

Selective quenching of magnetic field effect for radical ion pairs with widely different hyperfine couplings

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ABSTRACT

The effect of selective quenching of magnetic field effect by a non-selective chemical reaction due to different rates of spin evolution in radical pairs is demonstrated. In the case of several parallel radical pairs a more rapid disappearance of magnetic signal from a pair does not mean a faster chemical decay of the underlying pair, if the hyperfine couplings in the pairs are significantly different. The presence of two signals with different sensitivity to quencher in the spectrum gives the effect of internal standard and helps to extract quantitative information from the intensities rather than widths of signals in spectra.

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1. Introduction

One of common approaches to measure the rates of chemical reactions is measuring the efficiency of quenching in a certain process as a function of quencher concentration, followed by determination of the quenching rate constant from the slope of the efficiency vs. concentration plot. A convenient method to estimate the rates of fast reactions involving short-lived radical ion pairs in non-polar solution is provided by Magnetically Affected Reaction Yield (MARY) spectroscopy [1,2] based on spin effects in reactions of spin-correlated radical ion pairs. The method takes advantage of a narrow feature ('line') on the curve of stationary magnetic field effect (MFE) in the vicinity of zero field, which arises due to degeneracy of spin levels of the radical pair in zero magnetic field [3–5]. The width of the line depends on the coherent lifetime of the pair as B_{pp} (mT) = $\frac{6.6}{\tau(\text{ns})}$ and increases with decreasing the lifetime, e.g., as a result of a chemical reaction leading to decay of the radical ions [6]. The width is determined by exponential processes, such as reaction with a quencher M with pseudo monomolecular rate constant $k[M]$, spin relaxation ($T_1 = T_2 = T_0$ in weak field), and monomolecular decay (with characteristic time τ_0), scaled by power-law geminate recombination kinetics [7]. In the conditions of a pseudo isolated zero field line, when its width is much less than the width of magnetic field effect $B_{1/2} = 2 \frac{\sigma_1^2 + \sigma_2^2}{\sigma_1 + \sigma_2}$, the contributions of these processes are additive. Thus the rates of reactions can be measured from the plots of the measured width of MARY line vs. quencher concentration M [8,1]. Here σ_1^2 and σ_2^2 are the second moments of ESR spectra of the two pair partners

$\sigma = \sqrt{1/3 \sum a_i^2 I_i(I_i + 1)}$, a_i are hyperfine coupling constants with nuclei of spin I_i , and the sum runs over all magnetic nuclei in the corresponding radical ion. For convenience the values $\sigma_{1,2}$ will be further referred to as effective hyperfine couplings. This approach has been used, e.g., to measure the rate constants of the reaction of alkane radical cations with alcohols [9] and the rate constant of radical ion quenching by molybdenum hexacarbonyl [10], which were found to be close to the diffusion controlled limit.

Determination of rate constants from line broadening in MARY spectra is in general similar to using line broadening in ESR. However, as opposed to magnetoresonance techniques, in MARY spectra all magnetic field effects and all MARY lines, if present, are centered at the zero of magnetic field and thus all overlap. This requires particular attention when using a narrow MARY line for determination of rate constants in radiation chemistry, taking into account the unavoidable multitude of the types of radical ion pairs under high-energy irradiation.

The key processes that proceed in X-irradiated alkane solutions when taking a MARY spectrum can be represented by the following scheme:



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where S is the solvent and PTP is an aromatic luminophor and charge acceptor, in this case *para*-terphenyl-*d*₁₄. Its functions are to form the radical ion partner of the pair via an almost instantaneous capture of free electrons produced by ionization (reaction 2), and then to recombine with the radical cation emitting a quantum of luminescence (reaction 3). The deuteration of PTP helps reduce intrinsic hyperfine couplings (HFC) in the radical anion to simplify spin evolution of the pair, which in this case is driven by its radical cation.

