

# Magnetic Field Dependence of the $^{31}\text{P}$ CIDNP in the Photolysis of a Benzyl Phosphite. Evidence for a $T_{-}-S$ Mechanism

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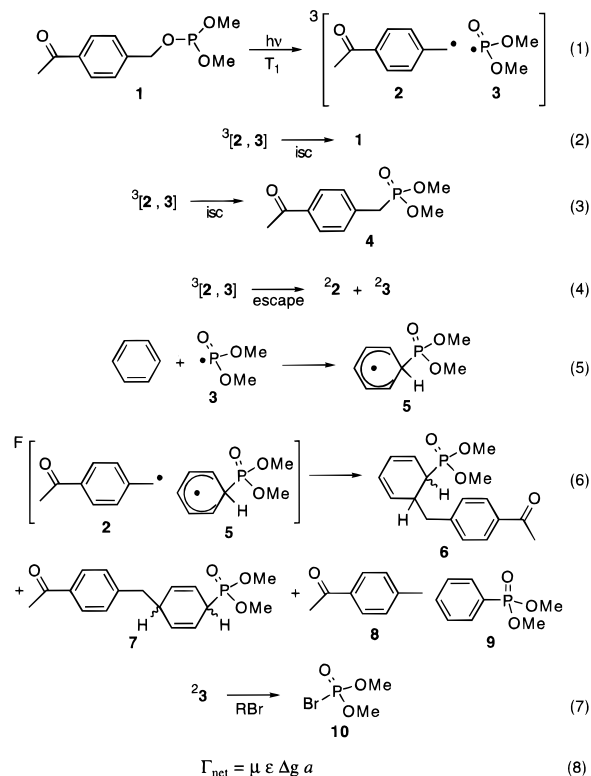
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$^{31}\text{P}$  chemically induced dynamic nuclear polarization (CIDNP) studies of the photochemistry of *p*-acetylbenzyl dimethyl phosphite (**1**) provide evidence for the operation of the relatively rare  $T_{-}-S$  intersystem crossing mechanism for a photochemically generated triplet free radical pair. The mechanism of intersystem crossing of the triplet radical pair *p*-acetylbenzyl (**2**) and dimethoxyphosphonyl (**3**), generated from **1**, is influenced by the large  $^{31}\text{P}$  hfcc of **3** and switches from the  $T_{-}-S$  mechanism in a relatively low magnetic field (18.8 kG) to the conventional  $T_0-S$  pathway at a higher field (58.8 kG). This change in mechanism is evidenced by the photolysis of **1** in the presence of radical scavengers (halocarbons, thiophenol) which yields the corresponding products from atom abstraction by **3** that has escaped the initial radical cage. These escape products are *absorptively polarized* at high field ( $T_0-S$ ) but are *emissively polarized* at lower field ( $T_{-}-S$ ) in a particularly well-defined display of the effect of magnetic field strength on intersystem crossing mechanism for a geminate radical pair. Photolysis of **1** in  $\text{C}_6\text{D}_6$  solution yields emissively polarized dimethyl *p*-acetylbenzylphosphonate (**4**) from combination of radical pair [2,3] in the initial solvent cage and following diffusive formation of [2,3] free pairs. Cage recombination and disproportionation of secondary F pairs, comprised of **2** and the phosphorus-substituted cyclohexadienyl radical (**5**), affords several emissively polarized products (**6**, **7**, and **9**) via the  $T_0-S$  mechanism at both magnetic fields. The polarization of **4** remains emissive at both magnetic fields regardless of the presence of radical scavengers, a finding which is argued to be consistent with the above results.

