SHORT PAPER

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Spin trapping chemistry of the diphenylphosphinyl radical[†]

Yoshimi Sueishi and Yuko Nishihara

Department of Chemistry, Faculty of Science, Okayama University, 3-1-1 Tsushima Naka,
Okayama 700-8530, Japan

The diphenylphosphinyl radical ($\cdot PPh_2$), produced from hydrogen atom abstraction of diphenylphosphine by 2,2-diphenyl-1-picryl-hydrazyl, was trapped by several kinds of spin trap and the relative reactivities of the $\cdot PPh_2$ radical toward the five kinds of spin trap were determined by competitive reactions using DMPO as a reference.

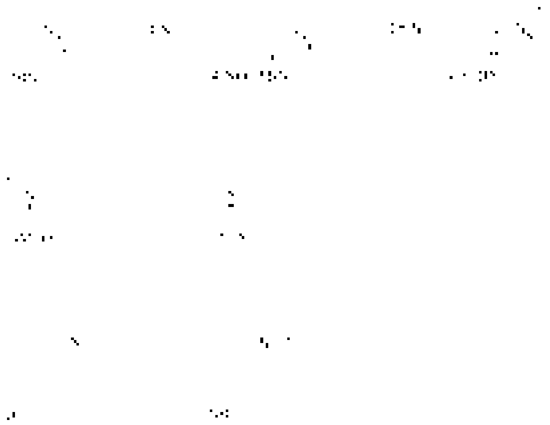
Keywords: spin trapping, diphenylphosphinyl radical

Phosphorus-centred radicals are involved in many processes of chemistry and biological interest.[1] However, since the phosphorus-centered radicals undergo subsequent α- and β-scissions,[2] it is difficult to detect the intermediate phosphorus-centred radicals at room temperature by means of EPR. The spin-trapping technique has been widely used to study radical intermediates in photochemical, radiation chemical, and thermal reaction systems.[3] The identification of spin adducts by EPR spectroscopy is rather difficult since the variation of the hyperfine coupling constants (hfccs) of spin adducts caused by the structural changes of trapped radicals is not very large. Recently, Janzen and Zhang[4] demonstrated several advantages of the phosphorus-labelled spin-trap, and the new phosphorus-containing nitroxide has attracted much attention. The phosphorus atom is a potentially useful probe because the phosphorus hyperfine structure (hfs) is normally large and is very sensitive to the structure of radicals.

There have many reports on the spin-trapping of carbon-centered, oxygen-centered, and nitrogen-centered radicals.[4] In contrast, only a few studies concerning spin-trapping of phosphorus-centered radicals have been reported.[5,6] In the present study, we have examined the spin-trapping efficiency of the phosphorus-centered radical (diphenylphosphinyl, $\cdot PPh_2$) by several kinds of spin trap. Further, the trapping rates of the $\cdot PPh_2$ radical were investigated kinetically by competitive reactions.

Experimental

Materials: Diphenylphosphine (Ph_2PH) was purchased from Aldrich Co. Ltd, and used without further purification. 2,2-Diphenyl-1-picrylhydrazyl (DPPH) was purchased from Tokyo Kasei Kogyo and recrystallized from a chloroform-ethanol mixture. The following compounds were used as spin-trapping reagents (Scheme 1).



Scheme 1

The seven kinds of spin trap were obtained from Aldrich and used as received. Reagent-grade solvents were dried over Molecular Sieves 4A-1/16 and distilled before use.

EPR measurements: A JEOL JES-FE3XG spectrophotometer equipped with 100-kHz field modulation was used for the EPR measurements. Reactant solutions of Ph_2PH(2.5×10^{-1} mol/dm^3), DPPH (2.5×10^{-2} mol/dm^3), and the traps ($6 \sim 25 \times 10^{-2}$ mol/dm^3) were separately charged into three glass tubes, which are connected with glass tubes in the shape of H with a side tube for EPR measurements. After the solutions were degassed by freezing and thawing under a vacuum, the three solutions were mixed and were transferred into the side tube. The EPR spectra were simulated and integrated with an attached computer. The integration of the EPR spectra was used to determine the relative concentration to the produced DMPO-adducts. The *g*-values were estimated with the aid of a frequency counter (Advantest TR5214) and the *g*-value of DPPH.