The primary solvent radical cation S⁺ could have been expected to participate in the observed reaction of recombination (reaction 3) as a partner with narrow ESR spectrum due to fast degenerate electron exchange with parent solvent molecules [11]. However, a fast process of capturing S⁺ always proceeds in *n*-alkane solvents to form a radical cation with a broad ESR spectrum S_b⁺ ascribed to radical cation of a branched isomeric alkane (reaction 2'). In our case chromatomass measurements show trace amounts of 2-methylnonane, 3-methylnonane, and 4-methylnonane, which cannot be removed from *n*-decane via the used purification procedures. The ionization potentials of branched alkanes are known to be lower than of their linear counterparts [12], which allows them to capture S⁺ and produce S_b⁺ in reaction 2'. The radical cations of branched alkanes have wider ESR spectra as compared to linear alkanes, because the unpaired electron in them is mostly confined to the C–C bond adjacent to the tertiary carbon atom, which produces substantial HFC from the protons of the hyperconjugated CH₃ groups [13–15]. So the actual spectra show not the reaction of recombination 3, but rather the recombination reaction (3') with a characteristic broad magnetic field effect and a pronounced zero field MARY line. A deliberate addition of isomeric alkane to the sample produces the exact same signal. The processes of sequential charge capture (reaction 4') do not show up in spectra, as in this case they lead to freezing of spin evolution [16] that does not transform the broad signal from the first pair into the narrow signal from the final pair. Finally, an additional process of solvent radical cation capture by PTP (reaction 4) always takes place. This is followed by recombination of the PTP⁺/PTP^{•-} pairs (reaction 5), which contributes a narrow magnetic field effect of the opposite phase relative to zero field MARY line from other pairs to the observed spectrum.

Thus the look of an experimental MARY spectrum is determined by the superposition of signals generated in reactions (3') and (5), with the narrow magnetic field effect due to reaction (5) overlapping MARY line generated in reaction (3'). This complicates the use of the line for estimation of the rates of chemical reactions involving pair radical ions, e.g., their reaction with a quencher, such as inorganic complex Mo(CO)₆ that will be used throughout this Letter as a typical example. Preliminary experiments demonstrated that the complex reacts with nearly diffusion-controlled rates with any radical ions present in the solution, thus leading to nonselective decay of all radical ion pairs present in the sample.

A common way to overcome these difficulties with signal overlap is lowering the concentration of luminophor to suppress reactions (4) and (5), sacrificing the signal to noise ratio for the useful signal (3') due to lower intensity of luminescence from the sample. Furthermore, relatively large broadenings visible in a noisy signal, i.e., high quencher concentrations, are required for reliable measurements, which is not always possible or desirable.

In this work we suggest to take advantage of the opposite limiting case of high luminophor concentrations, when both signals are prominent in the spectrum. It turned out that due to widely different rates of spin evolution in the pairs PTP⁺/PTP^{•-} (low HFC) and S_b⁺/PTP^{•-} (high HFC in S_b⁺) the efficiency of *magnetic field effect*

quenching in the two pairs as a result of chemical quenching with equal rates is significantly different, and the ratio of the *intensities* of the signals from the two pairs is very sensitive to the rate of pair decay. Quencher concentrations about an order of magnitude lower as compared to those required to produce sufficient spectrum broadening become sufficient, with better spectrum quality for the target pair. The important thing is the demonstrated and interpreted non-identity of the chemical decay of radical ions and the suppression of their observed signal in magnetic field effect curves, and the crucial role of hyperfine couplings in creating the reporter signal. It should thus be kept in mind that in the case of several parallel radical ion pairs a more rapid disappearance of MFE signal from a pair does not necessarily mean a faster chemical decay of the underlying pair, if the hyperfine couplings in the pairs are significantly different.

2. Experimental

The experiments were performed on a home-built setup described elsewhere [17] based on a modified CW-ESR spectrometer. The typical look of the MARY spectrum and its interpretation can also be found in the cited work. The presented MARY spectra are steady-state magnetic field effects on the intensity of recombination luminescence generated by X-ray irradiation. A sample in a quartz ampoule is placed in the magnetic field of a Bruker ED-200D ESR spectrometer equipped with an X-ray tube (BSV-27, Mo, 40 kV × 20 mA) for steady-state generation of radical ion pairs and a PMT (FEU-130) with quartz lightguide for registration of fluorescence, no optical spectral selection is employed. An additional shift coil with a dedicated power supply is placed on one of the poles of the ESR magnet to create a constant field opposing the scanned field of the magnet. In the presented spectra this shifted field is shown as 'negative'. As in conventional ESR spectrometer, field modulation and lock-in detection are used for producing the first-derivative spectra. The PMT signal is fed to a Stanford Research Systems SR-810 Lock-In Amplifier synchronized with the modulation unit of the spectrometer. The scanned field is modulated at 12.5 kHz with amplitude 0.2 mT. The output of the lock-in amplifier is fed to PC for averaging and storage. The field is scanned at a rate of 200 s/scan with time constant of the lock-in amplifier 1 s and 512 points per scan, a total of 20 scans per spectrum are accumulated. Prior to experiment all samples are degassed down to ~10⁻³ mmHg (0.1 Pa) with several 'freeze-pump-thaw' cycles to remove paramagnetic oxygen from the solution. All experiments were performed at room temperature in *n*-decane solutions. The solvent, *n*-decane was treated with sulphuric acid, potassium permanganate, washed with water, dried over calcium chloride, and passed through a column with a mixture of activated MgO and Al₂O₃ (all done by Mrs. N. Ivanova). *p*-Terphenyl-*d*₁₄ (Aldrich, 98 at.% D) and Mo(CO)₆ (Reakhim, Reagent grade) were used without additional purification.

