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Photochemistry of Stable Free Radicals: The Photolysis of Perchlorotriphenylmethyl Radicals

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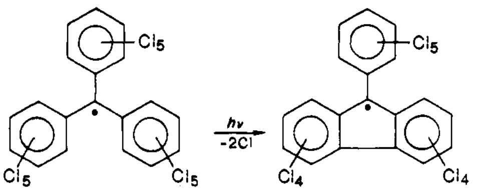
Abstract: The excitation of perchlorotriphenylmethyl radical (PTM) at 532 nm leads to an excited doublet, ^{2}PTM* (τ = 7 ns). The lifetime of this state is insensitive to oxygen, electron acceptors, and hydrogen-donating solvents. Electron donors (triphenylamine, *N,N*-dimethylaniline, and thianthrene) quench ^{2}PTM* at diffusion controlled rates. Cyclization to form perchloro-9-phenylfluorenyl radical (PPF) occurs with a quantum efficiency of 0.3 under 365-nm irradiation. Transient absorption spectroscopy shows that this ring closure proceeds via two intermediates. The first decays in a unimolecular process (k_2 = 3.8 ± 0.4 × 10^6 s^{-1}) to produce the second which also decays unimolecularly (k_3 = 4.6 ± 0.5 × 10^4 s^{-1}) to yield PPF.

Our interest in visible light induced electron transfer reactions of organic dyes[1-13] has prompted us to investigate the excited state behavior of stable free radicals. We hoped to examine whether unique oxidative and/or reductive redox chemistry might ensue upon photoexcitation and whether the steady state photoreactions of stable radicals would provide useful models for the excited state chemistry of transient free radicals, a subject of current interest of several other research groups.[14-19] Ballester and co-workers have suggested that several paramagnetic perchlorinated organic compounds be classified as "inert free radicals" to emphasize their minimal reactivity, since they have half-lives on the order of decades and high thermal and chemical stability.[20] Contrary to common chemical intuition, this family reacts slowly even with typical free radical traps such as molecular oxygen and hydrogen-donating solvents. They have even been used as mass spectral standards in the range *m/e* 300–700 since they show only successive loss of chlorine with very little fragmentation of the carbon skeleton.[21]

In the last decade, the thermal chemistry of these inert free radicals has been increasingly better established, but the course and efficiency of their photoreactions have not been extensively investigated. To alleviate this deficiency, we chose to examine the photochemsitry of perchlorotriphenylmethyl (PTM), a prototypical member of the series whose thermal chemistry has previously been investigated.[22]

That PTM is photoreactive has been previously reported. Luckhurst and Ockwell first described the light-induced ring closure of PTM in 1968,[23] concluding from ESR experiments that the major product formed was the perchloro-9-phenylfluorenyl radical (PPF), eq 1. In 1974, Buchachenko and Bogatyreva investigated the photolysis of PTM, also by ESR techniques.[24] They concluded that the rate-determining step in the decay of the PTM radical on exposure to light was hydrogen atom abstraction from the solvents employed in their work (vis., toluene, benzene, ethylbenzene, and cumene).



PTM PPF 63%

(1)

Neither of these preliminary studies made an attempt to decipher the mechanism of photochemical ring closure. No attempts at product isolation or quantitation were made, and product assignments were based solely on ESR data. Our work investigates the photophysics and photochemistry of PTM primarily in non-hydrogen-donating solvents, e.g., carbon tetrachloride. We are particularly interested in characterizing its excited state behavior and in establishing the mechanism of PPF formation since this is a rare example of an electrocyclic ring closure in an odd electron system.

Experimental Section

Perchlorotriphenylmethyl radical (PTM), perchlorotriphenylmethane (PTM-H), and perchloro-9-phenylfluorenyl (PPF) radicals were prepared by the method of Ballester et al.[20] Rose Bengal (Eastman Kodak), Aberchrome 540[25] (Aberchromics Ltd.), and carbon tetrachloride (Fisher Spectroanalyzed) were used without further purification. *N,N*-Dimethylaniline (Aldrich 99%) was distilled under vacuum. Triphenylamine (Aldrich 98%) was recrystallized once from absolute ethanol and then from diethyl ether. Thianthrene (Aldrich 97%) was recrystallized twice from glacial acetic acid. Cyclohexane (Fisher reagent grade) was stirred over several portions of concentrated H_2SO_4 and then over saturated Na_2CO_3. It was then washed with dilute KOH and water, dried over $MgSO_4$, and distilled from sodium metal. Acetonitrile (Fisher

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reagent grade) was purified by the method of Mann et al.[26] Duroquinone, purified by sublimation, was a kind gift from Dr. Stephan Hubig.

Steady-State Irradiations. Aliquots of a solution of freshly purified PTM (0.01 M) in redistilled spectral grade CCl_4 were placed in septa-sealed Pyrex test tubes and were deoxygenated by bubbling with a slow nitrogen or argon stream for 15 min to 1 h. The resulting solution was then sealed and irradiated with a sunlamp (Westinghouse, 150 W tungsten lamp) in a temperature-controlled bath (14 °C). After 5 min, the red color of PTM had faded and after 10 min the green color of PPF was apparent. After 1.3 h, irradiation ceased and the solvent was removed. The residue was purified on an alumina column with hexane as eluent. Products (see Results section below) were identified by spectroscopic analysis and by comparison with authentic samples. A parallel procedure was followed for the other irradiations reported below: (a) without degassing for air-saturated samples; (b) by replacing the CCl_4 with cyclohexane, methanol, or $CHCl_3$:CCl_4 mixtures; or (c) by replacing PTM with PPF. Rigorous purification of PTM (chromatographic removal of its precursor PTM-H:silica gel with CCl_4 eluent) was necessary for clean conversion to PPF.

