparatively fast, thus resulting in a narrower time frame in which to determine the relative mobility of the geminate ions. Besides, *p*TP solubility was low in this case, especially at lower temperatures, where the concentration was close to its solubility limit. As a result, it seems probable that at 253 K charge carriers in solution in DEE are capable of forming aggregates, which are both more voluminous and slower than dimeric complexes.

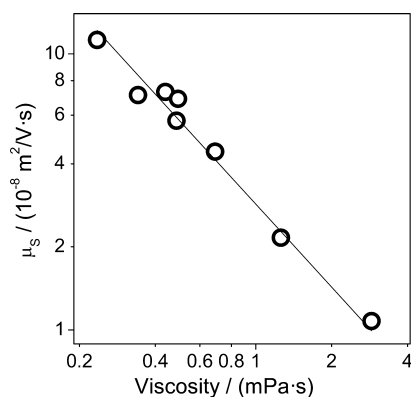
**Viscosity Dependence.** Figure 5 shows that the relative mobility of *p*TP radical ions in the studied ethers is approximately reciprocally proportional to solvent viscosity, i.e., that it approximately follows the well-known Walden's rule,  $\mu\eta = \text{constant}$ . Since the accuracies of the apparent activation energies for both the solvent viscosity and the mobility are comparatively low, it appears likely that Walden's rule can be considered as valid over the studied temperature range.

The results of our work can be compared with the results of diffusion coefficient measurements of lithium salts of polycyclic aromatic hydrocarbons in perdeuterated tetrahydrofuran at 298 K obtained by using the NMR spectroscopy technique.<sup>22</sup> Among the compounds studied in that work were 9,10-dimethylantracene and 9-phenylantracene, with molecular volumes of 124 and 142  $\text{cm}^3/\text{mol}$ , respectively, as determined from the data given in ref 23. The molecular volume of *p*TP amounts to 135  $\text{cm}^3/\text{mol}$ , so the diffusion coefficients of the corresponding anions are expected to be similar. The diffusion coefficients of 9,10-dimethyl-9-hydroanthracene monoanion, 9,10-dimethylantracene dianion, and 9-phenylantracene dianion were reported to be  $9.1 \times 10^{-10}$ ,  $9.1 \times 10^{-10}$ , and

**Table 1.** Values of Solvent Viscosity,  $\eta$ , with Apparent Activation Energy of Reciprocal Viscosity,  $E_v$ , and Relative Mobility,  $\mu_s$ , of Secondary Radical Ions in Concentrated *p*TP Solutions with Mobility Activation Energy  $E_a^a$ 

solvent	$\eta$ /(mPa·s)	$E_v$ /(kcal/mol)	$\mu_s$ ( $\pm 10\%$ )/ $10^{-8}$ m <sup>2</sup> /(V·s)	$E_a$ /(kcal/mol)
diethyl ether DEE	0.235 <sup>b</sup>	1.7	11.2	2.9
methyl <i>tert</i> -butyl ether, MTBE	0.34 <sup>c</sup>	1.9	7.1	1.9
monoglyme, MG	0.44 <sup>d</sup>	2.0	7.3	2.2
tetrahydrofuran, THF	0.485 <sup>e</sup>	1.6	5.7	2.1
methyltetrahydrofuran, MTHF	0.492 <sup>f</sup>	1.9	6.9	2.1
dibutyl ether, DBE	0.69 <sup>g</sup>	2.3	4.4	2.7
dioxane, DO	1.26 <sup>e</sup>	2.8	2.2	4.3
eucaliptol, EC	2.9 <sup>h</sup>	3.9	1.1	5.8

<sup>a</sup>All parameters are given for 293 K. <sup>b</sup>Reference 28. <sup>c</sup>Reference 29 <sup>d</sup>Reference 30. <sup>e</sup>Reference 31. <sup>f</sup>Reference 32. <sup>g</sup>Reference 33. <sup>h</sup>Reference 34.

**Figure 5.** The dependence of the relative mobility of secondary charge carriers in *p*TP solutions at  $T = 293$  K vs ether viscosity (circles). The lines show the approximation of the mobility values according to a  $\propto 1/\eta$  dependence.