3. Results and discussion

Figure 1 shows normalized to maximum MARY spectra for solutions of PTP in *n*-decane for increasing concentration of PTP taken in otherwise identical conditions. At low PTP concentration the noisy spectrum contains practically only the signal from pair S_b⁺/PTP^{•-} looking like a broad magnetic field effect and an inverted line in zero field. As demonstrated in [10], upon introduction of a quencher (Mo(CO)₆) into such a solution the zero field MARY line broadens proportionally to its concentration, which yields the rate constant for the reaction with the quencher. In this case it was found to be 2 × 10¹⁰ M⁻¹s⁻¹, which is about twice the diffusion controlled limit for *n*-decane (≈ 7 × 10⁹ M⁻¹s⁻¹) due to reaction

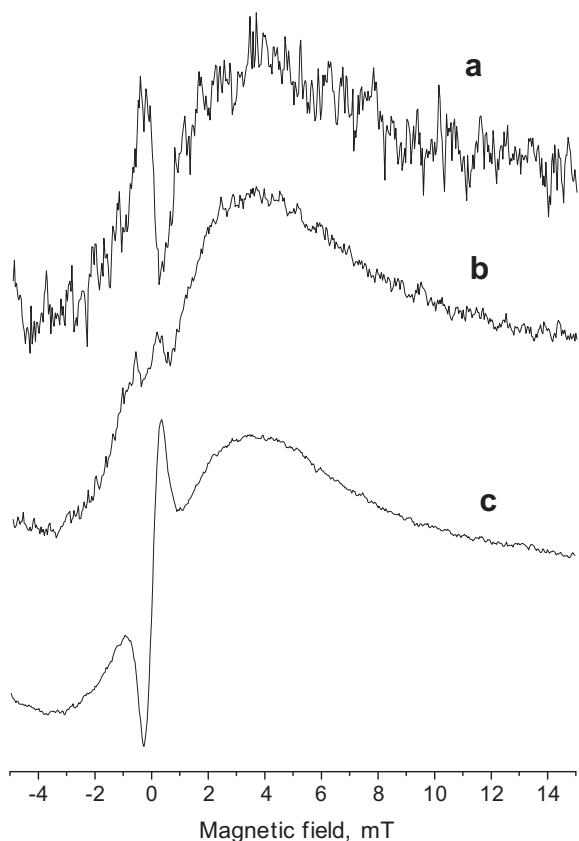


Figure 1. MARY spectra for solutions of PTP in *n*-decane with increasing PTP concentration: (a) 3×10^{-5} M, (b) 2×10^{-4} M, (c) 9×10^{-4} M.

of $\text{Mo}(\text{CO})_6$ with both partners of the pair. To obtain this rate constant the concentration of the quencher had to be brought up to several mM, suppressing the already not spectacular signal to noise ratio of the spectrum even further.

With increasing PTP concentration the signal to noise ratio grows better, and gradually a narrow MFE signal from pair $\text{PTP}^+/\text{PTP}^-$ appears overlapping the zero field MARY line and having the opposite phase to it. A modeling shows that all such spectra can be represented as a sum of two fixed spectra with varied weights. The first spectrum in such a superposition is the spectrum from the pair $\text{S}_b^+/\text{PTP}^-$ from Figure 1a, for which a model spectrum was calculated to simplify spectrum manipulation. Figure 2a shows the modeling of the experimental spectrum for solution of $3 \cdot 10^{-5}$ M PTP in *n*-decane (Figure 1a) in the model of equivalent nuclei with turning on of spin evolution [18] that describes the capture of the primary solvent radical cation by an acceptor with a broad ESR spectrum of the resulting radical cation S_b^+ . In this modeling, to simplify the calculations, the real (and unknown) hyperfine structure of the radical ion is replaced with a sufficiently large number of equivalent spin-1/2 nuclei producing the same second moment of the ESR spectrum for the radical ion, which is obtained from the experimental spectra. To avoid a side-effect of this approximation, a pronounced inflection at triple HFC constant of the equivalent nuclei in the model spectrum [19,4] that is not present in the experimental spectrum, a sufficiently large number of nuclei with appropriately low HFC should be taken. The shown spectrum was obtained using the following parameters: $n_1 = 10$, $a_1 = 0.04$ mT, which corresponds to $\sigma_1 = 0.06$ mT, known for PTP^- , $n_2 = 100$, $a_2 = 0.83$ mT, which corresponds to $\sigma_2 = 4.1$ mT, where $n_{1,2}$ is the number of equivalent nuclei in radical ions with HFC coupling $a_{1,2}$. The parameters chosen for the second partner are

