Indications for unequal rates of ion-molecular charge transfer reaction for biphenyl radical anion and cation from MARY and OD ESR spectra

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Abstract

MARY and Optically Detected ESR techniques were used to infer that radical cation and radical anion of biphenyl in concentrated hexane solutions have substantially different second moments of their ESR spectra. This observation is interpreted in terms of different types of processes between the two radical ions and the neutral parent molecule. It is suggested that dimerization is prevalent for biphenyl radical cation, while biphenyl radical anion is rather involved in fast ion-molecular charge transfer reaction.
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1. Introduction

The processes of degenerate electron exchange (DEE) between a radical ion and its parent molecule (ion-molecular charge transfer) in solution are one of the simplest model processes that a charge and spin can participate in. They are also often an intrinsic property of the system, and play an important role in the studies of primary radiation chemical reactions in irradiated non-polar solutions that involve radical ions. Often correct interpretation of experimental data is impossible without due account of the DEE. In non-polar solutions DEE processes are normally diffusion-controlled, and thus the rate constant for DEE reaction is a universal characteristic of the solvent and its temperature, provided that sizes of the species do not differ substantially. However, generally the rate constant for DEE reaction is specific for each type of radical ion in each particular solvent, and does not necessarily have to be equal for radical anion (1) and radical cation (2) of the same substance, although this has not been often described.

$$A + A^- \Longleftrightarrow A^- + A \qquad (1)$$

$$D + D^+ \Longleftrightarrow D^+ + D \qquad (2)$$

This work reports such a peculiar behaviour of biphenyl radical ions in liquid *n*-hexane, observed by Optically Detected ESR and MARY spectroscopy.

Biphenyl is the simplest possible representative of *para*-phenylene oligomers, charge transfer in which is now being thoroughly examined in view of their suggested application of molecular wires [1]. Biphenyl molecule in *n*-hexane solution can accept both negative and positive charge to produce radical anion and radical cation, respectively, and has appreciable quantum yield of fluorescence, which is required by the optically detected techniques. Biphenyl also dissolves in hexane in concentrations up to hundreds of mM, which is required to cover a range of DEE rates.

2. Experimental

Optically detected magnetic field effects and ESR under X-irradiation were recorded in stationary conditions as described in [2,3], respectively. The sample, containing about 1 ml of degassed solution in a quartz cuvette, is put into magnetic field of a Bruker ER-200D CW X-Band ESR spectrometer equipped with an X-ray tube for sample irradiation (Mo, $40\,kV \times 20\,mA$), a pair of coils with a separate current source to provide constant 'negative' shift of the field (for MARY experiments), and a PMT for fluorescence detection. The scanned magnetic field is modulated at a frequency of 12.5 kHz with an amplitude up to 1 mT. A Stanford SR-810 Lock-In Amplifier and computer averaging over 20–40 scans are used to get MARY and ODESR spectra, obtained as the first derivatives of the actual field dependencies. Microwave power for OD ESR experiments was 0.2–0.3 W. MARY experiments were carried out without microwave pumping. All experiments were carried out at room temperature ($20 \pm 3\,°C$).

The solvent – *n*-hexane – was stirred with concentrated sulphuric acid, washed with water, distilled over sodium and passed through a column of activated alumina. Biphenyl ($C_{12}H_{10}$) served as electron and hole acceptor and was used without further purification.

3. Results

3.1. Experimental MARY spectra

A first-derivative MARY spectrum in the vicinity of zero field consists of the zero field line and conventional magnetic field effect (MFE) in the opposite phases [4]. The width of the MFE B_p (the distance from the zero of the field to the maximum of the first derivative) is determined by second moments of the ESR spectra of radical ions of the pair. As shown in the works [5,6], in the assumption of Lorentzian shape of the conventional MFE B_p is given by the following expression:

$$B_p = \frac{2(\sigma_1^2 + \sigma_2^2)}{\sigma_1 + \sigma_2}, \tag{3}$$

where

$$\sigma_k = \sqrt{\sum_i \frac{a_{ik}^2 I_{ik}(I_{ik}+1)}{3}} \tag{4}$$

is the second moment of radical k, a_{ik} and I_{ik} are the hyperfine coupling constant and nuclear spin of the *i*-th nucleus of radical k, and the sum runs over all nuclei in the radical. If $\sigma_{1,2}$ of the pair partners are close to each other and do not exceed about 1 mT, the zero field line does not develop, and MARY spectrum consists solely of the MFE [7]. Qualitatively, the presence of the

zero field MARY line for $\sigma_{1,2}$ of that order of magnitude indicates that they are substantially different.

