Photoionization of Diarylmethyl Radicals in Acetonitrile and Alcohol–Water: Laser Flash Production of Diarylcarbenium Ions

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Diarylmethyl radicals $Ar_2CH^•$ were produced by 248-nm laser photolysis (20 ns) of diphenylmethane, diphenylmethanol, and diarylmethyl halides in acetonitrile and water:alcohol mixtures. A few microseconds after their generation, the radicals were subjected to a laser pulse (20 ns) of 308-nm light. As products of the photolysis of the radicals, the electronically excited radicals, $Ar_2CH^{•*}$ (D_1 state), and the corresponding cations, Ar_2CH^+, were identified. The electronically excited radicals decay with emission of light (≈550 nm in the case of $Ph_2CH^{•*}$) to their ground state (D_0), whereas the cations react with solvent or (other) nucleophiles. The formation of cation from $Ar_2CH^•$ requires *two* photons (is biphotonic) and proceeds by photoionization of $Ar_2CH^{•*}$. The photoejected electrons were directly observed in aqueous alcohol. In acetonitrile, the yield of photoionization of $Ar_2CH^•$ (as measured ≥20 ns after the 308-nm pulse) can be increased by the electron scavenger *n*-butyl chloride, which does *not* react with $Ar_2CH^{•*}$. In contrast, CCl_4, which *does* react with $Ar_2CH^{•*}$, does *not* lead to an increase in cation yield.

Introduction

In many photochemical reactions, free radicals are important intermediates, resulting from (homolytic) abstraction, fragmentation, and ionization processes. Under conditions of low intensity of exciting light, in solution the stationary concentration of the radicals is typically $<10^{-9}$ M, due to their usually large rates of chemical reaction (radical-radical termination rates 10^9–10^{10} M^{-1} s^{-1}). As a result, absorption of light by the radicals can be neglected compared to that by the parent compounds, even if the extinction coefficients of the radicals are up to 10^3–10^4 times higher. However, the situation is different if high intensity (pulsed) methods such as, e.g., laser photolysis are used to generate radicals which permit initial radical concentrations in the μM to mM range to be easily produced. Under these conditions, the photolysis of radicals cannot be neglected and it becomes necessary to understand their photochemistry in order to obtain a complete picture.

The photochemistry and photophysics of diaryl[2–6] and triarylmethyl[7] radicals in solution have previously been investigated using the "tandem pulse" technique[8] and other[9–11] methods. In the more recent studies, the diphenylmethyl (DPM) radical was produced by irradiation of diphenylmethyl chloride with an electron pulse[5] or by photolysis of 1,3-diphenylacetone,[6] and photolyzed with 347- or 337-nm light. The excited state of the DPM radical thus produced is quite long-lived (lifetime 280 ns) and highly fluorescent ($\Phi_f = 0.30$) from its lowest excited state (D_1).[5] The fluorescence quantum yield was found to be virtually independent of the nature of the solvent. However, in several polar solvents, after decay of the excited state, the recovery of the ground-state DPM radical is not complete, which means that an irreversible photochemical reaction occurs. In line with this is the fact that the fluorescence quantum yield decreases at higher laser light intensities, from which it was concluded that the photochemical process leading to incomplete ground-state recovery arises from the absorption of a second photon by the first excited doublet state, in a consecutive process. It was tentatively suggested that upon further excitation of the D_1 state homolytic cleavage of the C–H bond occurs with formation of the corresponding carbene.[5b] However, since the carbene would abstract a hydrogen atom from the solvent giving the ground-state radical,[6a] this mechanism does not account for the incomplete recovery of the ground-state radical.

We have previously found that it is possible to ionize a neutral radical, such as *tri*phenylmethyl radical, in a polar solvent, such as water, and to make the resulting carbocation visible.[7] In the present work we demonstrate that the same reaction takes place also with (substituted) *di*phenylmethyl radicals,[12] i.e., that the permanent destruction of the ground-state radical under conditions of high light intensities is due, at least in polar solvents, to its photoionization. On the basis of the ionization potentials of diarylmethyl radicals,[13] this type of reaction is thermodynamically possible with 308-nm light (quantum energy 4.0 eV), if the solvation energies of the ions are >3 eV.[14]

Experimental Section

Para-substituted diphenylmethyl (benzhydryl) chlorides were prepared from the corresponding alcohols (from Lancaster) by treatment with HCl in CH_2Cl_2,[15] and they were purified by fractional distillation or recrystallization. Benzhydryl bromide (from Aldrich) was zone refined to a purity >99%. Benzophenone (>99%) and diphenylacetic acid (>98%) were from Fluka, diphenylmethane (>99%) from Aldrich. Acetonitrile (≡AN), dichloromethane, isopropanol, and tetrachloromethane (Merck) and *n*-butyl chloride (Fluka) were spectroscopic grade.

Solutions of the substrates (A/cm ≈ 0.2–2) were flowed (rates ≈ 1–6 mL/min) through a 2 mm (in the direction of the laser beam) by 4 mm (in the direction of the analyzing light, 90° geometry) Suprasil quartz cell and photolyzed with 20-ns pulses (denoted as P1, 1–100 mJ, as measured at the position of the cell, typical values are 10 mJ) of 248-nm light from a Lambda Physik EMG103MSC excimer laser, and the time-dependent optical changes were recorded with Tektronix 7612 and 7912 transient recorders interfaced with a DEC LSI 11/73+ computer, which also controlled the other functions of the instrument and performed on-line analysis of the experimental data. A few microseconds after the first pulse, the solution was subjected to a second 20 ns laser pulse (denoted as P2, 1–60 mJ, at an angle of ≈10° to the analyzing light) of 308 nm from a Lambda Physik EMG150E laser. To convert the mJ numbers given in the text or in the Figures into mJ/cm² at the position of the cell, the numbers given for the 248-nm pulses should be multiplied by 2, those for the 308 nm pulses by 0.9. The delay between the first pulse and the second could be varied from 10 ns to the ms range by a computer-controlled delay generator. Time-dependent absorption spectra ΔA vs λ or kinetics refer to the situation after the first (P1, the

