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Mobility of geminate radical ions in concentrated alkane solutions as measured using electric field dependence of delayed fluorescence

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Abstract

A method using the effect of external electric field on the delayed luminescence of solutes was applied to measure the drift mobility of geminate radical ions. The mobilities of a number of radical ions in alkanes with viscosities varying from 0.24 to 35.4 cP were determined. Mobilities of radical ions were found to correlate with their molecular size but for similar species only. As a specific case, radical cations of polycyclic aromatic molecules were found to exhibit significantly lower mobilities than the olefin and alkane radical cations. (© 2002 Published by Elsevier Science Ltd.

Keywords: Radical ions; Mobility; Recombination fluorescence

1. Introduction

Reactions of radiolytically generated radical ions determine many subsequent stages of chemical transformation of irradiated materials. Since radical ions are very reactive species, the rates of their bimolecular reactions in liquids in many cases are limited by their diffusion mobility. That is why the study of the transport properties of radical ions has been the subject of intense experimental and theoretical efforts for decades. However, up to now, investigation of the diffusion process is still far from its completion (Terazima, 2000; Holroyd and Nishikawa, 2002) and an important reason for that is a scarcity of data on radical ion mobilities due to experimental difficulties in studying of the transient species. Several methods have been developed for determining ion mobility in nonpolar

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liquids. Most common are the direct current (DC) conductivity (e.g., Beck and Thomas, 1972; Allen et al., 1976; Schmidt et al., 1983; Sauer et al., 1996), the microwave (MW) conductivity (e.g., Warman et al., 1977, 1991) and the time-of-flight (TOF) techniques (e.g., Winokur et al., 1975; Haber and Albrecht, 1984; Lim et al., 1994).

The TOF technique is the most direct method, because the quantity measured is the time of drift over a known distance. It is the method in which the ions that escaped geminate recombination move in complete absence of counterions, and the anion or cation mobility can be measured separately with good accuracy. However, because of milliseconds drift times of molecular ions, it is difficult to be certain of the ion identity since there is a possibility of the charge transfer reaction with impurities during the flight (Lim et al., 1994).

To study the migration of ions on a shorter time scale (e.g., nanoseconds) after their formation, the two other techniques, giving nanosecond (MW conductivity) or subnanosecond (DC conductivity) time resolution, should be employed. Because on the nanosecond time scale geminate recombination is the main pathway for

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disappearance of the ions, computer simulation should be used to analyse the signals (Schmidt et al., 1983; Sauer et al., 1996). For mobility measurements, these techniques are less direct than the TOF method, because the quantity extracted from experiments is the sum of the mobilities of anions μ^- and cations μ^+ :

$$\mu_{\rm S} = \mu^- + \mu^+$$

This is an inevitable restriction because at a short time scale, an ion is at a relatively short distance from its counterion and both of these oppositely charged ions contribute to the conductivity signal.

In spite of the variety of the mobility measurement techniques, there are some discrepancies in the reported values of radical ion mobilities. For instance, for concentrated biphenyl solutions in *n*-hexane at room temperature, the $\mu_{\rm S}$ values of $0.72 \times 10^{-3} \,{\rm cm}^2$ (V s) (Winokur et al., 1975) and $2.0 \times 10^{-3} \,{\rm cm}^2$ (V s) (van den Ende et al., 1984) were reported.

A new experimental approach to the investigation of transport properties of radical ions in nonpolar solutions was developed in our recent works (Borovkov et al., 1995, 1997). It uses the transient quenching of delayed radiofluorescence decay curves by a static external electric field and is referred to as time-resolved electric field effect (TREFE).

It is well established that the main reaction pathways leading to solute fluorescence in solutions of aromatic additives under irradiation are given by the following reaction scheme:

$$\mathbf{RH} \rightarrow \mathbf{RH}^{+} + \mathbf{e}^{-}, \tag{1}$$

$$\mathbf{R}\mathbf{H}^{+} + \mathbf{e}^{-} \to \mathbf{R}\mathbf{H}^{*},\tag{2}$$

$$e^{-} + A \rightarrow A^{-}, \tag{3}$$

$$\mathbf{R}\mathbf{H}^{+} + \mathbf{D} \rightarrow \mathbf{R}\mathbf{H} + \mathbf{D}^{+},\tag{4}$$

$$\mathbf{D}^+ + \mathbf{e}^- \to \mathbf{D}^*,\tag{5}$$

$$\mathbf{R}\mathbf{H}^{+} + \mathbf{A}^{-} \rightarrow \mathbf{R}\mathbf{H} + \mathbf{A}^{*}(\mathbf{R}\mathbf{H}^{*} + \mathbf{A}), \tag{6}$$

$$D^{+} + A^{-} \rightarrow D^{*} + A(D + A^{*}),$$
 (7)

$$\mathbf{A}^* \left(\mathbf{D}^* \right) \to \mathbf{A} \left(\mathbf{D} \right) + hv. \tag{8}$$

Here RH is solvent molecule, reaction (1) proceeds under ionizing irradiation, A and D are acceptors of excess electrons (e^-) and solvent holes (RH⁺), respectively. A^{*} and D^{*} are the solutes in their singlet excited states. The fluorescence from the solute singlet excited states indicates that radical ion pair recombination has occurred. This scheme is deliberately simplified. In particular, energy transfer from excited solvent molecules to A or D molecules is not included. For the purposes of the present paper, it does not lead to serious errors, because in concentrated alkane solutions, this process is important only within the first several nanoseconds (Sauer et al., 1991).