$9.4 \times 10^{-10}$  m<sup>2</sup>/s, respectively. Most probably, the absence of a correlation between the size of a diffusant and its diffusion coefficient is to some extent due to measurement uncertainties.

In this work, the individual mobility of the *p*TP radical anion was estimated, assuming that it is the same as that of the radical cation since, at present, there are no data to suggest the difference is significant. Upon dimerization of radical cations the ion's characteristic size increases, thus resulting in reduced mobility. For aromatic ions in alkanes, dimerization decreases the charge carrier mobility by a factor of 1.2–1.6.<sup>3,10</sup> It appears likely that a significant part of the scatter is due to the comparatively low accuracy of the corresponding measurements. In this work, it was assumed that dimerization results in doubling the charge carrier volume and increasing the effective Stokes radius of the cation by a factor of  $\sim(2)^{1/3} \approx 1.3$ . Thus, by using this estimate, it was assumed that anions diffuse by a factor of 1.3 faster than dimeric *p*TP radical cations; that is, the value of  $\mu_a$  was assumed to be 57% of  $\mu_s$  as determined in the experiment. Recalculating the diffusion coefficient of the *p*-terphenyl radical anion by using the viscosity<sup>22</sup> of perdeuterated THF at 298 K based on Walden's rule gave a value of  $8.2 \times 10^{-10}$  m<sup>2</sup>/s.

On the one hand, the results of this work and ref 22 are in quite good agreement since the mobility of the *p*TP radical anion, which is an open shell species, is expected to be slightly lower than the mobility of ions with closed electron shells studied in ref 22. Such an effect of the open shell can be expected based on studies of the diffusion of neutral radicals (ref 24 and works cited therein), where it was found that the diffusion coefficients of molecules are usually larger than those

of radicals with similar volumes formed after hydrogen atom abstraction. On the other hand, a direct comparison of the mobility values is not valid since in solutions of metal salts of polycyclic aromatic hydrocarbons there is always an alkali metal cation in close proximity to the anion. As the example of 9-phenylanthracene showed,<sup>22</sup> substituting a Li cation with other alkali metal cations leads to changes in the observed diffusion coefficient of the negative charge carrier in the range from  $8.1 \times 10^{-10}$  m<sup>2</sup>/s to  $10.6 \times 10^{-10}$  m<sup>2</sup>/s. Therefore, at this stage, the agreement between the different approaches for determining ion diffusion coefficients in THF is only semiquantitative.

It looks likely, the demonstration that there is no essential effect of solvent polarity on diffusion of the radical ions, since the dielectric constants of the solvents used varied from 2.3 (DO) to 7.5 (THF) at 298 K, is the most interesting result of the measurements performed in this work. It is a rather surprising one because changes in the dielectric properties of solvent are expected to change the relative contributions of different components of the friction coefficient, which are viscous friction, the electrostrictive effect on viscous friction, and dielectric friction (see, e.g., ref 25). These components together determine the ion diffusion coefficient. In particular, such a change would be expected for the contribution associated with the electrostrictive effect on friction that was proposed<sup>26</sup> to be the reason for ion diffusion slowing down in nonpolar alkanes.

Data on the transport properties of metal salts of aromatic hydrocarbons reported in ref 22 and mentioned above give additional evidence for the complexity of the problem concerning the effects of solvent polarization around a charge carrier on the diffusion of the latter. In that work, as in many others (see, e.g., ref 27 and references therein), it was observed that in going from neutral molecules to ions the diffusion coefficient in low viscosity solvents typically decreases by a factor of 1.5–2. However, this looks like a threshold effect, since on going from monoanions to dianions the diffusion coefficients are not changed significantly. Most likely, these experimental observations indicate that the mobility of charge carriers in organic solutions is strongly dependent on short-range ion–solvent interactions, which are not properly taken into account in continuum models of the ion transport problem. An obvious approach to clarify experimentally the issue is a detailed analysis of the dependence of ion mobility on the ion's size in various solvents, when such a database can be collected.