appropriate to reproduce the experimental spectrum well and are reasonable for S_b^+ . The times used in the model are $\tau_0 = 7$ ns and $\tau_c = 110$ ns, where τ_0 is the effective recombination time in exponential recombination model that also accounts for internal relaxation and monomolecular decay of the pair partners, and τ_c is the characteristic time of charge transfer from the narrow partner S^+ to the broad partner S_b in reaction (2').

The second spectrum, shown in Figure 2b, was obtained as follows: from the total signal at high concentration of PTP (Figure 1c) normalized to maximum of the broad magnetic field effect envelop was subtracted the normalized signal of pair the $\text{S}_b^+/\text{PTP}^-$ from Figure 2a. Thus obtained narrow magnetic field effect is well modeled as described above with the known magnetic parameters for the pair $\text{PTP}^+/\text{PTP}^-$: $n_{1,2} = 10$, $a_{1,2} = 0.04$ mT, which corresponds to $\sigma_{1,2} = 0.06$ mT known for both PTP^- and PTP^+ , and a somewhat longer $\tau_0 = 20$ ns. It turned out that any experimental spectrum for a solution of PTP in *n*-decane can be modeled as a sum of spectra from Figure 2a and b, an example of such modeling for a typical 'middle-range' spectrum is shown in Figure 2c. As the figure demonstrates, the 'sum of spectra' representation is more conveniently done with clean model spectra rather than with noisy original traces. Finally, Figure 2d shows the dependence of the relative contribution of the signal from pairs $\text{PTP}^+/\text{PTP}^-$ (the weight of spectrum Figure 2b in superposition) on the concentration of PTP. Thus, MARY spectra for solutions of deuterated PTP in *n*-decane and other similar alkanes are simple superpositions of two fixed-shape signals with so vastly different parameters that their correct decomposition into two components and analysis of their relative contributions becomes possible. The signals themselves correspond to pairs with widely different hyperfine couplings.

Now let us see what happens when a quencher that non-selectively reacts with any radical ion is added to such a solution. Molybdenum hexacarbonyl will be used below as an example, but similar results were also obtained with other quenchers, such as molecular oxygen, copper acetylacetonate, cluster $[\text{Fe}_3(\mu_3\text{-Se})_2(-\text{CO})_9]$, that non-selectively react with any radical ion present in the system. A similar effect of differential quenching, left unexplained, was also observed for quenching by nitroxyl radicals in [20]. Figure 3 shows a selection of spectra for a solution of 5×10^{-4} PTP in *n*-decane with a gradually increasing concentration of $\text{Mo}(\text{CO})_6$. A relatively high concentration of PTP was selected to have an intense initial signal from pairs $\text{PTP}^+/\text{PTP}^-$ and thus a sufficient dynamic range for varying the concentration of the quencher.

It can be seen that the relative intensity of the narrow signal rapidly drops already at quencher concentration of about 10^{-4} M. All spectra in the presence of the quencher were decomposed into superpositions of the same spectra from Figure 2a and b. The most apparent effect of the quencher is a reduction of the relative contribution from the signal of pairs $\text{PTP}^+/\text{PTP}^-$. Although the spectra should experience some broadening due to reduction of the lifetime of the pair, this is below 0.1 mT at the highest used quencher concentration, which is completely buried within the modulation amplitude of 0.2 mT and noise for the line with a 1 mT width. The spectra were evaluated as follows: all spectra we normalized to the intensity of the broad signal and then modeled as a superposition of the normalized model spectrum of pairs $\text{S}_b^+/\text{PTP}^-$ from Figure 2a with unity weight and normalized model spectrum of pairs $\text{PTP}^+/\text{PTP}^-$ from Figure 2b with varied weight, which is the sought relative contribution of the narrow signal v . Convenient coordinates to plot these data were found to be the reciprocal value $1/v$ vs. quencher concentration. As Figure 4a shows, these coordinates produce a linear plot, and the value of $1/v$ doubles already at the quencher concentration of the order of 10^{-4} M.