Fig. 1 shows a selection of MARY spectra for solutions of biphenyl in *n*-hexane for several concentrations of the acceptor.

It can be seen that at the lower concentrations of acceptor (top curves) the spectra show only MFEs (and an apparent inflection that is reproduced in simulations, see Fig. 4), which first widen and then grow narrower, until at 10^{-1} M (trace d) the zero field line appears.

Such a behaviour of the spectra is consistent with transformations of $\sigma_{1,2}$ caused by DEE. At low concentrations the processes of exchange are not important, and the observed spectra come from pairs with individual radical anion and radical cation of biphenyl. Hyperfine couplings for the two radical ions are known: 4H:0.315 mT; 4H:0.051 mT; 2H:0.63 mT for Biph$^+$ [8] and 4H:0.264 mT; 4H:0.037 mT; 2H:0.532 mT for Biph$^-$ [9], yielding $\sigma_1 \approx 0.55$ mT, $\sigma_1 \approx 0.46$ mT, and $B_p \approx 1.05$ mT, consistent with trace a. The transformations of MFE follow the transformations of σ as the system passes through the region of slow charge transfer (widening) into the region of exchange narrowing. However, the zero field line present at the lowest trace indicates that the second moments of the two partners became substantially different. The tentative explanation
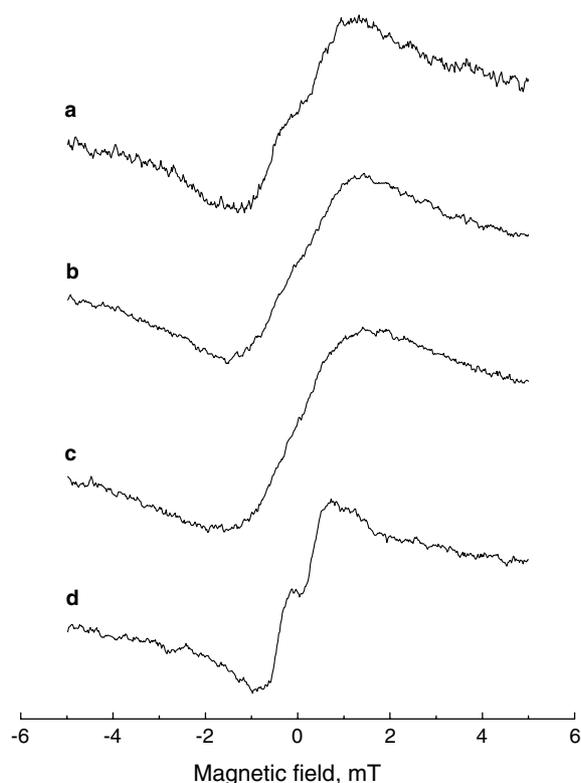
Fig. 1. MARY spectra of hexane solutions of biphenyl at concentration: (a) 1.6×10^{-3}, (b) 10^{-2}, (c) 3×10^{-2}, (d) 10^{-1} M.

for this experimental observation is that the rate of DEE reaction is different for radical cation and radical anion of biphenyl in *n*-hexane.

3.2. Experimental OD ESR spectra

Further support for the suggestion on different rates of DEE reaction for the two species came from OD ESR spectra of biphenyl solutions in *n*-hexane for different concentrations of the acceptor, a selection of which is shown in Fig. 2.

As can be seen, increasing solute concentration up to 10^{-1} M (Fig. 2(d)) leads to substantial narrowing of the spectra. The figure also shows the results of simulations of the spectra as superposition of spectra from two species A and B in WinSim free simulation package [10], with the results collected in Table 1.

Here, LS is the characteristic of the line shape (0 for pure Gaussian, 100 for pure Lorentzian, and inbetween for their superposition), and LW is the characteristic of the line width, which in our case of unresolved single line is equal to σ for Gaussian line and $\sigma\sqrt{3}$ for Lorentzian line.