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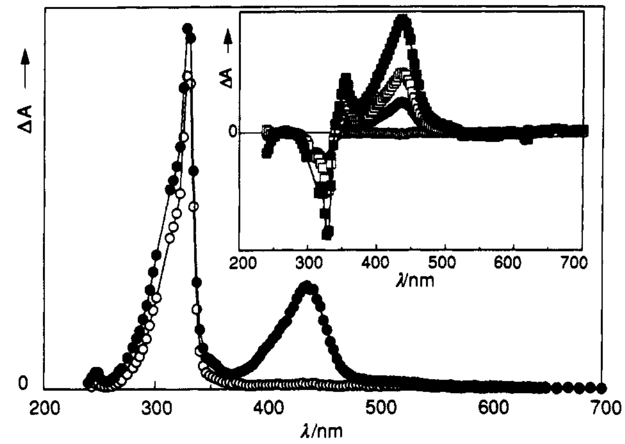


Figure 1. Time-resolved absorption spectra generated by 248-nm photolysis (14 mJ/pulse) of 1.1 mM Ph_2CHBr in acetonitrile, saturated with argon, recorded 50 ns (full circles) and 2.5 μs (open circles) after the pulse. Inset: Spectra from the same solution upon two-pulse laser photolysis (PI = 248 nm, 14 mJ, P2 = 308 nm, 60 mJ, delay = 3 μs), recorded at 85 ns (full squares), 270 ns (open squares), 470 ns (full circles), and 2.5 μs (open circles) after P2.

"synthesis"[6]) or after the second (P2, the "photolysis"[6]) pulse, as indicated in the figures or text.

Results and Discussion

A. Formation of Diarylmethyl Radicals. Diarylmethyl radicals were produced basically by two different processes:[16] Photohomolysis of Ar_2CH-Y (Ar = para-substituted benzene, Y = Hal, OH) by 248 nm light:

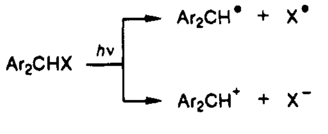
$$Ar_2CH\text{-}Y \rightarrow Ar_2CH^{\bullet} + Y^{\bullet} \qquad (1)$$

or side-chain fragmentation[17] of diarylmethyl radical cations $Ar_2CH^{\bullet+}Y$ (Y = H, CO_2^-), formed by biphotonic (λ = 248 nm) ionization from diarylmethane derivatives:

$$Ar_2CRY + 2h\nu/\text{-}e^- \rightarrow Ar_2CR^{\bullet+}Y \rightarrow Ar_2CR^{\bullet} + Y^+, \quad R = H, OH \qquad (2)$$

The advantage of using these simple, nonconjugated "alkylbenzenes", which have a strong π–π^* absorption at 248 nm, the wavelength of the "synthesis pulse" (P1), is that they essentially have *no* absorption at 308 nm, the wavelength of the "photolysis pulse" (P2). Photolysis at this wavelength, therefore, leads to excitation of only the *products* of the 248 nm photolysis (provided, of course, that they absorb at 308 nm), but not of their parent compounds.

Photohomolysis (Eq 1). *Diarylmethyl Halides.* On 248-nm photolysis in acetonitrile (AN), diarylmethyl halides undergo efficient homolysis (eq 3, Φ_{hom} = 0.1–0.39) and heterolysis (eq 4, Φ_{het} = 0.05–0.32) to yield the corresponding radicals and cations.[18] The latter react rapidly with acetonitrile (lifetimes ≤ μs). Since the electronically excited radicals[5,6] that result from biphotonic excitation at 248 nm in these systems[18] also have a short lifetime (<μs),[5,6,18] after a few microseconds, the ground state radicals are the only transient species remaining (see Figure 1). In the absence of oxygen, their lifetime typically is ≥ ms. In Table I are listed some spectroscopic and kinetic data of the transients from the benzhydryl halides used.



$$Ar_2CHX \xrightarrow{h\nu} Ar_2CH^{\bullet} + X^{\bullet} \qquad (3)$$

$$Ar_2CHX \xrightarrow{h\nu} Ar_2CH^{+} + X^{-} \qquad (4)$$

Diphenylmethanol. For the results, see eq 8.

Side-Chain Fragmentation of Radical Cations (Eq 2). *Diphenylmethane and Diphenylacetic Acid.* These compounds were photolyzed with 248-nm light (pulse 1, P1) in acetonitrile, water, ethanol, or mixtures of these solvents. The diphenylmethyl radical, $Ph_2CH^{\bullet}$ ($DPM^{\bullet}$), was formed, as judged by its characteristic absorption spectrum with λ_{max} at 330 nm. The formation of $DPM^{\bullet}$ requires *two* quanta, as concluded from the quadratic dependence of the $DPM^{\bullet}$ yield (measured as ΔA at 330 nm) on the laser light intensity I ($\Delta A = \text{const}\cdot I^2$). With $Ph_2CHCO_2^-$ in aqueous solution,[19] the formation of e^-_{aq} was observed on photolysis, showing that $DPM^{\bullet}$ formation is initiated by photoionization. In agreement with the idea of $DPM^{\bullet}$ production proceeding via the radical cation of the aromatic (eqs 6, 7) is the fact[18] that the radical can be generated independently by reaction of the one-electron oxidant $SO_4^{\bullet-}$ with $Ph_2CHCO_2^-$. From the observation that there is no delay in the formation of $DPM^{\bullet}$ after the 20 ns pulse, the rate of deprotonation of $Ph_2CH_2^{\bullet+}$ or of decarboxylation of $Ph_2CHCO_2^{-\bullet+}$ is $>5 \times 10^7\ s^{-1}$. Similar conclusions have previously been drawn for phenyl acetates[20,21] and triphenyl acetate:[7]

$$Ph_2CH_2 + 2h\nu \rightarrow Ph_2CH^{\bullet} + H^+ + e^-_{solv} \qquad (5)$$

$$Ph_2CHCO_2^- + 2h\nu/\text{-}e^- \text{ or } +SO_4^{\bullet-}/\text{-}SO_4^{2-} \rightarrow Ph_2CH^{\bullet} + CO_2 \qquad (6)$$

$$Ph_2CHR^{\bullet+} \rightarrow Ph_2CH^{\bullet} + R^+; \quad R = H, CO_2^-; \quad k \geq 5 \times 10^7\ s^{-1} \qquad (7)$$