## CONCLUSION

As demonstrated by the effects of external electric and magnetic fields on the fluorescence decay curves, the fluorescence

response of irradiated ethereal solutions of *p*-terphenyl is mainly due to the recombination of partially spin-correlated radical ion pairs. Except for dimethoxyethane solutions, the formation rate of the radical cation of aromatic solute is comparable to the rate of binary encounters of molecular species in the solvent. The analysis of magnetic field effects in concentrated luminophore solutions in THF showed the positive charge carrier in the solution to be, very probably, a dimeric complex between a radical cation and a neutral molecule of the solute.

A computer simulation of the ion recombination provided an estimation of the relative mobilities of *p*TP radical ions in the studied ethers. The evaluated mobilities of the *p*TP radical anions in tetrahydrofuran were found to be in semiquantitative agreement with data on the diffusion coefficients of similar anions as obtained by using another technique. The values of relative mobility for the ions are in an approximately reciprocal dependence on the ether viscosity as prescribed by Walden's rule.

Therefore, experiments with *p*-terphenyl solutions have demonstrated that the method of the Time-Resolved Electric Field Effect in recombination fluorescence is applicable for studying transport properties of radical ions generated by ionizing irradiation in polar aprotic solutions such as aliphatic ethers.

## ■ APPENDIX A

In this work, we used a computer model described in ref 35, without accounting for the presence of free radicals or the interaction between ions and solute excited states. The starting point of the simulation is the positioning of four primary positive charge carriers within a sphere with a radius of 2 nm. Solvated electrons were positioned somewhere around corresponding cations with an exponential distance distribution, at an average distance of 4 nm. As mentioned above, particular parameters of the primary spur structure do not noticeably affect the calculated TR EFE curves. Actually, nearly the same results would be obtained even for an isolated primary ion pair. However, with these spur parameters in media with a dielectric constant of 7.5 (THF), the probability of the ions escaping recombination amounts to approximately 0.2. A similar escape probability can be obtained if one puts the initial yield of ion pairs at 4 per 100 eV while the yield of free ions is 0.5 ion pairs per 100 eV, that is, the average value according to data given in ref 36. Besides, at these parameters of the spur, the fraction of recombining geminate ion pairs is nearly the same as is required to provide the experimentally observed plateau level in the time-resolved magnetic field effect ( $\approx 1.25$ , see Figure 3a). Note that this level is very similar to that observed for liquid alkanes.

The electron mobility value was always put at  $1.25 \times 10^{-7} \text{ m}^2/(\text{V}\cdot\text{s})$ . This is the electron mobility in THF at ambient temperature as estimated in ref 37. Changing the electron mobility by a factor of 3 in the model did not affect the calculated curves of the field effects within the accuracy of the stochastic modeling.

Let us note that in our experiments secondary radical ions of aromatic solutes are formed due to scavenging of charged precursors. These precursors are solvated electrons and unknown positive charge carriers. In this work the nature of the latter has not been explored. We assumed without justification that the mobility of the primary positive charge carrier is double the mobility of the solute radical cation. The

scavenging radius of primary charges by the solute was taken to be equal to 1 nm. As was found in the experiments (see discussion of the TR MFE results), in solution one of the carriers quickly forms a dimer complex with a molecule. The dimerization reaction radius in the model was approximately twice as much as the van der Waals radii of *p*-terphenyl molecules, 7 nm. According to the results of ref 10, in cases of such efficient dimerization of charge carriers, it is the dimeric carrier that determines the relative mobility of the geminate ion pairs.

## ■ APPENDIX B

In *p*-terphenyl radical ions, the spin of the unpaired electron interacts with quite a large number of magnetically non-equivalent protons. To describe the evolution of the spin state of a pair consisting of such radicals, the quasi-classic approximation was used.<sup>38</sup> According to the approximation, the probability of finding the radical ion pair in the singlet spin state in the absence of spectral exchange in either a strong (eq B1) or zero (eq B2) magnetic field is given by the following expressions

$$\rho_{ss}^B(t) = \frac{1}{4} + \frac{1}{4} \exp(-t/T_1) + \frac{1}{2} \exp(-t/T_2) G_c^B(t) G_a^B(t) \quad (\text{B1})$$

$$\rho_{ss}^0(t) = \frac{1}{4} + \frac{3}{4} \exp(-t/T_0) G_c^0(t) G_a^0(t) \quad (\text{B2})$$