Absorption spectra were measured on a Hewlett-Packard 8450A diode array spectrophotometer. All spectra were recorded under yellow safety lights. Quantum yield measurements were performed under red safety lights. The quantum yield for formation of PPF was measured by irradiating an optically opaque solution of PTM (2.2×10^{-3} M in CCl_4) in a 1-cm cuvette with an Oriel 200 W medium-pressure Hg arc lamp through a grating monochromator set at 365 nm. A 2-cm^2 window was placed in front of the cuvette and the solution was continuously stirred with a small bar magnet. The changes in optical density at 564 and 618 nm were recorded every 2 min during 30 min of irradiation. Under our conditions, less than 10% conversion of the starting material occurs. Aberchrome 540[25] and potassium ferrioxalate[51] were used as actinometers.

Steady-state emission spectra were recorded on a Perkin-Elmer LS-5 spectrofluorometer. All spectra were measured in the dark. The quantum yield of fluorescence of PTM in CCl_4 (1.3×10^{-4} M) was measured by comparison to Rose Bengal (3.0×10^{-6} M) in ethanol.[27]

Cyclic voltammetry was performed with a BAS-100 electrochemical analyzer and a Houston Instruments DMP40 digital plotter. Measurements were reported against a $Ag/AgNO_3$ reference and were done in the dark. Solutions were approximately 1 mM PTM in acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate as supporting electrolyte.

Time-resolved emission and flash photolysis experiments were performed on either a frequency doubled mode-locked Nd:YAG laser (Quantel YG402, 200-ps pulse, approximately 30 mJ at 532 nm) or a frequency doubled Q-switched Nd:YAG laser (Quantel YG581, 10-ns pulse, approximately 80 mJ at 532 nm). The sample was changed at least every five shots and appropriate cut-off filters were placed immediately in front of and behind the cuvette. Transient absorptions were monitored with a conventional xenon lamp, monochromator, photomultiplier arrangement. Digitized signals were passed to a PDP 11/70 computer for analysis. The system has been described more fully elsewhere.[28]

Photoacoustic measurements were made at The Univeristy of Colorado (Boulder) with a previously described apparatus.[29] In the photoacoustic measurements the optical density of PTM in cyclohexane at 337 nm was approximately 0.1 absorption units.

Results and Discussion

Steady-State Photolysis. Visible light photoexcitation of an intensely red solution of PTM in CCl_4 produces a green paramagnetic product PPF in up to 63% isolated yield (eq 1) together with α-hydroperchloro-9-phenylfluorene, PPF-H ($\sim$12%), and small quantities of hexachlorobenzene (trace). Larger fractions of PPF-H were obtained in hydrogen-donating solvents or if the carbon tetrachloride was not rigorously purified. Independent irradiation of purified PPF induced fading, with high yield conversion to PPF-H. PTM and PPF have visible absorption maxima at 564 and 618 nm, respectively.

The conversion of PTM to PPF via steady-state photolysis ($\lambda > 420$ nm) as monitored by absorption spectroscopy is shown in Figure 1. The quantum yield of PPF formation was measured as 0.3 ± 0.1 by comparison to Aberchrome 540 and ferrioxalate actinometers.[52] Three of the four isosbestic points are quite stable and plots of A (at 564 and 618 nm) versus irradiation time are linear.[30] Changes in optical density were monitored at both 564 and 618 mm since the extinction coefficients had been measured for pure samples of PTM ($\epsilon_{\mathrm{PTM,564nm}} = 760\ \mathrm{cm^{-1}\ M^{-1}}$) and PPF ($\epsilon_{\mathrm{PPF,618nm}} = 150\ \mathrm{cm^{-1}\ M^{-1}}$) at these wavelengths.

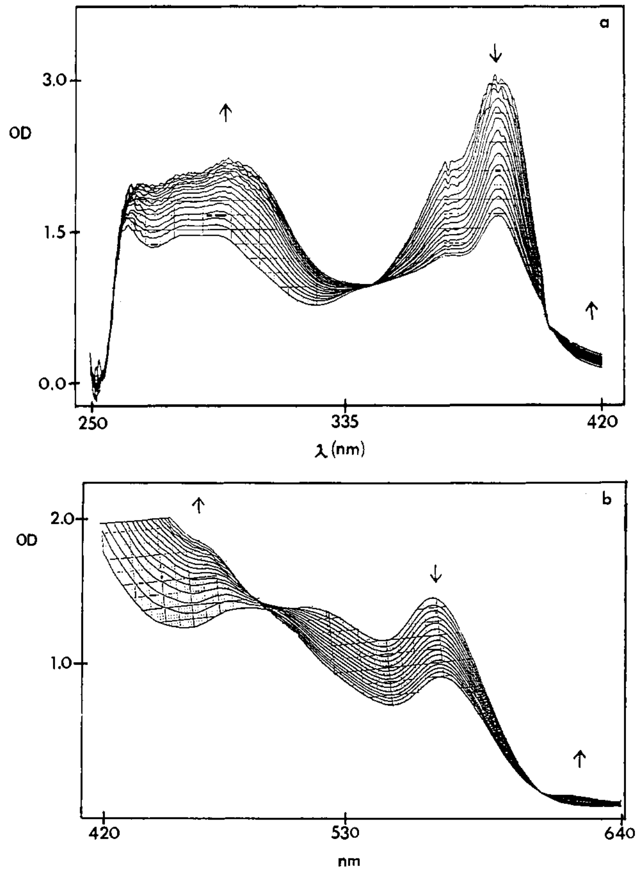

Figure 1. Irradiation of (a) 10^{-4} M and (b) 10^{-3} M solutions of PTM with a Hg pen lamp ($\lambda > 420$ nm) for 30 min. Spectra were recorded every 2 min on a Hewlett-Packard 8450A spectrophotometer.

If the steady-state irradiation is conducted under oxygen, no green color developed. A complex mixture of products was formed from which PPF-H and hexachlorobenzene became major products. Irradiation of the initial photoproduct (PPF) as a pure sample under oxygen produced a comparable mixture.

PTM has an emission maximum at 605 nm which is independent of the wavelength of excitation. The quantum yield of fluorescence at room temperature was measured as 0.015 ± 0.005 by comparison to Rose Bengal.