Several mechanisms can be operative in the generation of both chemically induced dynamic electron (CIDEP) and nuclear polarization (CIDNP) observed in the ESR spectra of radical intermediates and in the NMR spectra of radical-derived products, respectively.<sup>1–3</sup> For radical pairs (RP) in solution, the most commonly encountered mechanism responsible for both phenomena is the  $T_0-S$  mixing of spin states. Much more rarely the  $T_{-}-S$  mechanism prevails, and usually requires the mobility of the partners in the pair to be restricted, e.g., as in highly viscous solvents<sup>4</sup> or in biradicals.<sup>5</sup> However, the  $T_{-}-S$  mechanism can be operative for a RP in solution at ambient temperature<sup>6,7</sup> if one of the radicals possesses an unusually large hyperfine coupling constant (hfcc). Time-resolved ESR studies<sup>8</sup> have implicated the possible involvement of  $T_{-}-S$  transitions in CIDEP phenomena observed on generation of the triplet primary RP [2,3] by photolysis of *p*-acetylbenzyl dimethyl phosphite (**1**) in solution in a 3.5 kG magnetic field (eq 1, Scheme 1). Indeed, the hfcc of phosphonyl radical **3** is large ( $ap \approx 700$  G)<sup>8–10</sup> and could facilitate intersystem crossing by the  $T_{-}-S$  pathway. However, a unique interpretation of the CIDEP data could not be made due to the simultaneous action of several electron polarization mechanisms.

In this letter we report definitive steady-state  $^{31}\text{P}$  CIDNP<sup>11,12</sup> evidence for the involvement of  $T_{-}-S$  intersystem crossing in the triplet RPs [2,3] generated from photolysis of **1** in benzene solution at ambient temperature. The key observation is the

## SCHEME 1



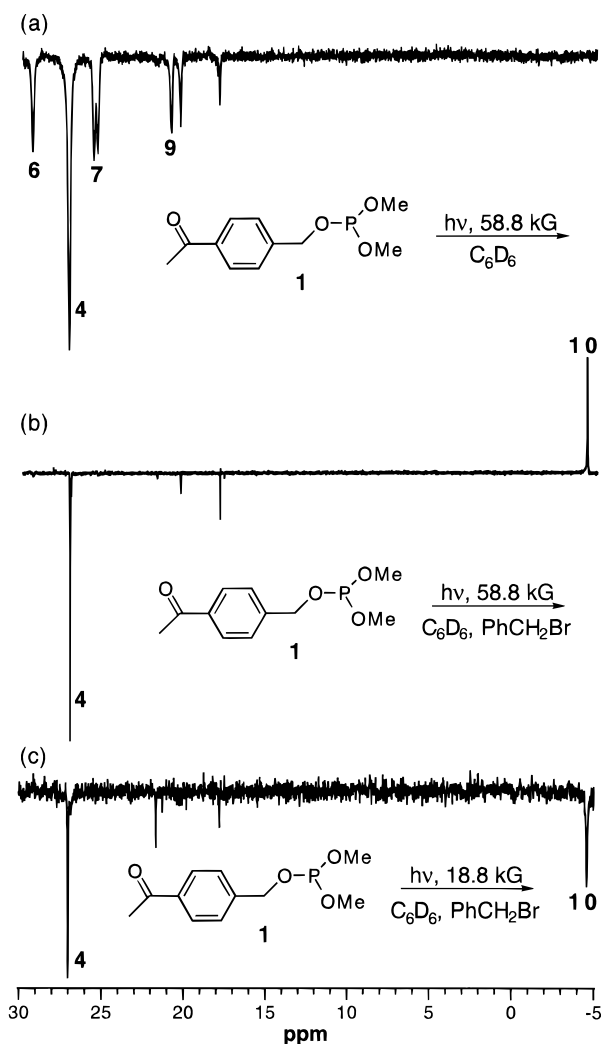
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magnetic field strength dependence of the net polarization of product **10** formed on trapping of cage-free phosphonyl radical



**Figure 1.**  $^{31}\text{P}$  CIDNP spectra recorded at high field (101.26 MHz, 58.8 kG) during the photolysis of deoxygenated 0.1 M benzene- $d_6$  solutions of **1** (a) in the absence and (b) in the presence of 0.2 M benzyl bromide. Part (c) is the  $^{31}\text{P}$  CIDNP spectrum recorded at low field (32.44 MHz, 18.8 kG) during the photolysis of a deoxygenated 0.1 M benzene- $d_6$  solution of **1** in the presence of 0.4 M benzyl bromide.

**3** by benzyl bromide (eq 7) and other radical scavengers which switched from *absorption* at 58.8 kG ( $T_0$ -S) to *emission* at 18.8 kG ( $T_-$ -S).

