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Magnetic Field Effects on the Photodissociation Reaction of Triarylphosphine in Nonviscous Homogeneous Solutions

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The magnetic field effects (MFEs) on the photodecomposition reactions of triphenylphosphine and its halogen and methyl derivatives are investigated in fluid solutions. The yield of diarylphosphinyl radicals decreased with increasing magnetic field from 0.1 to 5 T but was stationary below 0.1 T and above 5 T. The MFE becomes larger by the substitution of halogen atoms and the 3- or 4-methyl group. In cyclohexane, the yields of the escaped diarylphosphinyl radicals at 1 T are reduced to 0.69, 0.55, 0.59, and 0.56 of those at 0 T for triphenylphosphine and its tris(4-chloro), tris(3-methyl), and tris(4-methyl) derivatives, respectively. This magnetic field dependence was ascribed to originate from the deactivation process of the excited triplet state, which is a variant of the d-type triplet mechanism originally proposed by Steiner. The interaction between the closely lying nπ* and $\pi\pi$* states makes their solvent dependence complicated.

1. Introduction

Most of the magnetic field effects (MFEs) of chemical reactions in the liquid phase have successfully been explained in terms of the radical pair mechanism (RPM).[1−3] A radical pair (RP) consists of two radicals surrounded by solvent molecules. The component radicals are interacting weakly with each other. Figure 1 shows the reaction scheme of an RP generated photochemically by bond fission. Here, triarylphosphine (Ar_3P) was taken as an example. This reaction scheme is confirmed in section 3.1.

In this scheme, four possibilities (A−D) of the magnetic field-dependent processes are shown. The first two (A, B) are the intersystem crossing (ISC) processes to depopulate and to populate the excited triplet state. To discriminate between them, we use the words depopulation and population type (d- and p-type) mechanisms for processes A and B.[4] Usually, processes A and B are not considered in the MFEs on chemical reactions in the liquid phase. In a contact RP, which appears immediately after the fission or just before the collision of an RP, the energy separation between its singlet and triplet states becomes larger than the magnetic interactions. Therefore, the spin conversion between the singlet and the triplet states is blocked, where the recombination of the pair proceeds through the singlet state. The spin-forbidden recombination process, C, is sometimes considered in the RP including heavy atoms, and this process is usually considered to be independent of a magnetic field. Although this does not mean that processes A−C are not possible origins of the MFEs, almost all efforts have been devoted to process D, the ISC of separated RPs.

Because the energy separation between the singlet and triplet states of a separated RP is much smaller than that of contact RPs, the magnetic interaction can induce a sizable effect on separated RPs. Thus, most MFEs on chemical reactions through RPs have been explained in terms of the RPM. The hyperfine coupling mechanism (HFCM), the Δg mechanism (ΔgM), the relaxation mechanism (RM), and the level-crossing mechanism (LCM) are variants of the RPM. The lifetime of the RP and hence the magnitude of its MFE are largely dependent on the confinement of the RP (i.e., the "cage effect") of its solvent. Therefore, the MFE becomes smaller if the solution becomes more fluid.

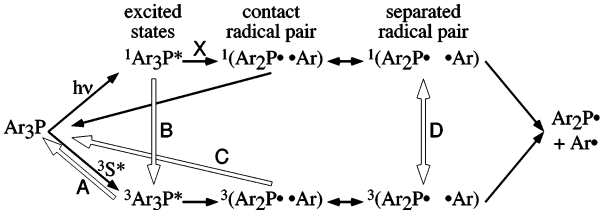

Figure 1. Four possible pathways (A−D) of the magnetic field-dependent processes in the photodecomposition reaction of triplet triarylphosphine. $Ar_2P^\bullet$, $Ar^\bullet$, and $^3S^*$ stand for the diarylphosphinyl radical, the aryl radical, and a triplet sensitizer. Path X is excluded in the real reaction scheme.

In 1979, Steiner reported large MFEs in the electron-transfer reactions between thiazine dyes and electron donors containing heavy atoms.[5] Such large MFEs and the field dependence of the effects could not be ascribed to the HFCM, ΔgM, RM, and LCM. He ascribed the origin of their MFEs to the spin-forbidden back-electron-transfer process of triplet exciplexes, which competes with the escape to the free radicals.[6,7] Although Figure 1 is presented for neutral RPs, the magnetic field-dependent decay of these triplet exciplexes corresponds to process C because each triplet exciplex is a contact RP-type intermediate formed from the excited triplet state of the dye.[6] This mechanism has been called the d-type triplet mechanism (TM), where spin−orbit coupling (SOC) plays an important role. Because the recovery of the ground-state molecule from each exciplex must compete with the diffusive separation, the reaction rate of the backward electron transfer in the triplet exciplexes must be very large. Steiner's group reported and analyzed several MFEs due to this d-type TM.[8,9] Tero-Kubota's group expanded this

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mechanism to chemically induced dynamic electron spin polarization (CIDEP).[6,7,10,11] As far as we know, however, there has been no example of the MFE in process C for a contact RP of neutral radicals. By investigating the CIDEP of the photolysis of 2,2′-azobisbutyronitrile in solution, Paul's group found a d-type TM polarization of molecular origin.[12,13] Recently, they found MFEs and CIDEP for the sensitized photodecomposition reaction of azocumene in fluid solutions and explained them in terms of the d-type TM operating in the photoreactive triplet state[14] as anticipated by Steiner.[6] The origin of this MFE corresponds to process A in Figure 1.

In 1995, we reported large MFEs for the photodecomposition reaction of triphenylphosphine (Ph_3P) in fluid solutions below 1.34 T.[15] The magnitude of the MFEs was anomalously larger than usual MFEs of neutral RPs in fluid solutions. Tentatively, we ascribed the MFEs of Ph_3P to ΔgM. In 1997, we found that the MFEs at higher fields (1.5−10 T) did not obey the field dependence due to ΔgM. Therefore, we started to apply the d-type TM to our reactions.[16] The MFEs found by Paul's group encouraged our analyses.

In this article, we report on the reconsideration of the MFEs of Ph_3P using its halogen and methyl derivatives. Our conclusion for the origin of the MFEs of the photodecomposition reactions of Ar_3P is the d-type TM in the photoreactive molecular triplet state. This is analogous to the mechanism put forth by Paul and co-workers. However, we considered all four alternatives (A−D) for MFEs and consequently eliminated three of them. In each of our reactions, the solute is dissolved in a fluid solvent at low concentration. These are the simplest reaction conditions for the observation of MFEs in the condensed phases and for practical applications.

2. Experimental Section

Triphenylphosphine (Ph_3P, elemental analysis grade, Merck), tris(4-chlorophenyl)phosphine (4-$ClPh_3P$, Aldrich) and its 3-analogue (3-$ClPh_3P$, Aldrich), 4-bromophenyldiphenylphosphine (4-$BrPhPh_2P$, Aldrich), tris(2-methylphenyl)phosphine (2-$MePh_3P$, Aldrich) and its 3- and 4-analogues (3, and 4-$MePh_3P$, Aldrich), and tetrafluoro-1,4-dicyanobenzene (F_4DCNB, Aldrich) were applied without further purification. 1,4-Dicyanobenzene (DCNB, TCI) was recrystallized from an ethanol−benzene mixture. 2-Propanol, cyclohexane (high-performance liquid chromatography grades, Cica-Merck), *n*-hexane (high-performance liquid chromatography grade or UV analysis grade, Cica-Merck), *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane (99+% grades, Aldrich) were used as solvents without further purification.