PTM shows a reversible reduction at −430 mV (Figure 2). It has been shown that alkali metals and ascorbic acid rapidly reduce PTM to the corresponding anion.[31] No oxidation was observed between +2 and −2 V, probably because of the cumulative effect of 15 inductive electron-withdrawing groups. (Perchlorotriphenylcarbonium hexachloroantimonate has been isolated but this salt was prepared under rather vigorous conditions ($SbCl_5$ in SO_2Cl_2).)[32,33]

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(30) The point at ~475 nm shifts approximately 5 nm during the irradiation. This may indicate the formation of another product, but it must be formed with a very low quantum yield, considering the minimal shift in the isosbestic point. A small amount of perchlorotriphenylmethane, PTM-H, can be isolated from the irradiation of PTM in chloroform. Therefore, our observed shift in the isosbestic point at 475 nm may be from the slow formation of PTM-H derived from chloroform impurity in our carbon tetrachloride.

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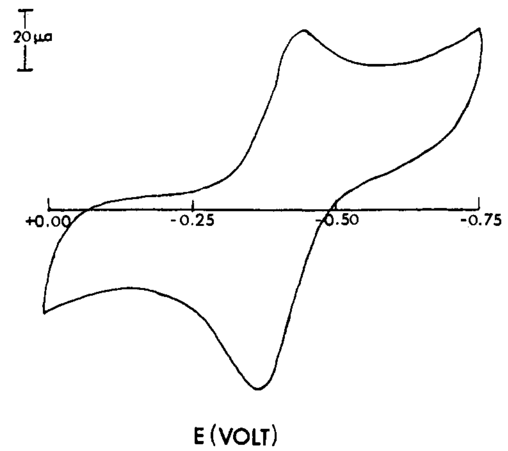

Figure 2. Cyclic voltammogram of PTM (10^{-3} M in acetonitrile containing 0.1 M TBAP). Potentials are reported against a Ag/$AgNO_3$ reference and were measured in the dark.

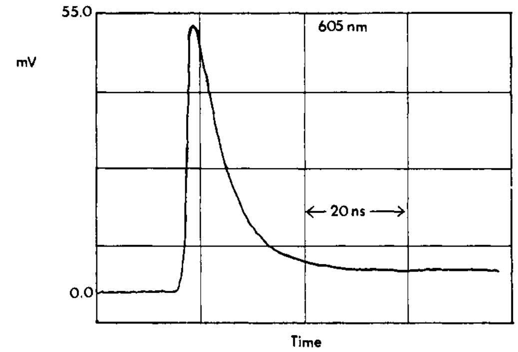

Figure 3. Fluorescence decay of excited PTM in CCl_4 (λ_{exc} = 532 nm).

Table I. Fluorescence Quenching of ^{2}PTM* by Electron Donors

donor	$10^{-10}k_q$,[a] M^{-1} s^{-1}	$10^{-8}k_0$,[b] s^{-1}
N,*N*-dimethylaniline (DMA)	1.55	1.60
triphenylamine (TPA)	1.03	1.61
thianthrene (THAN)	1.45	1.87

[a,b] Values calculated from slope[a] and intercept[b] of best fit line from Figure 4. Typical errors in observed rate constants are 15%.

Time-Resolved Measurements. Because PTM is a ground-state doublet, the lowest energy spin allowed excitation in the visible region is to the first doublet excited state. The observed rate of emission from PTM upon excitation at 532 nm, monitored at 605 nm, was measured as 1.4 ± 0.1 × 10^8 s^{-1} (Figure 3). Electron donors, specifically, *N*,*N*-dimethylaniline, triphenylamine, and thianthrene, quench the excited doublet state at approximately a diffusion-controlled rate (Table I). The observed emission rate constant, k_{obsd} was measured at varying electron donor concentrations, [Q], and was plotted according to

$$k_{obsd} = k_0 + k_q[Q] \qquad (2)$$

where k_0 is the rate of decay in the absence of quencher and k_q is the bimolecular rate constant. The rate constants k_0 and k_q can be obtained respectively from the intercept and slope of this plot (Figure 4). Table I lists k_0 and k_q values, calculated by least-squares analysis, for each electron donor. The average value for k_q was 1.3 × 10^{10} M^{-1} s^{-1} and for k_0 it was 1.7 × 10^8 s^{-1}, a value that is comparable with the previously observed rate of emission in the absence of quenchers (1.4 × 10^8 s^{-1}).

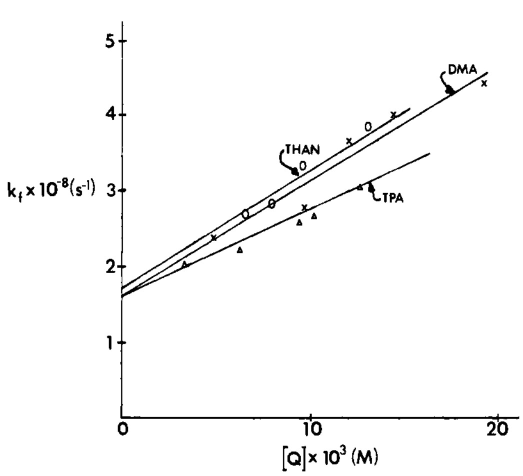

Figure 4. Plot of fluorescence quenching by electron-donating quenchers (Q): *N*,*N*-dimethylaniline (DMA), thianthrene (THAN), and triphenylamine (TPA).