Results and discussion

Spin trapping of the diphenylphosphinyl radical: The stable free radical DPPH has been used both as a radical scavenger and also as a hydrogen acceptor. In a previous paper,[6] we have reported that DPPH abstracts the hydrogen atom of Ph_2PH to produce the phosphorus-centred radical, diphenylphosphinyl ($\cdot PPh_2$). However, the EPR signal of the $\cdot PPh_2$ radical could not be observed at room temperature. When the trap PBN was added to the Ph_2PH/DPPH system, one kind of EPR signal appeared, as shown previously.[6] Based on the *g* value and the hyperfine structure (hfs) of the EPR spectra, we have suggested that the formed phosphinyl radical is trapped by PBN as a nitroxide radical. The following reaction occurs:

$$Ph_2PH + DPPH \rightarrow \cdot PPh_2 + DPPH_2 \quad (1)$$

$$\cdot PPh_2 + PBN \rightarrow PBN\text{-}PPh_2 \quad (2)$$

The spin-adduct PBN-PPh_2 exhibits the characteristic splitting into a large doublet caused by a phosphorus atom.

When the substituted PBN (4-NO_2-PBN and 4-POBN) was added to the Ph_2PH/DPPH system, EPR spectral patterns similar to that of the Ph_2PH/DPPH/PBN system were observed. The observed EPR spectra were assigned to the diphenylphosphinyl adducts (4-NO_2-PBN-PPh_2 and 4-POBN-PPh_2); the EPR parameters are given in Table 1. These spin adducts also show the characteristic hfcc caused by the phosphorus atom. The A_N values of the spin adducts reflect the electronic properties of the captured radicals. Abe *et al.*[7] reported on the EPR parameters for spin adducts of aryl and alkyl radicals trapped by several kinds of substituted PBN. The A_N values for the

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* To receive any correspondence. E-mail: ysueishi@cc.okayama-u.ac.jp

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 EPR parameters for adducts observed in benzene at 25°C

Adduct	A_P(mT)	A_N(mT)	A_H(mT)	g value
PBN–PPh_2	1.82	1.41	0.38	2.0060
4-NO_2–PBN–PPh_2	1.89	1.40	0.28	2.0060
4-POBN–PPh_2	1.94	1.42	0.26	2.0062
DMPO–PPh_2	3.72	1.36	1.83	2.0057
TMPO–PPh_2	2.50	1.36	2.72	2.0060
NB–PPh_2	1.04	0.91	0.23(*o*,*p*-H) 0.08(*m*-H)	2.0064

spin adducts of oxygen-centred radicals (1.33–1.42 mT) are smaller than those of carbon-centred radicals (1.43–1.49 mT). The smaller values of A_N can be attributed to the higher degree of electronegativity of the captured oxygen-centred radicals. In examining the data in Table 1, we compared the A_N values of the $\cdot PPh_2$ adducts trapped by the PBN traps in benzene with those of the oxygen-centred radicals. The data suggest that the PPh_2 moiety in the spin adduct reduces spin density around the aminoxyl function, causing a decrease in the A_N values.

Previously, we have reported that the $\cdot PPh_2$ radical is efficiently trapped by DMPO.[6] The formed spin-adduct DMPO-PPh_2 has an EPR signal pattern similar to that trapped by PBN. The spin adduct exhibits the remarkably large hfcc, compared with the hfcc of PBN-adducts. Analogous with DMPO, TMPO also traps the $\cdot PPh_2$ radical. The EPR parameters of DMPO-PPh_2 and TMPO-PPh_2 are listed in Table 1. Although TMPO has the same 5-membered molecular skeleton as does DMPO, the A_P value of the spin adduct trapped by TMPO having methyl groups at the 3 and 5 positions is smaller than that of DMPO. As suggested by Janzen and Zhang,[4] the dihedral angle between the *p* orbital of the aminoxyl nitrogen atom and C_2-P bond is directly related to the hyperfine splitting constant A_P. The above results of the A_P values are responsible for the difference in the equilibrium position of $–PPh_2$ in the spin adducts.

When BNB was used as a trap reagent, the EPR signal of the spin adduct could not be obtained in the Ph_2PH/DPPH/BNB system. In the case of BNB, the steric circumstances around the nitroso group are severe, and the bulky $\cdot PPh_2$ radical may not be trapped. When NB was used in the place of BNB, one kind of EPR signal was observed (Fig. 1(1)). Judging from the *g*-value in Table 1, the spin adduct can be regarded as a nitroxide radical and can be assigned to the NB-PPh_2 adduct, trapped by NB. The hfs of the NB-PPh_2 adduct can be assigned to A_P=1.04 mT, A_N=0.91 mT, $A_{o,p\text{-}H}$=0.23 mT, and $A_{m\text{-}H}$=0.08 mT. Using these EPR parameters, the observed EPR spectrum is easily reproduced (Fig. 1 (2)). Compared with the A_P and A_N values trapped by PBN and DMPO, the small A_P and A_N values suggest the flow of spin into the benzene ring.