The radical pair theory of CIDNP<sup>13</sup> predicts that under conditions of  $T_0$ -S mixing the net polarization ( $\Gamma_{\text{net}}$ , emission or absorption) of a product is dependent upon four parameters (eq 8): the initial spin multiplicity of the radical pair ( $\mu$ ), the mode of product formation ( $\epsilon$ , in-cage or escape), the sign of the difference in  $g$  factors of the two radicals ( $\Delta g$ ), and the sign of the hfcc ( $a$ ) of the nucleus whose polarization is observed. Thus the sign of the polarization will depend on whether product formation from a given polarized radical occurs before or after it exits the initial solvent cage. By contrast the  $T_-$ -S intersystem crossing mechanism requires that *all* polarized resonances arising from a triplet-born RP show *emission*.<sup>1-3</sup> Therefore, CIDNP can serve to identify conclusively the principal  $T$ -S mixing channel.

Figure 1a,b shows  $^{31}\text{P}$  CIDNP spectra taken at 101.26 MHz (58.8 kG) upon photolysis of **3** in  $\text{C}_6\text{D}_6$  without (Figure 1a) and with (Figure 1b) added benzyl bromide ( $\text{PhCH}_2\text{Br}$ ). Figure 1c displays the CIDNP spectrum with added benzyl bromide obtained on a low-field NMR spectrometer (32.44 MHz, 18.8 kG). (A spectrum recorded at 32.4 MHz (18.8 kG) in the absence of benzyl bromide was very similar to Figure 1a except

for some small changes in relative line intensities and the disappearance of one of the unassigned lines observed in Figure 1a). With the exception of the resonance due to **1** (not shown,  $\delta = 141.1$  ppm), all signals in Figure 1 correspond to strongly polarized products and disappear entirely when the light is turned off. The nuclear polarization parameters (eq 8) for radical pair [**2,3**] (eq 1) can be assigned unambiguously based on: its triplet origin ( $\mu > 0$ ); the  $g$  factors of radicals **3** ( $g = 2.0018^{10}$ ) and **2** ( $g = 2.00292^{14}$ ,  $\Delta g < 0$ ); and the positive value of  $ap$  for **3** ( $\approx +700$  G).<sup>8-10</sup> The strongest emissive signal in Figure 1a-c ( $\delta = 27.0$  ppm) is that of *p*-acetylbenzyl dimethyl phosphonate (**4**), which accounts for 10–12% of the products formed at low conversion of **1** in the absence of radical scavengers.<sup>8</sup> The observed emissive polarization of **4** ( $\Gamma_{\text{net}} < 0$ ) is predicted by both the  $T_0$ -S and  $T_-$ -S CIDNP mechanisms for the formation of **4** either from combination of the primary [**2,3**] pair (eq 3) or combination of [**2,3**] free pairs formed on random encounter after cage escape ( $\epsilon > 0$ ; cage yield of **4**, ca. 3%).

Very significantly, during photolysis of **1** in the presence of benzyl bromide (Figure 1b,c), the polarized resonances due to **6**, **7**, and **9** (see below) are no longer present. As benzyl bromide is an effective trap for phosphonyl radical **3**, converting it to dimethyl phosphorobromidite (**10**,  $\delta = -4$  ppm),<sup>15,16</sup> the missing resonances can be very reasonably assigned to products formed by **3** following its escape (eq 4) from the primary [**2,3**] caged pair (see below). The *absorptive polarization* of **10**, formed from cage-escaped **3** ( $\epsilon < 0$ ), along with the emissive polarization of cage product **4**, points unambiguously to the *predominance of the  $T_0$ -S mechanism at the higher field* (101.3 MHz, 58.8 kG). In striking contrast, however, in the low field spectrum (Figure 1c) both **4** (in-cage;  $\epsilon > 0$ ) and **10** (escape product;  $\epsilon < 0$ ) are *emissively polarized*. This result can only be reconciled with the CIDNP paradigm by assuming *the predominance of  $T_-$ -S mixing*. The observation of CIDNP due to the  $T_-$ -S mechanism in the magnetic field of an NMR spectrometer in nonviscous solution is rare indeed, especially when it originates from photolytically generated primary geminate RPs. This study represents a particularly clear cut example of the effects of magnetic field change on the mechanism of nuclear polarization of products of a photoreaction proceeding via RPs.

