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Photoreaction of 7-Me₂-germanorbornadiene to tetraphenylnaphthalene

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Abstract

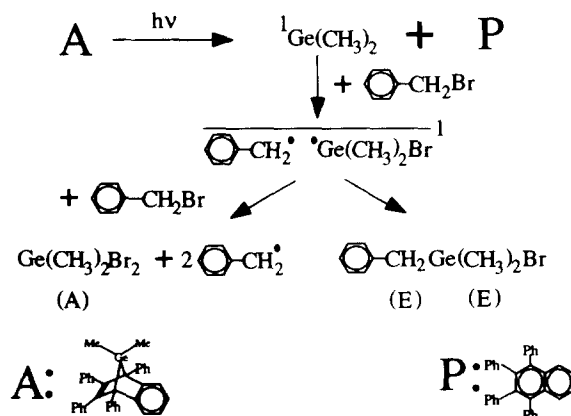
The photoreaction of 7-dimethylgerma-1,2,3,4-tetraphenyl-5,6-benzonorbornadiene (**A**) into 1,2,3,4-tetraphenylnaphthalene (**P**) and dimethylgermylene (Me₂Ge) was studied in dilute solution. The quantum yields in several solvents at room temperature and in methylcyclohexane at 77 K were found to be in the range 0.35–0.5. Time-resolved UV spectroscopy showed that the **A** → **P** photoconversion occurs within 100 ns. The main observed transient is assigned to the triplet state of **P**, while Me₂Ge escaped spectroscopic observation. The appearance of radical-type transients could be excluded by ¹H chemically induced dynamic nuclear polarization (CIDNP) during irradiation of **A** in benzene-*d*₆ using laser pulses and an r.f. technique.

Keywords: ¹H chemically induced dynamic nuclear polarization (CIDNP); Photolysis; Germynes

1. Introduction

The chemistry of germynes and stannylenes has been studied extensively and reviewed by Neumann [1]. A key intermediate in the thermal and photochemical reactions of germynes is dimethylgermylene (Me₂Ge) [2–18]. A convenient source of generation of Me₂Ge is 7-dimethylgerma-1,2,3,4-tetraphenyl-5,6-benzonorbornadiene (**A**). Neumann and coworkers [1,3,15,16] have shown that, at elevated temperatures, **A** decomposes into Me₂Ge and 1,2,3,4-tetraphenylnaphthalene (denoted as **P**). Photolysis of **A** in solution at room temperature also yields stable **P** [16]. Several details of this photoreaction are unclear, e.g. the spectroscopic and kinetic properties of Me₂Ge and the quantum yield ($\Phi_{\mathbf{A} \rightarrow \mathbf{P}}$).

During continuous UV irradiation of **A** in the presence of benzyl bromide in benzene-*d*₆, emission has been observed by ¹H chemically induced dynamic nuclear polarization (CIDNP) of the methylene and methyl protons of the insertion product of Me₂Ge into the C–Br bond, indicating a singlet state of reacting germylene followed by a two-step radical reaction. ¹H CIDNP has not been observed in **A** itself with or without benzyl bromide or in **P**, showing the absence of any radical precursor [3]. It has therefore been postulated that the formation of Me₂Ge occurs in a one-step reaction (Scheme 1). In contrast, Nefedov and coworkers [8] have reported the occurrence of ¹H CIDNP in **A** and **P** under similar conditions. To explain this, a biradical has been postulated, formed by C–Ge bond scission. In a second step, a further



Scheme 1. Photo-CIDNP reactions of **A** in the presence of benzyl bromide (E, emission; A, enhanced absorption).

C–Ge bond may be split on formation of Me₂Ge and **P** or **A** may be re-formed by recombination [8].

To distinguish between these possibilities, ¹H CIDNP experiments were carried out by excitation with laser pulses and using an r.f. pulse technique. This allows the nuclear magnetic resonance (NMR) signals of the protons in **A** and **P** to be suppressed and therefore a more precise detection of CIDNP than before. Moreover, we aim to elucidate the mechanism of the photoreaction. For this purpose, we studied **A** → **P** photoconversion in dilute media, determined $\Phi_{\mathbf{A} \rightarrow \mathbf{P}}$ and applied time-resolved UV spectroscopy to characterize the observable transients.

