Photohomolysis and Photoionization of Substituted Tetraphenylethanes and C–C Fragmentation of 1,1,2,2-Tetra(*p*-R-phenyl)ethane Radical Cations ($R = H, CH_3, OCH_3, Cl$)

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Abstract: On photolysis of a series of tetraphenylethanes in 2,2,2-trifluoroethanol (TFE) solution with 248 nm light, homolysis of the central C–C bond occurs to yield the corresponding substituted diphenylmethyl radicals, in a process requiring one quantum of light. A second process takes place under conditions of high photon fluxes, namely biphotonic photoionization to produce a radical cation, which subsequently undergoes efficient C–C scission of the aliphatic central bond to yield the radical and carbocation fragments. Photoionization and photohomolysis are the preferred processes of excited state deactivation in the solvents acetonitrile, TFE, and 1,1,1,3,3,3-hexafluoroisopropanol. The lifetime of the radical cation could be directly determined by following the formation rates of the fragments in solution. The cations were characterized by their UV absorption spectra and electrophilic reactivities.

Keywords: carbocations • photochemistry • radical ions • radicals • reaction mechanisms

Introduction

Photoionization of organic substrates in solution leads to the formation of the corresponding radical cations. For aromatic molecules with an aliphatic side chain, weakening of the side-chain $C_\alpha - C_\beta$ σ bond occurs,[1] and it has been found that upon electron removal the strength of the C–C bond is decreased by as much as 20 kcal mol^{-1}.[2–4] Subsequently, the weakened bond may cleave rapidly leading to radical and cation fragments (separation of charge from spin).

The most widely used route to effect oxidative C–C bond cleavage is through photoinduced electron transfer,[5–9] with electron-deficient aromatic compounds as electron acceptors. However, under these conditions one important reaction which competes with fragmentation is back electron transfer from the reduced acceptor.

When the radical cations are generated in polar solvents by photoionization, back electron transfer is no longer important, since the photoejected electron is readily solvated. In this case C–C bond cleavage only has to compete with the usual reactions of deprotonation,[1, 10] adduct formation or rearrangements.[7] In spite of these advantages, the method of generating aromatic radical cations by photoionization has up to now not found widespread use.[1a, 11, 12] One of the reasons for this is that photoionization is not easy to achieve. It depends strongly on the ionization potential of the substrate and on the nature of the solvent. Obviously, for photoionization to be possible in solution, the energy of the interacting photons plus the energy of solvation of the resulting species (the electron and the radical cation) must overcome the gas-phase ionization potential of the substrate.

The tetraarylethanes which are the target of this study (Scheme 1) do meet these energetic requirements. The interest in these systems stems from the possibility that if photoionization-induced side-chain fragmentation occurs, this should be an efficient route to generate the corresponding diphenylmethyl-substituted cations in solution. The interest in the characterization and reactivity of carbocations is one field of very active[13] research owing to their importance as intermediates in many organic reactions. Diarylmethyl cations have been previously generated in different solvents in several different ways, for example in acetonitrile by photoheterolysis of the corresponding halides,[14, 15] and by photoionization of the corresponding radicals,[16, 17] in acetonitrile/water and in trifluoroethanol by photoheterolysis of acetates and 4-cyanophenyl ethers,[13a] in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) by photoprotonation of the carbinol,[16] and in various alcohols by the protonation of a photogenerated diarylcar-

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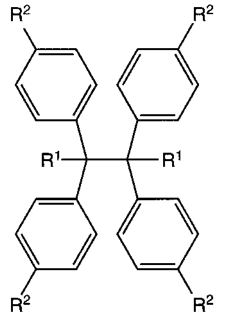

	1	2	3	4	5
R^1	H	H	H	H	OCH_3
R^2	H	CH_3	OCH_3	Cl	H

Scheme 1. The tetraarylethanes studied.

bene.[18] As shown in this paper, photoionization of tetrarylethanes does indeed provide an additional method for obtaining these important cationic intermediates. One of the novel features of this work is that the precursor cation radical can actually be observed on the nanosecond time scale, and rate constants can be directly measured for the fragmentation to diarylmethyl cation and radical.

