

# Single-phase primary electron spin polarization transfer in spin-trapping reactions

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Time-resolved (TR) ESR was employed to investigate the reaction of diphenylphosphinoyl reactive free radicals with N-phenyl-tert-butyl nitron (PBN), which were produced by laser flash photolysis (YAG laser, 355 nm) of diphenyl-2,4,6-trimethylbenzoyl phosphine oxide (DPO). The TR ESR and continuous wave (cw) ESR spectra of the nitroxide spin adduct of diphenylphosphinoyl radicals and PBN were investigated, and both spectra of the adduct show the same hyperfine-splitting and relative line intensities. The TR ESR spectra of the spin adduct as well as the initial diphenylphosphinoyl radicals are absorptively polarized, corresponding to a net electron spin polarization transfer. The requirements for spin polarization transfer in radical addition reactions and the TR and cw ESR spectrum of the spin adduct are discussed.

## 1. Introduction

The photochemistry of benzoyl phosphine oxides (general structure  $\text{ArCO}(\text{O})\text{R}_2$ ) is of interest for a number of reasons. Type I  $\alpha$  cleavage produces an aroyl phosphonyl radical pair ( $\text{ArCO}\cdot\cdot\text{P}(\text{O})\text{R}_2$ ) which is formally analogous to the radical pair produced by the photolysis [1–4] of aryl alkyl ketones [ $\text{ArCO}\cdot\cdot\text{CR}_3$ ]. However, the phosphonyl radical,  $\cdot\text{P}(\text{O})\text{R}_2$ , possesses a number of important structural features which give the  $\text{ArCO}\cdot\cdot\text{P}(\text{O})\text{R}_2$  radical pair potentially novel magnetic properties compared to those of the radical pairs produced by the photolysis of aryl alkyl ketones. For example, the electron–nuclear hyperfine coupling between the odd electron and the 31-P nucleus is enormous ( $a_{\text{P}} \approx 400$ –1000 G) relative to most carbon centered radicals ( $a_{\text{C}} \approx 20$  G) [5]. This feature is important because a large value of  $a$  can serve as a mechanism for  $\text{S-T}_{-1}$  mixing of the radical pair as it separates from a collision pair and becomes a separated pair. Another important difference is that the phosphonyl radical,  $\cdot\text{P}(\text{O})\text{R}_2$ , is exceedingly reactive compared to typical carbon centered radicals. For example, the

rate of addition of  $\cdot\text{P}(\text{O})\text{R}_2$  radicals to carbon–carbon double bonds is often several orders of magnitude faster than the addition of typical unstabilized carbon  $\cdot\text{CR}_3$  radicals to carbon–carbon double bonds [1,6,7]. Also, from the standpoint of spectral analysis, the 31-P atom has spin 1/2 and through appropriate substitution of neighboring atoms may exhibit only weak coupling with other magnetic nuclei, thereby leading to a simple hyperfine doublet split by hundreds of gauss [3,5] that is readily recognized and analyzed because of its clean separation from the lines of other species. Finally, a feature which has not yet been addressed, the P atom in a phosphorous radical may possess a much slower stereochemical interconversion than a carbon radical, a feature that may be tested in typical radical clock experiments.

Because of our interest in the use of electron polarization transfer as a mechanistic tool in organic photochemistry [8], we have initiated an investigation of the photochemistry of a benzoyl phosphine oxide [1–4], diphenyl-2,4,6-trimethylbenzoyl phosphine oxide, DPO, by TRESR. A goal of these investigations was to check for any unusual properties of P-centered free radicals in polarization transfer reactions.

Electron spin polarization (ESP) can be transferred in chemical reactions. For example, reactive

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free radicals, which bear multiplet or net polarization, can transfer spin polarization to the reaction products – secondary radicals (or spin adducts) [6–12]. The relatively new phenomenon of ESP transfer (ESPT) in a reaction such as addition,



is the consequence of the principle of conservation of spin angular momentum [8,13,14]. The symbol # is used here and below for designation of electron polarization, i.e. a non-Boltzmann population of electronic spin levels in an external magnetic field. For non-viscous liquids near room temperature electron spin polarization typically relaxes to the Boltzmann distribution within a few microseconds so that it is readily studied by TR ESR but is not usually amenable to investigation by cw ESR.