2. Experimental details

A and **P** were prepared as described previously [1,15]. The solvents were used as available commercially (cyclohexane, benzene- d_6 , benzene, acetonitrile; Uvasol) or were purified by distillation (methylcyclohexane (MCH), methanol). The molar absorption coefficient of **P** is $\epsilon_{308} = 1.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in benzene and $\epsilon_{308} = 8.6 \times 10^3$ and $\epsilon_{242} = 5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in acetonitrile. The molar absorption coefficient of **A** is much smaller, e.g. $\epsilon_{308} = 1.4 \times 10^3$ and $\epsilon_{242} = 2.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in MCH and acetonitrile. The samples (absorbance $A = 0.5\text{--}2 \text{ cm}^{-1}$ at λ_{irr}) were freshly prepared, and for the transient absorption measurements the irradiated volume was exchanged after each flash. High performance liquid chromatography (HPLC) measurements were carried out on a Nucleosil 5-C18 column (4.6 mm \times 125 mm) with a mobile phase of methanol and water (5:1).

For the determination of the quantum yield ($\Phi_{\text{A} \rightarrow \text{P}}$) with $\lambda_{\text{irr}} = 222, 248$ or 254 nm , the uridine actinometer was used, where $\Phi = 0.018$ for chromophore loss in aerated aqueous solution [19,20]. Continuous irradiation at 222 nm was carried out by a KrCl excimer lamp (Lichttechnisches Institut, Universität Karlsruhe) and at 254 nm by a low-pressure mercury lamp. For direct excitation and sensitized measurements, we used $\lambda_{\text{irr}} = 353 \text{ nm}$ from an Nd laser and $\lambda_{\text{irr}} = 248 \text{ nm}$ from an excimer laser with 20 ns pulses respectively; the laser photolysis apparatus was the same as reported previously [20,21]. The emission properties were studied by standard procedures, e.g. on a Spex-Fluorolog; the quantum yields of fluorescence (Φ_f) and phosphorescence (Φ_p) were obtained using 9,10-diphenylanthracene in ethanol ($\Phi_f = 1.0$ at 77 K) as reference [21,22].

A detailed description of the experimental pulse technique for CIDNP detection is given in Ref. [23]. A solution of **A** (1.3 mg) in 0.5 ml benzene- d_6 in a 5 mm quartz tube was irradiated in the probe of a 200 MHz NMR spectrometer with ten pulses of an excimer laser at 308 nm. The pulse width was 15 ns and the energy within the probe was 28 mJ. The irradiated volume was 0.08 ml. Before pulsing, the NMR signals were removed by four saturation pulses within 6 s; 1 ms after the laser flash, the detection of nuclear polarization was performed with a 90° r.f. pulse and a free induction decay within 4.1 s. After that, the probe was removed, shaken and irradiated again. The procedure was repeated 104 times. To determine the decay rate of **A**, NMR spectra were taken before and after irradiation; four r.f. pulses were accumulated for this purpose. The delay time between the pulses was 90 s. It was found that 17% of **A** was decomposed by irradiation.

A description of the continuous irradiation technique for CIDNP detection is given in Ref. [3] and the references cited therein. Solutions of **A** (5 mM in benzene- d_6) were irradiated with the light of a 1000 W Hg-Xe high-pressure lamp filtered by an aqueous solution of NiSO_4 (1.1 M), CoSO_4 (0.20 M) and H_2SO_4 (0.01 M). ^1H NMR spectra were taken before, during and after irradiation using an equal number of r.f. pulses.

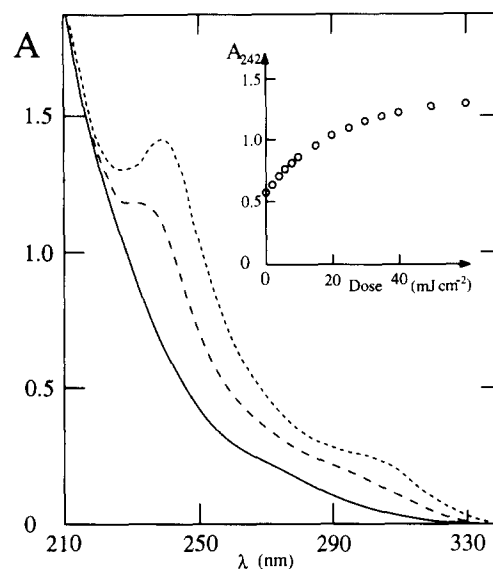


Fig. 1. Absorption spectra of **A** (—), **P** (---) and a mixture during photoconversion (---) in MCH at room temperature; inset: increase in A_{242} with increasing dose ($\lambda_{\text{irr}} = 245 \text{ nm}$).