The table shows that for the lowest included concentration (1.6×10^{-3} M) the widths of the two superimposed spectra are close to each other and are consistent
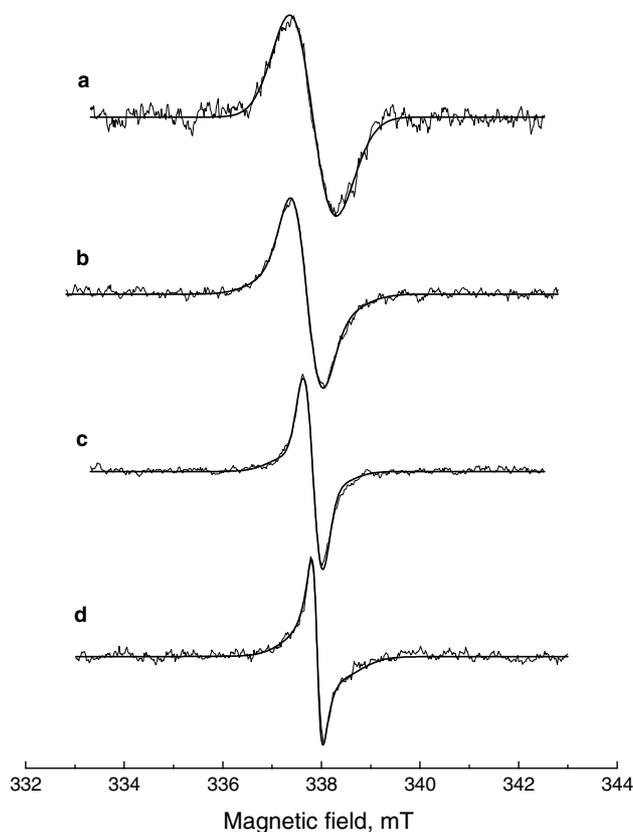
Table 1
Results of OD ESR spectra simulation

Concentration (M)	1.6×10^{-3}	10^{-2}	3×10^{-2}	10^{-1}
LW_A (mT)	0.56	0.60	0.51	0.49
LS_A	0.0	0.0	0.0	0.0
LW_B (mT)	0.48	0.31	0.21	0.18
LS_B	0.0	0.0	0.0	94.5

See text for discussion.

with the second moments of the ESR spectra of individual biphenyl radical ions ($\sigma \approx 0.55/0.46$ mT). As the concentration is increased, line width of the first partner LW_A first slightly increases and then goes down by about 20%. The line of the second partner LW_B becomes substantially narrower, and at concentration of 10^{-1} M the best fit for the experimental spectrum is produced with the widths of the two lines differing nearly three times. A plausible explanation is that as the concentration is increased, one of the partners goes into the region of slow to intermediate charge transfer (this is indicated by a certain increase in LW_A at concentration 10^{-2} M) and stays there, while the rate of DEE for the second partner grows steadily, as it enters the region of fast charge transfer.

Further indications come from the line shape parameter $LS_{A,B}$. The spectra for the lower concentration are best fit with Gaussian lines (zero LS), corresponding to inhomogeneous ESR spectra of both partners, while at the highest displayed concentration the line for partner B becomes practically Lorentzian ($LS = 94.5$). This means that at high concentration of acceptor the spectrum of partner B becomes practically homogeneous, as it should be in the region of fast DEE.

3.3. Comments on Simulation of OD ESR spectra

OD ESR spectra were modelled in standard ESR simulation package WinSim [10] intended for simulation of conventional ESR spectra rather than OD ESR spectra. However, the package allows superposition of spectra from several independent radicals, and with sufficient accuracy for this work the OD ESR spectrum can be represented by superposition of two spectra corresponding to two partners of the radical ion pair. Each partner was represented by a single unresolved line, for which shape and width were determined from fitting the experimental spectra. To reduce the number of the varied parameters to a minimum the fractions of the two spectra were kept fixed and equal to 50%, corresponding to equal amounts of biphenyl radical anions and radical cations in the recombining pairs – a valid assumption at high concentration of the acceptor.

The main goal of the simulations was verification that spectra for samples with high concentration of biphenyl (Fig. 2(d)) consist of two superimposed lines

Fig. 2. OD ESR spectra of hexane solution of biphenyl at concentration: (a) 1.6×10^{-3}, (b) 10^{-2}, (c) 3×10^{-2}, (d) 10^{-1} M (noisy traces) and their simulation (smooth curves).

with substantially differing widths. In principle, such a featureless spectrum can be fit with a single line, but we know that these particular spectra consist of two lines from the two partners of the pair. When two lines are introduced into simulation, the fitting reproducibly yields different lines with parameters given in Table 1.