Because the external electric field affects the motion of ions and decreases the recombination probability, it also quenches the fluorescence intensity. To analyse the transient influence of the electric field, the ratio $I_{\rm E}(t)/I_0(t)$ of the fluorescence decay curves detected with applied static electric field and without it was proposed to be used. The ratio was shown to be determined by sum of geminate ion mobilities and to be insensitive to the initial distribution of ions (Borovkov et al., 1995; Anishchik et al., 1996). The TREFE technique also allows studying radical ions of additives that do not display noticeable yield of fluorescence from the excited state if their counterion is a good luminophor.

In this paper, results on the measurements of mobilities of a number of radical ions by the TREFE method are presented. The studied radical ions were believed to be relatively stable and they were chosen first of all for fluorescence properties of corresponding molecules. Many of the obtained values are published for the first time.

2. Experimental

The luminescence of alkane solutions was observed by single photon counting using the X-ray fluorimeter described elsewhere (Anishchik et al., 1989; Borovkov et al., 1997). The duration of the ionizing pulse was < 2 ns. The light was collected using an optical bandpass filter (260-390 nm). The cuvette for measuring the effects of external electric field was constructed from diamagnetic materials and was described elsewhere (Borovkov et al., 1997). Electric field strength of up to 45 kV/cm was used. To decrease the influence of instrumental drift. fluorescence decays were recorded for periods of 250s, alternatively, with and without electric field using computer control. In this work the method of timeresolved magnetic field effect was also applied (Brocklehurst, 1997; Klein and Voltz, 1977; Bagryansky et al., 2000). The magnetic field effect curves were obtained by the same procedure that was used for electric field effects. In such case the cuvette was placed into the external magnetic field instead of electric one. Zero magnetic field was adjusted to within $\pm 0.05 \,\mathrm{mT}$; a nonzero magnetic field as large as 0.1 ± 10^{-3} T was applied.

To exclude nonsaturated impurities, normal and cyclic alkane solvents (Aldrich, Fluka) were stirred with concentrated sulphuric acid, washed with water, distilled over sodium and passed through a 1 m column of activated alumina. *iso*-Octane and 2,3-dimethylbutane were passed through a 1 m column of activated alumina only. Using gas chromatography, we found that the hydrocarbon solvents used contained alkane isomers.

These alkane isomers could not be removed from alkane solvents with the purification method used. However, these impurities are expected not to affect our measurements of mobilities of solute radical ions. The concentration of unsaturated hydrocarbon impurities was < 10 ppm.

Tolan (diphenylacetylene), 2,5-diphenyl-1,3,4-oxadiazole (PPD), *trans,trans,*-1,4-diphenyl-1,3-butadiene, 1,4diphenylbutadiyne, hexafluorobenzene (C₆F₆), benzene, 2,3-dimethyl-2-butene (TME), 2,3-dimethyl-1,3-butadiene, 1-pentene, 1-heptene, 1-octene, 1-decene, *c*hexene, *cis*-cyclooctene, 2,4,4-trimethyl-2-pentene, 9,10octalin (1,2,3,4,5,6,7,8-octahydronaphthalene), 2,6,10, 15,19,23-hexamethyl-2,6,10,14,18,22-tetracosahexaene (squalene), were used as recieved from Aldrich. 1^2 , 2^3 , 3^2 , 4^3 -tetramethylquaterphenyl (TMQP) was synthesized in the Institute of Chemical Kinetics and Combustion of Sibirian Branch of RAS.

The solutions were degassed by repeated freezepump-thaw cycles. All measurements were made at 293 ± 0.5 K.

3. Results and discussion

3.1. Mobility of radical ions as estimated by the method of electric field effect

According to our previous work (Anishchik et al., 1996), the influence of an external electric field on delayed fluorescence of solutes is independent of mobilities of primary electrons and solvent holes if a solute concentration is 10^{-2} M or more. Even though the solvent holes are captured with the rate of a diffusion-controlled reaction for solvents with viscosity of about 1 cP and the time range of the caption exceeds the resolution of the experimental set-up, the difference between the mobilities of the holes and the solute radical cation has no time to become apparent at this concentration. Taking it into account, in the present work, solute concentrations of both aromatic and nonaromatic compounds ranged from 10^{-2} to 10^{-1} M when possible.

Fig. 1 shows experimental curves of the ratio $Q(t) = I_{\rm E}(t)/I_0(t)$ at 36 kV/cm for solutions of 10^{-2} M tolan in various alkanes on a semilogarithmic scale. Here $I_{\rm E}(t)$ and $I_0(t)$ are intensities of fluorescence decay curves detected from these solutions with applied static electric field and without it, respectively. According to data on electron affinity and gas-phase ionization potential (IP) of tolan molecules (Werst, 1996; Kondratyev, 1974), excess electrons and solvent holes are captured by the solute effectively in alkane solutions. The generation of the tolan radical cations (reaction 3) is much slower than the formation of anions (reaction 2). However, the typical time of the radical cation formation at used

Fig. 1. Time dependence of the ratio of fluorescence intensities at 36 kV/cm and zero electric field for 10^{-2} M of tolan in *n*-hexane (1), *n*-octane (2—solid line), methylcyclopentane (2—circles), *iso*-octane (2—triangles), *n*-decane (3), cyclohexane (4), cycloheptane (5), hexadecane (6) and squalane (7).

acceptor concentration does not exceed 10–20 ns except for the case of squalane. Thus, the fluorescence within the time domain used for Fig. 1 corresponds mainly to recombination of secondary geminate radical ions that arise after scavenging of the primary charge carriers by tolan molecules.