Diphenylmethanol. The spectrum obtained upon photolysis of diphenylmethanol in acetonitrile (Figure 2a) is very similar but not identical to that of the DPM radical. In particular, there is a weak band at 550 nm which is not from $Ph_2CH^{\bullet}$. This band indicates the presence of the α-hydroxydiphenylmethyl radical which can be obtained quantitatively by, e.g., hydrogen abstraction by excited benzophenone from a hydrogen donor such as 2-propanol. The spectrum (Figure 2b) observed under these conditions (lifetime of the excited triplet state[22] of benzophenone 46 ns) matches that measured in acetonitrile (λ_{max} = 328 nm, $\epsilon = 3.0 \times 10^4\ M^{-1}\ cm^{-1}$).[23] There was no evidence for formation of the diphenylmethyl *cation* in acetonitrile, which means that photo*heterolysis* does not occur in this solvent. The absorption band of α-hydroxydiphenylmethyl radical at 328 nm (Figure 2b) is very similar to that of the diphenylmethyl radical at 330 nm (Figure 1, 2.5 μs after the pulse).

It was found that the signal intensity as measured at 330 nm increased with the laser intensity I in a supraproportional way, the relation being $\Delta A = \text{const}\cdot I + \text{const}'\cdot I^2$. This suggests that the species absorbing at 330 nm is (are) produced in a monophotonic *and* in a biphotonic way. These processes are assigned to photohomolysis of the C–OH bond (eq 8, *one* photon required) and photoionization (eq 9, *two* photons necessary) followed by deprotonation of the resulting radical cation (eq 10):

$$Ph_2CHOH \xrightarrow{h\nu} Ph_2CH^{\bullet} + OH^{\bullet} \qquad (8)$$

$$Ph_2CHOH \xrightarrow{2h\nu} Ph_2CHOH^{\bullet+} + e^- \qquad (9)$$

$$Ph_2CHOH^{\bullet+} \rightarrow Ph_2C^{\bullet}OH + H^+, \quad k \geq 5 \times 10^7\ s^{-1} \qquad (10)$$

Photohomolysis (eq 8) could be very clearly seen in the unpolar solvent cyclohexane, where ionization is certainly very unfavorable. The spectrum observed in this solvent at 4 μs after the pulse was identical with that in Figure 1 (open circles). The occurrence of ionization (reaction 9) was tested by photolyzing Ph_2CHOH in aqueous solution which led to the characteristic absorption of the hydrated electron, e^-_{aq}, in a biphotonic reaction. Reaction 10 is

TABLE I: Absorption Maxima of Diarylmethyl Radicals and Cations $(4\text{-}RC_6H_4)_2CH$. Rate Constants for Reaction with O_2 of the Ground and Excited State Radicals and for Decay of the Cations in Acetonitrile

R_1, R_2	$Ar_2C^{\bullet}H$[a] (λ_{max}/nm)	$k(O_2)$ (10^9 M^{-1} s^{-1})	$[Ar_2C^{\bullet}H]^{*}$[a] (λ_{max}/nm)	k(decay) (10^6 s^{-1})	$k(O_2)$ (10^9 M^{-1} s^{-1})	$Ar_2C^{+}H$[a] (λ_{max}/nm)	k(decay) (10^6 s^{-1})
H, H	330	1.7 (0.6)[b]	355, 435[c]	3.6	8.7[b]	435	2.4
CH_3, CH_3	335	1.9	365, 474[c]	4.8	12	465	0.22
CH_3O, CH_3O	350	2.0	380[d]	5.8	17	500	[e]
Cl, Cl	340	1.3[f]	370, 474[c]	6.5	9.4[f]	475	3.0
Cl, H	334	1.2	361, 445[c]	5.3	9.6	457	3.3

[a] Similar to the numbers given in ref 18 and references therein. [b] In cyclohexane, from ref 6a. [c] Broad band of weak intensity (~30–40% of that at the lower λ). [d] Band at longer λ not measurable. [e] Cation decays bimolecularly by combination with anion, see ref 18. [f] Taken from ref 18.

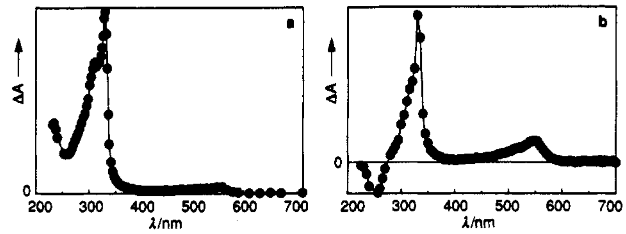


Figure 2. (a) Absorption spectrum measured 4 μs after 248-nm photolysis (P1, 24 mJ) of 3.6 mM Ph_2CHOH in acetonitrile, saturated with argon. (b) Absorption spectrum recorded 425 ns after 248-nm photolysis (P1, 8 mJ) of 32 μM Ph_2CO in 2-propanol, saturated with argon.

in line with the dramatically enhanced Brönsted acidity of radical cations[24–26] compared to their parent compounds.

To summarize, in the polar solvent acetonitrile diphenylmethanol undergoes a *mono*photonic C–OH homolysis and a *bi*photonic ionization, whereas in a nonpolar solvent such as cyclohexane only homolysis is observed.