3. Results

3.1. Fluorescence

The absorption spectra of **P** and **A** are shown in Fig. 1. Because of the substantial $\Phi_{\text{A} \rightarrow \text{P}}$ values and the larger ϵ values of **P** than **A** over the whole UV range, all observations concerning **A** are limited to small conversions. It therefore seems necessary to characterize the emitting and transient properties of **P** as well.

P shows fluorescence in several solvents examined at 297 and 77 K ($\lambda_{\text{exc}} = 250$ or 310 nm). The spectrum has one band with a maximum around 360 nm at 297 K which is slightly blue shifted to 356 nm in frozen MCH at 77 K (Figs. 2(a) and 2(b) respectively). The quantum yields of fluorescence Φ_f are 0.09 and 0.25 respectively. Virtually the same was found in ethanol. The fluorescence lifetime in aerated MCH or ethanol ($\lambda_{\text{exc}} = 290 \text{ nm}$) was estimated to be 2.9–3.2 ns at 297 K. When **A** is photoconverted into **P** (e.g. to 50% by irradiation at 254 nm), the same fluorescence spectrum was detected as for neat **P**. Back-extrapolation of the signal at 360 nm to zero conversion indicates weak fluorescence (about 20% with respect to that of **P**). Moreover, freshly dissolved **A** shows a fluorescence peak in the 320–400 nm range during the laser pulse ($\lambda_{\text{exc}} = 248 \text{ nm}$).

3.2. Phosphorescence

P shows phosphorescence at 77 K, e.g. in MCH ($\lambda_{\text{exc}} = 250$ or 310 nm); the spectrum has maxima at 506, 544 and 587 nm (Fig. 2(b)). The quantum yield of phosphorescence is $\Phi_p = 0.3$ and the phosphorescence lifetimes is approximately 2 s. Virtually the same was found in ethanol. A measurable amount of phosphorescence at 297 K is not expected since

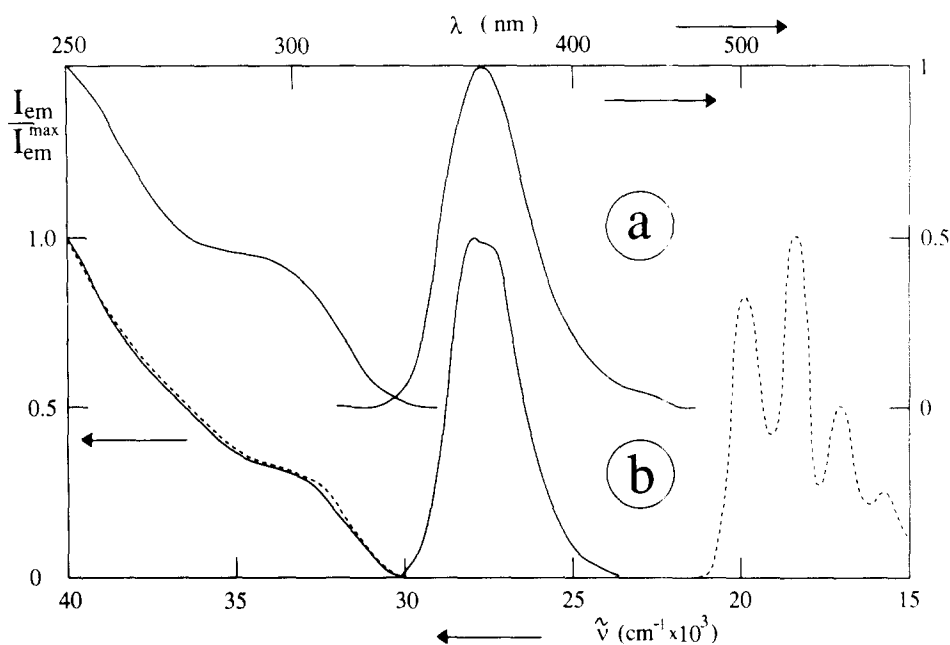


Fig. 2. Emission and excitation spectra of **P** in MCH at 297 K (a) and 77 K (b): fluorescence (middle curve) and phosphorescence (right) ($\lambda_{\text{exc}} = 250 \text{ nm}$). Note that the excitation spectra (left) are the same for $\lambda_{\text{em}} = 510\text{--}600 \text{ nm}$ and $340\text{--}380 \text{ nm}$ for phosphorescence and fluorescence respectively.