Phosphine compounds are rather sensitive to oxygen in air. Although triarylphosphines are not pyrophoric, the weighing, the dissolution in solvents, and the preservation during the measurement were carried out in a glovebox filled with nitrogen gas. All solvents were degassed by sonication before the dissolution under nitrogen. The sample solution was supplied to the quartz flow cell by a Teflon tube surrounded by a rubber tube. Nitrogen gas flowed in the rubber tube to prevent the permeation of oxygen to the Teflon tube. The irradiated solution was not reused. No Tygon tube was applicable to the present experiments.

Laser flash photolysis experiments were performed at 293 K. They were basically the same as described previously.[17] The sample solutions were excited with the fourth (266 nm) harmonic of a Quanta-Ray GCR-1 or a GCR-103 Nd:YAG laser. The external magnetic fields (B) of 0−1.75 T were generated by a Tokin SEE-10W electromagnet. Those of B = 0−10 T were generated by an Oxford 37057 superconducting magnet with a PS120-10 power supply. The experiments under the lowest magnetic field (B < 0.2 mT for the electromagnet, B < 0.3 mT for the superconducting magnet) are denoted as those in the absence of a magnetic field.

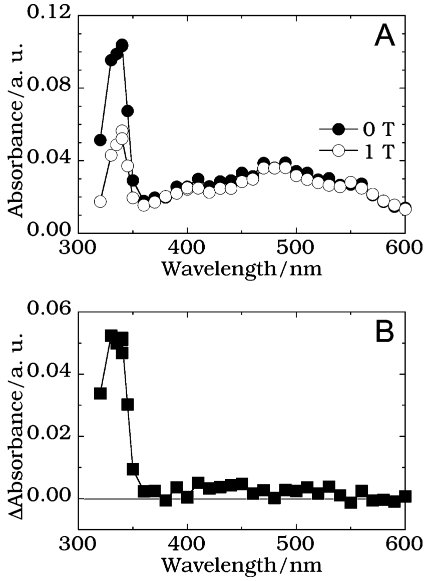

Figure 2. (A) Transient absorption spectra of 4-$ClPh_3P$ in *n*-dodecane in the absence (●) and presence (○) of a magnetic field of 1 T. (B) MFE spectrum, the difference in the above spectra.

In the present experiments, the time profiles of the transient absorbance, $A(t, B)$ curves, were measured in the absence and presence of a magnetic field. Because the magnetic field modified the immediate $A(t = 0 \text{ ns}, B)$ values, we could not use them as an internal standard to calibrate the fluctuation of laser power. To reduce the fluctuation of the power of each laser shot, we averaged the data over 10 shots. To avoid long-term variation of the laser power, we measured the $A(t, 0 \text{ T})$ curves frequently during the measurements of $A(t, B)$ ones. Using a second- or third-order polynomial fit for all $A(t, 0 \text{ T})$ measurements, we estimated the long-term variation of the laser power. Then we normalized all data assuming that the laser power was changing smoothly during the measurements at other fields between the measurements at 0 T.

3. Results and Discussion

3.1. Reaction Scheme. The $A(t, B)$ curves were measured for Ph_3P, 4-$ClPh_3P$, and 4-$BrPhPh_2P$ in nonviscous homogeneous solutions upon laser excitation (λ = 266 nm) at 293 K. Here, we concentrate on those of 4-$ClPh_3P$ because we described those of Ph_3P in the preliminary report.[15] The transient absorption spectra of 4-$ClPh_3P$ (1×10^{-3} mol dm^{-3}) observed in *n*-dodecane 200 ns after excitation in the absence and presence of a magnetic field of 1 T are shown in Figure 2A. Each spectrum shows a sharp peak at 340 nm and a broad one around 480 nm. The shape of each spectrum shown in Figure 2A was not changed during t = 0 ns and ∼4 μs. However, the magnetic field dependence of the peak at 340 nm is different from that at 480 nm. In Figure 2B, we plotted the MFE spectrum,[18] which is derived from the difference $A(t, 0 \text{ T}) - A(t, 1 \text{ T})$. This spectrum corresponds to the species whose yield is affected by the magnetic field. In this MFE spectrum, the peak at around 480 nm is missing. The spectrum shown in Figure 2B is very similar to the spectrum of the diphenylphosphinyl radical ($Ph_2P^\bullet$) observed in the reaction of Ph_3P,[15,19] although the peak position is shifted from 320 to 340 nm. Thus, we can definitely conclude

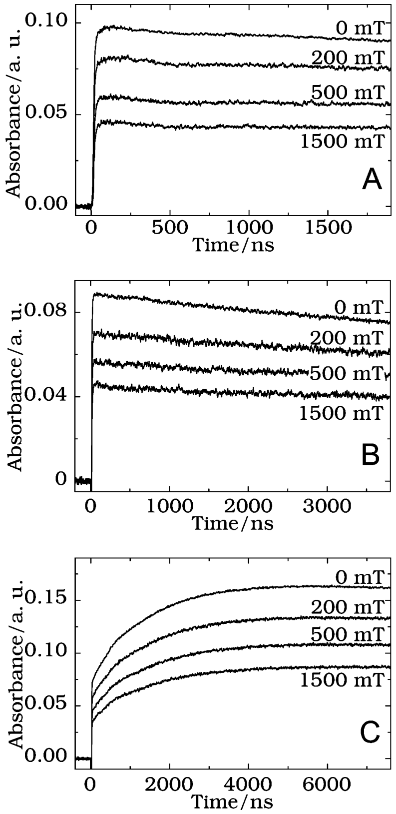

Figure 3. $A(t)$ curves observed at 340 nm for (A) 4-ClPh$_3$P in *n*-dodecane, (B) 4-ClPh$_3$P in 2-propanol, and (C) 4-ClPh$_3$P with F$_4$DCNB in 2-propanol.

that the peak at 340 nm is due to the bis(4-chlorophenyl)-phosphinyl radical (4-ClPh$_2$P$^\bullet$). Because the absorption around 480 nm shows no MFE and it was not observed in the reactions of Ph$_3$P and other derivatives, we shall not discuss it further.

The transient absorption spectrum of 4-BrPhPh$_2$P (1×10^{-3} mol dm^{-3}) in cyclohexane observed 200 ns after the excitation showed a sharp peak at 330 nm and a weak absorption up to 600 nm (data not shown). The resemblance and clear shift of the spectrum from that of Ph$_2$P$^\bullet$ implies that the observed sharp peak can be assigned to the 4-bromophenylphenylphosphinyl radical (4-BrPhPhP$^\bullet$).

Figure 3A shows the typical $A(t, B)$ curves observed in the dodecane solution of 4-ClPh$_3$P at 340 nm in the absence and presence of magnetic fields. Figure 3B shows those observed in a 2-propanol solution. Each of these $A(t)$ curves consists of a very fast rise and a slow decay. The slow decay is ascribed to the simple disappearance process of escaped radicals, a bimolecular process. Consequently, we can conclude that all processes prior to the escape of the RPs are completed before the decay of $A(t)$ curves, and we can safely use the $A(t)$ values later than 50 ns as the measure of the yield of the escaped Ar$_2$P$^\bullet$ radical.