The dependence of Q(t) curves presented in Fig. 1 on time is evidently close to exponential and the slope of these curves obviously relates to solvent viscosity that ranges from 0.31 cP for *n*-hexane (curve 1) to 35.4 cP for squalane (2.6.10.15.19.23-hexamethyltetracosanecurve 7) at 293 K. It is in accordance with results of our previous works (Borovkov et al., 1995, 1997), where the dependence of the ratio Q(t) on time, external electric field strength E and the sum of the mobilities of geminate radical ions $\mu_{\rm S}$ was estimated. It was shown that the dependence was close to exponential and this was determined by the product $(E^2 \mu_{\rm S} t)$ when recombination of the geminate radical ion pairs was a diffusioncontrolled process. The dependence of O(t) curves on the electric field strength in the studied time range was tested for field strength from 24 to 45 kV/cm and the agreement with results of the previous works (Borovkov et al., 1995, 1997) was observed. Besides, one can estimate by scaling of time axis for the slope of the Q(t)curves that they are approximately proportional to inverse solvent viscosity that corresponds to expected dependence for solute radical ions in accordance with Walden's rule (Schmidt, 1997).

Figs. 2a and b demonstrate electric field effect curves for *n*-decane solutions of different additives and

1.0



dependencies of the curves on solute concentrations. In Fig. 2a, solid lines 1 and 2 show the Q(t) curves for 10^{-2} M solutions of tolan and TMOP, respectively. Scatter plots corresponding to 10^{-1} M solutions of the same additives follow in the same relative position and indicate that the relative mobility of the ions becomes lower with increasing solute concentration. In Fig. 2b the O(t) curves for *n*-decane solutions of *c*-hexene as solvent holes acceptor and hexafluorobenzene (C_6F_6), as electron acceptor and luminophor, are shown. The solid line corresponds to 10^{-2} M of the solutes. With an increase in the *c*-hexene concentration up to 10^{-1} M, no changes take place in Q(t) curves (shown with circles) unlike the case of C_6F_6 when such increase results in slowing the radical anions mobility (shown with triangles).

Using the ratio of the slopes of the Q(t) curves for a 10^{-2} M solution, one can estimate that the $\mu_{\rm S}$ values for 10^{-2} M solutions of TMQP, tolan and C₆F₆ with *c*-hexene are related as 0.6:1:1.5, respectively. This difference in their mobilities apparently results from different radii of the radical ions. For 10^{-1} M solutions, the $\mu_{\rm S}$ values within a time range up to 100 ns are lowered by a factor of 1.14, 1.25, and 1.4, for tolan, C₆F₆, and TMQP solutions, respectively. Moreover, these factors for the two last solutions display a tendency to increase at a longer time range.

In regard to the process responsible for the decrease in aromatic radical ion mobilities, it is dimer or cluster radical ion formation that comes to mind first. Such aggregate ions for many of both anions and cations were observed (see, e.g., Kira and Imamura, 1979; Desrosiers and Trifunac, 1985, 1986; Mehnert, 1991; Werst, 1996; Lim et al., 1994; Majima et al., 1997) and the formation of these species should be taken into account.

A simple estimation based on Stoke's law gives that dimer formation results in doubling of the ion volume and in lowering of the mobility of the ion, would be lowered by a factor of about $2^{1/3} \approx 1.26$. If only one of the ions composing a radical pair dimerizes, then μ_s value would be lowered by a factor of about 1.12. Thus, it is likely for tolan solutions that only one kind of the ions composing a radical pair dimerizes. The decrease in $\mu_{\rm S}$ value by a factor of 1.4 for TMQP solution seems to be caused by such process for both cation and anion radicals. In the case of hexafluorobenzene solutions, it should be taken into account that this solute forms a radical anion and does not capture solvent holes due to high ionization potential (Kondratyev, 1974). Thus, any concentration-dependent decrease in μ_s value for the solutions is to be assigned to a process involving negative charge carriers only. For this case, one can estimate that the corresponding decrease of the radical anion mobility is about 1.5. Such values are within the range 1.2-1.6 experimentally obtained by Lim et al. (1994) for the ratios of monomer anion mobilities to dimer ones for various acceptors calculated using the data presented in Table 1 in the mentioned work.

As for the case of c-hexene radical cations, it is known that many olefins dimerize in alkane solutions (Desrosiers and Trifunac, 1986; Mehnert, 1991) effectively and the dimerization is a diffusion-controlled reaction. As



Fig. 2. Time dependence of the ratio of fluorescence intensities at 36 kV/cm and zero electric field for *n*-decane solutions: (a) of 10^{-2} and 10^{-1} M of tolan (solid line 1 and circles, respectively), and of 10^{-2} and 10^{-1} M of TMQP (solid line 2 and rectangles, respectively); (b) of 10^{-2} M C₆F₆ and 10^{-2} M c₆F₆ and 10^{-2} M C₆F₆ and 10^{-1} M c₆F₆ and 10^{-2} M c₆F₆ and 10^{-2}

was mentioned above, if such a high rate were so, the cation mobility measured in concentrated solutions of olefins would correspond to the cation formed last, i.e. to the dimer cation. That is why no changes in Q(t) curve take place with increase in the concentration of *c*-hexene. Results on nonaromatic compounds are discussed in more detail below.