the triplet lifetime, which is $3\text{--}5 \mu\text{s}$ in oxygen-free solution at 297 K (using triplet–triplet (T–T) absorption, see below), should be reduced by a factor of 10^5 or more. When **A** was converted into **P** (by irradiation at either 297 or 77 K), the same phosphorescence spectrum and lifetime as for neat **P** were detected at 77 K. Freshly dissolved **A** in MCH at 77 K shows a similar phosphorescence spectrum, but with a much weaker signal.

3.3. Steady state photolysis

When **A** in solution at 297 K is irradiated at 254 nm, the absorption spectrum increases over the spectral range 200–340 nm, as expected for the **A** \rightarrow **P** photoconversion. Results from HPLC measurements with **A** in acetonitrile were found to be consistent with those from UV spectroscopy. The increase in absorbance (e.g. at 242 or 290 nm) with increasing dose (fluence) is downward curved, this being due to the much higher ϵ_{254} value of **P** than of **A** (inset in Fig. 1). The initial slope of A_{242} vs. dose is similar in several solvents (MCH, acetonitrile or methanol), indicating comparable quantum yields. In fact, $\Phi_{\text{A} \rightarrow \text{P}}$ is independent of the solvent properties such as polarity (Table 1). Oxygen has no discernible effect on $\Phi_{\text{A} \rightarrow \text{P}}$, e.g. in MCH or acetonitrile. Virtually the same $\Phi_{\text{A} \rightarrow \text{P}}$ values were obtained for $\lambda_{\text{irr}} = 222 \text{ nm}$. The effect of temperature on $\Phi_{\text{A} \rightarrow \text{P}}$ was studied in aerated MCH. The decrease in $\Phi_{\text{A} \rightarrow \text{P}}$ at 77 K is only about 20% with respect to the value at room temperature. This strongly suggests that volume changes are unimportant for the photoreaction since both temperature and viscosity have only a small effect.

Table 1
Quantum yield of **A** \rightarrow **P** conversion^a

Solvent	λ_{irr} (nm)	$\Phi_{\text{A} \rightarrow \text{P}}$
Cyclohexane	254	0.4
MCH	254	0.46
MCH	254	0.48 ^b
MCH	254	0.37 ^c
Benzene	308	≥ 0.1 ^d
Methanol	254	0.38
Acetonitrile	254	0.42
Acetonitrile	254	0.44 ^b
Acetonitrile	248	0.35
Acetonitrile	222	0.38

^a In aerated solution at room temperature (unless indicated otherwise) obtained under conditions of less than 10% conversion.

^b In argon-saturated solution.

^c At 77 K.

^d Limit, due to conditions of substantial conversion.

3.4. ¹H CIDNP measurements

Using the laser pulse technique, no CIDNP effects could be observed at room temperature in **A**, **P** or any reaction product of Me_2Ge . During continuous UV irradiation for 20 s (four scans), the intensities of the NMR signals due to **A** were similar to those before and after irradiation. This indicates the absence of any ¹H CIDNP effect as reported earlier [3]. During and after irradiation for 120 s (30 scans), the methyl proton signals of **A** were smaller than before irradiation because of the decay of **A**. After shaking the probe, the signals were nearly the same as before irradiation, as the probes were only partially illuminated [3]. In addition, signals due to **P** appeared during irradiation which were greatly diminished by shaking the probe before taking the spectrum.