In the study of Ph$_3$P in 2-propanol, we reported a sharp rise and decay immediately after the excitation together with a slow decay.[15] Preliminary picosecond laser photolysis revealed that the lifetime of the excited Ph$_3$P in solution was much shorter than the pulse width of our nanosecond laser. This means that the sharp rise observed in the 2-propanol solution is the integrated one of the singlet and/or triplet excited states during our nanosecond-laser pulse. However, we could not find such an absorption for 4-ClPh$_3$P on the nanosecond scale, which indicates that the lifetime of its precursor excited state should be shorter than that of Ph$_3$P.

In the previous report, we proposed the observed MFEs to be due to the triplet state from the polarization of the CIDEP spectra observed in the 2-propanol solution of Ph$_3$P. We can further confirm this conclusion using F$_4$DCNB in the sensitization experiments. Figure 3C shows the $A(t)$ curves observed at 340 nm for the 2-propanol solutions of 4-ClPh$_3$P (1×10^{-3} mol dm^{-3}) and F$_4$DCNB (1×10^{-3} mol dm^{-3}). The reaction dynamics changed drastically from that without F$_4$DCNB (cf. Figure 3B). Nevertheless, the observed transient absorption spectrum was not changed from that without F$_4$DCNB. Each of the $A(t)$ curves in Figure 3C consists of an immediate rise and a gradual rise that continues up to $\sim$5 μs. The immediate rise can be ascribed to the reaction by the direct excitation of 4-ClPh$_3$P. However, the slow rise was observed only in the presence of F$_4$DCNB. Because the lifetime of the singlet excited state of DCNB is reported to be merely 8.8 ns in acetonitrile,[20] the slow rise is not attributed to the sensitized decomposition of 4-ClPh$_3$P by the excited singlet state of F$_4$DCNB but to that of the excited triplet state. Similar behavior was observed in the reaction of Ph$_3$P with F$_4$DCNB or DCNB in 2-propanol, but the slow rise terminated within 1.5 μs. Therefore, we can draw the reaction scheme shown in Figure 1. Here, path X, which is the dissociation from the singlet excited state, is excluded, and ^{3}S* indicates ^{3}F$_4$DCNB* or ^{3}DCNB*.

Transient optical absorption spectra and their kinetic behavior for 2-MePh$_3$P, 3-MePh$_3$P, and 4-MePh$_3$P in cyclohexane solutions were also measured upon laser excitation ($\lambda = 266$ nm) at 293 K. Spectra similar to that of Ph$_3$P in cyclohexane were observed. The peak positions were 325, 325, and 330 nm for 2-, 3-, and 4-derivatives, respectively. The reaction scheme shown in Figure 1 is also applicable to these compounds.

3.2. Magnetic Field Dependence. In Figure 4A, the magnetic field dependence of the ratio $R(B) = A(t, \mathrm{B})/A(t, 0\ \mathrm{T})$ observed for Ph$_3$P in 2-propanol, cyclohexane, and *n*-hexane solutions is plotted against log(B/T). Here, the observation time, t, is taken to be 200 ns after laser excitation. This figure also shows the dependence of $R(B)$ observed at $t = 5\ \mu$s for Ph$_3$P with F$_4$DCNB (1×10^{-1} mol dm^{-3}) in 2-propanol. The results in *n*-hexane and cyclohexane were obtained at 320 nm. The others were obtained at 330 nm. The selection of each observation wavelength was determined by respective experimental conditions. These $R(B)$ values correspond to the magnetic field dependence of the yield of the escaped Ph$_2$P$^\bullet$. The smooth lines are the best-fit curves based on the d-type molecular triplet mechanism, which is discussed later.

From Figure 4A, we observed the following peculiar MFEs for Ph$_3$P:

(a) The $R(B)$ values are almost constant between 0 and 0.1 T.

(b) Above 0.1 T, they start to decrease with increasing B.

(c) Their decrements become smaller above 1 T and are almost stationary above 5 T.

(d) The yields of the escaped Ph$_2$P$^\bullet$ at 10 T become as small as 0.68, 0.62, and 0.75 of those at 0 T in 2-propanol, cyclohexane, and *n*-hexane, respectively.

(e) If we take the $R(B)$ values at 10 T as limiting values, then the half fields of the effects, $B_{1/2}$, in 2-propanol, cyclohexane, and *n*-hexane are 0.4, 0.5, and 0.7 T, respectively.

(f) The sensitized reaction with F$_4$DCNB showed the same magnetic field dependence as that without F$_4$DCNB within experimental error.

In Figure 4B, the magnetic field dependence of the $R(B)$ values observed for 4-ClPh$_3$P in 2-propanol ($t = 200$ ns), cyclohexane ($t = 100$ ns), and *n*-hexane ($t = 100$ ns) solutions

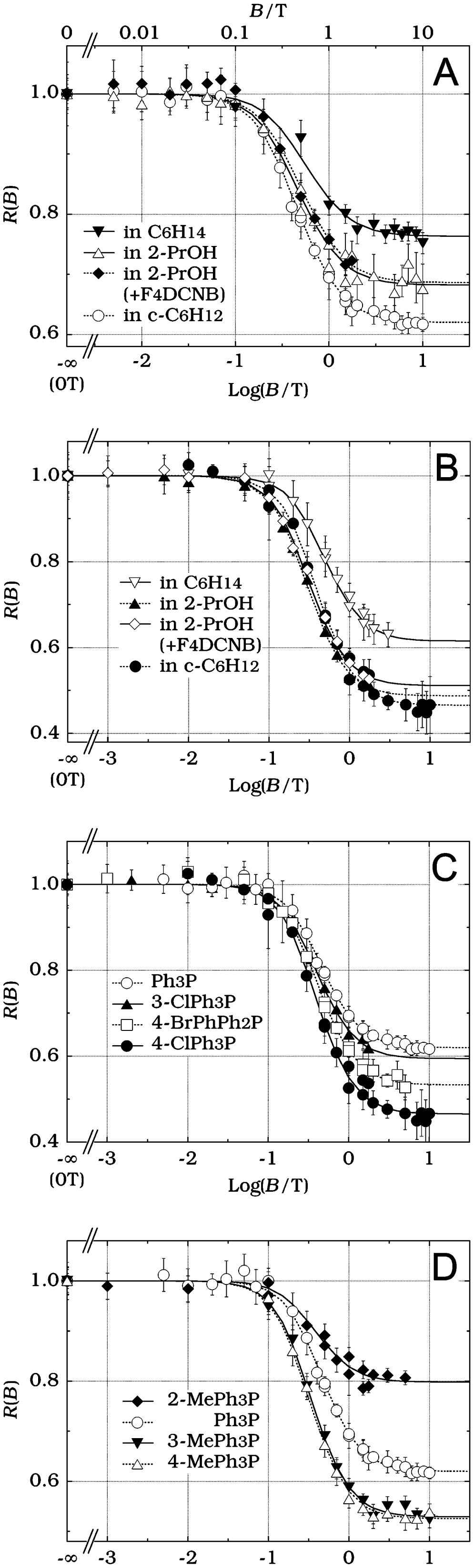

Figure 4. $R(B)$ values versus $\log(B/\mathrm{T})$ of (A) Ph_3P in *n*-hexane and cyclohexane and in 2-propanol in the absence and presence of F_4DCNB, (B) $4\text{-}ClPh_3P$ in *n*-hexane and cyclohexane and those in 2-propanol in the absence and presence of F_4DCNB, (C) Ph_3P, $3\text{-}ClPh_3P$, $4\text{-}BrPhPh_2P$, and $4\text{-}ClPh_3P$ in cyclohexane, and (D) Ph_3P, $2\text{-}MePh_3P$, $3\text{-}MePh_3P$, and $4\text{-}MePh_3P$ in cyclohexane.