Photolysis of DPO is reported to yield a strong absorptive electron polarization of both primary radicals at early times. This absorptive polarization converts into E/A\* polarization, mainly of the P-centered radical,  $\cdot P(O)(C_6H_5)_2$ , at later times [3], and finally transforms a single E line at low field at the longest times accessible to measurement. We have confirmed these results and also have found that the diphenylphosphonyl radical adds to N-phenyl-tert-butyl nitron (PBN) and transfers its polarization to the nitroxide produced by addition.

The two-phase (or multiplet) ESPT has been observed in reactions of addition to double bonds [6,7,9–11]; the direct transfer of single-phase (or net) polarization was reported only for hydrogen-atom transfer reactions [15] and for reactions with stable nitroxyl radicals [8,16] to the best of our knowledge<sup>#1</sup>. To our knowledge the present work is the first observation of single-phase primary ESPT in an addition reaction such as eq. (1).

## 2. Experimental

The TR ESR measurements and description of the instrument are described in detail in ref. [16]. The

<sup>#1</sup> The electron transfer between polarized radical-anion and parent molecule leading to pure single-phase polarization [17] may be considered also as single-phase (or net) polarization transfer.

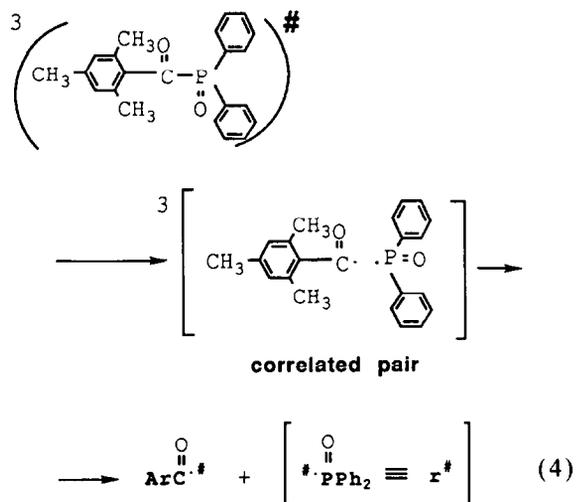
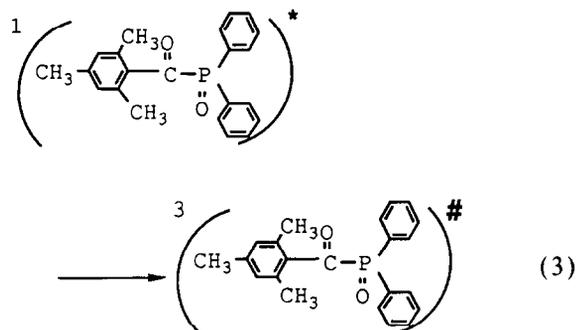
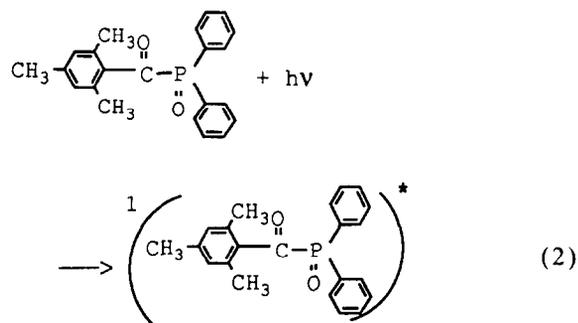
instrument consists of a Bruker ER 100 D spectrometer, a PAR model 4402 digital boxcar integrator, a Quanta Ray DCR 2A Nd:YAG laser (third harmonic  $\lambda_{ex} = 355$  nm, 8 ns fwhm, typical laser energy 10–15 mJ), and a Bruker broad band preamplifier with response time of 60 ns. Typical sampling gates were 50–300 ns. We present TR ESR spectra below specifying  $\Delta t = A-B$  (in s) where  $A$  is the beginning of sampling after the laser pulse, and  $B$  is the end of the sampling, and the  $B-A$  value is the sampling gate. The “true” or effective response times were estimated at  $\approx 200$  ns. The experiments, which were done with a flow system, included a flat thin (0.5 mm) quartz cell. Flow rates were chosen in the range of 2–5 ml/min unless stated otherwise. cw ESR spectra were recorded with the same Bruker spectrometer in the same cell.