Results and Discussion

Laser photolysis (248 nm) of 1,1,2,2-tetraarylethanes:

Photolysis in TFE: The spectrum shown in Figure 1 (solid circles), measured at 160 ns after photolysis of a deoxygenated TFE solution of 1,1,2,2,-tetra(4-methylphenyl)ethane (0.11 mM) with a 100 mJ pulse of 248 nm light, displayed a strong peak at 340 nm and a symmetrical band at 460 nm. Below 240 nm, the bleaching of the parent compound was clearly visible. This bleaching persisted even after complete decay of the 460 nm band (Figure 1: spectrum at 154 µs, open squares), which indicates that the parent is not regenerated by the decay of the 460 nm species. The decay of the absorption peaking at 340 nm was found to follow second-order kinetics, and it was accelerated when O_2 was admitted to the solution. This peak has previously been identified as resulting from the di(4-methylphenyl)methyl radical, which was produced in CH_3CN by photohomolysis of the corresponding di(4-methylphenyl)methyl halide.[14] The decay of the 460 nm absorption was found to follow first-order kinetics with an observed rate constant of $5.5 \times 10^4\ s^{-1}$ (Table 1), and not to be dependent on the presence of O_2, which means that this band is not due to a triplet or to a neutral radical. This band has also previously been identified as resulting from the di(4-methylphenyl)methyl cation, produced in CH_3CN by photoheterolysis of the corresponding di(4-methylphenyl)methyl halide,[14] and in trifluoroethanol by photoheterolysis of the 4-cyanophenyl ether.[13a]

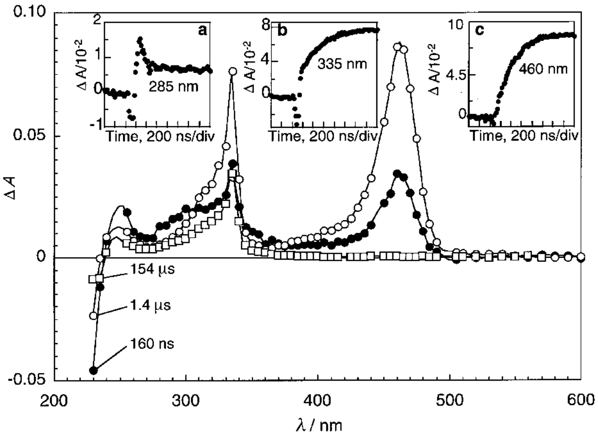

Figure 1. Time-resolved spectrum recorded upon laser photolysis (248 nm) of a TFE solution of a 0.11 mM 1,1,2,2-tetra(4-methylphenyl)ethane degassed with Ar, taken at 160 ns (●), 1.4 µs (○) and 154 µs (□). Insets: a) kinetic traces monitored at 340 nm for the above solution; b) kinetic traces monitored at 460 nm for an identical solution saturated with oxygen.

Table 1. Absorption characteristics of the intermediates genereated upon laser photolysis of the teraarylethanes **1**–**4** in solution(CH_3CN and TFE) under argon; decay rates of the species.[a]

Substrate	Solvent	Intermediate	λ_{max} [nm]	k_{obs} [s^{-1}]
1	CH_3CN	$Ph_2CH^{\bullet}$	330	[b]
		Ph_2CH^+	436	1.5×10^6
	TFE	$Ph_2CH^{\bullet}$	330	[b]
		Ph_2CH^+	436	2.5×10^6
				3.2×10^6[c, d]
2	CH_3CN	$(p\text{-}CH_3C_6H_4)_2CH^{\bullet}$	340	[b]
		$(p\text{-}CH_3C_6H_4)_2CH^+$	466	1.6×10^5
	TFE	$(p\text{-}CH_3C_6H_4)_2CH^{\bullet}$	340	[b]
		$(p\text{-}CH_3C_6H_4)_2CH^+$	460	5.5×10^4
				2.4×10^4[c]
3	CH_3CN	$(p\text{-}CH_3C_6H_4)_2CH^{\bullet}$	347	[b]
		$(p\text{-}CH_3C_6H_4)_2CH^+$	500	[b]
	TFE	$(p\text{-}CH_3C_6H_4)_2CH^{\bullet}$	347	[a]
				14[c]
		$(p\text{-}CH_3C_6H_4)_2CH^+$	500	[b]
4	CH_3CN	$(p\text{-}ClC_6H_4)_2CH^{\bullet}$	340	[b]
		$(p\text{-}ClC_6H_4)_2CH^+$	470	1.6×10^5