is plotted. This figure also shows the $R(B)$ values observed at $t = 4$ μs for $4\text{-}ClPh_3P$ and F_4DCNB (2×10^{-1} mol dm^{-3}) in 2-propanol. The observation wavelength is 340 nm except for the low-field data in cyclohexane (335 nm). As is the case for Ph_3P, the $R(B)$ values are almost constant between 0 and 0.05 T. Above 0.05 T, they start to decrease with increasing B. Their decrements become smaller above 1 T and are almost stationary above 5 T. The $R(10\ \mathrm{T})$ values for the escaped $4\text{-}ClPh_2P^{\bullet}$ become as small as 0.46 ($B_{1/2} = 0.4$ T) and 0.62 ($B_{1/2} = 0.5$ T) in cyclohexane and *n*-hexane, respectively. The $R(1.75\ \mathrm{T})$ value in 2-propanol is 0.5, and its $B_{1/2}$ is estimated to be 0.3 T. The sensitized reaction with F_4DCNB gave the same magnetic field dependence as the direct one within experimental error.

In Figure 4C and D, we compared the magnetic field dependence of the $R(B)$ values observed for Ph_3P, $3\text{-}ClPh_3P$, $4\text{-}ClPh_3P$, and $4\text{-}BrPhPh_2P$ in cyclohexane and that of Ph_3P and 2-, 3-, and $4\text{-}MePh_3P$ in cyclohexane, respectively. The observation wavelengths are 320, 330, 325, 325, and 330 nm for $3\text{-}ClPh_3P$, $4\text{-}BrPhPh_2P$, $2\text{-}MePh_3P$, $3\text{-}MePh_3P$, and $4\text{-}MePh_3P$, respectively. The data of Ph_3P and $4\text{-}ClPh_3P$ are the same as those presented in Figure 4A and B, respectively. The $B_{1/2}$ values for $3\text{-}ClPh_3P$, $4\text{-}BrPhPh_2P$, $2\text{-}MePh_3P$, $3\text{-}MePh_3P$, and $4\text{-}MePh_3P$ in cyclohexane are estimated to be 0.4, 0.4, 0.4, 0.4, and 0.3 T, respectively.

The above-mentioned MFEs are very unique as compared with the ordinary MFEs observed in fluid solutions. The present MFEs are characterized as follows:

(i) The magnitudes of the present MFEs ($1\text{-}R(B)$) are much larger than the conventional ones. Even in the most fluid solvent examined, *n*-hexane, the $R(10\ \mathrm{T})$ values attained such small values as 0.75 and 0.62 for Ph_3P and $4\text{-}ClPh_3P$, respectively. The magnitudes of the MFEs (25 and 38% decreases) are much larger than those of conventional MFEs in fluid solutions (usually less than 10%).

(ii) There is no detectable MFE below 0.1 T for Ph_3P and $2\text{-}MePh_3P$ and below 0.05 T for $3\text{-}ClPh_3P$, $4\text{-}ClPh_3P$, $4\text{-}BrPhPh_2P$, $3\text{-}MePh_3P$, and $4\text{-}MePh_3P$, respectively. However, the effects converge below 10 T for all Ar_3P species investigated. A magnetic field dependence such as that observed in the present study is completely different from those expected from the conventional mechanisms, as explained later.

(iii) The solvent dependence of the magnitude of the MFEs for Ph_3P and $4\text{-}ClPh_3P$ (*n*-hexane < 2-propanol < cyclohexane) does not correlate with the viscosity (0.313, 2.379, and 0.9751 cP, respectively). Furthermore, the effects of 2-propanol compared to those of cyclohexane for Ph_3P and $4\text{-}ClPh_3P$ are very different from each other.

(iv) The magnitude of the MFEs becomes larger by the substitution with heavy atoms. The magnitude of the MFEs of halogen-containing Ar_3P species is larger than that of Ph_3P, and the effect of one para-bromine substitution in $4\text{-}BrPhPh_2P$ is almost the same as that of three para-chlorine substitutions in $4\text{-}ClPh_3P$. This heavy-atom effect is also position-dependent. The para substitution of chlorine atoms exhibited a larger effect than the meta substitution.

(v) The 3- and 4-methyl substitutions also enhanced the MFEs in the same way that heavy atoms did. However, the 2-methyl substitution reduced the magnitude of the MFE to be smaller than that of Ph_3P.

Previously, we reported results on MFEs of neutral RPs in fluid solutions. In the photochemical electron-transfer reactions between triplet xanthone and *N*,*N*-diethylaniline in 2-propanol, we observed $R(1.5\ \mathrm{T}) = 1.13$ for the escaped aniline cation radical.[21] However, no MFE was observed beyond experimental error for the hydrogen-abstraction reaction between triplet xanthone and xanthene in 2-propanol.[21] The absence of an MFE in the last reaction is ascribed to the lack of a Coulombic attraction between the component radicals in a pair. In a very viscous solution of glycerin, the hydrogen-abstraction reaction between triplet benzophenone and phenol forming a neutral RP showed an increase of up to 1.28 at 0.34 T.[22]

In micellar solutions, we could observe larger MFEs than in fluid solutions. In the photochemical hydrogen-abstraction reactions of triplet 1,4-naphthoquinone in a sodium dodecyl sulfate (SDS) micelle, R(10 T) for the escaped semiquinone radical became 2.26.[23] In the photodecomposition reaction of triplet (2,4,6-trimethylbenzoyl)diphenylphosphine oxide, a phosphorus-containing compound, in an SDS micelle, R(1.2 T) for the escaped diphenylphosphonyl radical was 1.12.[24] It is clear that the present MFEs observed for Ar_3P species in fluid solutions are almost as large as those observed in micellar solutions. This must be related to the origin of the present MFEs.

3.3. Mechanism of the Magnetic Field Effects. The most probable origin of the MFE of chemical reactions in the liquid phase is the RP, process D in Figure 1, which should be considered at first. The MFEs in this process have been explained by HFCM, ΔgM, RM, and LCM.[1,3,27] The absence of an MFE in the present reactions at fields lower than 0.1 or 0.05 T is interesting. The mechanism to induce MFEs in such low fields is ascribed to the HFCM. According to our CIDEP results, the hyperfine coupling (hfc) constant of ^{31}P in $Ph_2P^\bullet$ is 8.73 mT.[15] The proton hfc constants of $Ph^\bullet$ are reported to be 1.743 mT for the 2 and 6 positions, 0.625 mT for the 3 and 5 positions, and 0.204 mT for the 4 position.[25] We can estimate $B_{1/2}$ due to the HFCM using the following equation:[26]

$$B_{1/2}(\text{hfc}) = \frac{2(B_{\text{Ph}_2\text{P}^\bullet}{}^2 + B_{\text{Ph}^\bullet}{}^2)}{(B_{\text{Ph}_2\text{P}^\bullet} + B_{\text{Ph}^\bullet})} \qquad (1)$$

where

$$B\ \text{radical} = (\Sigma_j I_j(I_j + 1)a_j^{\,2})^{1/2}$$

Using the above hfc constants, we obtained a $B_{1/2}$(hfc) value of 12.7 mT for an RP consisting of $Ph_2P^\bullet$ and $Ph^\bullet$. Because the largest hfc constant in $Ar_2P^\bullet$ is the one for ^{31}P and other contributions such as that of protons at the 4 position of $Ar^\bullet$ are negligible, this value is applicable to all compounds in the present study. Consequently, the absence of an MFE below 50 mT means the absence of a contribution from the HFCM beyond experimental error.