Diphenylmethanol was also photolyzed in the non-nucleophilic[27] and acidic solvent 1,1,1,3,3,3-hexafluoroisopropanol (HFIP, $pK_a = 9.3$[28]), which has been shown to be able to protonate substituted benzenes,[29,30] styrenes,[31] and phenylacetylenes[32] upon their electronic excitation. The spectrum observed after the pulse was that of the benzhydryl *cation*, Ph_2CH^+. It was formed *mono*photonically and there was *no* evidence for production of the corresponding *radical*, as supported by the finding that the spectrum was the same in the absence or presence of oxygen. This means that in the only weakly polar solvent HFIP ($\epsilon = 16.6$)[33] photo*heterolysis* is the predominant reaction, in contrast to the situation in the much more polar solvent acetonitrile ($\epsilon = 37.5$). The increase in *polarity* in going from HFIP to acetonitrile is thus not sufficient to compensate for the lack of *acidity* of acetonitrile. Thus, acidity seems to be the decisive property in enabling heterolysis to occur. The easiest way to understand this is in terms of protonation of the OH group, caused by its increased basicity in the excited state.[34] As a result, the bad leaving group OH^- ($pK_a(H_2O) = 15.7$) is converted into the excellent one H_2O ($pK_a(H_3O^+) = -1.7$):

$$Ph_2CH\text{-}OH^{*} + (CF_3)_2CHOH \xrightarrow{-(CF_3)_2CHO^-} Ph_2CH\text{-}O^+H_2 \rightarrow Ph_2CH^+ + H_2O \quad (11)$$

Using the number 4.4×10^4 M^{-1} cm^{-1} for the ϵ of Ph_2CH^+ at 435 nm and aqueous $K_2S_2O_8$ for actinometry[35] with $\Phi\epsilon(SO_4^{\bullet-}) = 2770$ M^{-1} cm^{-1} at 445 nm,[36] the quantum yield for formation of the benzhydryl cation was determined to be 0.013.

B. 308-nm Photolysis of Diarylmethyl Radicals. *Diarylmethyl Halide Precursors.* In Figure 1 are shown the absorption spectra of $Ph_2CH^{\bullet}$ ($\lambda_{max} = 330$ nm) and of Ph_2CH^+ ($\lambda_{max} = 435$ nm) resulting from 248-nm photolysis (pulse 1, P1) of Ph_2CHBr in acetonitrile (eqs 3 and 4). It is evident that after 2.5 μs, the cation has disappeared (by reaction with solvent),[18] whereas the radical concentration has hardly changed. At 3 μs after P1, a pulse of 308 nm light was applied (pulse 2, P2). As seen in the inset, P2 leads to: a) a "negative absorption" (depletion) with a maximum at 330 nm; b) a positive optical density change (formation) peaking at 350 nm; c) a strong positive band with λ_{max} at 435 nm; and d) a weak negative signal in the 550 to 600 nm region. With the exception of the negative absorption at 330 nm, the optical density changes return to zero within 3 μs.

Identification of the P2-Induced Phenomena. A "negative absorption" *after* P2 means that more light is seen by the photomultiplier relative to the situation *before* P2. This can be caused by a larger transmittance of the solution, i.e., by photobleaching, or it can be due to light emission (fluorescence). Since the negative absorptions in the 330–350-nm region (for $Ph_2CH^{\bullet}$ and the substituted benzhydryl radicals) are perfect mirror images of the absorption spectra of the radicals (see Figure 3, inset a, for the case of $(4\text{-}ClC_6H_4)_2CH^{\bullet}$), these negative absorption changes are identified in terms of depletion of the ground-state radicals.

In contrast, the negative signals observed at 500–600 nm can *not* be explained in terms of bleaching since at these wavelengths the radicals have no absorption (see Figure 1). Therefore, they must be due to emission induced by P2. This was demonstrated by working without analyzing light, which made the detection of the emission much easier. On the basis of the similarity of the spectra of these emissions with those[6b] previously measured, they are identified as fluorescence from the first electronic excited state (D_1) of the benzhydryl radicals. In support of this assignment is the fact that the fluorescence decay rates are exactly the same as those measured for decrease of the excited state absorptions or for recovery of the ground-state radicals (vide infra).

The most conspicuous P2-induced absorption changes are those due to the electronically excited diarylmethyl radicals in the 330 to 370 region and those of the cations between 435 and 500 nm. As previously shown,[18,37] the cations have a very high reactivity with halides ($k = (1\text{–}2) \times 10^{10}$ M^{-1} s^{-1}). Therefore it is possible to quantitatively scavenge the cations with relatively small concentrations of halides. Alternatively, alcohols or water can be used as reactive nucleophiles.[18,37] In experiments of this type, it was found that after complete removal of the cations, there remained absorptions in the 435–500-nm region. An example for this is shown in Figure 3, inset b. These absorptions decayed with the same rates as those in the 350 to 370 nm range, as those of the ground-state recovery, and as those of the fluorescence in the 500 to 600 region (see Figure 3, insets d–g). The absorptions could be removed with oxygen, again with the same rates as those in the lower wavelength region. The conclusion is thus that the (broad) absorption bands that extend from 400 to 500 nm under conditions of cation scavenging are due to the excited radicals. These absorptions have been seen previously.[6a] The excited state radicals, $Ar_2CH^{\bullet *}$, have a much higher reactivity with oxygen (for the case of $(4\text{-}ClC_6H_4)_2CH^{\bullet *}$, $k = 9.4 \times 10^9$ M^{-1} s^{-1}) than the ground-state ($k = 1.3 \times 10^9$ M^{-1} s^{-1}),[38] and they can be scavenged with 1,3-cyclohexadiene,[18] which shows no reactivity with the ground-state radicals.