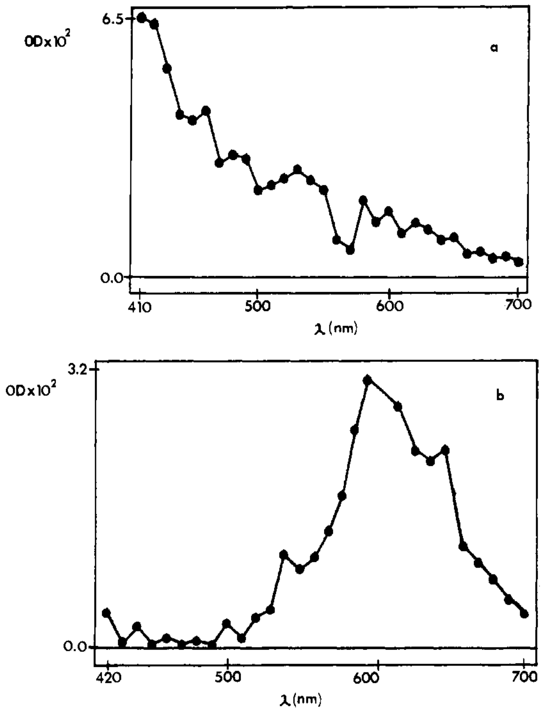

Figure 5. Absorption spectra of donor cation radicals formed by quenching ^{2}PTM*: (a) *N*,*N*-dimethylaniline (0.32 M) and PTM (1 mM) approximately 2 μs after pulse (λ_{exc} = 532 nm); (b) triphenylamine (0.42 M) and PTM (1 mM) in CCl_4 approximately 3 μs after pulse (λ_{exc} = 532 nm).

Because the spectra of the radical cations of both *N*,*N*-dimethylaniline[35,36] and triphenylamine[36,37] are observed immediately upon excitation of solutions of millimolar PTM in the presence of each electron donor (0.5 M) (Figure 5), we conclude that emission quenching is via electron transfer to PTM. Both of the radical cations decay to the base line via second-order kinetics. The decay rates were shown to be bimolecular by attenuating the laser intensity and measuring the rate constant and half-life of the radical cation. The first half-life of these decays increased as the beam energy decreased, while the bimolecular rate constant remained unchanged, within experimental error. The second-order rate constant for decay of the dimethylaniline cation radical, k_d, is calculated as 1.0 × 10^{10} M^{-1} s^{-1} when the previously reported extinction coefficient is used.[36] No growth of absorption was observed upon decay of the radical cation, thus excluding dimerization as a possible decay route. This observation suggests that k_d measures the rate of back electron transfer to the donor radical cation from PTM^-.

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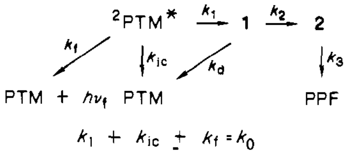
Table II. Observed Rate Constants in Hydrogen-Donating Solvents

	$CHCl_3$:CCl_4 (2:3 v/v)	cyclohexane
$k_0{}^a$	$1.42 \pm 0.10 \times 10^8$ s^{-1}	$1.44 \pm 0.10 \times 10^8$ s^{-1}
k_2	$3.25 \pm 0.30 \times 10^6$ s^{-1}	$3.71 \pm 0.40 \times 10^6$ s^{-1}
k_3	$4.74 \pm 0.50 \times 10^4$ s^{-1}	$4.55 \pm 0.50 \times 10^4$ s^{-1}

[a] Observed rate of emission.

Scheme I. Proposed Mechanism for the Photochemical Conversion of PTM to PPF



The observed rate of emission did not change in the presence of duroquinone ($k_0 = 1.5 \pm 0.1 \times 10^8$ s^{-1}, [duroquinone] = 3×10^{-2} M). Although no oxidation of PTM was observed between −2 and +2 V, the excited-state oxidation potential of PTM should approximate its ground-state reduction potential (−430 mV) when corrected by a dielectric work function term. Since duroquinone has a redox potential of −235 mV, it should be able to accept an electron from excited PTM on thermodynamic grounds, and our failure to observe excited-state quenching by acceptors was not anticipated.

The excited doublet state is not quenched by oxygen even though this process is spin allowed ($k_0 = 1.4 \pm 0.1 \times 10^8$ s^{-1}) in oxygen-saturated solution. Given that the maximum concentration of O_2 in CCl_4 is 1.3×10^{-2} M,[38] the oxygen quenching rate constant must be less than 5×10^8 M^{-1} s^{-1} (or at least 40 times slower than diffusion control) since as little as 10% quenching could easily have been observed. Buchachenko and Bogatyreva did not observe any change, in fact, in the ESR signal of PTM other than paramagnetic broadening in the presence of O_2. They attributed this behavior to a short lived electronically excited state.[24]

Space-filling models of PTM show an approximate 60° tilt of the phenyl rings with respect to each other leading to extremely weak overlap of the phenyl π orbitals with the p orbital of the trivalent carbon.[39] ESR data show that the odd-electron density resides mainly on the trivalent carbon.[40] Localization of electron density usually enhances the reactivity of radical centers. However, due to the tilt of the phenyl rings, the central carbon is completely shielded by six ortho chlorines, making it virtually unapproachable for collisional quenching. Electron-transfer quenching can occur, however, over distances as large as 15 Å and therefore this process represents a major degradative pathway for excitation energy when electron donors are present.

Although Buchachenko and Bogatyreva have stated that the production of PTM-H is the rate-determining step in the loss of PTM radicals on photolysis in hydrogen-donating solvents,[24] our flash-photolysis studies show that neither the rate of emission nor the rates of decay of any intermediate change upon changing the solvent from carbon tetrachloride to cyclohexane to $CHCl_3$:CCl_4 mixtures (Table II). If PTM-H is formed photochemically, this process must occur with a very low quantum yield so as to make only such small changes in the observed rate constants that they would be within the experimental error of our measurements.

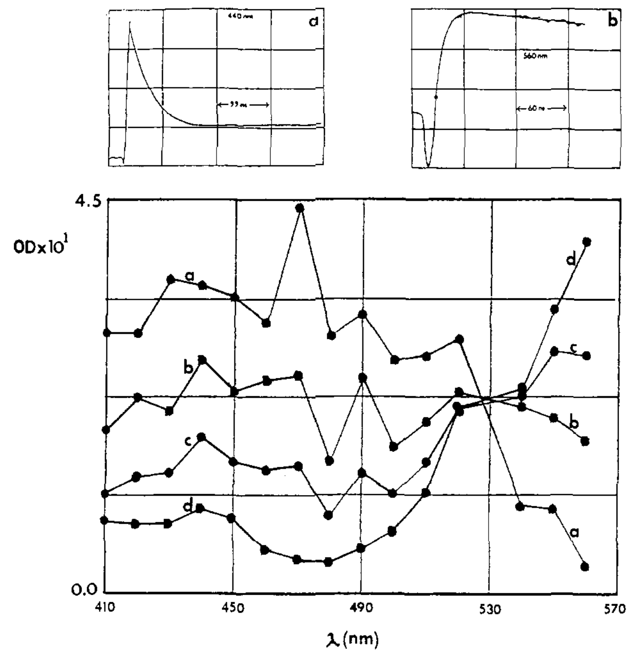


Figure 6. Transient absorption spectrum after 532-nm excitation of PTM in CCl_4 (OD_{532nm} = 1.0). Curves correspond to spectra taken at various delay times after the excitation pulse: (a) 390 ps, (b) 2.4 ns, (c) 5.1 ns, and (d) 10.5 ns. Insets: (a) decay of the doublet excited state ^{2}PTM*; (b) growth of intermediate **1**.