[a] In the case of the cations, the first-order processes are due to reaction with solvent. The more stabilized cations, however, react by combining with anions (second-order kinetics).[15] [b] Second order. [c] See ref. [13a]. [d] Same number also for diphenylcarbene in TFE.[18]

The spectrum at the shortest time in Figure 1 was recorded 160 ns after the laser pulse. Immediately after the laser pulse, there was a much smaller absorbance for the radical at 335 nm, and no absorbance for the cation. There was an additional weak absorption band in the region 250–300 nm. Over the initial 100 ns following the laser pulse, the absorbance at 250–300 nm decayed (inset a, Figure 1), and the radical (inset b, Figure 1) and the cation (inset c, Figure 1) grew in, all three processes with comparable rate constants. These facts suggest that the species at 250–300 nm is a common precursor of both radical and cation. As can be clearly seen, radical formation (inset b, Figure 1) arises from two separate processes. After some initial emission, there is a fast jump that is complete within the time of the laser pulse; this is then followed by delayed build-up. Cation formation, however, occurs by a single process which has the same rate as that of the delayed build-up of the radical.

The 248 nm photons have an energy (5 eV) well above the bond dissociation energy of the central C–C bond of the studied tetraphenylethanes (2.07 eV for 1,1,2,2-tetraphenylethane).[3, 6, 19] On this basis it is not surprising that the primary photoprocess in solution is photohomolysis (to give the corresponding radicals), reaction (1). In addition, a biphotonic photoionization takes place in which the radical cation is produced, reaction (2).

$$Ar_2CHCHAr_2 \xrightarrow{h\nu} 2\,Ar_2CH^{\bullet} \qquad (1)$$

$$Ar_2CHCHAr_2 \xrightarrow{2h\nu} Ar_2CHCHAr_2^{\bullet +} + e^-_{solv} \qquad (2)$$

The radical cation undergoes side-chain fragmentation to yield (more) radicals and cations,[20] reaction (3), whereas the radicals produced in reaction (1) decay by a second-order process (as mentioned above) resulting from radical–radical reaction (4). The electron formed in reaction 2 is probably trapped by the solvent (see below).

$$Ar_2CHCHAr_2^{\bullet +} \rightarrow Ar_2CH^{\bullet} + Ar_2CH^{+} \qquad (3)$$

$$2\,Ar_2CH^{\bullet} \rightarrow \text{combination and disproportionation products} \qquad (4)$$

In order to obtain a more detailed picture of the formation mechanism of the photolysis products, the dependence of the yield of both radical and cation on the energy of the laser pulse was determined in the solvent TFE for the diarylethane **2**. In the case of the di(4-methylphenyl)methyl radical, the dependence of its yield (measured at 340 nm) was determined for both processes, that is, the initial jump and the delayed build-up. The results are shown in Figure 2.

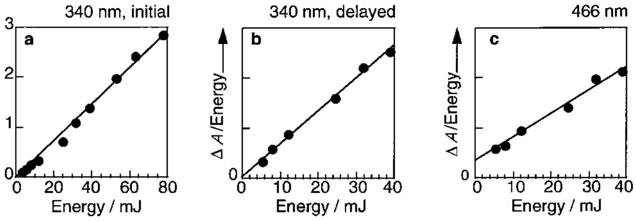

Figure 2. Dependence on laser power of the yield of the intermediates obtained upon photolysis (248 nm) of a solution containing 0.22 mM 1,1,2,2-tetra(4-methylphenyl)ethane in TFE. Radical formation: a) for the initial jump measured at 340 nm; b) for the delayed build-up at 340 nm. Cation formation: c) at 466 nm in a TFE solution deoxygenated with Ar.