Although TREFE measurements give only the sum of the mobilities of anions and cations, it is possible to conclude what kind of the charge carriers dimerize effectively in tolan solutions. Both electron affinity and ionization potential for C₆F₆ molecules are higher as compared to tolan ones (Werst, 1996; Kondratyev, 1974). When both of these acceptors are present simultaneously in the solution, recombination fluorescence will arise from recombination of the pairs ($C_6F_6^-/$) tolan⁺). The concentration-dependent change in μ_s value was determined for n-decane solutions of tolan in a concentration ranging from 10^{-2} to 10^{-1} M in the presence of 10^{-2} M C₆F₆. The presence of C₆F₆ molecules was found not to influence noticeably the decrease in the $\mu_{\rm S}$ value. Thus, if radical ion dimerization takes place in the solution of tolan, then the radical cations dimerize more effectively as compared to the radical anions.

3.2. Study of dimerization of tolan and TMQP radical ions using the method of magnetic field effect

To clarify the nature of geminate radical ions for the tolan and TMQP solutions, the method of time-resolved magnetic field effect in the fluorescence of excited luminophor molecules being formed by recombination of spin-correlated radical ion pairs was used (Brocklehurst, 1997; Klein and Voltz, 1977; Bagryansky et al., 2000). This method analyses the ratio $I_{\rm B}(t)/I_0(t)$ of the fluorescence decay curves detected with applied static magnetic field $I_{\rm B}(t)$ and without the field $I_0(t)$. The method allows to get information on ESR spectra of the short-lived radical ions in solutions under the same conditions and within the same time scale as those used for electric field effect experiments. In this work, the method of magnetic field effect is used for a qualitative study only to avoid an unwieldy presentation.

Figs. 3a and b demonstrate the time-resolved magnetic field effect curves $I_{\rm B}(t)/I_0(t)$ at $B=0.1 \,{\rm T}$ for *n*decane solutions of tolan and TMQP in concentrations of 10^{-2} M (solid curves 1) and 10^{-1} M (circles), respectively. Curves 2 in the Figs. 3a and b correspond to 10^{-3} M solutions of the same additives in cyclohexane. For acceptor concentrations being equal to both 10^{-3} and 10^{-2} M, magnetic field effect curves exhibit a shape that is typical of the case when radical pair partners have unresolved ESR spectra and the contribution of phase relaxation to spin dynamics is not very large (Schulten and Wolynes, 1978). If ESR spectra of radical ions composing geminate pairs differ considerably, then the time position of the maximum on the curves is determined by ESR spectrum width σ of the radical that has a wider spectrum and the position is of about $1.6/(\gamma\sigma)$ where γ is the gyromagnetic ratio (Borovkov et al., 2002). In the case when the counterion also has a wide spectrum so that their spectrum widths are approximately equal, the maximum time position becomes shifted to the moment of about $1/\sigma$.



Fig. 3. Time dependence of the ratio of fluorescence intensities at 0.1 T and zero magnetic field: (a) for solutions of tolan in concentration of 10^{-2} M in *n*-decane (solid curve 1); 10^{-3} M in cyclohexane (solid curve 2); 10^{-1} M in *n*-decane (circles); (b) or solutions of TMQP in a concentration of 10^{-2} M in *n*-decane (solid curve 1); 10^{-3} M in cyclohexane (solid curve 2); 10^{-1} M in *n*-decane (circles).

In cyclohexane solutions, radical ions of most aromatic compounds are formed very quickly due to a very high mobility of primary solvent holes and electrons, and the magnetic field effect is determined by the dynamics of the spin state of the radical pair which includes radical anion and radical cation of solutes (Bagryansky et al., 2000). For the purposes of this work, it is important that in the cyclohexane solutions the magnetic field effect curves have the maximum at approximately the same time as compared to 10^{-2} M solutions in *n*-decane. Thus, in these solutions, radical ions that recombine within the first 50 ns are likely to be the same. The rate of constant of diffusioncontrolled reaction in cyclohexane at room temperature is of about $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and at the solute concentration as large as 10^{-3} M, it is improbable that the radical ions of tolan and TMOP in this solution within the first 50 ns are more complex than monomer radical ions. This suggests that in 10^{-2} M *n*-decane solutions, the geminate radical ions also exist mostly as monomers. This also implies that the rate of the possible reaction between the radical ions and neutral solute molecules in n-decane is lower than the diffusion-controlled one at least by an order of magnitude because radical ion dimerization is known to lead to a delocalization of an unpaired electron spin density over two molecules that is to result in time displacement of the maximum of magnetic field effect curve towards a later moment.

When the solute concentration is increased up to 10^{-1} M, the radical ions dimerize/aggregate faster and narrowing of ESR spectra of radical ions is to become apparent at an earlier moment. ESR spectrum widths of radical cations and anions of even alternant hydrocarbons are known not to differ significantly (Carrington and McLachlan, 1967). This is believed to be valid for the radical ions studied, too. If only one of the radicals dimerizes then its spectrum width becomes decreased by a factor of $(2)^{1/2}$ and the magnetic field effect curve changes slightly. The opposite case is that when both cations and anions aggregate and considerable delocalization of spin density takes place and maximum on the curve of field effect becomes shifted to a large extent.

As it is easy to see from Figs. 3a and b, at the highest concentration used, the maximum of magnetic field effect curve for TMQP solutions, unlike solutions of tolan, becomes shifted considerably towards longer times. This shift should be interpreted as narrowing of ESR spectra of both radical cations and radical anions. Thus, in agreement with the electric field results, in solutions of TMQP both radical cations and radical anions display a tendency to form aggregates including several species whereas the only type of radical ions of tolan is likely to dimerize.