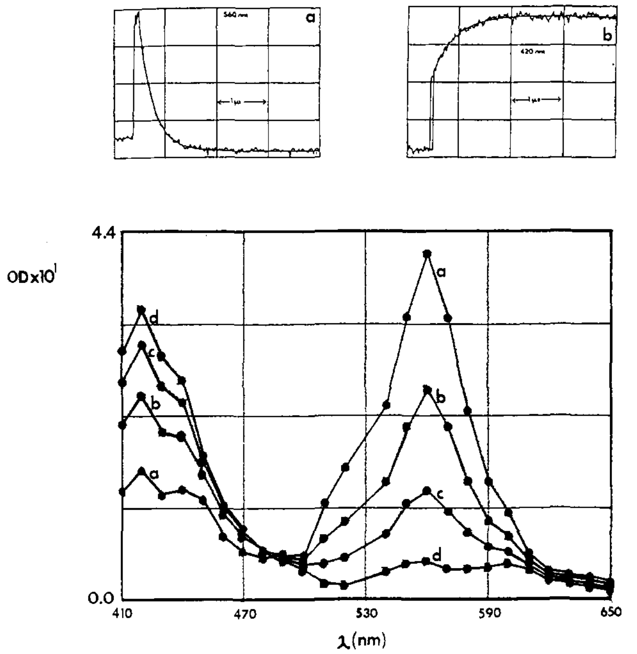


Figure 7. Transient absorption spectrum after 532-nm excitation of PTM in CCl_4 (OD_{532nm} = 1.0). Curves correspond to spectra taken at various delay times after the excitation pulse: (a) 20 ns, (b) 140 ns, (c) 260 ns, and (d) 320 ns. Insets: (a) decay of **1**; (b) growth of intermediate **2**.

Proposed Mechanism. Excitation of PTM at 532 nm leads to several transient absorptions. The initial absorption (^{2}PTM*) is shown in Figure 6 (curve A) at 390 ps after the pulse, the earliest time measured. As can be seen, this absorption decays (Figure 6, insert a, 440 nm) concomitant with a growth of absorption at longer wavelengths (Figure 6, insert b, 560 nm). An isosbestic point is observed at 530 nm. The decay rate at 440 nm was measured as $1.3 \pm 0.2 \times 10^8$ s^{-1} in agreement with the rate of absorption growth at 560 nm. This rate compared to the observed emissive rate, $k_0 = 1.4 \times 10^8$ s^{-1}, leads to its assignment as the first doublet excited state which decays to an intermediate, **1** (Scheme I).

Intermediate **1** decays on a longer time scale (Figure 7). The decay rate of this intermediate at 560 nm (Figure 7, insert a) was measured as $3.8 \pm 0.6 \times 10^6$ s^{-1} with a concomitant growth at 420 nm (Figure 7, insert b) having a rate constant of $3.3 \pm 0.6 \times 10^6$ s^{-1}. Neither the rate of decay at 560 nm nor the rate of growth at 420 nm is dependent on the initial ground-state concentration of PTM, making unlikely the assignment of **1** as an

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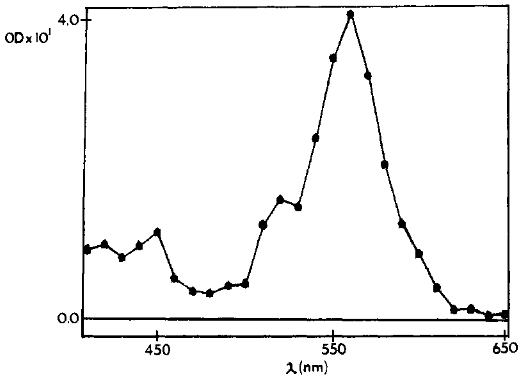


Figure 8. Absorption spectrum of **1** in CCl_4.

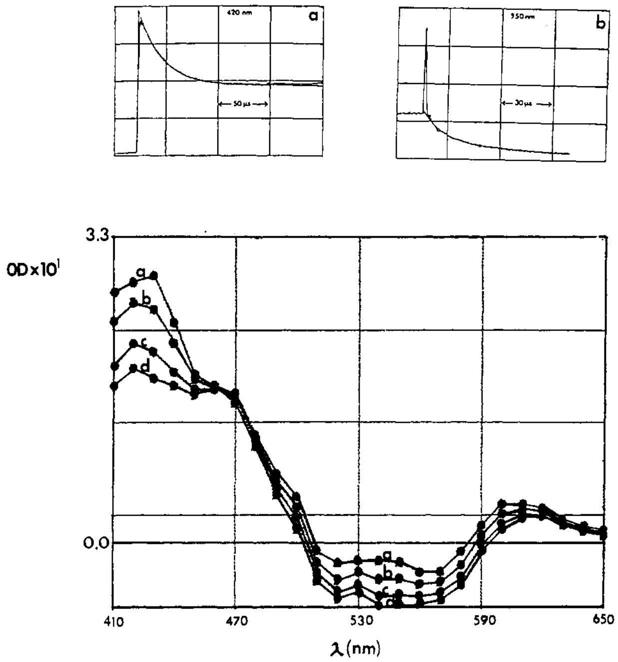


Figure 9. Transient absorption spectrum after 532-nm excitation of PTM in CCl_4 (OD_{532nm} = 1.0). Curves correspond to spectra taken at various delay times after the excitation pulse: (a) 4 μs, (b) 13 μs, (c) 22 μs, and (d) 37 μs. Insets: (a) decay of **2**; (b) bleaching, photoproduct formation.