Finally, the pronounced bell-shaped bands with the maxima at 435 to 500 nm are identified as the ground-state (substituted) benzhydryl cations. Not only are the absorption spectra identical with those previously determined[39] for the cations in acidic media,

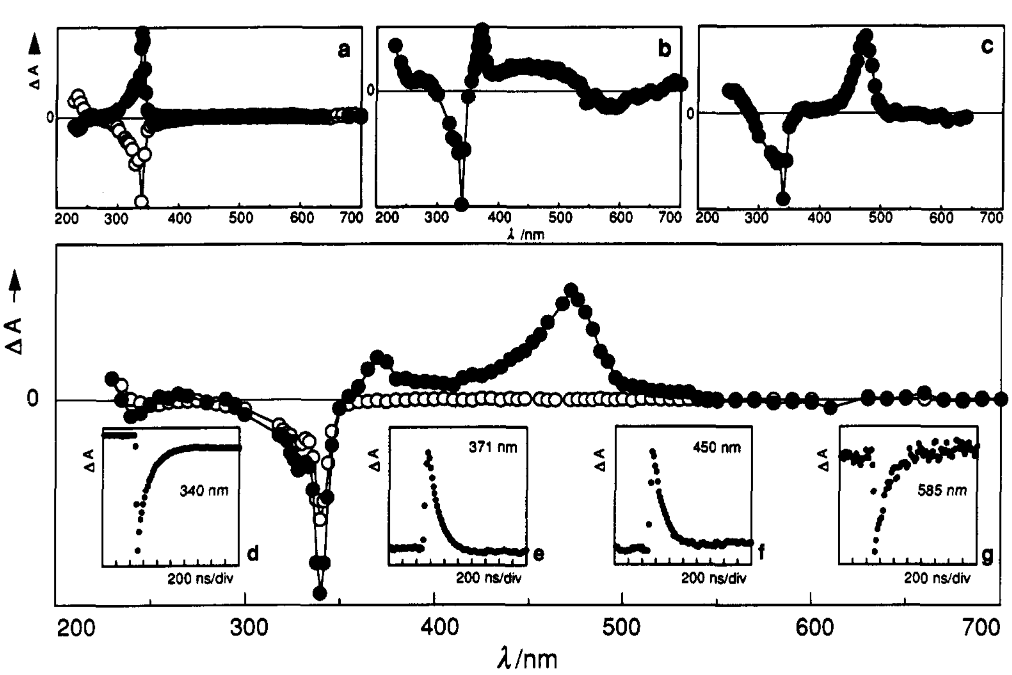


Figure 3. Time-resolved absorption spectra generated upon two-pulse laser photolysis (P1 = 248 nm, 10 mJ, P2 = 308 nm, 60 mJ, delay = 3 μs) of 0.2 mM $(4\text{-ClPh})_2CHCl$ in acetonitrile, saturated with argon, recorded 75 ns (full circles) and 3.0 μs (open circles) after P2. Insets: (a) Absorption spectrum recorded at 2.5 μs after P1 (full circles), and spectrum measured at 5 μs after P2 (delay 3 μs) (open circles). (b) Spectrum measured at 130 ns after P2 (delay = 3 μs) in $(4\text{-ClPh})_2CHCl$ in acetonitrile containing 4 mM $(n\text{-Bu})_4NCl$, saturated with argon. (c) Spectrum recorded at 220 ns after P2 (delay = 3 μs) in $(4\text{-ClPh})_2CHCl$ in acetonitrile, saturated with an argon:oxygen mixture (1.7 mM O_2). (d)–(g) Kinetic traces recorded in the presence of 4 mM $(n\text{-Bu}_4NCl$ showing the recovery of the ground state radical (d), the decay of the excited state radical (e and f), and the decay of emission from the excited state radical, all with $k = 6.4 \times 10^6$ s^{-1}.

or upon photoheterolytic formation in acetonitrile,[18] but also the electrophilic reactivities are the same as those[18,37] measured after heterolytic production. Concerning their absorption spectra, there is overlap with the spectra of the electronically excited radicals, as mentioned above. These can, however, be selectively scavenged by *small* concentrations of molecular oxygen (≤2 mM; with O_2-saturated solutions ($[O_2]$ = 8 mM), the ground-state radical precursor to the cation will be trapped), leading to a pure spectrum of the cation (see Figure 3, inset c, for the case of $(4\text{-ClPh})_2CH^+$). This procedure utilizes the difference of reactivity between the excited and the ground-state radicals with molecular oxygen (for the rate constants, see Table I). Note that in inset c the amplitude of ground-state radical bleaching is similar to that of cation formation. Under the condition that the reaction of the excited state radical with oxygen leads to recovery of the ground-state radical (by energy transfer) and that the extinction coefficients of the two species are comparable,[5,6a] this result means that the depletion of radical is caused by its conversion into cation (ionization).

Diphenylmethyl halides substituted at the para-position of the ring(s) by only one Cl, and by Me and MeO were also studied (for identification of the systems, see Table I). In all cases, after P2, very intense negative absorptions (which are due to P2-induced depletion of the corresponding radicals, for the λ_{max} and ϵ values, see ref 18) were seen between 330 and 350 nm, peaks with absorption maxima between 340 and 360 nm (due to the electronically excited radicals), intense absorptions between 435 and 500 nm (representing the cations),[18] and very weak but observable negative changes above 500 nm (resulting from fluorescence of the excited radicals). For an example, see Figure 3.

Diphenylmethane and Diphenylacetic Acid as Precursors. As pointed out above, the benzhydryl cations are derived from the radicals by photoionization. In this process, by definition, an electron is formed, and it is therefore tempting to try to demonstrate directly the production of the electron. To see this species, the presence of electron scavengers should be avoided, and it is for this reason that diphenylmethane, diphenyl acetate, and diphenylmethanol (see later), which all have low rate constants for reaction with the electron, are suitable precursors for the benzhydryl radical from which the electron is to be photoejected.

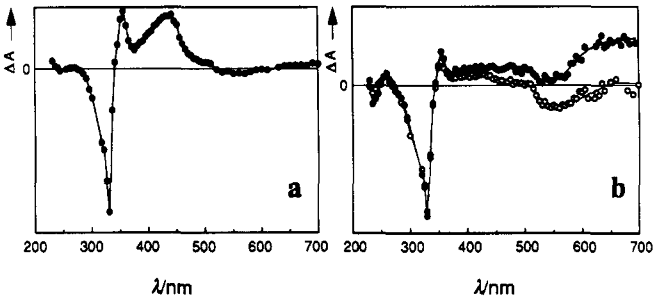


Figure 4. (a) Spectrum recorded at 150 ns after P2 (40 mJ, delay 3 μs) in a 3 mM solution of Ph_2CH_2 in AN saturated with Ar. (b) Spectrum recorded at 70 ns after P2 (60 mJ, delay 2 μs) in 3 mM Ph_2CH_2 in W:EtOH (1:3 v/v). Full circles: Ar saturated. Open circles: N_2O saturated.