A linear dependence is clearly seen in the first process (i.e., the initial jump, Figure 2a), indicating that the radical is formed in a monophotonic process. As the extinction coefficients for the radicals under study are known in CH_3CN,[15] the quantum yields for radical formation in the first step can be determined (Table 2) with the assumption that the extinction coefficients are not significantly different in TFE.

From reaction 1 it is evident that one photon gives rise to two diarylmethyl radicals. Thus the quantum yield for homolytic scission is half of the quantum yield of radical formation (Φ_{RAD1}), as given in Table 2.

Table 2. Quantum yields for radical formation by reaction (1) (Φ_{RAD1}) and quantum yields (at 40 mJ pulse) for cation formation (Φ_{CAT})[a] in TFE solutions.

Substrate	Φ_{RAD1}	$\Phi_{CAT} = \Phi_{RAD2}$
1	0.045	0.040
2	0.038	0.102
3	0.028	0.109
5	0.190	[b]

[a] This yield is same as that for formation of the corresponding radical from the delayed process (Φ_{RAD2}), cf. reactions (2) and (4). [b] See Figure 4 and text.

For the second process of radical formation, Δ*A* values were determined as the difference between the absorbance *A* at the end of the initial jump and that at the end of the delayed formation. The Δ*A* versus laser energy dependence in this case is curved upwards in a parabolic way. As shown in Figure 2b, the plot of Δ*A*/(laser energy) versus (laser energy) is linear with a zero intercept. This means that the delayed process leading to additional radical formation requires two photons (i.e., it is biphotonic).

Like the delayed process of formation of the radical, the yield of formation of the di(4-methylphenyl)methyl cation measured at 466 nm is curved upwards with increasing laser power (Figure 2c).[21] Since the dependence is not linear, no absolute quantum yields can be determined. However, knowing the extinction coefficient for the cations in CH_3CN and using a similar approach as in the case of the radical, we can obtain a yield at a given laser power (Table 2). In this way it is possible to characterize the effect produced by introducing an electron-donating substituent at the *para* position of the phenyl ring. The conclusion is that the yield of cation production is enhanced by the presence of such groups.

Looking at the kinetics, numerical evaluation of the first-order build-up of radicals (delayed process only) and of cations (see insets b and c in Figure 1) leads to the same value, $2.7 \times 10^6\ s^{-1}$, for these processes (Table 3). The observation of a similar rate for the build-up of both intermediates supports the contention that cation and radical are generated from a common precursor. The common precursor is the radical cation produced upon ionization of the parent substrate [reaction (2)].

Table 3. Kinetics of delayed formation for the cation and radical measured at their maximal absorption.

Substrate	Solvent	k_{obs} [s^{-1}]
1	CH_3CN	2.0×10^6
	TFE	$> 3.0 \times 10^7$
2	CH_3CN	7.5×10^5
	TFE	2.7×10^6
3	CH_3CN	0.9×10^5
	TFE	2.1×10^5

The involvement of a radical cation precursor has previously been reported, but under conditions where a sensitizer was used to oxidize the substrate.[2, 7] It is reasonable to assume that the introduction of electron-donating or -withdrawing groups changes the ionization potential of the parent

1,1,2,2-tetraphenylethane without strongly affecting the dissociation energy of the central bond, and therefore reactions (1) – (4) can be expected also for systems **1** – **4**. The *para*-methyl and *para*-methoxy groups will stabilize both the parent radical cation and the products, especially the cationic product. The observation that the lifetime of the radical cation increases with increased electron donation shows that the effect on the radical cation is more important. Similar observations were made for the other substrates, the transients formed being identified by comparison with the spectra in CH_3CN from the literature.[14]