Because of a considerably wider ESR spectrum of $C_6F_6^{-\bullet}$ as compared to hydrocarbon species, it is difficult

to carry out a conclusive study for hexafluorobenzene solutions by the way just described for solutions of tolan and TMQP. However, $C_6F_6^{\bullet}$ radical anion is known to exhibit an ability to form a cluster including several neutral molecules (Nakajima et al., 1993) and decreasing of the anion mobility with increasing concentration of C_6F_6 may be explained as well as for the case of radical ions of tolan and TMQP.

3.3. Mobility of aromatic radical ions as determined with computer simulation

To determine radical ion mobility values, we use a computer simulation of geminate ion recombination by the same way that was described in a previous work (Anishchik et al., 1996). Briefly, the simulation was started from a single (electron/solvent hole) pair. The initial distance between the ions was varied from one realization to the next in accordance with the literature data on electron thermalization distance (Freeman, 1987). The movement of the charge carriers due to random diffusive motion and to the drift in attractive Coulombic force and the external field was calculated using the known parameters of the charged species and of the solvents. The capture of the charge carriers was described by changing their mobility values according to the rates of reactions (3) and (4). If the positive and negative ions reacted, the calculation for that ion pair was terminated. The intensity of recombination fluorescence at a certain moment of time was determined as the number of ion pairs with luminophor as one of the partners that recombined at the moment. Besides, dynamics of the spin state of radical ion pairs is independent of electric field and this factor was not taken into account.

To estimate the individual mobilities of geminate radical ions using $\mu_{\rm S}$ value, an additional assumption concerning the relative magnitude of counterion mobilities is needed. There is some experimental evidence that radical cations and anions of polyaromatic molecules have approximately equal mobilities in nonpolar solution. Several authors have reported the mobilities of anions and cations in *n*-hexane solution of diphenyl at room temperature to be nearly identical (Allen et al., 1976; Winokur et al., 1975). It was also demonstrated with the improved TOF technique (Lim et al., 1994) that the mobilities of pyrene radical anions and cations in *n*hexane coincided within the experimental accuracy of $\pm 5\%$. Taking this into account, we assume the mobilities of radical cations (μ^+) and radical anions (μ^{-}) of aromatic molecules used as charge acceptors to be the same and to be equal to $(\mu^+ + \mu^-)/2$. As it will be shown below, the assumption is in accordance with the TREFE experiment.

Fig. 4 shows the experimental (solid line) and simulated (scatter plots 1, 2 and 3) Q(t) curves for the



Fig. 4. Time dependence of the ratio of fluorescence intensities at 36 kV/cm and zero electric field for solution of 10^{-2} M tolan in *n*-decane at E=36 kV/cm (solid line) and simulated curves for $\mu^+ = \mu^- = 2.3 \times 10^{-4}$ cm²/V s (triangles) and $\mu^+ = \mu^- = 2.0 \times 10^{-4}$ cm²/V s (rectangles), no dimerization; for $\mu^+ = \mu^- = 2.3 \times 10^{-4}$ cm²/V s for monomers and $\mu^+ = 1.6 \times 10^{-4}$ cm²/V s for dimer radical cations (circles). The rate constant of reaction (9) was 6×10^8 M⁻¹ s⁻¹.

solution of 10^{-2} M of tolan in *n*-decane. The values of 0.038 and $3.8 \times 10^{-4} \text{ cm}^2/\text{V}$ s were chosen for mobility of excess electrons (Freeman, 1987) and solvent holes, respectively. The procedure of the measuring of the latter value by TREFE method will be described below. The corresponding reaction rate of capturing of the primary charges were about $10^{12} \text{ M}^{-1} \text{ s}^{-1}$ for electrons and about $2 \times 10^{10} \,\mathrm{M^{-1} \, s^{-1}}$ for holes. Changes in the mobility values by a factor from 0.3 to 3 did not result in noticeable modification of Q(t) curves. Simulated curves 1 and 3 were computed assuming that no changes of mobilities of secondary radical ions generated via reactions (3) and (4) occurred. The values of the fixed mobilities were equal to 2.3×10^{-4} and 2.0×10^{-4} cm²/ Vs, respectively. It is evident that the experimental Q(t)curve cannot be covered with the theoretical ones under this assumption. To improve the agreement, taking into account the concentration dependence of O(t) curves in tolan solutions, a dimerization of radical cations was included:

$$\mathbf{D} + \mathbf{D}^+ \to \mathbf{D}_2^+. \tag{9}$$

The cation D_2^+ was assumed to participate in reactions (5) and (7) in a similar way as D^+ cation, but with a different reaction rate due to its lower mobility. In other words, both the yield of solute excited states in these reactions and the fluorescence yield in

reaction (8) were assumed to be independent of the nature of the charge carrier. The assumption is not expected to introduce significant errors into the results of the measurements, because variations of the quantum yield of recombination are independent of comparatively weak electric field used in our experiments. The variations in fluorescence yield appear identically in the numerator and the denominator of the Q(t) definition as time-dependent multipliers. If the fluorescence yield difference is not dramatic, then the I(t) curves change but the Q(t) curve does not.

In the present work, we have restricted the computer model to the simple case of radical ion dimerization as introduced by reaction (9). However, the reaction seems also to be the simplest way to take into account both the process of the dimerization and the process of aggregation, which can progress in time. If the computer simulation gave a too large decrease in the mobility of the dimer radical ion as compared to monomer ion, it would be an evidence of the radical ion aggregation.