Such a high sensitivity of the narrow line to low quencher concentrations for equal rates of chemical reaction with the quencher is caused by the different rates of the development of spin

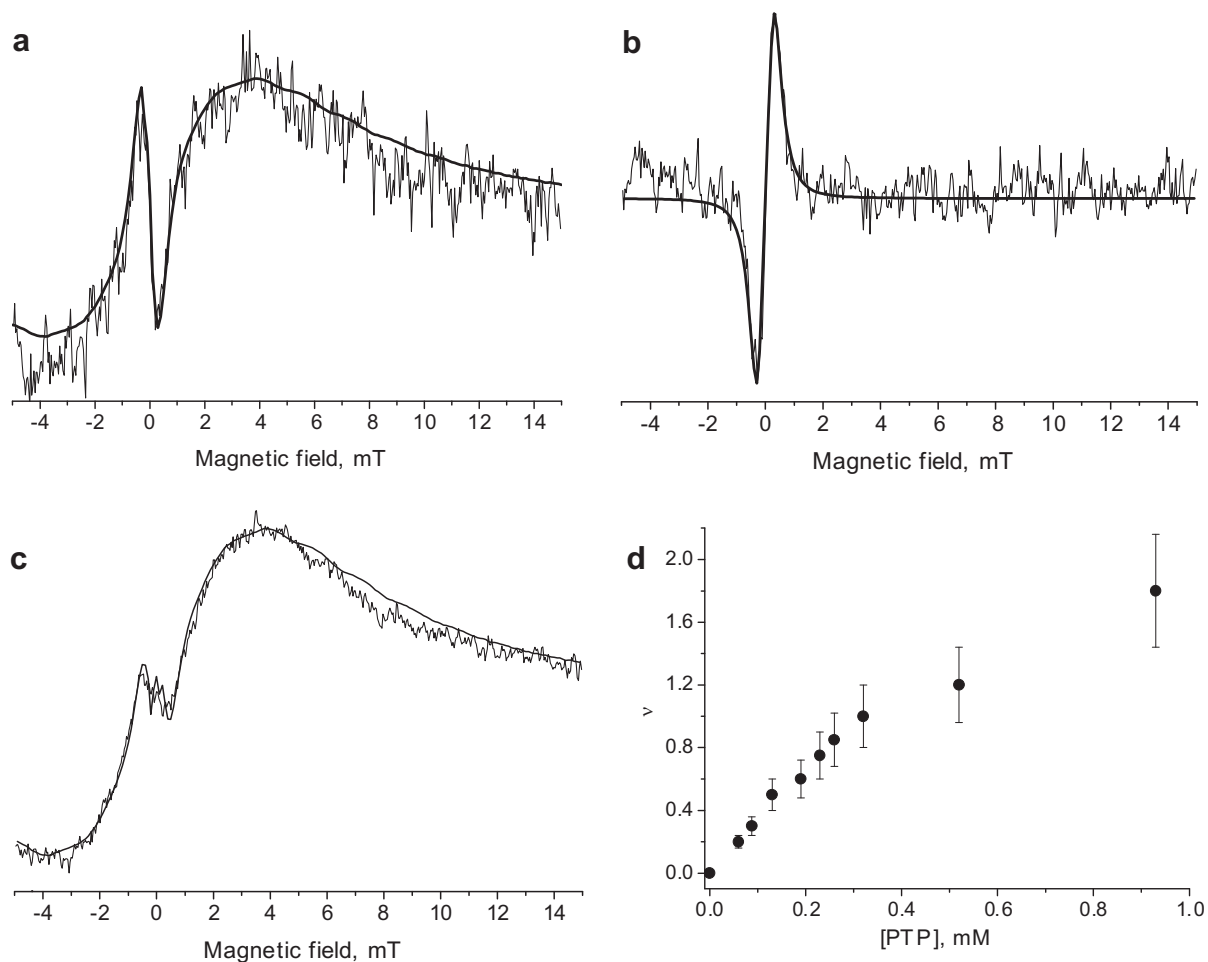


Figure 2. (a) Modeling experimental spectrum for solution of 3×10^{-5} M PTP in *n*-decane (noisy curve) in the approximation of equivalent nuclei with switching on of spin evolution for parameters $n_1 = 10$, $a_1 = 0.04$ mT, $n_2 = 100$, $a_2 = 0.83$ mT, $\tau_0 = 7$ ns, $\tau_c = 110$ ns (smooth curve). (b) Narrow signal obtained by subtracting the signal from pair S_d^+/PTP^- from the total signal (noisy curve) and its modeling with parameters $n_1 = 10$, $a_1 = 0.04$ mT, $n_2 = 10$, $a_2 = 0.04$ mT, $\tau_0 = 20$ ns corresponding to pair PTP^+/PTP^- (smooth curve). (c) MARY spectrum for solution of 2×10^{-4} M PTP in *n*-decane (noisy curve) and superposition of model spectra from pairs $(S_b^+/PTP^-) + 0.6 \cdot (PTP^+/PTP^-)$ (smooth curve). (d) Contribution of signal from pairs PTP^+/PTP^- vs. concentration of PTP.

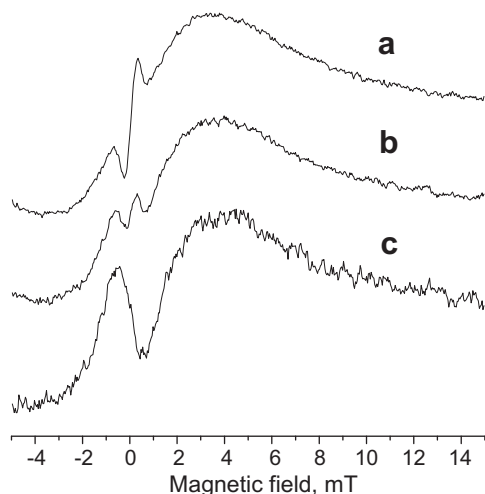
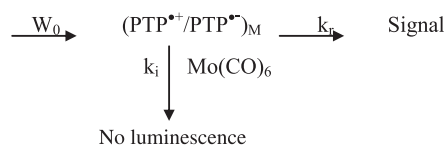


Figure 3. MARY spectra for solution of 5×10^{-4} M PTP in *n*-decane for increasing concentration of $Mo(CO)_6$: (a) 0, (b) 1×10^{-4} M, (c) 7×10^{-4} M.