Relative spin-trapping efficiency: When Ph_2PH was mixed with DPPH in the presence of two kinds of traps (for example, PBN and DMPO), the EPR spectrum shown in Fig. 2 was observed. The observed spectrum was easily reproduced by means of the superposition of the simulation using the EPR parameters of two kinds of the spin adducts (PBN-PPh_2 and DMPO-PPh_2). The reaction scheme in the Ph_2PH/DPPH/PBN-DMPO system is given below.

$$Ph_2PH + DPPH \rightarrow \cdot PPh_2 + DPPH_2 \qquad k_1 \qquad (1)$$

$$\cdot PPh_2 + PBN \rightarrow PBN\text{-}PPh_2 \qquad k_2 \qquad (2)$$

$$\cdot PPh_2 + DMPO \rightarrow DMPO\text{-}PPh_2 \qquad k_3 \qquad (3)$$

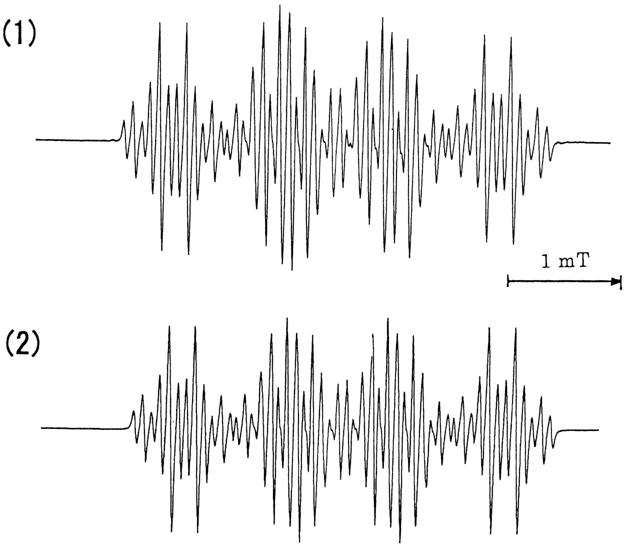

Fig. 1 EPR signals of the Ph_2PH/DPPH system in the presence of (1) NB in benzene at 25°C and (2) simulated spectrum using EPR parameters of the NB–PPh_2 adduct.

Fig. 2 (1) EPR signals of the Ph_2PH/DPPH system in the presence of PBN and DMPO in benzene at 25°C. (2) Simulated spectrum.

To determine the reaction rate between Ph_2PH and DPPH, it is instructive to examine the UV–VIS absorption spectra. DPPH shows a strong absorption in the vicinity of 520 nm. When Ph_2PH was mixed with DPPH, the absorption band at 520 nm decreased as time went by, and 2,2-diphenyl-1-picrylhydrazine ($DPPH_2$) was formed. From following the change in the visible absorption spectra, the rate constant for the abstraction of hydrogen atoms by DPPH was estimated to be 1.93×10^{-3} dm^3/mol/s in benzene at 25°C. We observed that the reaction rate between Ph_2PH and DPPH is not influenced by the addition of spin traps (PBN and DMPO) and $DPPH_2$ to the reaction solution, which suggests that the hydrogen-abstraction reaction by DPPH is not reversible.

We considered that the rate constant for the trapping reaction of the $\cdot PPh_2$ radical is fast compared with the abstraction reaction of the hydrogen atom by DPPH, and therefore the first step is determining the rate. Since the present rate analysis for the formation of spin adducts at the initial stage is the so-called initial rate method, it is not necessary to consider that the spin adducts are formed reversibly. The ratio (R_P/R_D)

of the formation rates for PBN–PPh$_2$ and DMPO–PPh$_2$ adducts at the initial stage can be expressed as follows.

$$\frac{R_P}{R_D} = \frac{(d[\text{PBN-PPh}_2]/dt)_{t\to 0}}{(d[\text{DMPO-PPh}_2]/dt)_{t\to 0}} = \frac{k_2\,[\text{PBN}]_0}{k_3\,[\text{DMPO}]_0} \qquad (4)$$

where [PBN]$_0$ and [DMPO]$_0$ denote the initial concentration of traps. Since the two kinds of phosphorus-containing adducts can easily be distinguished from each other because of the characteristic phosphorus hfs, the relative concentrations of the spin adducts formed can be determined from the EPR spectra of the competing reactions. Figure 3 (1) shows the time dependence of the concentrations of the PBN–PPh$_2$ and DMPO–PPh$_2$ adducts formed during the initial stage. During the initial stage, the concentrations of the formed spin adducts increase linearly with time, and the slopes of the linear plots correspond to the formation rates (R_P and R_D) of the spin adducts. The relative spin-trapping efficiency (k_2/k_3) can be determined from the slopes of the linear plots (the formation rates of adducts) and the concentration of the two dissolved spin-trap reagents. As predicted by equation (4), plotting R_P/R_D against [PBN]$_0$/[DMPO]$_0$ gives a straight line with slope k_2/k_3 and passes through the origin (Fig. 3(2)), suggesting that the above estimation of the relative rate constant is reasonable. The relative reactivities of the ·PPh$_2$ radical toward five kinds of spin traps were determined in benzene and chloroform using DMPO as a reference (Table 2): 4-POBN was not sufficiently soluble in benzene for the measurement of the relative rate.