The rate of effective paramagnetic relaxation, both longitudinal ( $1/T_1 = 1/T_{1a} + 1/T_{1c}$ ) and transverse ( $1/T_2 = 1/T_{2a} + 1/T_{2c}$ ) is the sum of the rates of the corresponding relaxation rates in a strong magnetic field, and  $1/T_0$  approximates the total phase relaxation rate of the radical ion pair in zero magnetic field. The functions  $G^{B,0}(t)$  depend on the parameters of the radical cation (c) and anion (a) and these are described by the following expression:

$$G^B(t) = \exp[-(\gamma\sigma t)^2/2] \quad (\text{B3})$$

$$G^0(t) = \frac{1}{3} [1 + 2(1 - (\gamma\sigma t)^2) \exp[-(\gamma\sigma t)^2/2]] \quad (\text{B4})$$

where  $\sigma^2$  is the second moment of the ESR spectrum of the studied radicals, and  $\gamma$  is the gyromagnetic ratio for the radicals. For *p*TP and *p*TP-*d*<sub>14</sub> radical cations the value  $\sigma_c$  was put at 0.357 mT<sup>39</sup> and 0.074 mT, respectively. For the radical anions  $\sigma_a$  was put at 0.332 mT<sup>20,21,40</sup> and 0.069 mT, respectively. The values for the deuterated radical ions were calculated by using hyperfine coupling constants as determined for protiated compounds. It is assumed that the *g*-values of the radical ions are equal.

To take the self-exchange reaction 3 into account at an arbitrary rate of the reaction, the  $\rho_{ss}(t)$  functions can be calculated numerically. According to ref 38, instead of the  $G_a^{B,0}(t)$  functions the functions  $\Gamma_a^{B,0}(t)$  as determined by eq B5 should be used

$$\Gamma_a(t) = \sum_{n=1}^{n=\infty} G_a^{(n)}(t) \quad (\text{B5})$$

where  $G_a^{(n)}(t) = \tau^{-1} \int_0^t G_a^{(1)}(t') G_a^{(n-1)}(t-t') dt'$  is the term corresponding to the contribution of the random realization of  $(n-1)$  acts of self-exchange by time  $t$ ,  $\tau$  is the mean time between electron jumps, and  $G_a^{(1)}(t) = G_a(t) \exp(-t/\tau)$ .



The TR MFE curves were calculated according to eq B6, which is the convolution of the calculated recombination rate of ion pairs in the singlet spin state with the lifetime distribution of singlet excited luminophores and the apparatus response function

$$I_{B,0}(t) = \frac{1}{\tau_{fl}} \int_{-\infty}^t dt' \exp\left(-\frac{t-t'}{\tau_{fl}}\right) \int_{-\infty}^{t'} dt'' \left[ \theta \rho_{ss}(t'') + \frac{1}{4}(1-\theta) \right] g(t'-t'') F(t'') \quad (B6)$$

Here  $\tau_{fl} = 1$  ns is the luminophore lifetime,  $g(t) = \exp(-t^2/\gamma^2)/(\gamma\pi^{1/2})$  is a function accounting for the time resolution of the experimental setup ( $\gamma \approx 1.2$  ns), and  $\theta \approx 0.25$  is a parameter determining the relative contribution of the pairs born in the singlet-correlated state.  $F(t)$  is a function to approximate the recombination rate of the radical pair, which was assumed to be the same for spin-correlated and noncorrelated radical ion pairs. The recombination rate was approximated by using the expression

$$F(t) \propto \frac{1}{(t_0 + t)^{3/2}} \quad (B7)$$

where the parameter  $t_0 \approx 1$  ns was selected to achieve a visual similarity between the experimental  $I(t)$  curves and that obtained according to eq B6. It should be noted that changing this parameter by a factor of 3 did not noticeably affect the calculated TR MFE curves.

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### Notes

The authors declare no competing financial interest.

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