Simulated curve 2, giving a good agreement with the experiment, was computed assuming reaction (9) occurred with a rate constant of $6 \times 10^8 \,\mathrm{M^{-1}\,s^{-1}}$, i.e. about one-tenth of the diffusion-controlled reaction rate. Mobility value for D_2^+ was assumed to be lower than that for D^+ by a factor of 1.4. A similar agreement with experiment could be achieved using a rate constant ranging from 0.3×10^9 to $10^9 \,\mathrm{M^{-1}\,s^{-1}}$. To fit the experimental curve at a larger (lower) value of the constant, the mobility value for D_2^+ should be increased (decreased) by a factor of about 1.15–1.2. These variations do not influence significantly the most suitable value of the monomer radical ion mobility.

To test the assumption of the equality of mobilities of oppositely charged radical ions of tolan and to compare the TREFE method with the improved TOF technique (Lim et al., 1994), the measurements of μ_S values in solutions of 10^{-2} M tolan with and without 10^{-2} M hexafluorobenzene in *n*-hexane at 24° were carried out. These experimental conditions correspond to that of TOF experiments (Lim et al., 1994) where for the $C_6 F_6^{-6}$ radical anion mobility, the value of $8.9 \times 10^{-4} \text{ cm}^2/\text{V} \text{ s}$ was determined with an accuracy of about $\pm 5\%$. As was pointed above, when both tolan and C_6F_6 molecules are present simultaneously in the solution, the measured $\mu_{\rm S}$ value corresponds to the sum of tolan⁺ ($\mu_{\rm T}$) and $C_6F_6^{-\bullet}$ (μ_{HFB}) mobilities. The value of μ_T may be estimated using $\mu_{\rm S}$ value for 10^{-2} M tolan solution. In this solution, the value of $(1.26\pm0.1)\times10^{-3}$ cm²/V s was obtained for the sum of geminate radical ion mobilities. Using the tested assumption, one can estimate the value of $\mu_{\rm T}$ to be about $(6.3 \pm 0.05) \times 10^{-4} \,{\rm cm}^2/{\rm V}\,{\rm s}$. After adding 10^{-2} M C₆F₆, the $\mu_{\rm S}$ value increases to $(1.49\pm0.15)\times10^{-3}$ cm²/Vs and for the mobility of radical anion $\mu_{\rm HFB} = \mu_{\rm S} - \mu_{\rm T}$, a value of $8.6 \times 10^{-4} \, {\rm cm}^2/$ Vs was obtained with an accuracy of about 10%.

Table 1

Computer simulation for this case included the reaction of radical anion dimerization:

$$\mathbf{A} + \mathbf{A}^{-} \to \mathbf{A}_{2}^{-}.\tag{10}$$

Properties of the radical anion A_2^- except for its mobility were assumed to be the same as those of the anion A⁻. A better agreement between simulation and experiment was achieved when the rate of reaction (10) was about one-tenth of a diffusion-controlled one and the mobility value of A_2^- was assumed to be lower than that of A^- by a factor of about 1.5. According to results obtained by Lim et al. (1994), in n-hexane solution the mobility of the dimer radical anion $(C_6F_6)_2^{-\bullet}$ is lower by a factor of 1.2 as compared to the monomer one. It is unclear what causes a larger value of the factor in TREFE experiment. However, variations of mobility value of dimer radical anion A_2^- within the range up to 30% make worse the agreement between the experimental curve and the theoretical ones beyond 150 ns but do not result in a noticeable change in monomer mobility that is mainly determined by the earlier part of Q(t) curve.

The good agreement between the values of $C_6F_6^-$ radical anion mobility obtained with different techniques allows us to conclude that the assumption of the equality of mobilities of oppositely charged radical ions of tolan is adequate. Besides, the described procedure of the mobility measurement of $C_6F_6^-$ is believed to be appropriate for using in cases of other solvents. It is notable that the use of TMQP as acceptors instead of tolan results in a close value for the anion mobility but accuracy of such measurements is lower due to larger influence of radical ion aggregation.

The computer simulation was also performed for solutions of tolan in various alkanes. Table 1 summarizes the obtained values of $\mu_{\rm S}/2$ that are assigned to the tolan monomer ions in the solvents. The mobilities of radical ions of several luminophores in *n*-decane and some other alkanes were determined with the procedure as described above for the tolan radical ions. The results are presented in Table 2. For polyaromatic molecules other than tolan and diphenylbutadiyne, a better accordance between the simulated and experimental Q(t) curves was achieved when reactions (9) and (10) took place simultaneously. Their rates were obtained to be about one-tenth of the diffusion-controlled reaction rate and the mobility values of radical ions A_2^- and D_2^+ were lower than that for monomer radical ions by a factor of about 1.4-1.5. In the case of TMQP solutions, this value was as large as 1.6. Such a rather high value is likely to be the consequence of the aggregation of the radical ions that cannot be described adequately by reactions (9) and (10).

As shown in Table 2, the relative mobility values of radical ions of used aromatic solutes apparently correlate with their molecular size. Though magnetic Estimated mobilities ($\mu_{\rm S}/2$) of tolan ions in liquid alkanes at 293 K

Mobility, $10^{-4} \text{ cm}^2/\text{V} \text{ s},$ $\pm 10\%$	Solvent viscosity ^a at 293 K (cP)
6.8	0.24
5.4	0.31
5.0	0.44
3.8	0.51
3.7	0.55
3.4	0.34
3.8	0.51
2.9	0.71
2.9	0.73
2.3	0.91
1.9	0.98
1.6	1.50
1.4	1.5 ^b
1.1	2.12
0.9	2.2 ^b
0.8	3.45
0.7	3.37
0.13	35.4
	Mobility, $10^{-4} \text{ cm}^2/\text{V s}$, $\pm 10\%$ 6.8 5.4 5.0 3.8 3.7 3.4 3.8 2.9 2.9 2.9 2.3 1.9 1.6 1.4 1.1 0.9 0.8 0.7 0.13

^a Alkane viscosities at 293 K were taken from Tatevski (1960) and Chu and Thomas (1990).