From an inspection of the data in Table 2, we notice that spin trapping of the ·PPh$_2$ radical by PBN is more favourable than that by DMPO. The low efficiency of trapping by TMPO may be attributed to steric hindrance of methyl groups. There have been some reports about relative spin-trapping efficiency. Schmid and Ingold[8] reported the relative rate constant for spin trapping of 5-hexenyl to be PBN:4-NO$_2$-PBN=1:2.2. For spin trapping of oxygen-centred radicals, PBN: 4-NO$_2$-PBN=1:0.45 is reported for the PhCOO· radical[9] and PBN: 4-NO$_2$-PBN=1:0.62 is reported for the Bu^{t}O· radical.[7] Our observation for spin trapping of the phosphorus-centred radical is similar to that of 5-hexenyl, while the relative rate for spin trapping of the oxygen-centered radical exhibits an opposite tendency. Hirota and co-workers[7,10] have calculated molecular orbits in order to rationalise the spin-trapping reaction theoretically and suggested that spin trapping of 5-hexenyl has nucleophilic reactivity toward the traps of PBN. As in the case of the trapping reaction of 5-hexenyl, we consider that the nucleophilic addition of the ·PPh$_2$ radical occurs toward the spin traps.

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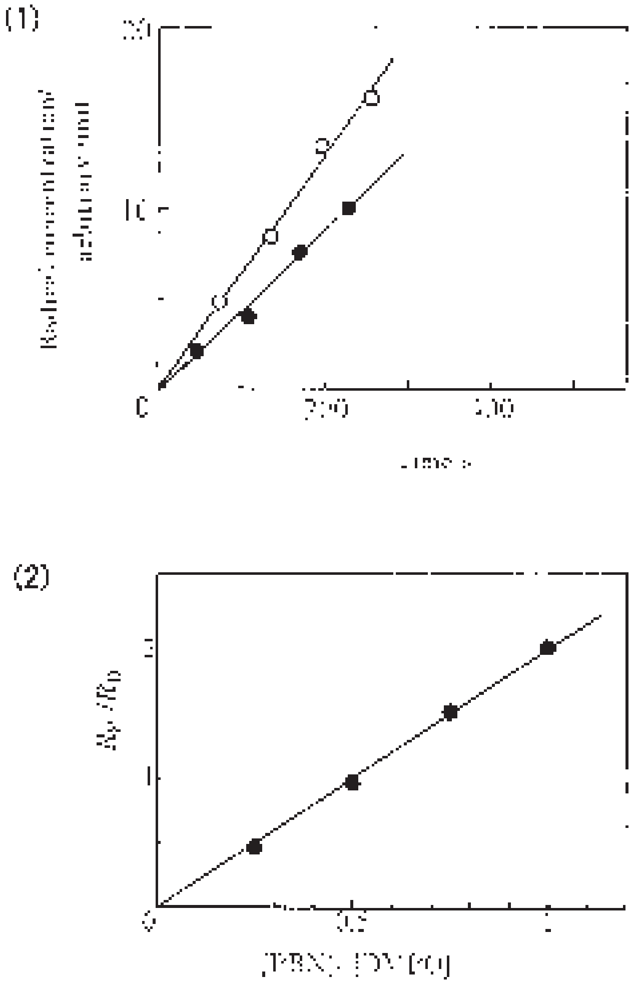

Fig. 3 (1) Time dependence for spin trapping of the ·PPh$_2$ radical by (○) PBN and (●) DMPO in benzene at the initial stage: [PBN]$_0$/[DMPO]$_0$=0.75. (2) Plots of R_P/R_D against [PBN]$_0$/[DMPO]$_0$ in benzene at 25°C.

Table 2 Relative rate constans for spin trapping of ·PPh$_2$

Spin strap	k_2/k_3	
	In benzene	In chloroform
PBN	2.0	1.2
4-NO$_2$–PBN	2.5	3.4
4-POBN	–	1.4
TMPO	<0.1	<0.1
DMPO	1.0	1.0

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