evolution in the pairs PTP^+/PTP^- and S_b^+/PTP^- which have effective hyperfine couplings $\sigma_{1,2}$ of 0.06 mT and 4.1 mT for PTP^{\pm} and S_b^+ , respectively. Although the underlying molecular carriers may decay at the same rate, the observed magnetic field effect

needs time inversely proportional to $\sigma_{1,2}$ to develop [21,22]. Therefore, for the same nominal amounts of radical pairs the number of 'magnetically live' pairs with lower σ values will be lower until the slower magnetic field effect has fully developed, and will be more sensitive to quenching. This dependence can be qualitatively reproduced in the following very simple kinetic model for the formation of magnetic field effect, which highlights the widely different rates of development of spin evolution in otherwise having identical chemical fate pairs: the pairs PTP^+/PTP^- and S_b^+/PTP^- are both formed instantaneously, the magnetic field effect in the 'broad' pair S_b^+/PTP^- is formed instantaneously, the magnetic field effect in the 'narrow' pair PTP^+/PTP^- is formed with a constant rate W_0 , the observed signal is formed from the magnetic field effect in the corresponding pair in a monomolecular reaction with the rate constant k_i and is quenched in a bimolecular reaction with the rate constant k_j :



Then, using a quasi-stationary approximation for the magnetically live PTP^+/PTP^- pairs, it follows that the contribution of the