The CIDNP behavior observed with benzyl bromide was confirmed by the formation of polarized product of trapping by other phosphonyl radical scavengers. Thus,  $\text{BrCCl}_3$  yielded **10** and  $(\text{MeO})_2\text{P}(\text{O})\text{Cl}$ . The latter was also formed, along with  $(\text{MeO})_2\text{P}(\text{O})\text{CCl}_3$ , in the presence of  $\text{CCl}_4$ . Radical **3** was trapped by  $\text{PhSH}$  to afford  $(\text{MeO})_2\text{P}(\text{O})\text{H}$ . *In all cases the in-cage product **4** ( $\epsilon > 0$ ) is emissively polarized, while the polarization of the corresponding product of phosphonyl radical escape ( $\epsilon < 0$ ) switches from absorption in the high-field spectra to emission in the low-field ones.*

The entirely emissive appearance of the spectra recorded in the absence of benzyl bromide *at both magnetic fields* is at first glance inconsistent with the benzyl bromide trapping experiments at the higher field that would seem to require the *absorptive polarization* of all products formed from **3** that had escaped the initial solvent cage. However, more careful consideration allows the emissive polarization of the cage-escape products **6**, **7**, and **9** to be attributed to their formation via secondary radical pairs (eqs 5 and 6) in which the absorptive cage-escape polarization of radical **3** has been lost. As argued below the polarization of **6**, **7**, and **9** evolves via the  $T_0$ -S mechanism at both fields.

Thus, phosphonyl radical (**3**) reacts with benzene (eq 5) to yield cyclohexadienyl radical **5**,<sup>17</sup> which becomes associated

with radical **2** as the free pair [2,5] (eq 6). The CIDNP spectrum of Figure 1a displays peaks corresponding to the products known<sup>8</sup> to arise from reactions of free pair [2,5] (eq 6), namely, the 1,2-coupling product **6** ( $\delta = 29.2$  ppm), two diastereomers (cis and trans) of the 1,4-coupling product (**7**,  $\delta = 25.3$  and  $25.5$  ppm), and dimethyl phenyl phosphonate (**9**,  $\delta = 20.8$  ppm<sup>18</sup>). The emissive polarization of **6**, **7**, and **9** at both magnetic fields is consistent with  $T_0$ -S mixing in the secondary, caged F pair [2,5] ( $\mu > 0$ ) in both instances, followed by in-cage ( $\epsilon > 0$ ) recombination or disproportionation<sup>19</sup> and requires that the  $^{31}\text{P}$  hfcc in **5** be positive ( $a > 0$ ) and the  $g$  factor difference be negative ( $\Delta g < 0$ ).<sup>20</sup> The emissive escape polarization of **3** generated in the primary RP, expected to impart emissive polarization to products **6**, **7**, and **9**, evidently is lost due to the expected long lifetime of **5** and/or its fast nuclear relaxation. Evidently, and not surprisingly, the phosphorus hfcc in cyclohexadienyl radical **5** ( $ap \approx 110$  G)<sup>17</sup> is not large enough to induce  $T_0$ -S mixing.

In conclusion, we have shown that the relatively rare  $T_0$ -S intersystem crossing mechanism is operative for the RP [2,3] in nonviscous solutions, not only in ESR magnetic fields (3.5 kG), but also is the dominant contributor to  $^{31}\text{P}$  CIDNP effects at the 18.8 kG field of an NMR spectrometer. The operation of this mechanism no doubt results from the very large  $ap$  value for **3** ( $\approx 700$  G). At a higher magnetic field (58.8 kG),  $T_0$ -S mixing predominates. This unambiguous interpretation of the  $^{31}\text{P}$  CIDNP polarization patterns arises from the effects of the addition of phosphonyl radical scavengers that prevent the formation of secondary phosphorus radicals from reactions of cage-escaped **3** with solvent benzene. This study clearly demonstrates the application of magnetic field changes to the discernment of the mechanism of spin polarization of RPs.

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- (21) Dimethyl phenyl phosphonate (**9**) can also be formed via a slow disproportionation reaction following escape of cyclohexadienyl radicals **5** from the geminate F pair. Such a process would lead to an absorptive component of polarization in **9** and, thus, plays a minor role in this case.
- (22) This assignment apparently contradicts the  $g$  factors in the literature.<sup>9,17</sup> However, the reported values are too close for an unambiguous conclusion.

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