To help see that the spectrum is indeed the declared superposition, Fig. 3 shows its components at the background of experimental spectrum from Fig. 2(d): only the narrow line (a), only the broad line (b), the two lines shown separately (c), and the two lines added together with equal weights (d), producing the simulated curve of Fig. 2(d). The two components of the simulation were in fact obtained simultaneously by fitting the experimental spectrum and are shown individually only to help visualize the results of modelling.

When analysing results collected in Table 1 it should also be taken into account that the produced parameter LW for Gaussian and Lorentzian line shapes differs by $\sqrt{3}$ for lines of the same peak-to-peak widths. This in turn means that at concentration 10^{-1} M the actual line width for the partner B with LS = 94.5 is still lower.

Finally we note that the values of the line shape parameter LS in Table 1, although given with one decimal place as produced by computer fitting, should not be taken as an accurate measure of the line shape. These are provided to demonstrate the trend for only one of the partners to assume Lorentzian line shape with increasing concentration of the acceptor, which is indicative for the region of fast charge transfer.

3.4. Simulation of MARY spectra

To obtain numerical parameters of the rates of DEE reaction for the two biphenyl radical ions, we attempted to simulate experimental MARY spectra. The theoretical counterpart of the MARY spectrum, the singlet product yield function $G_s(B)$, can be written as:

$$G_s(B) = \int_0^\infty \rho_{ss}(B,t)f(t)\,\mathrm{d}t, \tag{5}$$

where $\rho_{ss}(B,t)$ is population of the singlet state of the radical ion pair, and $f(t)$ is its recombination kinetics.

Assuming diffusion model of the recombination kinetics, $f(t)$ is written as:
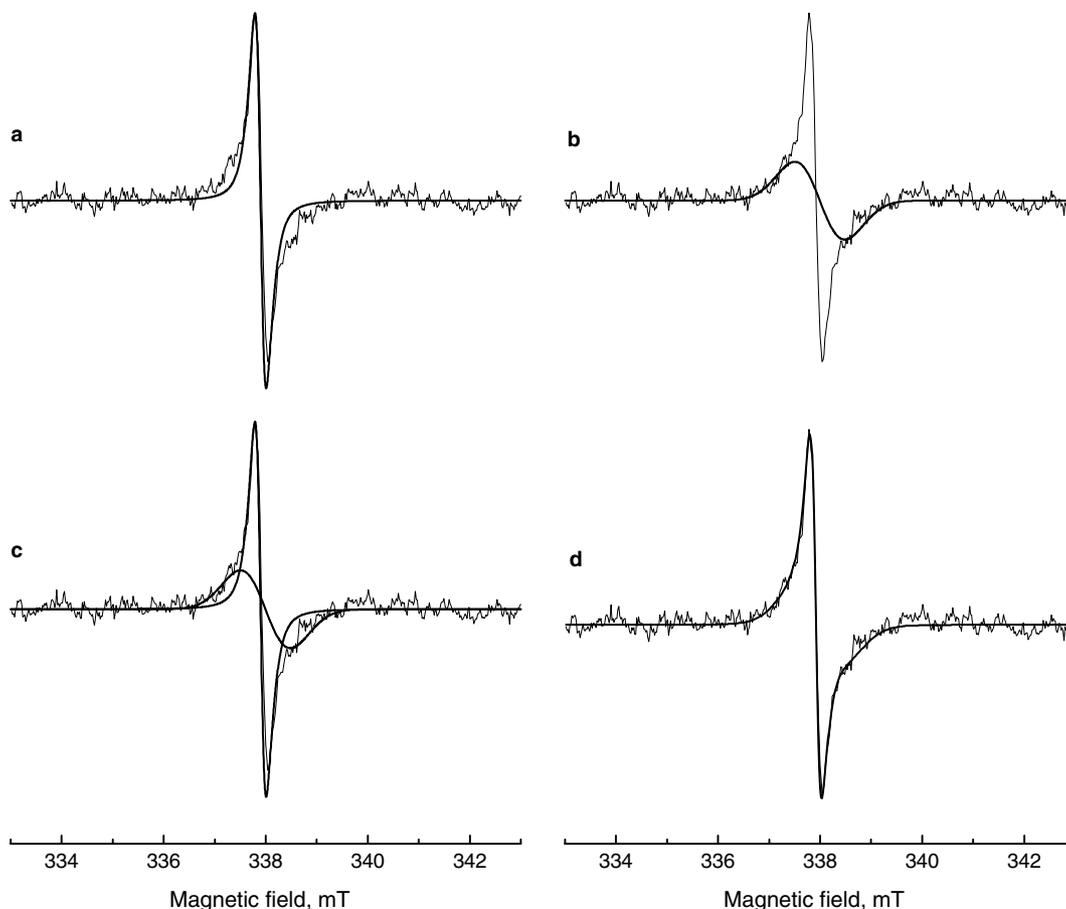
Fig. 3. Breaking down the simulated spectrum from Fig. 2(d) into individual components: (a) only the narrow line, (b) only the broad line, (c) the two lines shown separately, (d) the two lines added together with equal weights.