The nanosecond laser flash photolysis system has been described [18]. Solutions were photoexcited with the third harmonic of a YAG laser with pulse energy and pulse duration comparable to those presented above. All of the solutions were deoxygenated by prolonged argon bubbling. The experiments were performed at room temperature.

The reagents diphenyl-2,4,6-trimethylbenzoyl phosphine oxide (DPO, BASF), PBN, styrene (both Aldrich), solvents dichloromethane and acetonitrile (both Fisher) were used as received. The concentration of DPO was  $\approx 10^{-3}$ – $10^{-2}$  M, that of PBN was  $8 \times 10^{-3}$ – $5 \times 10^{-2}$  M, and that of styrene 0.05–1.0 M.

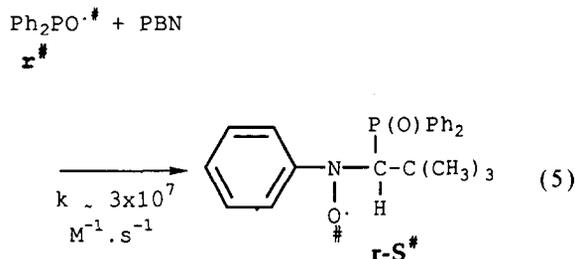
## 3. Results and discussion

Laser flash photolysis of DPO leads to the appearance of a transient absorption band in the region of  $\lambda = 320$ – $370$  nm with  $\lambda_{max} \approx 330$  nm in agreement with published reports [1,2]. The observed absorption is assigned to the diphenyl phosphonyl radical ( $r^{\#}$ ) formed through reactions as



(The substituted benzoyl radical absorbs light at shorter wavelengths [1]). The electron spin polarization of  $r^{\#}$  in a magnetic field will be described below.

In the presence of PBN the rate of decay of  $r^{\#}$  is accelerated due to the spin trapping of this radical to form the adduct nitroxide radical,  $r\text{-S}^{\#}$ ,



The decay of  $r^{\#}$  obeyed pseudo first order kinetics when  $[\text{PBN}] > 1 \times 10^{-3} \text{ M}$ . The measured dependence of the first-order  $r^{\#}$  decay on  $[\text{PBN}]$  allows computation of the rate constant for the addition step of eq. (5):  $k_5 = (3.0 \pm 0.5) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  in methylene chloride. The magnitude of this rate constant is quite large for an addition of a radical to a multiple bond. In fact, the radical  $r^{\#}$  is known to be very reactive in addition to double bonds [1,6,7]. The measured  $k_1$  for  $r^{\#}$  and a number of vinyl monomers are of the order  $\approx 10^6\text{-}10^7 \text{ M}^{-1} \text{ s}^{-1}$ ; in particular for styrene  $k_1 = (6.0 \pm 0.3) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  [1]. The 2,4,6-trimethylbenzoyl radical is expected to add to PBN at a slower rate, since the rate constant for the addition of the unsubstituted benzoyl radical to PBN is  $\approx 8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  in benzene [19].

The TR ESR spectrum of photolyzed DPO shows absorptively polarized radicals at the shortest times of observation (fig. 1a). The same spectrum was reported earlier in refs. [4,5], but its time resolved behavior was not reported. The TR ESR spectrum at early times is very simple and consists of an absorptively polarized doublet with a typical phosphorous hyperfine splitting constant ( $a_p = 370 \text{ G}$ ) assigned to  $\cdot\text{P}(\text{O})(\text{C}_6\text{H}_5)_2$  and an absorptively polarized singlet, assigned to the 2,4,6-trimethylbenzoyl radical, in accordance with results reported earlier [3,4].