A convergence of the MFE at high fields was not observed in the previous study where the maximum magnetic field was 1.34 T. In the previous study, we ascribed the origin of the magnetic field dependence to ΔgM[15] because the yield of the escape radical from a triplet precursor should decrease because of ΔgM.[27] The photosensitization by F_4DCNB again supports the triplet precursor. However, the convergence of the dependence below 5 T cannot be rationalized by ΔgM. We can estimate the Larmor frequency difference from the g values of $Ph_2P^\bullet$ and $Ph^\bullet$. In the previous study, we reported the g value of $Ph_2P^\bullet$ to be 2.007, but a more accurate value taking into account the second-order effect is 2.0065. The g value of $Ph^\bullet$ is reported to be 2.00227.[25] Consequently, the Δg value between $Ph_2P^\bullet$ and $Ph^\bullet$ is estimated to be 0.00423, which implies a Larmor frequency difference of 59 kHz T^{-1}. Thus, the $S-T_0$ conversion takes 8.4 ns at 1 T or 0.84 ns at 10 T. Because the lifetime of an RP in fluid solutions is 0.1−1 ns, this interval seems to be too long to invoke a complete mixing between the S and T_0 states even at 10 T. Furthermore, the observed largest decrease down to 0.46 for 4-$ClPh_3P$ in cyclohexane is beyond the limit of ΔgM because its most optimistic estimation cannot exceed 0.67 ($^2/_3$). Therefore, we conclude that the magnetic field dependence of Ar_3P cannot be explained by ΔgM, which was tentatively proposed in the previous study.[15]

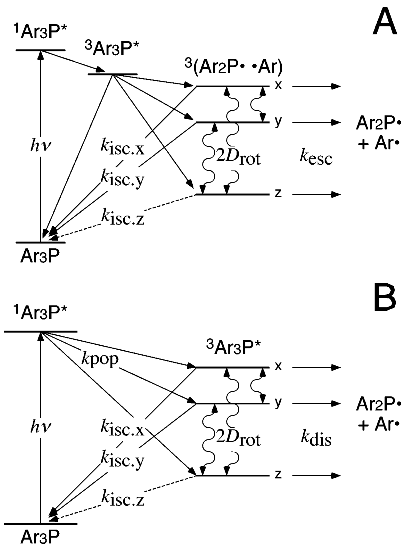

Figure 5. (A) Level diagram and kinetic constants to describe the d-type triplet mechanism proposed by Steiner. (B) Modified diagram and kinetic constants to describe the d-type molecular triplet mechanism.

The relaxation mechanism (RM) is the third one to describe the MFEs of RPs.[28] The estimated effect due to the RM for the photodecomposition reactions of Ar_3P in fluid solutions should be at least 1000 times smaller than the observed one[15] even if $Ph_2P^\bullet$ has a large anisotropy in its g tensor.[29] MFEs due to the LCM are sometimes observed in reactions of RPs, which have nonzero values for the exchange interaction.[27] The expected field dependence due to the LCM is, however, completely different from that observed in the present study. Consequently, the MFEs of Ar_3P cannot be interpreted by the conventional mechanisms, process D in Figure 1.

Next we consider the d-type triplet mechanism (TM) proposed by Steiner[8] for a contact RP, process C in Figure 1. In Figure 5A, we applied the d-type TM to the present reaction scheme. The key species in this mechanism is the triplet contact RP (radical pair complex), $^3(Ar_2P^\bullet\ {}^\bullet Ar)$ in this figure. In the absence of a magnetic field, each sublevel (x, y, z) of the triplet complex decays to the starting material with a different rate constant ($k_{\text{isc.}x}$, $k_{\text{isc.}y}$, $k_{\text{isc.}z}$). Under this anisotropic condition, the decay rate from each sublevel is assumed to be as follows:

$$k_{\text{isc.}z} = z \times k_{\text{isc}} \qquad (0 \le z \le 1) \qquad (2)$$

$$k_{\text{isc.}x} = k_{\text{isc.}y} = k_{\text{isc}} \qquad (3)$$

The slower recombination from the z sublevel causes a larger yield of the escaped radicals in the absence of a magnetic field. This anisotropy in the ISC process levels off with increasing B. In the limit of high field, the ISC process becomes isotropic so that the yield of the escaped radicals may be reduced. Therefore, the d-type TM for the contact RP predicts a decrease of the escaped radicals due to the transition from the anisotropic stage to the isotropic one. The yield of the escaped radicals, $Y(B)$, is expressed as follows:[7−9]

$$Y(B) = \frac{1 + (1/3)k'_{\mathrm{isc}} + 6D'_{\mathrm{rot}}(B)}{(1 + k'_{\mathrm{isc}})(1 + 4D'_{\mathrm{rot}}(B)) + 2D'_{\mathrm{rot}}(B)} \tag{4}$$

Here, $k'_{\mathrm{isc}} = k_{\mathrm{isc}}/k_{\mathrm{esc}}$, $D'_{\mathrm{rot}}(B) = D_{\mathrm{rot}}(B)/k_{\mathrm{esc}}$, and the magnetic field dependence of the rotational relaxation rate, $D_{\mathrm{rot}}(B)$, is described in the original article. k_{esc} is the rate constant of escape of the RP. In eq 4, $k_{\mathrm{isc},z}$ is assumed to be 0 (i.e., $z = 0$). The magnetic field dependence of $Y(B)$ predicted by eq 4 is similar to that shown in Figure 4, where the relative yield, $Y(B)/Y(0\ \mathrm{T})$ is plotted.

Two observations support the d-type TM: (1) The absence of the effect at low fields and the convergence at high fields depicted in feature ii. (2) The heavy-atom effect described in feature iv. However, we need to address several unique points that may not be affirmative for the d-type TM. The first point is that the key species is composed of two neutral radicals in the present reaction. This invokes two difficulties. Because the recombination process is spin-forbidden, the SOC interaction between the component radicals becomes important, which requires close interaction between the component radicals. A neutral RP has no special interaction to hold the component radicals as a relatively rigid complex.