^bExtrapolation from viscosities at 286 K (Tatevski, 1960; CRC Handbook of Chemistry and Physics, 1987).

field effect measurements were performed for the cases of tolan and TMQP solutions only, the correlation allows us to confirm the mobility values corresponding to monomer radical ions of aromatic solutes.

Two aromatic solutes that in most studied solvents capture only one of the primary charge carriers are also included in Table 2. Hexafluorobenzene does not capture solvent holes in most alkanes and the mobility of $C_6F_6^{-\bullet}$ radical anion was estimated as it was described above for *n*-hexane solution. The molecule of benzene does not form radical anions in hydrocarbon solutions, but it captures solvent holes effectively. The procedure of measuring of the ion mobilities in benzene solutions is described in the further sections.

3.4. Measurement of mobility of olefin radical cations

To study the transport properties of olefin radical cations, *n*-decane was chosen as a solvent. Decane solutions of $10^{-2}-10^{-1}$ M C₆F₆ and of $10^{-2}-10^{-1}$ M of olefins were used. Under these conditions, the delayed luminescence arised mainly from the recombination of C₆F₆⁻⁶ or (C₆F₆)² radical anions and positive charge carriers that originate from the capture of solvent holes by olefins. The mobilities of positive charge carriers were estimated as $\mu^+ = \mu_{\rm S} - \mu_{\rm HFB}$. The mobilities of radical cations of benzene as well as squalane and *trans*-decalin

Table 2 Estimated mobilities ($\mu_S/2$) of radical ions in alkanes at 293 K

Radical ion	Solvent	Mobility, $10^{-4} \text{ cm}^2/$ V s, $\pm 10\%$
Tolan ⁺⁽⁻⁾ (diphenylacetylene) ⁺⁽⁻⁾	<i>n</i> -Hexane	5.4
	<i>n</i> -Decane	2.3
	Squalane	0.13
2,5-Diphenyl-1,3,4- oxadiazole $^{+(-)}$ (PPD) $^{+(-)}$	<i>n</i> -Hexane	4.4
	<i>n</i> -Decane	1.9
	Squalane	0.12
$1^{2},2^{3},3^{2},4^{3}$ - Tetramethylquaterphenyl ⁺⁽⁻⁾ (TMOP) ⁺⁽⁻⁾	<i>n</i> -Hexane	3.8
(<i>n</i> -Decane	1.6
	Squalane	0.06
Diphenyl ^{+(-)a}	<i>n</i> -Decane	2.5
<i>trans,trans,</i> -1,4-Diphenyl-1,3 butadiene $^{+(-)}$	<i>n</i> -Decane	2.2
1,4-Diphenylbutadiyne ⁺⁽⁻⁾	<i>n</i> -Decane	2.0
Hexafluorobenzene ⁻ $(C_6F_6^-)$	<i>n</i> -Hexane	8.0
	Cyclopentane	6.0
	iso-Octane	4.5
	Methylcyclohexane	4.0
	<i>n</i> -Decane	3.4
Benzene ₂ ^{+ b}	<i>n</i> -Decane	3.7

^a The mobility value is determined with an error about $\pm 20\%$ because of a longer fluorescence lifetime of diphenyl molecules as compared with other aromatic solutes used.

^bSee discussion on measurement of olefin radical cation mobility.

having a sufficiently low IP to capture solvent holes in decane were measured in the same way. Electric field effect in *n*-decane solutions of C_6F_6 as the only solute was used to estimate the solvent hole mobility in *n*-decane. This value was obtained to be about $3.8 \times 10^{-4} \text{ cm}^2/\text{V} \text{ s}$ and it was used in computer simulations.

First of all it should be noted that the TREFE technique in the present work failed to detect any concentration-dependent decrease in the cation mobility in the solutions of used olefins except for *cis*-cyclo-octene. As it is mentioned above, it may be interpreted as the result of an effective dimerization of olefin radical cations (Mehnert, 1991).

Tał	ole 3
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Estimated mobilities ($\mu_{\rm S}-\mu_{\rm PFB}$) of positive charge carriers in decane solutions of various olefins at 293 K

Solute	Charge carrier detected	Mobility, $10^{-4} \text{ cm}^2/$ (V s), $\pm 10\%$
2,4,4-Trimethyl-2-pentene	Ol^+	4.2
cis-Cyclooctene	Ol^+	3.5
	Ol_2^+	2.7
2,3-Dimethyl-2-butene	Ol_2^+	3.7
(TME)		
Cyclohexene	Ol_2^+	3.7
2,3-Dimethyl-1,3-butadiene	Ol_2^+	3.1
1-Pentene	Ol_2^+	3.1
1-Heptene	Ol_2^+	2.8
1-Octene	Ol_2^+	2.6
1-Decene	Ol_2^+	2.3
9,10-Octalin	Ol_2^+	2.9
trans-Decalin ^a	$C_{10}H_{18}^+$	4.1
Squalene	Ol_2^+	2.2
Squalane ^a	$C_{30}H_{62}^+$	2.7

^aSee text for explanations.

Benzene radical cation is also believed to dimerize with a diffusion-controlled reaction rate (Kira and Imamura, 1979; Miyoshi et al., 1997). At the same time, there is also an acceptor, 2,4,4-trimethyl-2-pentene, which exhibits both no concentration dependence and a significantly larger mobility of its cation as compared to other similar molecules (e.g., 1-octene). This radical cation is not likely to dimerize in the time range studied due to the sterical hindrance. Radical cations of squalane and *trans*-decalin are also believed to form no dimers.