In the case of 1,1,2,2,-tetraphenylethane the spectrum recorded in TFE at 90 ns after the 248 nm pulse showed a strong peak at 330 nm, a shoulder at 350 nm, and a symmetrical band at 436 nm. Some emission in the 280 – 300 nm range and above 520 nm was also visible. At 195 ns after the pulse, the shoulder and the emission disappeared completely, and the remaining peak and band increased to their maximum amplitude. Emission at shorter wavelengths was very intense, occurring within 100 ns. The decay of the shoulder and of the emission were found to follow first-order kinetics and to be independent of the wavelength, suggesting that they belong to the same species. In fact the emission spectrum was identical to the fluorescence of the electronically excited diphenylmethyl radical,[22] which is known to absorb in the 350 nm range.[16]

Photolysis in CH_3CN: In order to substantiate our assignments, we also performed experiments in CH_3CN. From analysis of the kinetic traces it can be concluded that on 248 nm photolysis in CH_3CN, the tetraarylethanes undergo efficient homolysis and photoionization by the same process as in TFE [reactions (1) – (5)]. Again, the decay of the radicals follows second-order kinetics, while the cation decay follows first-order kinetics. These first-order decay rates are comparable in CH_3CN and TFE (Table 1); these solvents have similar nucleophilicities, although in general acetonitrile is slightly more reactive.[23]

As to the formation of the radical cation, only in the case of the more stabilized tetraarylethanes **2** and **3** were we able to see a weak absorption which we attribute to this species (see Figure 1). Two bands with maxima at 260 and 420 nm could be observed after the 248 nm photolysis of **3**. In the case of $\mathbf{2}^{\cdot+}$ (maxima at 260 and 360 nm) it was more difficult to observe such bands as they are weak and overlap with the radical and cation bands. In both cases these bands decay at the same rate as the formation of the radical and the cation, which supports their assignment as resulting from the radical cation precursors. These bands are not influenced by the presence of O_2, which further supports this identification.

The rate constants for radical cation fragmentation depend on the structure of the substrate and the fact that they are solvent-dependent. The radical cation is longer-lived in CH_3CN ($\varepsilon = 38$) than in TFE ($\varepsilon = 27$). This may result from the fact that the former is more polar. The fragmentation involves a migration of the positive charge within the molecule, and thus it will also involve a rearrangement of the solvation shell of the positive charge. This effect will be more important in the more polar solvent.

Finally, concerning the e^- released in the ionization reaction (2), in acetonitrile e^- is efficiently trapped by the solvent, forming a dimer radical anion $(CH_3CN)_2^{\cdot-}$, which has a very faint broad absorption between 400 and 700 nm,[24] and therefore is very difficult to observe.

Photolysis in HFIP: Reactive cations, including the diphenylmethyl cation, can be generated and observed in the acidic and very weakly nucleophilic solvent HFIP[25] ($\varepsilon = 17$). Compound **1** was photolyzed in Ar-saturated solution, and both radical and cation were formed, judged by their characteristic absorption spectra, with λ_{max} at 330 and 436 nm, respectively. The nature of these intermediates was confirmed by introducing selective scavengers. The band at 330 nm was efficiently quenched by the introduction of O_2, which supports the radical nature of this intermediate. On the other hand the decay at 436 nm was faster when a nucleophile such as MeOH was present, which agrees with the cationic nature of this intermediate. It was found that the formation of the diphenylmethyl cation requires two photons. This is in agreement with the idea that the cation is produced via the radical cation of the parent. However, the delayed build-up was almost imperceptible, suggesting that the radical cation precursor is very short-lived.

Reactivity of the carbocations: The substituted diphenylmethyl cations formed on photolysis of the tetraarylethanes react rapidly with typical nucleophiles, Nu. The second-order rate constants for reaction with Nu were measured as functions of the nucleophile concentration, monitoring the decay of the cation. The rate constants obtained are collected in Table 4.

Table 4. Rate constants for reaction of the diphenylmethyl cations with nucleophiles in TFE solutions ($k\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$).