In the presence of PBN the signals of  $r^{\#}$  diminish or disappear depending on  $[\text{PBN}]$ , and signals of the spin adduct with PBN formed through reaction (5) are observed (fig. 2a). The signals of the spin adduct are absorptively polarized (fig. 2a). The sign of polarization indicates that in both  $r^{\#}$  and in the spin adduct the  $\beta$ -Zeeman level of the unpaired electron is overpopulated, which results in the enhanced absorption (figs. 1a and 2a). This observation demonstrates experimentally that the next polarization

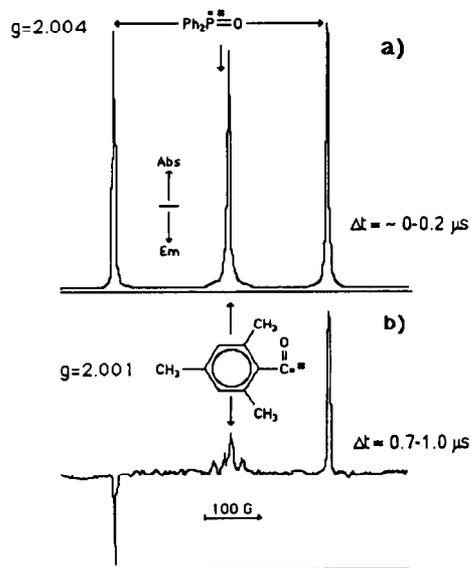


Fig. 1. TR ESR spectrum observed under pulsed ( $\approx 20$  ns) photolysis of DPO in dichloromethane at two different sampling gates: (a)  $\approx 0-0.2$   $\mu$ s and (b)  $\approx 0.7-1.0$   $\mu$ s. The lines at highest and lowest fields are assigned to the  $^{31}\text{P}$  hyperfine coupling and the central peak ( $g \approx 2.000$ ) is assigned to the 2,4,6-trimethylbenzoyl radical.

of the primary radicals is conserved in a chemical reaction (5), the most important observation made in the present work.

The spectrum of the spin adduct,  $r\text{-S}^\bullet$ , (eq. (5)) consists of 12 lines (fig. 2b) from which the following values of the pertinent hyperfine constants are computed:  $a_N = 15.0$  G;  $a_{\beta\text{-H}} = 3.8$  G and  $a_P = 17.0$  G. A more detailed analysis of the data reveals that there is also a measurable contribution of substituted benzoyl radical to the TR ESR spectra observed at short times ( $\approx 200-700$  ns). The 2,4,6-trimethylbenzoyl radical has absorptive signals overlapping with lines Nos. 8, 9 and particularly 10 of the TR ESR spectrum of spin adduct (cf. figs. 1a and 2). It was found that the benzoyl absorption persists at the same time scale, when signals of  $r^\bullet$  are almost fully replaced by spin-adduct signals. This observation confirms the conclusion that benzoyl radical attacks PBN at a slower rate than  $r^\bullet$ .

The spin trapping of  $r^\bullet$  and PBN was also investigated by cw ESR under the comparable experimental conditions employed for the TR ESR. The cw ESR spectrum of spin adduct can be observed (fig.

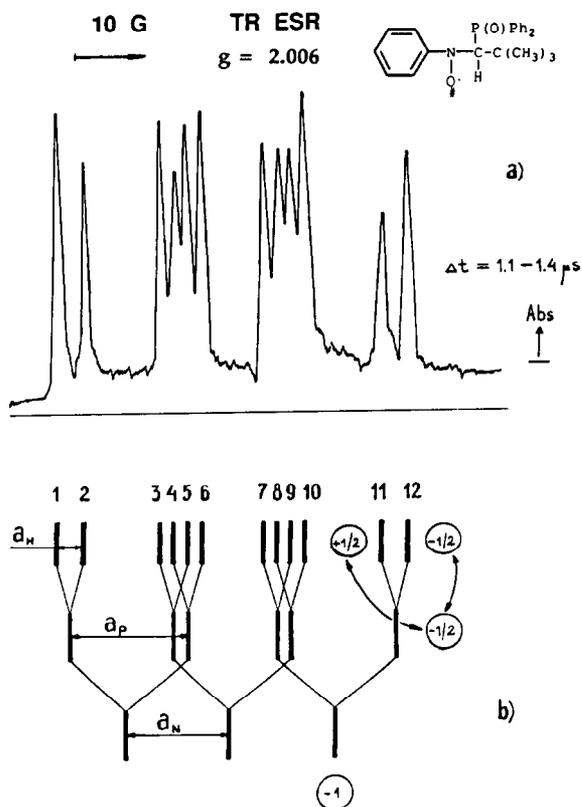


Fig. 2. TR ESR spectrum observed under pulsed ( $\approx 20$  ns) photolysis of DPO in dichloromethane in the presence of PBN at sampling gate  $\approx 1$   $\mu$ s. The calculated stick spectrum is shown below the observed spectrum. For a discussion of the lines marked with circles see text.