Steiner investigated the photoexcited electron-transfer reactions of thiazine dyes with electron donors and assumed triplet exciplexes, each of which consists of the neutral dye radical and cation radical.[8,9] Therefore, such an exciplex has a charge but no Coulombic interaction between them. The charge-transfer interaction between the charged molecule and the counterpart seems to support the rigid structure. Tero-Kubota et al. investigated the CIDEP spectra of similar systems[11] and found a special polarization, when the MFE of the system obeys the d-type TM. They found that no such polarization appeared when neutral radicals are produced. These results mean that a strong interaction, such as the charge-transfer interaction, is necessary between the component radicals for the d-type TM for contact RPs. No MFE due to this mechanism is expectable for neutral RPs such as $\mathrm{Ar_2P^\bullet}$ and $\mathrm{Ar^\bullet}$.

Another important issue is the nature of the depopulation process, which has to be competitive in rate with rotational relaxation. In the systems investigated by the groups of Steiner and of Tero-Kubota, the depopulation process corresponds to back-electron transfer, which apparently can be fast enough to compete with rotational relaxation. That σ-bond formation between two neutral radicals should be comparably fast seems at least doubtful. Furthermore, the escape of two neutral radicals should be faster than that of molecules held together by charge-transfer interaction. Faster escape, however, diminishes the magnitude of MFE.

The second point is the solvent viscosity dependence of the present reactions. This is the reason that we cast doubt on the d-type TM for the contact RP in a previous study.[15] According to Steiner's simulation, the magnitude of the MFE becomes larger when the solvent viscosity becomes larger. As described in feature iii, such dependences were not observed. This is contradictory to the expectation of the d-type TM for a contact RP. However, the strange effect of 2-propanol indicates that the solvent dependence of the present reaction is not simple.

Apart from the discrepancy in the viscosity dependence, several features observed in the present MFEs correspond well to the expectation by the d-type TM. Consequently, we investigated the viscosity dependence of the reaction of 4-$\mathrm{ClPh_3P}$ in detail. For that purpose, we chose *n*-alkanes as solvents. From *n*-hexane to *n*-hexadecane, their viscosity changes by more than a factor of 10, from $\eta = 0.313$ to 3.53 cP at 20 °C. However, their dielectric constant changes by merely a factor of 1.11, from 1.8371 to 2.0460 at 20 °C. Consequently, we can neglect the change in polarity that may be expected between cyclohexane and 2-propanol, although its contribution to the neutral RP is not clear.

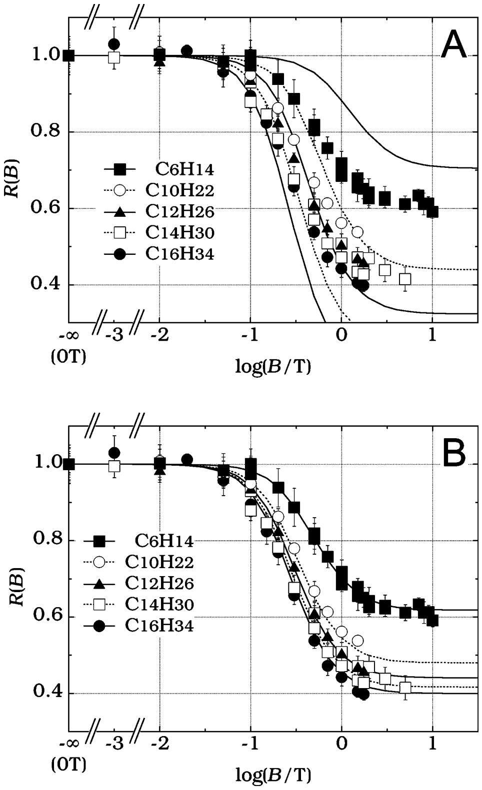

Figure 6. Results and simulation of the solvent dependence of $R(B)$ values of 4-$\mathrm{ClPh_3P}$. (A) Viscosity dependence of D_{rot} and k_{esc}. (B) Viscosity dependence of D_{rot} only.

In Figure 6A, the $R(B)$ values obtained for 4-$\mathrm{ClPh_3P}$ in these solvents are shown. To obtain these values, we used the $R(B)$ at $t = 100$ ns observed at 340 nm. The simulated $R(B)$ curves for the solvents are discussed later. The MFE becomes larger from *n*-hexane to *n*-hexadecane, and we can definitely conclude that this dependence originates from viscosity. The $R(B)$ values at 1.5 T range from 0.67 in *n*-hexane to 0.41 in *n*-hexadecane. This means that the magnitude of the MFE becomes 1.6 times larger when the viscosity increases by a factor of 11.

Steiner and Haas investigated the viscosity dependence of the MFE in the photochemical electron-transfer reaction between triplet methylene blue and *p*-iodoaniline in a mixture of methanol and ethylene glycol.[9] The mechanism of its MFE is interpreted by the combined effects of the d-type TM and ΔgM. They presented a simulation to extract the contribution of d-type TM. The comparison with their results and ours indicates that the viscosity dependence of methylene blue is much larger than that of 4-$\mathrm{ClPh_3P}$. The enhancement of the MFE of methylene blue observed in the increase of the viscosity by 3.5-fold seems much larger than that of 4-$\mathrm{ClPh_3P}$, which was observed to have an 11-fold viscosity increase. The shift of $B_{1/2}$ values in the increase of the viscosity by a factor of 3.5 is similar to ours when the viscosity increases by a factor of 11. A quantitative evaluation of the observed MFE may shed light on this discrepancy.

Using eq 4, we tried to fit the *relative* yields observed in the present reactions by calculating $R(B) = Y(B)/Y(0)$. In these fittings, k_{isc}, k_{esc}, D_{rot} are the variables to be optimized. Because the three independent parameters are still abundant, it is difficult to evaluate the validity of the obtained values for the data shown in Figure 4. As for the results shown in Figure 6A, the parameters are restricted by the viscosity. k_{esc} and D_{rot} are considered to be dependent on solvent viscosity. We made a global nonlinear least-squares fit of the whole data set shown in Figure 6A by adding the following limitations:

(1) k_{isc} is a common constant in all alkane solvents.

(2) k_{esc} and D_{rot} are inversely dependent on solvent viscosity.

The second assumption is well established, and theoretical expressions are given.[30,31] Instead of substituting such theoretical values, we fit a set of k_{esc} and D_{rot} values for *n*-hexadecane, and others are fixed to the values inversely dependent on their viscosity. With this assumption, we could fit the data shown in Figure 6A with the following values: $k_{\mathrm{isc}} = 3.25 \times 10^{11}$ s^{-1}, $k_{\mathrm{esc}} = 1.80 \times 10^{5}$ s^{-1}, and $D_{\mathrm{rot}} = 3.22 \times 10^{9}$ s^{-1} for *n*-hexadecane. The k_{esc} and D_{rot} values for other solvents are obtained by multiplying by the ratio η(*n*-hexadecane)/η(solvent).

The fitted curves are shown in Figure 6A. We note the large discrepancies on the low- and high-viscosity sides indicating that the viscosity dependence of the MFE of 4-ClPh$_3$P is smaller than expected for the d-type TM for a contact RP. The numerical simulations indicate that this size of the change can be explained by the viscosity increase by a factor of about 2.5, not 11. Furthermore, the fitted value of k_{esc} is 10^6 times smaller than that of k_{isc}, which means that there are almost no escaped radicals. Although we did not measure the quantum yields of the present reactions, it is very unlikely that we could observe radical formation with a quantum yield smaller than 10^{-6}. This result is, of course, due to the limitation of the fitting process to optimize the relative yield, $R(B) = Y(B)/Y(0)$, instead of the real yield, $Y(B)$. Similarly, we could have observed neither a kinetic process having a rate constant of 1.80×10^{5} s^{-1} in *n*-hexadecane nor a process having a rate constant of 2.03×10^{6} s^{-1} in *n*-hexane.