3.5. Laser flash photolysis

On pulsed excitation ($\lambda_{\text{irr}} = 248 \text{ nm}$) of **P** in MCH, acetonitrile or methanol at 297 K, one transient appears during the pulse or after the disappearance of the fluorescence signal. It shows a broad absorption spectrum with maxima at 330 nm or less and about 490 nm (Fig. 3(a)). The transient is assigned to the triplet state ($^3\text{P}^*$). It is known that the introduction of two phenyl groups on naphthalene broadens the T–T absorption spectrum and shifts the maximum from 430 nm towards approximately 500 nm [24]. The half-life for the decay of the triplet of **P** in the three solvents under argon is 1.5–4 μs . The decay is of mixed first and second order with a tendency to a shorter half-life with increasing laser intensity, i.e. $t_{1/2}$ decreases with increasing concentration of the transient. From the $t_{1/2}$ value under argon and the triplet lifetimes in oxygen- and air-saturated acetonitrile solution, a rate constant for quenching by O_2 of $1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was obtained. Very similar results were found with solutions of **A**, which were irradiated at 254 nm (e.g. 50% **A** \rightarrow **P** conversion) prior to time-resolved photolysis at 248 nm. Thus the photoproducts resulting from Me_2Ge do not interfere discernibly. For a comparison with the transient(s) obtained with **A**, other quenchers, such as 2,3-dimethylbutadiene (Me_2B) and methylbutadiene (MeB), were added to **P** in argon-saturated acetonitrile. With MeB , a rate constant for triplet quenching of $k_q = 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ was obtained at 450 nm, whereas quenching by Me_2B was found to be inefficient; the limit is $k_q \leq 0.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (Table 2).

When freshly dissolved **A** in MCH is excited, the main effect is an increase in absorbance in the 280–340 nm range

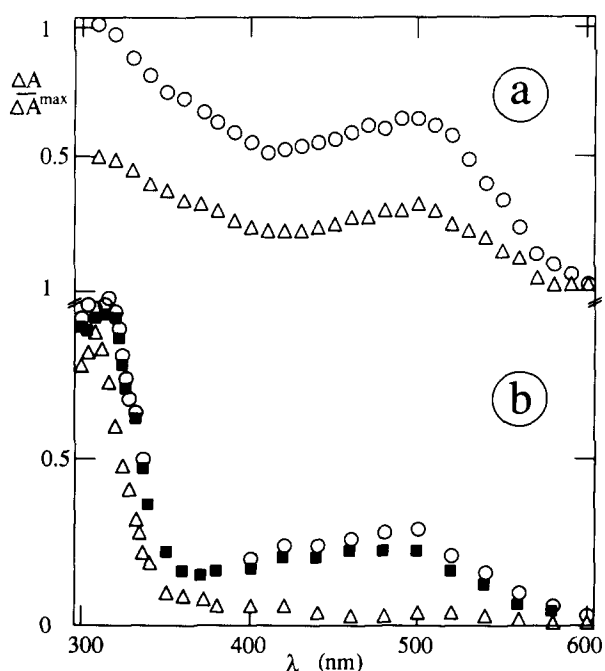


Fig. 3. Transient absorption spectra in argon-saturated MCH at 297 K: (a) for **P** at 0.2 μs (\circ) and 2 μs (\triangle) after the 248 nm pulse; (b) for **A** at 0.1 μs (\circ), 1 μs (\blacksquare) and 10 μs (\triangle) after the pulse.

Table 2

Rate constants for quenching of the transients of **A** and **P**^a

Compound	Quencher	k_q ($10^7 \text{ M}^{-1} \text{ s}^{-1}$)
A	O_2	≈ 150
P	O_2	120
A	CCl_4	≤ 0.01
A	Me_2B	≤ 0.02
P	Me_2B	≤ 0.05
A	MeB	≤ 0.2
P	MeB	≈ 0.2

^a In argon-saturated acetonitrile; $\lambda_{\text{irr}} = 248 \text{ nm}$; Me_2B , 2,3-dimethylbutadiene; MB , methylbutadiene.

at the end of the pulse (Fig. 3(b)). Part of this increase in absorbance (e.g. ΔA_{300}) decreases within $t_{1/2} = 2\text{--}3 \mu\text{s}$ under argon and a substantial part remains. The short-lived transient also absorbs in the 350–580 nm range and its decay is accelerated by O_2 ; a rate constant for quenching by O_2 of approximately $1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was obtained. The remaining part of ΔA at $\lambda < 340 \text{ nm}$, which was found to be constant for more than 2 s, i.e. it results from a permanent absorption increase, is due to the **A** \rightarrow **P** conversion (note that $A_{310}(\text{P}) \approx 6 \times A_{310}(\text{A})$). Similar spectra and kinetics ($t_{1/2} = 2\text{--}4 \mu\text{s}$ under argon) were observed in acetonitrile (Fig. 4(a)) and methanol (Fig. 4(b)). The temperature dependence of the transient(s) of **A** was studied in MCH. However, we failed to detect a transient which can unambiguously be attributed to originate from **A** (rather than from **P**) since, even at 77 K, due to $\Phi_{\text{A} \rightarrow \text{P}} = 0.37$ (Table 1), the initial conversion is too large under the applied conditions. It should