Nucleophile	Ph_2CH^+	$(p\text{-}CH_3C_6H_4)_2CH^+$	$(p\text{-}CH_3OC_6H_4)_2CH^+$
water	1.1×10^6	[a]	[a]
dioxane	1.3×10^6	–	–
isopropanol	7.8×10^6	–	–
methanol	1.0×10^7	1.6×10^6	[a]
ethanol	1.3×10^7	1.6×10^6	[a]
N_3^-	5.5×10^9	4.2×10^9	9.9×10^8
Cl^-	1.9×10^9	8.1×10^8	[b]
Br^-	6.5×10^9	2.3×10^9	[b]
I^-	7.5×10^9	9.2×10^9	[b]

[a] k_{obs} vs concentration plot is curved upwards. [b] Reaction is reversible.

The dependence of the rate constants on cation structure is as expected on the basis of the electronic effect of the substituents. In the case of the diphenylmethyl cation the rate constants for reaction with the halides and with azide are very high and close to diffusion control, whereas the values for the more stabilized cations are lower, suggesting activation control for these reactions. In the case of the very stable di(4-methoxyphenyl)methyl cation, there is a noticeable lack of reactivity with the halides in TFE. The explanation is probably that the addition reaction to halide is reversible, and followed by solvolysis of the resulting halide, as previously observed in the case of trityl cation.[13b] In this case there is no observable dependence of the rate on the concentration of halide.

Another observation concerns the reaction of the less reactive substituted diphenylmethyl cations with weaker nucleophiles such as the alcohols. In these cases the plot of k_{obs} versus [Nu] was curved upwards with a strong adherence to a quadratic dependence (Figure 3). This observation has precedents[25, 26] in cases where either the attacking species has a low nucleophilicity or the cation is quite unreactive.

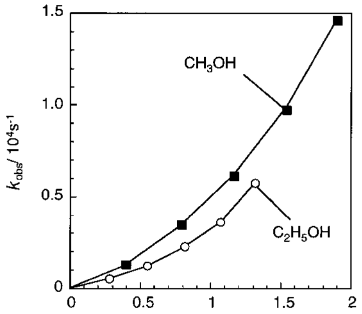

Figure 3. Dependence on [CH_3OH] and [C_2H_5OH] of k_{obs} for decay of (p-$CHO_3C_6H_4)_2CH^+$ in TFE.

Laser photolysis of 1,2-dimethoxy-1,1,2,2-tetraphenylethane: Our study was extended to a tetraphenylethane with an alkoxyl-substituted C–C central bond, namely 1,2-dimethoxy-1,1,2,2-tetraphenylethane. On photolysis with 248 nm light, in TFE solution deoxygenated with Ar, the absorption spectrum observed (Figure 4) is dominated by a very intense peak at 336 nm, with a faint band in the 470–550 nm range. The slow decay of the absorptions (by second-order kinetics, inset Figure 4) was found to be independent of the wavelength in both λ ranges, and drastically accelerated in the presence of O_2. The conclusion is thus that the peaks belong to only one species. The 336 nm and the 470–550 nm peaks have previously been identified as resulting from the diphenyl(methoxy)methyl radical, produced[27] in CH_3CN. The formation of the radical was complete within the laser pulse (20 ns). The dependence of the yield of the diphenyl(methoxy)methyl radical (measured at 336 nm) on the intensity of the 248 nm laser light is clearly linear (Inset b, Figure 4). The conclusion is that only one quantum of light is needed to produce the corresponding radical; this conclusion supports homolytic scission of the parent compound.