The lifetime, τ, of a neutral RP is estimated to be $\tau = 4r^2/D$.[31] Here, r is the radius of the component radical, and D is the sum of the diffusion coefficients of each radical. If we derive D from the Stokes−Einstein relation, then k_{esc} ($= 1/\tau$) is described as follows:

$$k_{\mathrm{esc}} = \frac{kT}{12\pi r^3 \eta} \tag{5}$$

Here, k is the Boltzmann constant, and T is the temperature. If we assume the radius of a radical to be 4.0 Å (this may be an overestimate, see below), then k_{esc} in *n*-hexadecane at 20 °C is estimated to be 4.8×10^{8} s^{-1}. This rate is 2.7×10^{3} times larger than the one derived by the optimization. These discrepancies seem to imply the invalidity of the model. Consequently, the experimental and theoretical arguments require us to discard the physical model of the original d-type TM for our reaction. Therefore, we can exclude process C in Figure 1.

3.4. d-Type Triplet Mechanism in the Photoreactive Molecular Triplet State. We obtained much better fitting curves shown in Figure 6B by introducing new limitations as follows:

(1) k_{isc} is a common constant in all alkane solvents.

(2) k_{esc} is also a common constant in all alkane solvents.

(3) D_{rot} is inversely dependent on the solvent viscosity.

With these assumptions, we obtained the following values: $k_{\mathrm{isc}} = 1.87 \times 10^{11}$ s^{-1}, $k_{\mathrm{esc}} = 1.90 \times 10^{10}$ s^{-1}, and $D_{\mathrm{rot}} = 7.02 \times 10^{8}$ s^{-1} for *n*-hexadecane. The D_{rot} values for other solvents are obtained by multiplying by the ratio η(*n*-hexadecane)/η(solvent).

For a contact RP, the independence of k_{esc} from solvent viscosity seems hardly acceptable, but the scheme becomes sensible by reassigning the origin of the present MFE to process A in Figure 1. This means that the excited triplet state of Ar$_3$P is affected by external magnetic fields, as is the case for Paul and co-workers.[14] This model is shown in Figure 5B. For convenience, we would like to call this mechanism the d-type molecular TM. In this scheme, the k_{esc} value is regarded as the dissociation rate, k_{dis}, of triplet Ar$_3$P. If this is the case, then we can consider the k_{dis} value not to be strongly dependent on solvent viscosity. At the same time, we can avoid the situation in which the obtained k_{esc} value (1.90×10^{10} s^{-1}) is much larger than the possible escaping rate of RPs (4.8×10^{8} s^{-1}).

For D_{rot}, this scheme also gives a reasonable value. According to Debye's derivation, the following relationship is expected:[30]

$$D_{\mathrm{rot}} = \frac{kT}{8\pi R^3 \eta} \tag{6}$$

Here, k is the Boltzmann constant, and R is the effective hydrodynamic radius of the rotating species. By substituting the D_{rot} and η(*n*-hexadecane) values, we get the R value of 4-ClPh$_3$P to be 4.0 Å for spherical geometry. Steiner and Haas obtained 3.6 Å for methylene blue/aniline complexes.[9] Considering the molecular structures of these compounds, we consider the present R value to be reasonable. The obtained rate constants based on this scheme show that the dynamic process that induces the present MFEs terminates within 1 ns after excitation, which is consistent with our observation. Therefore, theoretical calculations and experimental observations support the d-type molecular TM.

The model can further explain the strange solvent effect of 2-propanol indicated in feature iii. As mentioned in the previous study, Ph$_3$P has closely lying nπ* and $\pi\pi$* excited states.[32] Consequently, the locations of these two states are dependent on the solvent polarity and on the substituents, as is the case for aromatic carbonyl compounds. The change in mixing of these two states induces a variation in the character of their triplet sublevels and in the dissociation rate. This may be the reason for the difference between Ph$_3$P and 4-ClPh$_3$P in 2-propanol. Preliminary picosecond laser photolysis revealed that the lifetime of the excited singlet or triplet state of Ph$_3$P in 2-propanol is longer than that in cyclohexane. Although the character of this state has not yet been defined, this is clear evidence for the solvent dependence of the excited states.

The next evidence to support the d-type molecular TM is the MFEs of methyl-substituted compounds. As described in feature v, the observed MFEs of 3- and 4-MePh$_3$P are almost the same as that of 4-BrPhPh$_2$P. Because methyl substitution is not expected to have large SOC interaction, the large MFE without heavy atoms can be ascribed to the modification of the nπ* and $\pi\pi$* excited states as in the case of the solvent polarity. The absence of the difference between 3- and 4-substitution of the methyl group is clearly different from that of the chlorine atom as described in feature iv. This may also come from the difference in the mechanism (i.e., nπ*-$\pi\pi$* modification and a direct SOC contribution). However, large effects of methyl substitution in the RP are not expected. In the case of 2-MePh$_3$P, its small MFE may be ascribed to its steric hindrance if the triplet molecule itself is the origin of the MFE. For the RP formed in this case, its steric hindrance seems to be significantly reduced in comparison with that of the original molecule. Consequently, the smaller and strange viscosity dependence and

TABLE 1: Observed $R(B)$ Values at 1.5 T, Derived Rate Constants, and Estimated Yields of Escaped Radicals at 0 T

compound	solvent	$R(1.5\ \mathrm{T})$	$k_{isc}/10^{11}\mathrm{s}^{-1}$	$k_{dis}/10^{10}\mathrm{s}^{-1}$	$D_{rot}/10^{9}\mathrm{s}^{-1}$	$Y(0)$
4-ClPh$_3$P	*n*-hexadecane	0.41	1.87	1.90	0.702	0.360
4-ClPh$_3$P	*n*-tetradecane	0.45	1.87	1.90	(1.07)	0.344
4-ClPh$_3$P	*n*-dodecane	0.47	1.87	1.90	(1.64)	0.325
4-ClPh$_3$P	*n*-decane	0.54	1.87	1.90	(2.67)	0.298
4-ClPh$_3$P	*n*-hexane	0.67	1.87	1.90	(7.92)	0.228
Ph$_3$P	*n*-hexane	0.80	1.53	3.91	(7.92)	0.378
Ph$_3$P	cyclohexane	0.65	1.91	3.84	(2.54)	0.398
3-ClPh$_3$P	cyclohexane	0.64	1.75	3.08	(2.54)	0.374
4-BrPhPh$_2$P	cyclohexane	0.57	2.05	2.87	(2.54)	0.349
4-ClPh$_3$P	cyclohexane	0.53	2.27	2.38	(2.54)	0.316
2-MePh$_3$P	cyclohexane	0.80	1.02	3.84	(2.54)	0.497
3-MePh$_3$P	cyclohexane	0.56	1.69	2.17	(2.54)	0.327
4-MePh$_3$P	cyclohexane	0.55	1.61	1.98	(2.54)	0.318
Ph$_3$P	2-propanol	0.71	1.74	5.04	(1.04)	0.468
Ph$_3$P + F$_4$DCNB	2-propanol	0.72	1.88	5.56	(1.04)	0.472
4-ClPh$_3$P	2-propanol	0.51	1.67	2.27	(1.04)	0.373
4-ClPh$_3$P + F$_4$DCNB	2-propanol	0.54	1.64	2.38	(1.04)	0.383

the effect of methyl substitution seem to be enough for us to conclude that the species sensitive to the external magnetic field is the excited triplet state of Ar$_3$P and not their RP.