As seen in Figure 4a, the absorption spectrum observed upon double pulse laser photolysis of Ph_2CH_2 *in acetonitrile solution* saturated with Ar, recorded after P2, is qualitatively the same as that (see Figure 1) observed with Ph_2CHBr as precursor. Even the fluorescence emission of $Ph_2CH^{\bullet *}$ is visible at ≈550 nm. The fact that the amplitude of the cation (at 435 nm) relative to that of the electronically excited radical (at 350 nm) is smaller than in Figure 1, inset, is due to the intensity of the 308 nm pulse being less than in the former case (see photonity data in section B).

It is known that in acetonitrile the electron, which exists as the dimer radical anion $(AN)_2^{\bullet -}$,[40] has only a very weak absorption between 400 and 700 nm,[41] and is therefore difficult to detect in this solvent. To see the electron, it is necessary to use solvents in which e^-_{solv} absorbs strongly. This is the case with (aqueous) alcohols. In water:ethanol 1:3, the spectrum, obtained after P2 under the same conditions as in the case of acetonitrile solutions, is characterized by the bleaching of $Ph_2CH^\bullet$, the absorption and emission of its electronically excited state, and a new band with a maximum above 550 nm, but no cation band (Figure 4b). The

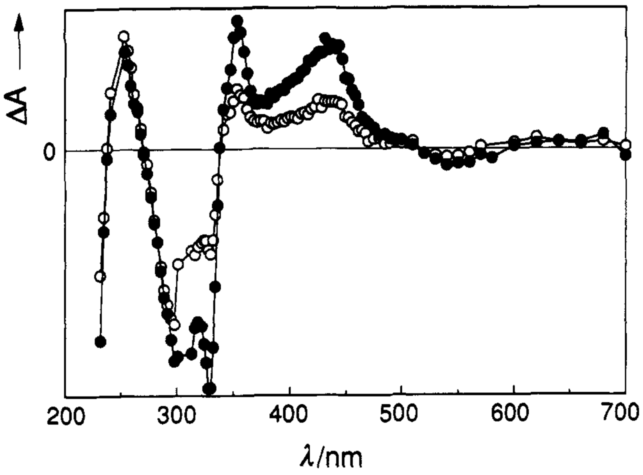


Figure 5. Spectrum observed after P2 (60 mJ, delay 6 μs; P1 24 mJ) in argon saturated 3.6 mM Ph_2CHOH in AN at 125 ns (full circles) and 250 ns (open circles).

550 nm band can be efficiently removed by N_2O, O_2, and 2-chloroethanol or other halogenated hydrocarbons, with bimolecular rate constants similar to those described[42] for e^-_{aq} reactions. This band is therefore identified as due to e^-_{solv}. In agreement with this is the fact that the subtraction of the spectra obtained in absence and in presence of N_2O results in a spectrum comparable to the absorption spectrum of the hydrated electron.

The fact that the cation band cannot be observed at ≥20 ns after P2 is due to the high reactivity of the nucleophilic solvent. The cation lifetime in water:EtOH 1:3 can be calculated to be ≈80 ps, using the bimolecular rate constants 1.2×10^8 M^{-1} s^{-1} for reaction with water and 8.5×10^8 M^{-1} s^{-1} for reaction with EtOH.[18]

The results obtained with $Ph_2CHCO_2^-$ in purely aqueous solution are similar to those described above for Ph_2CH_2 in W:EtOH.

Benzhydrol Photolysis. As reported in section A, 248-nm photolysis of diphenylmethanol (benzhydrol) in acetonitrile leads to the benzhydryl and to the α-hydroxydiphenylmethyl radical (eqs 8–10). In Figure 5 are shown the spectra observed after P2 in a diphenylmethanol solution in acetonitrile. The electronically excited benzhydryl radical is clearly recognizable by its absorption at 350 nm and its emission at 550 nm, and also the benzhydryl cation is present (λ_{max} = 435 nm). The difference to the situation with the other ground-state radical precursors is the wavelength region between 240 and 350 nm. Here, the negative band is much broader, and at 252 nm, there is a pronounced positive band which is very long lived (≥ms). On the basis of its shape and its lifetime of > 1 ms, this band is assigned to a stable product, i.e., to benzophenone, known to be formed[6d] by photoinduced rupture of the O–H bond in the α-hydroxydiphenylmethyl radical:

$$Ph_2C^{\bullet}O\text{–}H \xrightarrow{h\nu} Ph_2CO + H^{\bullet} \qquad (12)$$

The formation of $Ph_2CH^{\bullet *}$ and Ph_2CH^+ by P2 is confirmation for C–OH homolysis by P1 (eq 8), the production of benzophenone by P2 support for generation and deprotonation of radical cation (eqs 9 and 10).

Photon Demand for Formation of $Ar_2CH^{\bullet *}$ and Ar_2CH^+. With diarylmethyl halides as precursors, at constant intensity of P2, the photochemical yields of the transient products of P2, i.e., $Ar_2CH^{\bullet *}$ and Ar_2CH^+, were proportional to the intensity of P1, the synthesis pulse. This result is in agreement with expectation for the monophotonic[18] C-Cl bond homolysis induced by P1. Concerning P2, at low intensities the yield of $Ar_2CH^{\bullet *}$ was found to increase linearly with the intensity of P2, I(P2). However, at ≥10 mJ/pulse the yield starts to level off and at >30 mJ it decreases again (for an example involving $(4\text{-}ClC_6H_4)_2CH^{\bullet}$, see Figure 6a). The initial linear portion in the dependence on I(P2) is as expected on the basis of the observed[18] quadratic dependence on I(P1) from 248 nm photolysis (i.e., it takes *two* photons to produce $Ar_2CH^{\bullet *}$ from Ar_2CH–Cl, but only *one* from $ArCH^{\bullet}$). Concerning the formation of *cation* from the ground-state radical, it is interesting that *two* photons are required to achieve this. This is visible with the initial portion of the yield vs. intensity plot, which is curved upward. After this, there is a quasi-linear portion, due to incipient saturation effects.