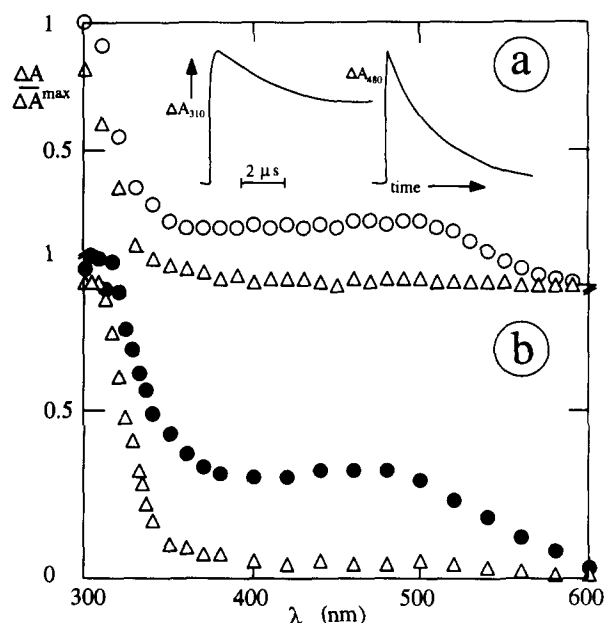


Fig. 4. Transient absorption spectra of **A** in argon-saturated solution at room temperature: (a) in acetonitrile at 0.5 μs (\circ) and 10 μs (\triangle) after the 248 nm pulse; (b) in methanol at 0.2 μs (\bullet) and 10 μs (\triangle) after the pulse inset: absorption signals at 310 and 480 nm vs. time.

be kept in mind that, after one flash, the irradiated volume already contains a significant amount of **P**.

In order to test whether or not the observed transient is Me_2Ge , CCl_4 was added to **A** in argon-saturated acetonitrile. From the small variations of the rate constant of decay at 480 nm vs. the CCl_4 concentration, an upper limit for the rate constant of quenching by CCl_4 of $k_q \leq 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ was estimated. In further experiments, dienes were added to **A**. With MeB, a rate constant for quenching of $k_q \approx 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ was obtained. Me_2B was found to be inefficient as with the triplet of **P** (see above); the upper limit is $2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ or less. These results exclude Me_2Ge as a possible transient under our conditions (see Section 4). For **A** in oxygen-saturated MCH or acetonitrile at room temperature, where the permanent absorption is observable 100 ns after the pulse, the ΔA_{310} value was found to be the same as under argon. This means that the observed transient cannot be the triplet state of **A** or an intermediate in the pathway from the excited state of **A** to **P**, because triplet quenching by oxygen should strongly reduce the formation of stable **P**, as measured by the increase in A_{310} after the pulse. We propose that the observed transient of excited **A** is due to T–T absorption, similar to that of **P**.

To test further for a triplet state, xanthone or benzophenone in acetonitrile and *p*-methoxyacetophenone in cyclohexane were used as high-energy donors ($\lambda_{\text{irr}} = 353 \text{ nm}$). On addition of **A** to an argon-saturated ketone solution, its triplet lifetime is reduced, as expected for energy transfer, but no transient was detected after this initial triplet decay (approximately $0.5 \mu\text{s}$). In contrast, with **P** under comparable conditions (Fig. 5), virtually the same T–T absorption spectrum in the 360–580 nm range was recorded as without the sensitizer. We therefore conclude that the observed transient on direct excitation of **A** is $^3\text{P}^*$ rather than $^3\text{A}^*$.