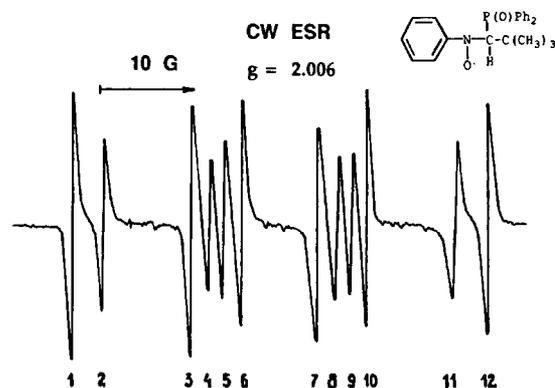


Fig. 3. cw ESR spectrum of spin adduct in dichloromethane. The numbers under the lines of the spectrum correspond to those of fig. 2. See text for discussion.

3) only under irradiation, as expected, since spin-trapped adducts with PBN are usually unstable [20]. Both the cw and TR ESR spectra have the same HFC pattern (figs. 2 and 3) in dichloromethane and acetonitrile. The values of  $a_N$  and  $a_P$  in the ESR spectra of spin adduct are very similar, since in acetonitrile  $a_N \approx a_P$ , both cw and TR ESR spectra consist of only eight lines.

We also succeeded in observing the cw ESR spectra of spin adducts of both substituted benzoyl (triplet of doublets) and diphenylphosphonyl radicals when irradiation of DPO was conducted under relatively fast flow (8–10 ml/min) conditions. However, the signals of spin adducts of substituted benzoyl radical are weaker than those of phosphonyl radicals, which is expected because of the lower rates of their formation and the faster rate of relaxation compared to that of phosphonyl radicals.

A marked peculiarity of the ESR spectra of the spin-adduct  $r-S^{\bullet}$  is the broadening of the internal lines Nos. 2 and 11 (figs. 2 and 3). This broadening is interpreted to be the result of an exchange of nuclear orientations of H and P atoms due to the rotation of the  $-CH(P)(C)$  fragment along the  $N-C$  bond. This exchange leads to an alteration of the local magnetic field of the unpaired electrons resulting from the change of nuclear fields under the exchange of conformations. For instance, the nuclear orientation corresponding to line No. 11  $-a_N + \frac{1}{2}a_{\beta-H} - \frac{1}{2}a_P$  changes into  $-a_N - \frac{1}{2}a_{\beta-H} + \frac{1}{2}a_P$  under an exchange of nuclear orientations of H and P atoms, which results in the broadening of this line (and similarly for line No. 2), see fig. 2b. At the same time an exchange of nuclear orientations of H and P atoms will not lead to a variation of local nuclear magnetic fields for electron Zeeman levels corresponding to components Nos. 12 and 1, and these lines are relatively narrow, see figs. 2a and 3. A similar observation has been made with other phosphorous containing nitroxyl radicals, which have broadened internal components [21].

From our results, we conclude that there are two important requirements for the observation of ESPT, even if a reactive radical is produced in a strongly polarized state. The first requirement for conservation of polarization during an elementary step chemical reaction, is a high reaction rate, and the second requirement is that the rate of addition compete with

relaxation of polarization to the Boltzmann level. Thus, the characteristic time of the reaction  $\tau = (k_1[S])^{-1}$  should be smaller or at least comparable, to the spin-adduct paramagnetic relaxation time  $T_1$ :

$$T_1 \gtrsim (k_1[S])^{-1}.$$

For very strong polarization of radicals and for measurement employing a high sensitivity spectrometer, the values of  $\tau$  and  $T_1$  may be of the same order of magnitude, and polarization still may be readily detected. From the values of  $[S]$  (vide supra, section 2) and the condition that  $k_1 = k_5$  (see above), one obtains  $\tau = 1.5\text{--}25 \mu\text{s}$ ; the observation of polarization is thus expected, since  $T_1$  for nitroxyl free radicals is usually present in the microsecond time domain [8–16]. From these considerations we observe that the photolysis of DPO in the presence of styrene, which is also very reactive towards  $r^{\bullet}$  ( $6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  [1]), is expected and is found to result in an absorptive TR ESR spectrum of the secondary adduct radical,  $r-S^{\bullet}$ .