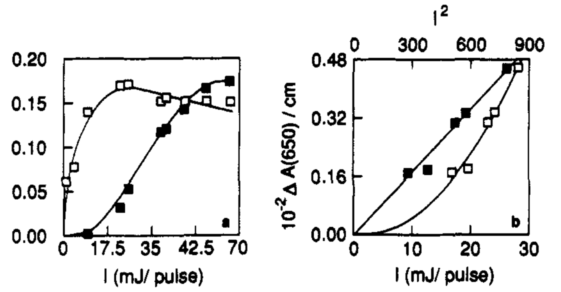


Figure 6. (a) Dependence of yield of excited state radical (open squares) and of cation (full squares) on the intensity (mJ/pulse) of P2 (delay 3 μs) in 0.3 mM $(4\text{-}ClPh)_2CHCl$ in AN saturated with Ar. (b) Open squares: Yield of e^-_{solv} (measured at 680 nm 30 ns after P2) as a function of I(P2), the intensity of P2, in a 1:3 (v/v) water:EtOH solution containing 1.1 mM Ph_2CH_2. Full squares: Yield of e^-_{solv} as a function if $I(P2)^2$.

It is interesting that the onset of saturation in the formation of $Ar_2CH^{\bullet *}$ occurs in the intensity range (≈10–30 mJ/pulse) where the increase in the formation of Ar_2CH^+ is most visibly curved upward. Also relevant is that the yield of $Ar_2CH^{\bullet *}$ goes through a maximum, i.e., that at higher laser intensities bleaching of $Ar_2CH^{\bullet *}$ occurs. This indicates that cation formation is at the expense of the excited radical. The conclusion is then that the cation is formed by absorption of a 308 nm light quantum *by the excited radical.* This process is apparently quite efficient. The susceptibility to photolysis within the same pulse is a consequence of the long lifetime (100–330 ns)[18] of $Ar_2CH^{\bullet *}$ (D_1 state).[5,6] If the lifetime was in the low ns range, as typical with excited *singlet* states of aromatics, the chances for photochemical transformation would be much less.[43]

To check the photonity of 2 found (from the quadratic portion of the yield vs intensity plot) for formation of *cation*, the yield of *electrons* produced by P2 was measured as a function of its intensity, using Ph_2CH_2 in water:ethanol as precursor for $Ar_2CH^{\bullet}$. The results, presented in Figure 6b, indicate that *two* photons are required for ionization of the radical, which is in support of the data for cation formation.

The results presented in the previous paragraph show that ionization of $Ar_2CH^{\bullet}$ takes place by photoexcitation of the excited radical, $Ar_2CH^{\bullet *}$, i.e., by a consecutive biphotonic process. In order to further investigate the nature of the ionization process and to judge the potential influence of the fate of the ejected electron on the yields of the transient products, the effects of electron scavengers was studied that react with the electron irreversibly, such as chloroalkanes, which undergo dissociative electron capture. In all cases, the effect of the scavengers on the lifetime of $Ar_2CH^{\bullet *}$ and on its yield and on that of permanent depletion of the ground-state radical (measured at >3 μs after P2) was also determined. It was found that none of the scavengers decreased the *lifetime* of $Ar_2CH^{\bullet *}$, except CCl_4, for which the rate constant for reaction with $Ar_2CH^{\bullet *}$ was measured to be 3.8×10^8 M^{-1} s^{-1}. This number is similar to that reported[6a] for the same reaction in methanol. However, all scavengers increased the degree of permanent depletion of $Ar_2CH^{\bullet}$ (by the factor ≈2). Results obtained for the case of $Ph_2CH^{\bullet}$ with *n*-butyl chloride (*n*-BuCl) and CCl_4 are contained in Figure 7a and b, respectively. In all cases the data have been corrected for influences of solvent on the yield of ground-state radical produced by P1.

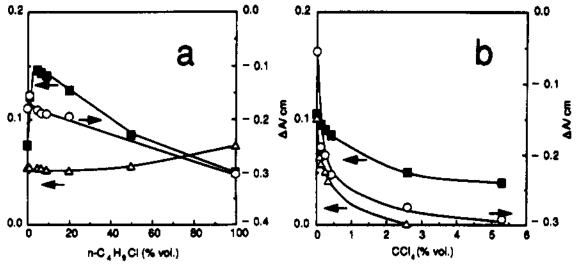


Figure 7. Effect of *n*-BuCl (a) and of CCl$_4$ (b) on the photochemical yield of Ph$_2$CH$^{\bullet *}$ (triangles), of Ph$_2$CH$^+$ (squares), and of permanent depletion of Ph$_2$CH$^{\bullet}$ (open circles), resulting from P2 (30–40 mJ) and measured as initial changes in A/cm at 350, 435 (at ≈30 ns), and 330 nm (at 4–6 μs after P2), respectively, in a solution of 0.3 mM Ph$_2$CHBr in AN, saturated with argon.

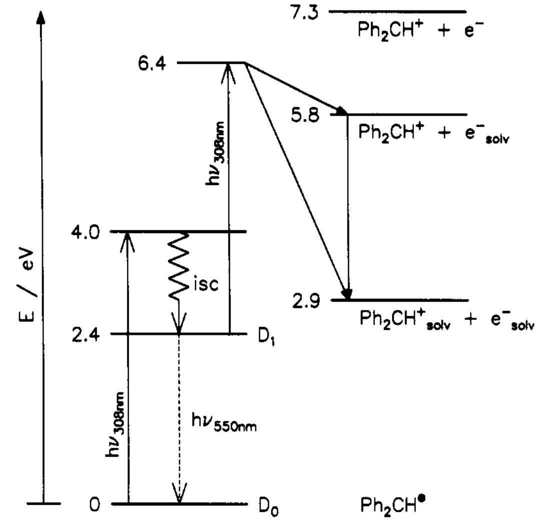
As seen, the effect of *n*-butyl chloride (Figure 7a) on the photochemical yield of cation is different from the effect of CCl$_4$ (Figure 7b). With *n*-BuCl, the yield of cation increases with [*n*-BuCl] to a maximum after which there is a decrease to a lower value in pure *n*-BuCl as compared to AN. The yield of Ph$_2$CH$^{\bullet *}$ is rather independent of [*n*-BuCl], whereas the permanent depletion of the ground-state radical increases with increasing [*n*-BuCl], without going through a maximum as in the case of the cation. A very similar effect of *n*-BuCl on ground-state, excited state, and cation yields was observed with the (4-MeC$_6$H$_4$)$_2$CH system (not shown).