Table III. Rate Constants of Decay and Formation of Intermediates Produced by 532-nm Excitation of PTM[a] in CCl_4

$k_f + k_{ic} + k_1$	1.43×10^8 s^{-1} [b]	$k_{form,2}$	3.29×10^6 s^{-1}
$k_f + k_{ic} + k_1$	1.32×10^8 s^{-1} [c]	$k_{decay,2}$	4.59×10^4 s^{-1}
$k_{form,1}$	1.00×10^8 s^{-1}	$k_{bleaching}$	4.21×10^4 s^{-1}
$k_{decay,1}$	3.78×10^6 s^{-1}		

[a] Typical errors in observed rate constants are 15%. [b] Observed rate of emission. [c] Decay of doublet–doublet absorption.

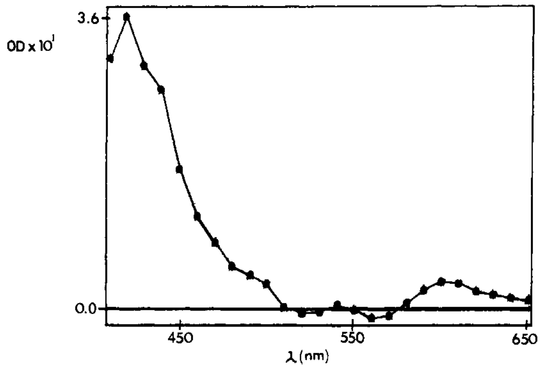
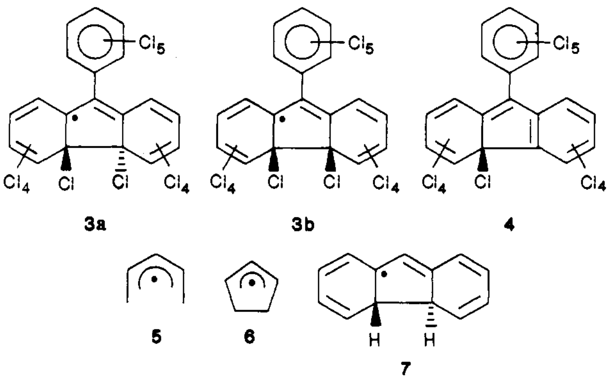


Figure 10. Absorption spectrum of **2** in CCl_4.

Chart I



absorptive excimer. The absorption spectrum of **1** (Figure 8) resembles that of PTM except that its most intense band is slightly red-shifted. It is possible, therefore, that it has somewhat greater charge-transfer character ($Ar_2C^+ - Ar^-$) than $^2PTM^*$. That this intermediate is a quartet formed via intersystem crossing from the initially formed first excited doublet is unlikely on energetic grounds (see below) if the perchlorinated radical bears analogy to the parent hydrocarbon radical.[17] As **1** decays, an isosbestic point is observed at 485 nm. With respect to our scheme, we attribute this to the conversion of **1** to another intermediate, **2**.

Longer time scales reveal the decay of **2** (Figure 9). This is shown by the decay at 420 nm (Figure 9, insert a) with an observed rate constant of 4.2 ± 0.5 × 10^4 s^{-1}. Accompanying the decay of intermediate **2**, bleaching is observed at 550 nm (Figure 9, insert b) with an observed rate constant of 4.2 ± 0.4 × 10^4 s^{-1}. Note that this loss of absorption indicates an irreversible loss of ground state, at least on these time scales, which we attribute to the formation of photoproduct PPF. Rate constants for these interconversions, where symbols are identified in Scheme I, are summarized in Table III.

Electron donors do not affect the rates of decay of intermediates **1** and **2** in contrast to their effect on the rate of decay of the first doublet excited state (Figure 4). Nor does the addition of $CHCl_3$ to solutions of PTM in CCl_4, the use of cyclohexane as solvent, or oxygen saturation affect the rates of decay of intermediates **1** or **2** (Table II). As with the parent hydrocarbon,[17] the chlorocarbon first excited doublet is apparently not the species from which hydrogen abstraction derives. Under our experimental conditions, biphotonic processes are not possible because we find a linear relationship between the observed optical density of **1** and **2** and the relative incident light intensity. Since oxygen and hydrogen donors do influence the chemical yield of PPF and H-PPF, and since the steady-state photolysis of PPF does indicate chemical sensitivity to these species, we infer that hydrogen atom incorporation occurs after ring closure and that decomposition ensues upon photolysis of PPF in the presence of oxygen.

Initially we hoped to assign structure to **2**, but since it has a lifetime of 22 μs, rapid spectroscopic methods are required and these seem to be insufficiently detailed to allow for unambiguous structural assignment. Since its absorption spectrum (Figure 10) exhibits a maximum at shorter wavelengths than either PTM or PPF, we suggest that conjugation is probably disrupted in this intermediate, as might be attained in a ring-closed PTM prior to the loss of two chlorines, i.e., **3**. This assertion reasonably ascribes similar chemistry to the excited states of PTM and those described earlier by Meisel and co-workers for the parent hydrocarbon.[17,18] Alternately, **2** could be a severely twisted precursor to cyclization or a distorted polyene **4** formed by loss of one clorine atom from **3**. If **1** does indeed have appreciable charge-transfer character, as was suggested earlier, such charge separation would provide a driving force for cyclization to **2**, the species to which **1** decays.