$$f(t) = at^{-3/2} \exp(-b/t) \qquad (6)$$

with

$$a = \frac{r_\sigma(r_0 - r_\sigma)}{r_0 \sqrt{4\pi D}} \qquad (7)$$

and

$$b = \frac{(r_0 - r_\sigma)^2}{4D}. \qquad (8)$$

The parameters of this model are the mutual diffusion coefficient D, the initial separation of the radicals r_0, and the recombination distance r_σ. Although these intrinsic parameters can not be directly applied in the situation of radiolysis in non-polar solution, meaningful values of effective parameters a and b can nevertheless be chosen [11]. These were taken to be $a = 0.06$ ns$^{1/2}$ and $b = 0.04$ ns in the presented simulations, although their particular values are not critical.

The patterns of equivalent nuclei in both radical cation and radical anion of biphenyl are identical (4:4:2) and coincide with the pattern for radical cation of pyrene treated in [6]. We thus used the approach developed for work [6] to perform the calculations of spin evolution with explicit consideration of the hyperfine structure of the biphenyl radical ions and DEE reactions for both ions, followed by numerical evaluation of the integral (5). The same pattern 4H:0.315 mT; 4H:0.051 mT; 2H:0.63 mT was used for both radical ions to simplify calculations, as the two sets of coupling are rather close to each other.

Fig. 4 shows the simulation of experimental MARY spectra for solutions of 1.6×10^{-3} M and 10^{-1} M biphenyl in *n*-hexane for several combinations of the two characteristic exchange times of the pair partners $\tau_{1,2}$ (the inverse of the exchange rate) in the range from 1 to 300 ns. As can be seen, the simulation yields conventional MFE curves with equal $\tau_{1,2}$, and the curve with large $\tau_{1,2}$, corresponding to negligible DEE, reproduces the low concentration spectrum including the inflection at zero field. The simulation also reproduces the zero field line at the trace for high concentration of acceptor fairly well when the two times are substantially different. However, the MFE portion of the simulated curve is always broader than the experimental trace: the B_p value for the experimental spectrum is about 0.7 mT, while the simulation produces 1.1–1.2 mT. Similar results were also obtained for simulations with several other diffusion-like recombination kinetics having $t^{-3/2}$ asymptotics [12], as well as exponential recombination kinetics. Thus we can state that irrespective of the model chosen to describe recombination of the pairs the simulations taking into account only DEE processes fail to reproduce the experimentally observed narrowing of the MFE at high concentrations of acceptor.
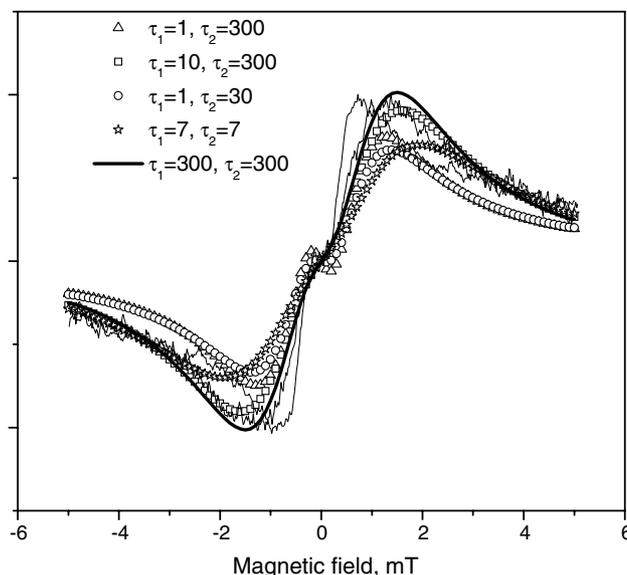
Fig. 4. Simulation of MARY spectra with different characteristic exchange times (nanoseconds) of the pair partners. The two noisy traces are experimental spectra for solutions of 1.6×10^{-3} M and 10^{-1} M biphenyl in *n*-hexane (the wider and the narrower spectrum, respectively).