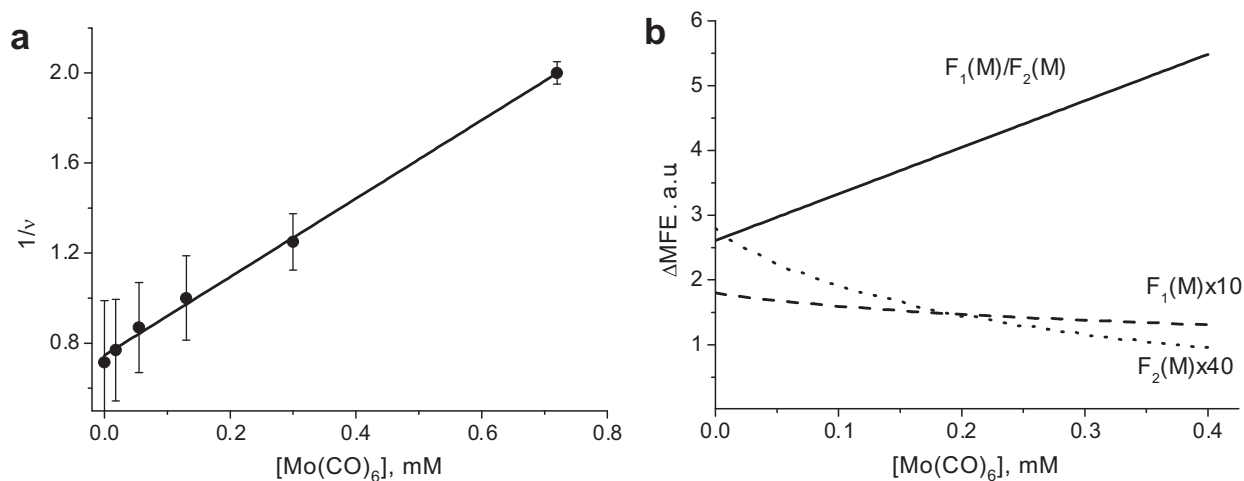


Figure 4. (a) Reciprocal contribution of narrow signal from pairs PTP^{+}/PTP^{-} to spectra vs. concentration of $Mo(CO)_6$ obtained from evaluation of experimental spectra. (b) Results of numerical calculation of functions $F_1(M)$ (dashed line), $F_2(M)$ (dotted line), and ratio $F_1(M)/F_2(M)$ (solid line) vs. concentration of M , modeled with parameters: $k = 4 \times 10^{10} M^{-1}s^{-1}$, $\sigma_1 = 4.1$ mT, $\sigma_2 = 0.06$ mT, $(T_1)^1 = (T_1)^2 = (T_2)^2 = (T_0)^2 = 1000$ ns (effectively infinity), $(T_2)^1 = (T_0)^1 = 20$ ns, $\tau = 3$ ns (see text for details).

magnetic field effect from the narrow pair to the observed signal can be written as:

$$v = \alpha \cdot [(PTP^{+}/PTP^{-})_M] = \frac{\alpha \cdot W_0}{k_r + k_i \cdot [Mo(CO)_6]}$$

where α is a proportionality factor. The quenching of the broad signal is taken into account automatically by normalizing to the broad magnetic field effect. The obtained dependence is seen to linearize in coordinates $1/v$ vs. $[Mo(CO)_6]$:

$$\frac{1}{v} = \frac{k_r}{\alpha \cdot W_0} + \frac{k_i}{\alpha \cdot W_0} \cdot [Mo(CO)_6]$$

A more correct but numerical evaluation explicitly taking into account spin evolution and recombination can be done as follows. Let us again assume that the radical cations of the two acceptors S_b^{+} and $/PTP^{+}$ are formed instantaneously and the quencher reacts with equal efficiency with all radical ions. Although the radical cations of both observed pairs are formed from the primary solvent radical cation S^{+} after a substantial delay (ca. 100 ns, *vide supra*), the primary pair S^{+}/PTP^{-} is nearly magnetically silent due to the lack of substantial HFC in the radical cation. The intrinsic σ value for the radical cation of *n*-decane is only 0.5 mT [11]. Furthermore, it is almost completely suppressed by fast degenerate electron exchange in *n*-decane matrix with rate constant approximately $3 \cdot 10^8 M^{-1}s^{-1}$ and concentration about 10 M [23]. So the radical pair dwells in an almost spin-frozen state until the radical cation is captured by S_b . The spin evolution in pairs S_b^{+}/PTP^{-} and PTP^{+}/PTP^{-} will be described in semiclassical approximation and assuming all *g*-values to be equal. The following analytical expressions for the time-dependent population of the singlet state of the corresponding pairs in the limiting cases of strong and zero magnetic field are available [15]:

$$\begin{aligned} \rho_{SS}^B(t) &= \frac{1}{4} + \frac{1}{4} e^{-t/T_1} + \frac{1}{2} e^{-t/T_2} G_C^B(t) G_A^B(t), \\ \rho_{SS}^0(t) &= \frac{1}{4} + \frac{3}{4} e^{-t/T_0} G_C^0(t) G_A^0(t), \end{aligned} \quad (5')$$

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

$$G^B(t) = e^{-\gamma^2 \sigma^2 t^2 / 2},$$

where subscripts C and A refer to the radical cation and radical anion of the pair, respectively, $T_{1,2}$ are the spin–lattice and spin–spin relaxation times for the corresponding radical ions in strong magnetic field, T_0 is the single spin relaxation time for the corresponding radical ion in zero magnetic field, the functions $G^{B,0}(t)$ describe spin evolution of the radical in a magnetic field much higher than its effective hyperfine coupling σ and in zero magnetic field, respectively, and γ is magnetogyric ratio.