4. Discussion

The literature concerning the transient intermediates in the $\text{A} \rightarrow \text{P}$ photoconversion is controversial and the findings are only partly consistent with the results presented. Kolesnikov et al. [7] have applied $5 \mu\text{s}$ flash photolysis to **A** in *n*-heptane at room temperature; the increase in ΔA_{320} has been ascribed to $\text{A} \rightarrow \text{P}$ conversion, and two transients, one with $\lambda_{\text{max}} = 380 \text{ nm}$ ($\tau = 0.3 \text{ ms}$) and a second with $\lambda_{\text{max}} = 460 \text{ nm}$ ($\tau = 2 \text{ ms}$), were assigned to Me_2Ge and a biradical respectively. Our results in several solvents (Figs. 3(b) and 4), showing an increase in ΔA at 300–330 nm after the pulse and a permanent absorption component within 0.1 and $5 \mu\text{s}$ in oxygen- and argon-saturated solution respectively, are in agreement with the assignment to $\text{A} \rightarrow \text{P}$ conversion. However, a calibration of the 380 nm transient in the 0.1 ms range with $\epsilon_{380} = 1.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ [7] must be rejected. A possible transient under our conditions of a low concentration of **A** (0.1 mM or less) at 0.1 ms and in the 380–460 nm range should yield 2% or less than the increase in A_{320} (Figs. 3(b)

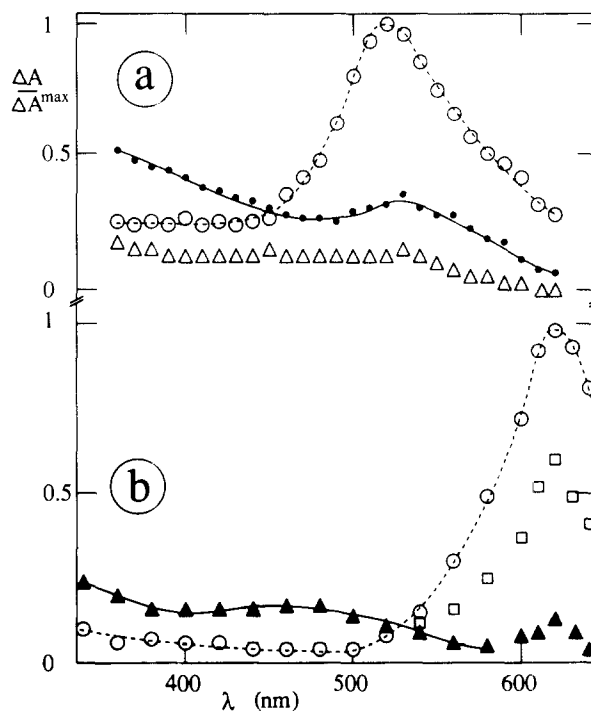
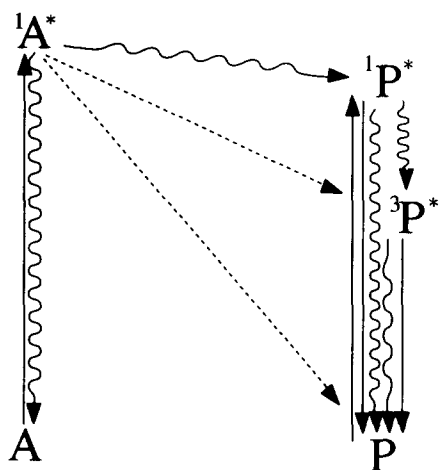


Fig. 5. Transient absorption spectra of **P** in argon-saturated acetonitrile at room temperature on sensitized excitation: (a) of benzophenone at $0.02 \mu\text{s}$ (\circ), $0.2 \mu\text{s}$ (\bullet) and $1 \mu\text{s}$ (\triangle) after the 353 nm pulse; (b) of xanthone at $0.02 \mu\text{s}$ (\circ), $0.2 \mu\text{s}$ (\square) and $1 \mu\text{s}$ (\blacktriangle) after the pulse.

and 4). This corresponds to a $\Delta \epsilon_{380}$ value of $120 \text{ M}^{-1} \text{ cm}^{-1}$ or less since the maximum ϵ value for the permanent increase in A_{320} is about $6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.