If intermediate **2** is the ring-closed isomer **3**, its stereochemistry would be interesting because there are no clear-cut rules for predicting conrotatory or disrotatory ring closures in $4n + 1$ π electron systems. Indeed, it has been claimed to be difficult to even qualitatively estimate activation energy differences for the

Table IV

s	τ (ns)	E (kcal/mol)[b]	τ (ns)[a]
0.74	10	62	7
0.30	290	25	285

[a] Observed values from flash photolysis. [b] Total heat emitted in corresponding τ. Errors in the photoacoustic experiment are approximately ±2 kcal/mol.

electrocyclic closure of radicals.[41] Since unambiguous experimental characterization of **2** proved to be impossible, we turned to semiempirical calculations to determine whether cyclizations such as the conversion of PTM to **3** should be stereoselective. In order to simplify the calculation, we stripped the system to its essential carbon skeleton, a pentadienyl to cyclopentenyl cyclization. The HOMO mnemonic predicts a ground-state disrotatory closure, whereas extended orbital correlation or the Zimmerman Mobius–Hückel predicts no stereochemical preference.[42] AM1 calculations[43] were used to attain geometry optimization for the *E,E*-pentadienyl radical **5** (H_f = 41.7 kcal/mol) and for the cyclopentenyl radical **6** (H_f = 24.6 kcal/mol). Although these heats of formation, when compared with experimentally derived values,[44] appear to be too low, the error seems to be systematic and attributable to overcompensation for electron correlation in radicals. A reaction profile was calculated by bringing together the two terminal carbons of **5** (distance = 3.21 Å) to the optimum bonding distance in **6** (1.51 Å). As the transition state was approached (E_A = 27 kcal/mol), conrotation of the termini was attained. The reaction profile motion was symmetric as the transition state was approached from either side. If a disrotatory motion was forced by symmetric motion of the C_4 and C_5 hydrogens of **6**, substantially higher barriers (E_A = 38 kcal/mol) were encountered. It is interesting to note that this ground-state stereopreference is opposite to that reported for the electrocyclization of the allyl radical.[45] Unfortunately, the excited-state surface, with geometric optimization, proved to be non-convergent. If we assume, however, that photolysis produces a charge-separated intermediate which closes thermally, we might expect that our photochemically induced cyclization might be stereochemically controlled and conrotatory. If this expectation also applies to the more complex perchlorinated PTM, we could expect formation of **3a** rather than **3b**. From either intermediate, rearomatization to PPF would be expected to occur, either through stepwise loss of chlorine atoms or concerted loss of Cl_2.[46] It is therefore possible that **4** might be involved, as well, in the conversion of PTM to PPF. It might reasonably be expected to be sensitive to oxygen- or hydrogen-donating solvents.

In any case, the observed cyclization is parallel to the similar photocyclization of diphenylamines, triphenylamines, and *cis*-stilbenes.[47] The similarity of our result and that seen by Meisel[17,18] suggests this route may have some generality and is probably *not* specific for a small group of highly chlorinated radicals.

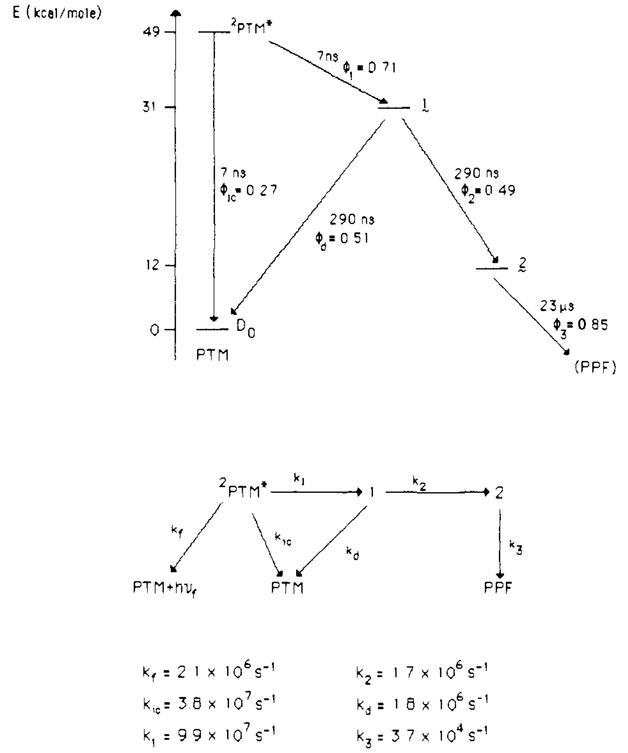


Figure 11. Energetic ordering, branching efficiencies, and rates of conversion of intermediates involved in the photochemical conversion of PTM to PPF. Note the ϕ_{ic} and ϕ_1 represent measured quantum efficiencies whereas ϕ_d, ϕ_2, and ϕ_3 represent dark partioning of decay paths available to **2** and **3**.

Measurements of the photoacoustic signal generated upon excitation of PTM at 337 nm in cyclohexane were made. The digitized data were analyzed by the method of Peters et al.[29,48] based on deconvolution techniques. The photoacoustic waveform for two consecutive first-order decays can be described as

$$V(t) = T(t)[a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2}] \tag{3}$$

where $V(t)$ is the experimentally measured voltage change as a function of time, $T(t)$ is a function of transducer response, a_1 and a_2 are the fractions of total heat emitted, and τ_1 and τ_2 are the lifetimes of the transients responsible for heat deposition. Table IV lists the fitted a and τ values. If the quantum yield of the non-radiative decay process, ϕ_i, is known, then the amount of heat deposited (in kcals/mole), E_Δ, can be calculated from

$$E_\Delta = a_i \phi_i E_{h\nu} \tag{4}$$

where $E_{h\nu}$ is the energy of the exciting photon (337 nm = 85 kcal/mol). Since the time scales for the conversions of ^{2}PTM* to **1** and of **1** to **2** fall within the response times of the photoacoustic measurements, we can specifically use time resolved heat deposition to characterize the energies of these intermediates and the quantum yields of their formation.

We assume that an exceedingly rapid vibrational cascade converts the initially formed vibrationally excited state to the lowest lying excited doublet with unit efficiency. From eq 3 and 4, we find that the total heat deposited within 10 ns after flash excitation of PTM is 62 kcal/mol. Since the 0,0 band of PTM at 590 nm corresponds to an energy gap of 49 kcal/mol, 36 kcal/mol is deposited in internal conversion from higher excited states to ^{2}PTM*.