4. Discussion

Briefly summing the experimental results, we see that the two radical ions of biphenyl at high concentrations of acceptor in *n*-hexane have different effective second moments σ (from MARY and OD ESR), and that the smaller σ corresponds to homogeneous line, while the larger σ corresponds to inhomogeneous line (from OD ESR). Furthermore, explicit consideration of the hyperfine structure of the partners and consistent description of DEE processes are not sufficient to reproduce the experimental observations in simulation (from MARY). Apparently some other processes should be involved. Finally, it is not clear whether it is the radical anion or the radical cation, for which the pronounced spectral narrowing is observed, although the spectra at low concentration of acceptor suggest that it is the radical anion.

First, we note that DEE is only one limiting case of the possible spectrum of interactions between radical ions and their parent neutral molecules in solution. The opposite limiting case is dimerization, or more generally, aggregation of neutral molecules around the radical ions. It is clear that there is a continuum of processes inbetween the two limits that differ by the relative stability of the formed encounter complex 'radical ion – neutral molecule', and theoretical treatment of the ensuing complexities can be found in [13]. We shall discuss here only the simple limiting case of pure dimerization that produces stable dimers and completely removes the radical ion from DEE.

Dimeric and higher aggregate radical cations have been repeatedly reported in literature and often called

upon to explain experimental results (see, e.g., [14–16] and references therein). Kinetic behaviour of the radical cation at rather high acceptor concentration is a common point of discussion since effective scavenging of positive charge in irradiated non-polar solution requires concentrations of hole acceptor about 10^{-2} M or higher, as opposed to scavenging of highly mobile electron, where concentration of electron acceptor of 10^{-4} M or lower are quite common. Pure dimerization leads to reduction of σ for the radical ion by at most $\sqrt{2}$ (for symmetric dimer) and leaves the line inhomogeneous. This inhomogeneity was clearly demonstrated when spin locking was observed in OD ESR spectra [14] at high concentrations of acceptor in similar systems (10^{-1} M biphenyl-d_{10} or naphthalene-d_8 in squalane). The theory of OD ESR [17] shows that had both partners of the recombining pair had homogeneous ESR spectra due to fast DEE, no locking would have been observed. Formation of aggregates including n molecules would reduce σ by at most $\sqrt{n}$.

The published quantum chemical calculations show that a neutral molecule of biphenyl is not planar, and the values ~40°–50° [18] were reported for the angle between the phenyl rings. A non-planar D_2 conformation with twist angle ~20° was reported for biphenyl radical cation on the basis of analysis of its resonance Raman spectra [19], while a planar D_{2h} structure is favoured for biphenyl radical anion. It is thus reasonable to suggest that it is the radical cation that is in more favourable conditions to form a stable dimer with its parent molecule. The situation is similar to description of bonding between two subunits in a molecule in terms of molecular orbital (MO) theory: other conditions being equal, the closer the geometry of electron distribution and the closer the two orbitals in energy, the stronger the interaction [20].

Dimeric radical anions have also been occasionally reported in non-polar solutions (see, e.g. [21,22] and references therein), but they are much less common than the ubiquitous radical cation aggregates. The published examples mostly refer to radical anions of fluorinated compounds such as octafluoronaphthalene [21]. As concluded in the detailed studies of concentrational behaviour of radical anions in n-hexane [22], DEE rather than dimerization is prevalent in these conditions for a broad range of organic electron acceptors.