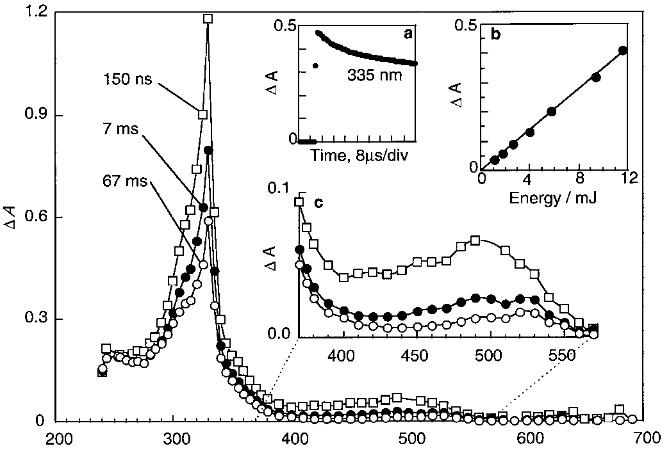

Figure 4. Time-resolved spectra recorded upon laser photolysis (248 nm) of a 1.1 mM solution of 1,2-dimethoxy-1,1,2,2-tetraphenylethane in TFE degassed with N_2O, taken at 150 ns (□), 7 µs (●) and 67 µs (○). Insets: a) kinetic traces monitored at 336 nm for the above solution; b) dependence of the yield of radical formation (at 336 nm) in deoxygenated TFE solution as function of the laser power (248 nm pulse); c) detail of the time-resolved spectrum showing the peak at 490 nm due to the absorption of the diphenyl(methoxy)methyl cation.

In contrast to the results for the substrates **1**–**4**, there was no prominent band visible in the range expected for the cation. However, close inspection of the absorption spectrum shows a band with a maximum at 490 nm, on the top of the radical shoulder (Figure 4). This absorption was completely absent in the presence of sodium azide, which is evidence for its cationic nature.[28] The signal was not strong enough to permit a good kinetic characterization.

The observations reported suggest that the primary process on photoexcitation of 1,2-dimethoxy-1,1,2,2-tetraphenylethane is homolysis, reaction (5).

$$Ph_2C(CH_3O)C(OCH_3)Ph_2 \xrightarrow{h\nu} 2\,Ph_2C^{\bullet}(OCH_3) \qquad (5)$$

The absorption measured just after the laser pulse was used to determine the quantum yield of homolysis, assuming that the molar decadic absorption coefficient ε ($M^{-1}cm^{-1}$) of the radical is 30000 (this is in fact the number given for ε of the $Ph_2C^{\bullet}(OH)$ radical[27]). The value obtained for the photohomolysis, taking into account the stoichiometry of the reaction, is 0.095.

Similar experiments carried out in CH_3CN and HFIP produced time-resolved spectra very similar to that in TFE (except for a small shift in the peak absorption observed in HFIP), indicating photohomolysis rather than photoionization in these solvents. The reason is probably the stabilization of the benzhydryl radicals by the α-methoxy groups.

Experimental Section

Substituted tetraphenylethanes and compound **5** are known compounds, and were prepared following standard literature methods.[3, 6a, 16]

Substituted tetraphenylethanes in solution were photolyzed with 20 ns laser pulses of 248 nm light (KrF* excimer). The intermediates produced in the laser flash photolysis experiments were detected by their optical signals in the UV/visible region, as previously described.[16] The laser energy indicated in the text and figures was measured at the cell position. Stock solutions were prepared dissolving the appropriate substrate in CH_2Cl_2, and injecting a few µL of this solution into the desired solvent, such as TFE, CH_3CN or HFIP. The final concentration of the organic substrate was typically 10^{-5}–10^{-3}M and the content of CH_2Cl_2 was less than 1% (v/v). The ground-state spectrum of the compounds is not very favorable for absorption of the 248 nm light owing to the fact that at 248 there is a minimum. The solutions had an A value of 0.1–0.6 cm^{-1} at 248 nm, and they were made to flow through a 2 mm (in the direction of the laser beam) by 4 mm (in the direction of the analyzing light) Suprasil quartz cell.

For determination of the photonities and quantum yields for excitation with the 248 nm light, the dependence of the yield of the intermediates measured at or close to their maxima on the intensity of the laser light was determined by attenuation of the light with neutral density filters.

Actinometry was performed with a $SO_4^{\bullet -}$ actinometer,[29] using a method previously described.[16]

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