Two non-emissive fates are available to ^{2}PTM*: non-radiative decay to the ground state or conversion to **1**. Simultaneous solution of eq 3 and 4 for the fast and slow heat depositions is possible if the heat of formation or the partitioning ratios for any of the heat-depositing conversions of **1** or **2** are known. These in turn are accessible if either of the extinction coefficients of **1** or **2** are known. Unfortunately, none of these values could be established independently by experiment and we again turned to calculations. The energy difference (12.3 kcal/mol) between the geometrically optimized diphenylmethyl radical and the *trans*-dihydrofluorenyl radical **7** calculated by UHF-MNDO methods[49] was assumed to reasonably approximate the energy difference between PTM and **3a**.[50] If this value is assigned to the intermediate **2**, the energies and quantum yields for the formation of the intermediates

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(50) The heat of formation of the diphenylmethyl radical was also calculated by RHF-MNDO methods. However, no reasonable minimum could be found on the RHF surface for the dihydrofluorenyl radical.

and products can be calculated directly. These quantum yields, together with the experimentally determined rates of Table III, allow for the determination of the individual rate constants shown in Figure 11.

The quantum yield of PPF from **2** was measured experimentally from the observed ground-state bleaching at 550 nm, using the extinction coefficient values at 550 nm for PTM and PPF previously measured for pure samples. The extinction coefficients of **1** ($\epsilon_{560\mathrm{nm}} = 1.71 \pm 0.08 \times 10^4\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$) and of **2** ($\epsilon_{430\mathrm{nm}} = 1.02 \pm 0.03 \times 10^4\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$) were measured by using the charge transfer excited state of $\mathrm{Ru(bpy)_3}^{2+}$ as an actinometer.[51]

From the initial heat deposition from $^2\mathrm{PTM}^*$ and from the energy of **1** (31 kcal/mol), we then solve for the partitioning between non-radiative internal conversion ϕ_{nr} (0.27) and formation of **1**, ϕ_1 (0.71). The additional 25 kcal/mol deposited in the next 280 ns, corresponding to the decay of **1**, occurs through only two routes (decay to PTM or conversion to **2**) since the conversion of **1** to **2** is clean (from the observed isosbestic point). We therefore know that the sum of the fractional branching between these two routes, ϕ_{d} and ϕ_2, respectively, is 1. From the energies of **1** and **2**, the solution of eq 3 and 4 gives $\phi_{\mathrm{d}} = 0.51$ and $\phi_2 = 0.49$. Since the photochemical quantum yield of PPF is known ($\phi_{\mathrm{PPF}} = 0.3$), we surmise that $\phi_3 = 0.3/\phi_1\phi_2 = 0.85$, a value that agrees exactly with an independent measurement based on the relative extinction coefficients of **2** and PPF. We summarize these results in Figure 11, a minimal representation of the energy levels, rate constants, and quantum efficiencies for the formation of the intermediates involved in the photoconversion of PTM to PPF. Because longer time scales could not be accessed in these experiments, PPF cannot be properly placed on this diagram, but it has been indicated as the product derived from **2** to complete the scheme.

Summary

In summary, we have delineated, with steady-state and time-resolved methods, the sensitivity of photoexcited PTM to electron transfer and radical trapping agents and have proposed a mechanism by which PTM is converted to PPF. The excited doublet state was shown to be unaffected by oxygen saturation, by electron acceptors, or by hydrogen-donating solvents. In contrast, it is quenched by electron donors at an approximately diffusion controlled rate. In the presence of donors, transient absorptions attributable to the donor radical cations were present immediately after excitation, leading us to assign the quenching process as involving electron transfer. We attribute the second-order decay of the radical cation to back electron transfer because the entire spectrum decays to the original base line with no concomitant growth of absorption.

The light-induced ring closure to PPF occurs via two intermediates, **1** and **2** which are encountered sequentially as PTM is converted to PPF. The decay of **2** is accompanied by an irreversible loss of PTM. Photoacoustic spectroscopy was used to calculate the relative energy differences between ground and excited states and intermediates formed in this system. From its absorption spectrum, we surmise that **1** is lower in energy than the initially formed doublet $^2\mathrm{PTM}^*$ and that it may possess internal charge-transfer character ($\mathrm{Ar_2{-}C^+{-}Ar^{\bullet-}}$). **2** is likely a ring-closed structure with disrupted aromaticity, as seen by the shorter wavelength absorption maximum relative to PTM or PPF, which ultimately loses two chlorine atoms, irreversibly, to generate PPF. AM1 calculations suggest that stereocontrol in the electrocyclization of the related pentadienyl radical is feasible. A complete photophysical description of the excited state surface could be derived from photoacoustic measurements, provided that the calculated energy of **2** can be stipulated.

Flash photolysis in hydrogen-donating solvents indicates that, contrary to previous studies, the loss of PTM by hydrogen abstraction in the lowest lying excited state must be an extremely inefficient process.

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(51) In this calculation $\epsilon_{360}(\mathrm{Ru(bpy)_3}^{2+}) = 2.1 \times 10^4\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ and $\phi_{\mathrm{isc}} = 1$ were assumed. There is some discrepancy in the literature concerning ϵ_{360} of $\mathrm{Ru(bpy)_3}^{2+*}$. Values range from $1.0 \times 10^4\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ (Benasson et al., *J. Am. Chem. Soc.* **1976**, *98*, 3722) to $2.2 \times 10^4\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ (Rongee et al. *J. Phys. Chem.* **1982**, *86*, 4404). Our value was measured by comparison to a *meso*-diphenylhelianthrene steady state actinometer (Hubig, S. M.; Atherton, S. J.; Gaillard, E., unpublished results). By measuring the optical density of $\mathrm{Ru(bpy)_3}^{2+*}$ at 360 nm ($\mathrm{N_2}$ saturated, $\mathrm{OD}_{532} = 0.12$), I_0 can be calculated. Then by measuring the optical density of **1** at 560 nm and of **2** at 430 nm, the extinction coefficients can be calculated. The reported values are derived from four separate determinations (ten averaged values per set) at three different laser intensities.

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