The general tendency for the radical anions to form less stable dimers than radical cations can also be rationalized using a MO analogy [20]: when two degenerate orbitals combine to form a bonding and an antibonding MO, energy gain in formation of the bonding orbital is always less than energy loss due to formation of its antibonding counterpart. Thus a removal of an electron from the lowest occupied antibonding MO to form 3e–2c bond, as in a radical cation dimer, should be preferable to addition of an electron to the upper nonoccupied

bonding MO to form 1e–2c bond, as in a radical anion dimer. The planar structure of biphenyl radical anion as opposed to twisted structure of the neutral molecule is an additional argument supporting this inference in our particular case of biphenyl, which was not studied in [22]. Thus, we suggest that radical anion is the partner that undergoes faster DEE, while radical cation is rather prone to dimerization.

Let us check the consistency of the observed OD ESR spectra with the suggested origins of spectral transformations. In experiment we see a substantial narrowing of one line (σ_B drops by about $3\sqrt{3}$, or about 5 times) that changes its shape from Gaussian (inhomogeneous) to Lorentzian (homogeneous), and a much smaller narrowing of the other line (by a factor of about 1.2) that remains Gaussian, when the concentration of acceptor is raised to 10^{-1} M. Assuming diffusion-controlled DEE reaction with rate constant 2.1×10^{10} M^{-1}s^{-1} for n-hexane at room temperature, and halving the rate constant because of probability 1/2 to pass electron in a single diffusion encounter of the radical ion with its parent molecule [23], we get characteristic exchange time $\tau_c \approx 1$ ns at concentration of acceptor 10^{-1} M. With $\sigma \approx 0.5$ mT this translates into $\sigma\tau_c \approx 10^{-1}$, and we thus fall in the region of fast charge transfer, where the line becomes homogeneous with $\sigma_{red} \approx \sigma^2\tau_c \approx 0.05$ mT. The two times greater value of 0.1 mT extracted from fitting OD ESR spectra implies that DEE in this case is not completely diffusion controlled, which is attributed to conformational difficulties: the same reasons that presumably prevent the radical anion from forming a dimer complicate DEE because of poor Frank–Condon factor and substantial medium reorganization that is required to switch from twisted to planar geometry and vice versa. The other, inhomogeneous, line with smaller reduction in σ can be ascribed to a dimer, probably participating in the DEE reaction but at a slower rate [13].

As has already been stated, the DEE reaction for both partners alone cannot account for the observed transformation of MARY spectra, see Fig. 4. However, the 5-fold reduction of σ_B by aggregation would require a cluster of at least 25 molecules, which is dubious, and thus aggregation alone also cannot describe the changes in experimental spectra. We thus, suggest that in this particular system different mechanisms, or rather different limiting cases, of interaction between the short-lived radical ion and its parent neutral molecule are realized: dimerization for the radical cation, reducing its σ by $\sqrt{2}$, and DEE for the radical anion, reducing its σ by a factor of 5. Although direct consistent simulation of the dimeric radical cation is currently not possible due to doubled number of magnetic nuclei in such a dimer, simple calculation using Exp. (3) shows that this reduction in $\sigma_{A,B}$ would indeed bring B_p down from 1.05 mT down to 0.66 mT, bringing simulation in agreement with

experiment in Fig. 4. Similar conclusions were also drawn in already cited study of spin locking [14], but on a different experimental ground. Although more direct experimental evidences are obviously desired, we believe this suggestion to be reasonable.

And in conclusion we would like to stress two points. First, although the numbers on which the reasoning of this work is based come mostly from OD ESR results, the motivation and clue of this study come from MARY spectra. As is often the case, OD ESR spectra for this system are featureless single lines, and it takes an external reason to try to analyse them in detail and decompose them into several components. In this case, the reason was provided by the zero field MARY line, which clearly indicated that $\sigma_{A,B}$ of the pair partners became substantially different. Certainly, 'better' spectra can be obtained in a more diluted, or more cooled, or more viscous solution, but this would have altered the system significantly. We were interested in this particular system – concentrated solution of biphenyl in warm *n*-hexane.

Second, these results and discussion once again show that often the explicit account of DEE, even the most involved and consistent, is not sufficient for reproduction of experimental data at high concentrations of hole acceptors as routinely found in experiment, and some other mechanisms should be called upon. The implication for an experimentalist is that in these situations it may be more adequate to revert to simple limiting cases such as slow DEE, fast DEE, pure dimerization, etc., which are very transparent and straightforward to apply, rather than indulge in very involved calculations that in effect do not cover the physics of the situation. Clearly a deeper understanding of the radical ion–neutral molecule interaction in concentrated solutions is required, and intuition should be developed – the points, already raised in works [13,16].

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