From Figure 7b it is evident that even very small concentrations of CCl$_4$ drastically decrease the yields of excited radical,[44] while leading to a pronounced increase in the ground state permanent depletion. In contrast to the effect of *n*-BuCl, *there is no increase in the yield of cation*, on the contrary, the cation yield decreases in a way similar to that of Ph$_2$CH$^{\bullet *}$. The conclusion is thus that neither Ph$_2$CH$^{\bullet *}$ (D$_1$) nor the state produced from the D$_1$ state by absorption of a 308 nm photon (denoted as Ph$_2$CH$^{\bullet **}$) react with CCl$_4$ to give cation measurable at ≥20 ns after P2. However, there must be a product-forming reaction between excited state radical and CCl$_4$, since there is a strongly increased yield of permanent depletion of ground-state radical with increasing [CCl$_4$]. This reaction cannot be electron transfer with subsequent solvation and separation of the ions formed, unless one assumes that CCl$_4$ reduces the lifetime of Ph$_2$CH$^+$ drastically. This is not at all the case, as was found by producing the cation by photoheterolysis (eq 4) with P1. No effect of CCl$_4$ on the cation lifetime was seen up to 5 vol %. It is therefore suggested that the reaction with Ph$_2$CH$^{\bullet *}$ or Ph$_2$CH$^{\bullet **}$ involves Cl-abstraction. An alternative is electron transfer followed by quantitative collapse in the solvent cage of the hypothetical ion pair formed.[45]

The effect of CH$_2$Cl$_2$ was also studied (with the Ph$_2$CH and the (4-ClPh)$_2$CH systems): CH$_2$Cl$_2$ had no effect on the lifetime of Ar$_2$CH$^{\bullet *}$, it increased the yield of permanent depletion of Ar$_2$CH$^{\bullet}$, but it did *not* lead to an increase of the yield of Ar$_2$CH$^+$. In pure CH$_2$Cl$_2$ the yield of cation (at ≥20 ns after P2) was much less than in AN.

Concerning the effect of *n*-butyl chloride (Figure 7a), after the initial increase in the cation yield, which can most easily be explained in terms of scavenging of the multiply excited radical, Ar$_2$CH$^{\bullet **}$, by electron transfer, there is a reduction with increasing [*n*-butyl chloride]. Unless a change of mechanism from electron transfer to transfer of a chlorine atom is invoked, the decrease can be understood in terms of increasing contributions of in-cage ion collapse (decreasing escape of ions) as the polarity of the solvent decreases as AN is replaced by *n*-butyl chloride. This interpretation is in agreement with the increased yield of permanent ground-state radical depletion.

SCHEME I: Energy Diagram for Ionization of Ph$_2$CH$^{\bullet}$ in CH$_3$CN



Summary and Conclusions

The key species in the photoionization mechanism is the excited state radical, Ar$_2$CH$^{\bullet *}$ (D$_1$ state),[5,6b,46] which is produced from the ground-state radical, Ar$_2$CH$^{\bullet}$, by absorption of one photon of, e.g., 308- or 248-nm[18] light. Ar$_2$CH$^{\bullet *}$ (lifetime in AN 100–330 ns) is chemically inert with respect to methyl chloride, *n*-butyl chloride, and dichloromethane, but it reacts with CCl$_4$, but not to give cation. Ar$_2$CH$^{\bullet *}$ is able to absorb a photon of, e.g., 308- or 248-nm[18] light. This process leads to ionization. The ionization yields (as measured at ≥20 ns) can be increased by *n*-BuCl, but not by CH$_2$Cl$_2$ or CCl$_4$. The result with *n*-BuCl indicates that in the initial cation-(solvated) electron pair there is some electron return (to yield radical) which can be intercepted by dissociative electron capture giving Cl$^-$. At higher concentrations of *n*-BuCl, the negative effect of the decreasing solvent polarity overcompensates that of the increased electron scavenging capacity of the solvent.

Scheme I represents a summary of the energetics of excitation and ionization of Ph$_2$CH$^{\bullet}$. The ionization potential of Ph$_2$CH$^{\bullet}$ is 7.32 eV.[13] If it is assumed that the solvation energy of the electron in AN is 1.5 eV, about half[47] of that (3.17 eV)[18] of Cl$^-$, and if the solvation energy of Ph$_2$CH$^+$ is taken as 2.91 eV,[18] it is evident that ionization of Ph$_2$CH$^{\bullet}$ with only *one* 308 nm photon (quantum energy 4.0 eV) is *thermodynamically* possible. In contrast, *without any* solvation, ionization is still uphill, even after absorption of a second 308 nm photon (by D$_1$. The assumption is made that after absorption of the 308 nm quantum by Ph$_2$CH$^{\bullet}$, relaxation to D$_1$ (see Scheme I) is very fast, $k > 10^{12}$ s^{-1}). For the system to profit from solvation, that process has to occur on the same timescale as ionization. Solvation times of organic molecules in AN have been determined to be 0.5 to 1 ps,[48] much longer than those of electron movement (<fs). The solvation time of the electron in AN is not known, but it is unlikely that this should be much less than that in water, which has been measured to be 550 fs.[49] Thus, to explain the occurrence of ionization of the multiply excited radical, Ph$_2$CH$^{\bullet **}$, it has to be assumed that its lifetime is in the fs to ps range, allowing for solvation of the (incipient) ions to take place and thereby fuel the ionization process.

From the above discussion, the important role of the solvent is evident in determining the fate of excited radicals formed under conditions of high light intensities. Thus, under these conditions, the solvent effect is two-fold: On the primary photoprocess of the parent[18] *and* on the further photoreactions of the intermediates.

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