For octaisopropylcyclotetragermane (Pr_2Ge)₄ in cyclohexane, Mochida and Tokura [13] have recently observed two transients, one with $\lambda_{\text{max}} = 560 \text{ nm}$ ($t_{1/2} \leq 0.2 \mu\text{s}$) and a longer lived form with $\lambda_{\text{max}} = 390 \text{ nm}$ ($t_{1/2} \geq 2 \mu\text{s}$); they were assigned to Pr_2Ge and $\text{Pr}_2\text{Ge}=\text{GePr}_2$ respectively. In analogy, we could assume that the lifetime of Me_2Ge in fluid solution is shorter than a few hundred nanoseconds. This would argue against the assignment of the observed transient of **A** (Figs. 3(b) and 4) to Me_2Ge . Recently, high molecular weight germanium compounds, such as $(\text{Et}_2\text{Ge})_n$, in cyclohexane were studied by flash photolysis [18]. Two transients with $\lambda_{\text{max}} = 430$ and 350 nm were attributed to Et_2Ge and polygermyl radicals respectively. In particular, they were quenched by CCl_4 with rate constants of $k_q = 1.0 \times 10^9$ and $0.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ respectively. Also, dienes were shown to scavenge both intermediates efficiently, the rate constants for quenching by Me_2B being $k_q = 8.4 \times 10^7$ and $8.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ respectively. Although the transient absorption spectra in Figs. 3(b) and 4 show some similarities with those of Mochida et al. [18], the observed transient should not be assigned to Me_2Ge due to the low rate constants for quenching by CCl_4 and Me_2B (Table 2). Instead, we assign the observed transient of **A** to a triplet state.

The results are interpreted as follows (Scheme 2). The first excited singlet state ($^1\text{P}^*$) shows fluorescence and undergoes intersystem crossing to $^3\text{P}^*$. An analogous conclusion cannot



Scheme 2. Proposed photoreaction for $^1A^*$ to $^1P^*$ (the broken lines refer to less likely possibilities to $^3P^*$ or P).

be unambiguously drawn for **A**, although the results indicate fluorescence and intersystem crossing, as observed by T–T absorption at 297 K and phosphorescence at 77 K. Because no triplet state could be detected on sensitized excitation of **A** in contrast with **P** (Fig. 5), we suggest that the first excited singlet state ($^1A^*$) is unable to undergo intersystem crossing to $^3A^*$. Owing to the similarity of the fluorescence properties of excited **A** and **P**, we tentatively propose that the fluorescence on excitation of **A** originates from $^1P^*$ rather than from $^1A^*$.

In any case, the photoconversion occurs directly from $^1A^*$ to **P**. This could be observed within a few microseconds (Figs. 3(b) and 4) or within 100 ns under oxygen. Once **P** is formed in a small amount, its fluorescence in fluid and rigid media and its phosphorescence at 77 K (Fig. 2) dominate over those from **A**. The time-resolved spectra on excitation of **A** at room temperature reveal a permanent absorption increase below 340 nm and a transient in the range 300–580 nm (Figs. 3(b) and 4). The former is attributed to the **A** → **P** conversion and the latter to $^3P^*$ rather than $^3A^*$. Otherwise sensitized excitation of **A** should have yielded a triplet state with a similar spectrum and lifetime as on direct excitation.

The large $\Phi_{A \rightarrow P}$ values, virtually unaffected by the medium (Table 1), point to a very rapid homolytic splitting reaction of the two Ge–C bonds. On the other hand, a fluorescence lifetime of 3 ns, as observed on excitation of **A**, seems to be incompatible with this efficient splitting. The proposed explanation is that all of the fluorescence of electronically excited **A** stems from $^1P^*$ after conversion (in the picosecond range) from $^1A^*$ concomitant with splitting (Scheme 2). This $^1A^* \rightarrow ^1P^*$ excited state process, rather than the ‘conventional’ one of $^1A^*$ to 1P , is proposed to be the key step which explains most of the puzzling results. Once $^1P^*$ is formed, the origin of further emission and absorption processes cannot be distinguished between **A** and **P**.

The results are consistent with the absence of a 1H CIDNP effect in **A** and **P**. We could not observe any transient which might be identified as the biradical postulated by Nefedov

and coworkers [8]. Their observations could be due to uncontrolled warming of their probes during irradiation and/or concentration changes of **A** and **P** during and after irradiation. We therefore believe that Me_2Ge is formed in a single step by a synchronous splitting of the two C–Ge bonds in **A** (see Scheme 2). Furthermore, a two-step mechanism seems unlikely because of energetic reasons and we are unaware of any comparable reaction described in the literature.

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