In Table 3, the mobility values estimated for monomer radical cations of olefins (marked as Ol⁺) and dimer radical cations (Ol₂⁺) are presented. These values were determined taking into account that the reaction of olefin cations dimerization (10) was diffusion-controlled, i.e. of about $10^{10} \text{ M}^{-1} \text{ s}^{-1}$, for all cases except for 2,4,4trimethyl-2-pentene and *cis*-cyclooctene. For the latter, the better accordance between experimental and simulation results was achieved when the rate of reaction (10) was assumed to be about one-fifth of this value.

It is possible to estimate approximately the mobilities of squalene and 9,10-octalin monomer radical cations. The mobilities of radical cations of squalane and *trans*decalin having similar structures may be used as references. The alkane solute concentrations were chosen high enough to prevent solvent hole decay. Though the solute alkane radical cations are expected to decay in nanosecond time domain, the only product of the decay, that yields fluorescence, would be a corresponding olefin cation isolated in alkane solvent (Mehnert, 1991). The mobilities of the cations are also included in Table 3. According to the results from the table, the decrease in the mobilities of the olefin cations after dimerization is approximately equal to factors of 1.2 for squalene, 1.3 for cyclooctene, and 1.4 for 9,10-octalin.

4. Concluding remarks

In this work, some measurements of the radical ion mobilities in liquid alkanes using the time-resolved electric field effect technique and computer simulation are presented. The mobilities of a number of radical ions in alkane solutions at 293 K were determined. To test the TREFE method, the mobility of hexafluorobenzene radical anion was measured in experimental conditions that were used in the time-of-flight experiments reported in (Lim et al., 1994). A very good agreement with the TOF technique results was obtained.

As reported in a previous work (Anishchik et al., 1996), no noticeable effect of a change in the electron thermalization distance on the shape of Q(t) curves was observed in the computer modelling. Now, it is confirmed experimentally by the example of *n*-octane, methylcyclopentane, and *iso*-octane solutions (curves 2 in Fig. 1). These solvents have close viscosities and corresponding Q(t) curves are almost identical, while the mean electron thermalization distances in these hydrocarbons are about of 6.4, ~7, and ~9 nm, respectively (Freeman, 1987).

It was observed that mobilities of radical ions in concentrated solutions of the aromatic solutes used became lower with time. This decrease in the mobilities may be described with computer simulation if the transformation of radical ions with a rate of about one-tenth of the diffusion-controlled reaction was included. The charge carrier mobility after the transformation was found to decrease by a factor of about 1.3–1.6. The value 1.6 is likely to display an aggregate radical ion formation.

For olefin radical cations, such factor for the decrease of the cation mobility due to dimerization was estimated to be about 1.2–1.4. These factors are similar to that obtained by Lim et al. for slowing down of radical anion mobility due to dimerization, and we conclude that radical ion dimerization is likely to be the main reason of the observed transient decrease in the ion mobility in the studied solutions.

It remains unclear why many of the estimated rate constants of dimer cation formation for the used aromatic solutes are about one-tenth of the rate of diffusion-controlled reaction. For instance, different radical cations are expected to dimerize with different rates, from diffusion-controlled rates to much slower ones, e.g. due to intramolecular rotation of phenyl group (Saik et al., 1985; Kira and Imamura, 1979). However, in the present work, the precision of the estimations of the transient decrease in mobilities of radical ions is quite low and the conclusion on the rate of an aggregation of radical ions with neutral solute molecules is not certainly proved.

According to the results of the present work, mobility values of ions correlate with their molecular sizes but for similar species only. By comparison of Tables 2 and 3, it is evident that cations of polycyclic aromatic molecules exhibit significantly lower mobilities than the olefin and alkane cations. As a specific example, radical ions of tolan and squalane have the mobilities of 2.3 and $2.7 \times 10^{-4} \text{ cm}^2/\text{Vs}$ despite the fact that van der Waals volumes for corresponding close-shell molecules are about 108 and 290 cm³/mol (Bondi, 1964), respectively. Within the studied olefins, straight 1-alkenes exhibit a lower mobility of radical cations as compared to other species. Probably, the observed difference in mobilities is determined by a different intermolecular charge polarization of the radical ions. Such an interaction is believed to result in a slow diffusion of radicals as compared with neutral molecules (Terazima and Hamaguchi, 1995; Okamoto et al., 1998). For long-chain species like squalane radical cations in solvent with smaller molecular size, it may be also an important factor that fragments of the cation move rather independently as compared with those of aromatic ions. Such long nonrigid ions seem to migrate "part by part" and their effective size becomes smaller.

In practical terms, though the mobility of radical ions exhibits the expected approximately inverse dependence on the solvent viscosity of order 1-10 cP, there are some deviations from linear dependence. For example, the viscosity values for n-hexane, n-decane and squalane relate as 0.34:1:39 but the reciprocal ion mobility values of tolan ion in these solvents relate as 0.43:1:18. respectively. For some branched alkanes, the deviation is even greater. Interestingly, the ratio between mobility values of a radical ion, as measured for two different solvents, is similar to that measured for the other ion. For instance, the ratio between the mobility values measured in n-hexane and n-decane for tolan, hexafluorobenzene, TMQP, and diphenyloxazole radical ions lies within 2.3–2.4. Using the ratio, one can estimate the radical ion mobility more precisely than using the ratio between solvent viscosities.

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