However, if we accept the fact that the fate of the excited triplet species is magnetic field-dependent, then we should be aware of another process that may exhibit anisotropy in addition to the depopulation process. That is the population process to the triplet state, the rate of which is k_{pop}, in Figure 5B. This corresponds to the p-type TM, process B in Figure 1. The result of the sensitization experiment allows us to assess the contribution of the p-type TM. If, in the intramolecular triplet population process, the zero-field sublevels were populated at different rates, then the triplet sensitization experiment should lead to an MFE that is different in size from that observed on direct excitation. As described above, the magnetic field dependence of the sensitized reaction is the same as that in the absence of sensitizer. Therefore we can certainly discard contributions from the p-type TM. The dissociation of the triplet state is definitely accomplished within the triplet manifold. There should be no anisotropy in k_{dis} of each triplet sublevel.

Consequently, we can draw the following conclusions:

(1) Our results are explained in terms of the MFE of the excited triplet molecules and not in terms of the succeeding radical pairs.

(2) Our results are explained by the magnetic field dependence of the depopulation kinetics of the excited triplet molecules and not by the magnetic field dependence of the population or dissociation kinetics.

This means that our results can be interpreted by the d-type TM in the photoreactive triplet state. In this paper, we exclude processes B−D in Figure 1 from the candidates for the present MFEs, and process A is ascribed to their origin. This elimination of possible mechanisms has been a lengthy procedure, but it was unavoidable to reach a reliable conclusion. As described in the Introduction, Paul and co-workers assigned the origin of the MFE of the sensitized photodecomposition of azocumene to the same mechanism.[14] Interestingly, the yield next to 0 T (maybe 0.1 T) shown in Figure 6 is clearly smaller than the yield at 0 T.[14] Of course, the starting field of the isotropic transition can be smaller than 0.1 T in the d-type TM; such field dependence, which starts smoothly from 0 T, can also originate from the RPM. The presented CIDEP spectrum of the cumyl radical is a little bit weaker on the higher-field side, which suggests a contribution of the RPM. Although the saturation of MFE at high fields seems to support their assignment, they did not explicitly exclude other possibilities.

3.5. Comparison among Compounds. In Figure 4, we presented the simulation curves of the experimental results. They are obtained under the following assumptions:

(1) The D_{rot} values are derived from that of 4-ClPh$_3$P in *n*-hexadecane by multiplying by $\eta(n\text{-hexadecane})/\eta(\text{solvent})$. The size difference has been neglected.

(2) The k_{isc} and k_{dis} values are the variables to be fit.

The $R(B)$ values at 1.5 T, the derived rate constants, and the estimated escaped radical yields at zero field, $Y(0)$, are shown in Table 1, where the data are arranged by solvents. The reasonable values of $Y(0)$ support the validity of the fitting processes optimizing $R(B) = Y(B)/Y(0)$. Of course, these values should be regarded as qualitative because the applied limitations are too restricted to derive the real parameters, particularly in the absence of recombination from the triplet z sublevel (the assumption that the z value in eq 2 is zero.). Many numerical simulations to interpret the effect of halogen or methyl substitution revealed that the most effective single parameter among k_{isc}, k_{dis}, and z is z when the others are taken to be common among the derivatives. Under such conditions, the optimized z value is generally small (0.01−0.09, except 0.23 for 2-MePh$_3$P), as expected. In these optimizations, 4-ClPh$_3$P had the smallest z value, which is in line with the expectation from the SOC. However, we have no choice but to set $z = 0$ to obtain a reliable D_{rot} of 4-ClPh$_3$P in *n*-hexadecane. Therefore, the interpretation of Table 1 must be done in keeping with these uncertainties.

In Table 1, we can see the following trends:

(1) The k_{dis} value of Ph$_3$P is larger than those of other compounds except for 2-MePh$_3$P.

(2) In the halogen-substituted compounds, the increase of MFE (1-$R(B)$) mainly reflects the increase in k_{isc}.

(3) In the methyl-substituted compounds, the increase of MFE (1-$R(B)$) mainly reflects the decrease in k_{dis}.

Observation 1 seems to indicate that any substitution tends to stabilize the triplet states. This may be due to the lowering of the energy levels of the excited triplet states by substitution. The increase of k_{isc} (observation 2) is in good agreement with the heavy-atom effects enhancing intersystem crossing. To some extent, the decrease of k_{dis} (observation 3) is also responsible for the increase of the MFE in the series of halogen-substituted compounds, but the changes in k_{dis} are smaller than those of the methyl-substituted compounds. However, observation 2 is not applicable to the methyl-substituted compounds. This supports the discussion in section 3.4 that the mechanisms to enhance the MFEs of halogen- and methyl-substituted compounds are different. For further discussion of these reactions, the determination of the lifetime of the excited states by picosecond photolysis system is needed, but this is beyond the scope of the present study.

4. Conclusions

The MFEs of triarylphosphines were found to be observable in dilute solutions, irrespective of the solvent polarity. The concentration of the substrate is arbitrary for the present MFEs because the reactions for the MFEs are unimolecular. Such requirements for large MFEs cannot be fulfilled by the d-type TM and the RPM of unchained RPs. From the MFE, it has to be concluded that the reaction rates of the triarylphosphines are very large. This means that it is very hard to quench these reactions. However, MFEs of the same magnitude appeared in the sensitized reactions. Last but not least, the magnitude of the MFEs of triarylphosphines was very large. The above conditions are very suitable to the practical application of the present MFEs. If we use triarylphosphine as an initiator of radical reactions, then we can almost freely settle the reaction condition by considering only the reactant. Some of the reactions that obey the d-type molecular TM may afford this option. The large MFE without heavy atoms other than phosphorus is still the excellent merit of triarylphosphines. Halogen atoms that pollute the environment if applied on a large (technical) scale are not required to induce the MFE for triarylphosphines.

The magnetic field effects on the photodecomposition reactions of triarylphosphines in fluid solutions were investigated in the present study. The yield of the diarylphosphinyl radicals was invariant from 0 to 0.05 T. Then it started to decrease up to 5 T and became invariant again above it. The magnetic field effect became larger by halogen substitution and by 3- and 4-methyl substitution. The viscosity dependence of tris(4-chlorophenyl)phosphine using *n*-alkanes revealed that the effect became larger with increasing solvent viscosity. This dependence was similar to that due to the d-type triplet mechanism reported by Steiner but was much smaller than the expectation of the standard mechanism for the triplet contact RPs. By assigning the magnetic field-dependent process to the excited triplet state as the precursor of the contact RP, the discrepancy was removed. The closely lying $^3n\pi^*$ and $^3\pi\pi^*$ states of triarylphosphine have been suggested to explain the difference in the solvent effect of polar and nonpolar solvents and the enhancement of the magnetic field effects of 3- and 4-methyl substitutions.

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