The second requirement for observation of ESPT is related to the structure of the polarized radicals and especially to the orbital configurations, explored during the course of reaction (1), which generate strong spin-orbit coupling (SOC). SOC is usually the source of a fast paramagnetic relaxation in radicals [22]. However, if reaction (1) proceeds via configurations, which are characterized by the quenched orbital momentum, the SOC will not enhance paramagnetic relaxation thus allowing the observation of ESPT. Quantum-mechanical calculations are required for a deeper analysis of individual cases [22].

Alternative mechanisms leading to the observed polarized species  $r-S^{\bullet}$  should be considered. For example, polarization may be transferred in bimolecular interactions of  $r^{\bullet}$  and the accumulated spin adduct, which may not have formed in a polarized state:



In other words, the observed polarization might not be a primary event as shown in eq. (1) but may be a secondary event, unrelated to direct addition as shown in eq. (6). Indeed, ESPT as described in eq. (6) has been reported [7,14] for radicals bearing net polarization and stable nitroxyl radicals ( $C \approx 10^{-3}$ –

0.1 M). However, the very low stationary concentration of photochemically-produced unstable nitroxyl radicals  $r-S$  ( $C \ll 10^{-3}$  M) as well as the independence of signal intensity upon the flow rate allow us to rule out reaction (6) as the significant mechanism for formation of  $r-S^{\#}$ .

The existence of both benzoyl radicals and  $r^{\#}$ , which are absorptively polarized at short times of observation, is consistent with the triplet mechanism (TM) of CIDEP as the dominant mechanism for the creation of the observed polarization [3], and a positive zero-field splitting value  $D$  in the triplet DPO [7]. The substituted benzoyl radical has a rather short effective relaxation time [8,17,23]; its signal disappears at  $t \geq 1 \mu s$ , and TR ESR spectrum of DPO at longer times of observation consists mainly of  $r^{\#}$ , cf. fig. 1b. Due to the contribution of  $S-T_0$  or RPM to the polarization, the low-field line of  $r^{\#}$  turns into emission. The present system manifests the principally known phenomenon of succession of RPM of CIDEP to TM [3,7,12,13]. However, these two mechanisms do not exhaust the possibilities for producing CIDEP of DPO. Due to the large values of  $a_p$ , the  $S-T_{-1}$  mechanism could contribute to the observed CIDEP [24] and lead to emissive CIDEP. In fact, at observation times of  $t \geq 1.5 \mu s$ , the TR ESR spectrum consists of only one low field line of  $r^{\#}$  in emission. Thus, the  $S-T_{-1}$  mechanism, which was observed at the longest possible times, completes the CIDEP phenomena in the system in accordance with similar observations of ref. [3].

To date, reports of ESPT in reactions of phosphorus-centered radicals have involved reactive radicals generated in *bimolecular* reactions, which led to multiplet polarization according to RPM [6,7,11]. In the present work the very reactive radicals were produced by a *unimolecular* reaction and their addition to PBN produces net polarization at the earlier times of observation. The transfer of single-phase (or net) primary polarization has the advantage of being a more straightforward way to follow radical reaction pathways rather than ESPT of two-phase (or multiplet) polarization, because the latter has many pitfalls in the interpretation of the CIDEP picture except in the simplest cases [9].

#### 4. Conclusions

Single phase ESPT was observed for the first time in a spin trapping reaction producing a nitroxide employing TR ESR. The observation of the cw ESR spectrum of spin adduct in the present case confirms the nature of TR ESR spectrum. However, an important possibility suggested by these results is that in a number of cases, where it is not possible to observe the cw ESR spectrum of spin adducts, the TR ESR spectrum of spin adduct may be observed. This possibility is due to the high polarization coefficients in CIDEP spectra, which allow the observation of concentrations of radicals too low to be detectable in cw ESR [8,9]. We believe that the ESPT method has the potential to enhance spin-trapping technique. ESPT is also expected to be a promising method for the study of photosynthesis [12] and other photoinduced free radical reactions.

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