To obtain the stationary magnetic effect, $\rho_{SS}(t)$ should be integrated with the distribution over the lifetimes of spin-correlated radical pairs $f(t)$ and the pair quenching kinetics [7]:

$$F(B) \propto \int \rho_{SS}(t) e^{-kMt} f(t) dt,$$

$$f(t) = \frac{1}{2} \frac{1/\tau}{(1 + (t/\tau))^3}, \quad (6')$$

where one of the standard functions for diffusion-controlled recombination of a pair of oppositely charged particles is taken as the recombination function, M is quencher concentration, and k is the rate constant of interaction with the quencher.

In general, to calculate MARY spectrum (the derivative $dF(B)/dB$) from expression Eq. (7), the function $\rho_{SS}(t)$ in an arbitrary field is required, and this problem still has not been solved analytically. However, in our case the evaluation of experimental spectra does not require the reproduction of the entire field dependence, and only the relative intensities of the two spectral components in the derivative form, from pairs PTP^{+}/PTP^{-} and S_b^{+}/PTP^{-} , are needed. Indeed, since the quencher concentrations used in the described experiments are so low, they do not cause any noticeable broadening of the spectrum and distortion of its shape. The relative changes in the derivative of any function upon its scaling without changing its shape are proportional to the relative changes in the differences of values of the function at any fixed pair of points. Then it follows that the relative changes in the intensities of the derivative spectra $dF(B)/dB$ as a function of quencher concentration will be proportional to the relative changes in the differences of values of function $F(B)$ Eq. (7) in any convenient pair of points, e.g., in strong field and in zero field. These can be calculated using functions Eq. (6). Thus, to describe the dependence of the relative contribution of the signal from pair PTP^{+}/PTP^{-} the following two functions can be evaluated:

$$F_1(M) = \int \frac{e^{-kMt}(\rho_{SS1}^B(t) - \rho_{SS1}^0(t))}{(t + \tau)^{3/2}} dt,$$

$$F_2(M) = \int \frac{e^{-kMt}(\rho_{SS2}^B(t) - \rho_{SS2}^0(t))}{(t + \tau)^{3/2}} dt,$$

where subscripts 1 and 2 refer to pairs S_b^+/PTP^- and PTP^+/PTP^- , respectively, M is quencher concentration. Then the ratio $F_1(M)/F_2(M)$ can be evaluated, which is the theoretical counterpart of the reciprocal of the contribution of the narrow signal $1/\nu$ as determined from experiment. The result of such a modeling for reasonable values of all relevant parameters is shown in Figure 4b. Thus estimated quenching rate constant is approximately $4 \times 10^{10} - M^{-1}s^{-1}$ and is close to diffusion controlled limit, although is somewhat higher. Such an overestimation is probably related to the assumed simplifications regarding the instantaneous formation of the parallel pairs S_b^+/PTP^- and PTP^+/PTP^- , which allowed reproduction of the observed effect of selective quenching of the magnetic field effect by a non-selective chemical reaction in such a simple and transparent model.

4. Conclusions

In this work we demonstrated the effect of selective quenching of the magnetic field effect by a non-selective chemical reaction due to different rates of development of spin evolution in radical pairs with widely different hyperfine couplings. This non-identity of the chemical decay of radical ions and the suppression of their observed signal in magnetic field effect curves should be kept in mind when interpreting experimental spectra. In the case of several parallel radical ion pairs a more rapid disappearance of MFE signal from a pair does not necessarily mean a faster chemical decay of the underlying pair, if the hyperfine couplings in the pairs are significantly different.

On the practical side, a new approach to measuring rate constants of radical ion quenching is suggested, which is based on the analysis of the relative intensities of contributions to the observed signal from two pairs with substantially different hyperfine couplings. The high sensitivity to reactions with quenchers allows determination of rates at low concentrations of the quencher and the probing acceptor, when the contributions of the two signals to the observed spectrum are additive and spectral broadening due to reaction of radical ions with the quencher can be neglected.

The presence of two signals with very different sensitivity to quencher in the spectrum gives the effect of internal standard immediately in the spectrum itself and helps to extract the quantitative information not from the widths, but from the intensities of signals in MARY spectra.

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