

Revealing Phenylum, Phenonium, Vinylenephenonium, and Benzenium Ions in Solution

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Abstract: The 4-methoxyphenylum ion has been generated in the triplet state ($^3\text{An}^+$) by photolysis of 4-chloroanisole in polar media and detected by flash photolysis ($\lambda_{\text{max}} = 400 \text{ nm}$). This is the first detection of a phenylum ion in solution by flash photolysis and the assignment is supported by time-dependent density functional theory (TD-DFT) calculations. In neat solvents, the cation was reduced to anisole, a process initiated by electron transfer from the starting compound ($^3\text{An}^+ + \text{AnCl} \rightarrow \text{An}^\bullet + \text{AnCl}^{+\bullet}$, with the radical cation detected at 470 nm, then $\text{An}^\bullet \rightarrow \text{AnH}$). Addition of π nucleophiles to

the $^3\text{An}^+$ cation offers a novel access to a number of other cationic intermediates under mild, nonacidic conditions. Two intermediates are successively formed with alkenes, a diradical cation and the phenonium ion, which are detected at 440 and 320 nm, respectively, by flash photolysis and are in accordance with calculations. Allylanisoles or β -alkoxyalkylanisoles are the

Keywords: aryl cations • carbocations • density functional calculations • photochemistry • reaction mechanisms

end products, with a small amount of α -alkoxyalkylanisoles that arises from a Wagner–Meerwein rearrangement to form benzyl cations. Further intermediates that have been predicted and detected are the phenylvinylum ion, possibly in equilibrium with the vinylenephenonium ion, with 1-hexyne ($\lambda_{\text{max}} = 340 \text{ nm}$) and the benzenium ion with benzene ($\lambda_{\text{max}} = 380 \text{ nm}$). The final products were anisylhexyne and methoxybiphenyl (an analogous product and intermediate were detected with thiophene).

Introduction

Of the conceivable intermediates in organic chemistry, divalent carbocations, and in particular, phenyl cations (phenylum ions) are among the less well-known.^[1] Two reasons explain the limited data available. The first is the scant synthetic application of this intermediate. Phenyl cations are known intermediates in some thermal or photochemical decomposition reactions of phenyldiazonium salts,^[2] and in some cases, phenyl triflates.^[3] The reactions occurring are mostly solvolysis processes that are moderately appealing from a synthetic point of view. This has led to the belief that the excessive reactivity of phenyl cations makes them unselective and of little preparative interest. On the contrary, the majority of synthetically useful reactions of diazonium salts (e.g., the Sandmeyer, Meerwein, and Gomberg reactions) do not involve the phenyl cation but the phenyl radical.^[4] Some indications of a more varied chemistry were obtained when the cation was generated by the decay of tritibenzenes,^[5] but this method is hardly suitable for synthesis.

The second reason is that mechanistic studies of the phenyl cation in solution have been hampered by the fact

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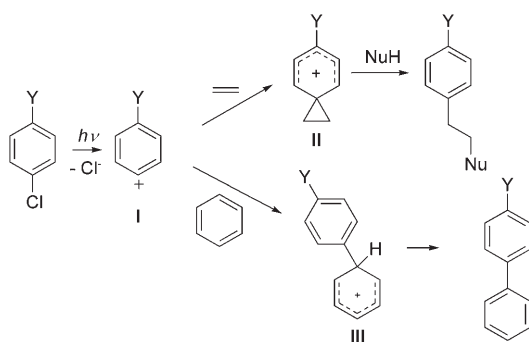
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Supporting information for this article is available on the WWW under <http://www.chemeurj.org/> or from the author. It contains methods of irradiation, characterization of photoproducts, details of flash photolysis measurements, optimized geometries listed in Cartesian format, energies calculated (B3LYP 6-31G(d)) for 4-chloroanisoles and adducts in the gas phase and in MeCN, and calculated spectra of the cations.

that this species appears to have no clear-cut UV absorption^[6] and thus flash photolysis, which has been instrumental in the study of other intermediates, such as carbenes and nitrenes, has been of limited value. Only a secondary intermediate, the benzenium ion (cyclohexadienyl cation), which results from the addition of the phenylium ion to benzene, has been detected in solution.^[7] Also, evidence for the formation of the phenyl cation in matrices is scarce. EPR spectra of the phenyl cation have been obtained by photolysis of some phenyl diazonium ions in EtOH at 77 K,^[8] and only recently, the IR spectrum of the phenyl cation was obtained by photolysis of phenyl iodide in an argon matrix at 4 K in which the phenyl radical is formed and gives the cation by ensuing electron transfer.^[9]

Recently, a class of reactions has emerged in which C–C bond formation has been achieved by the photolysis of electron-donating substituted aryl halides^[10] or esters^[11] in the presence of carbon nucleophiles, for example, alkenes, alkynes, or (hetero)aromatics, with little competing solvolysis. These reactions have been rationalized in terms of trapping of the triplet phenylium ion (**I**, Scheme 1), which generates



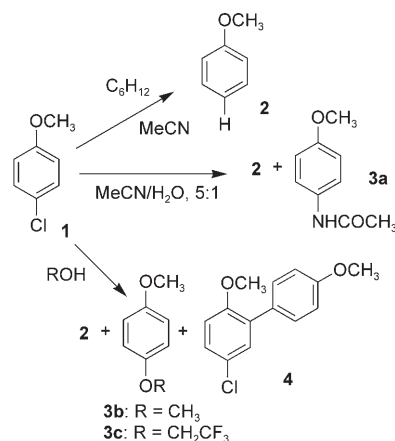
Scheme 1. Trapping of the phenylium ion by carbon nucleophiles.

further cationic intermediates, for example, the phenonium ion (the cyclopropanespirocyclohexadienyl cation, **II**) in the case of alkenes.^[10] This latter species is an intermediate in the solvolysis of phenethyl derivatives,^[12] but has mostly been directly detected under superacid conditions.^[13] As mentioned above, with benzene, the benzenium ion **III** is expected to be formed by trapping the phenylium ion with benzene.

If the overall picture invoked above is correct, then this photolytic reaction lends itself to the detection and study under neutral, mild conditions of various cations that have been invoked as intermediates, but rarely detected.^[14,15] Herein, we report a study aimed at the spectroscopic and kinetic characterization of the above cations by flash photolysis with the support of product and computational studies to prove their structures and roles.

Results and Discussion

Photoproducts in various solvents: 4-Chlorophenol has previously been studied in detail,^[14a,b,16] however, the studies were affected by the protolytic equilibrium of the OH group. Therefore, this work was carried out by using 4-chloroanisole (**1**, see Scheme 2).



Scheme 2. Photoproducts of 4-chloroanisole in various solvents.

Table 1. Quantum yields of the products formed by irradiation of 4-chloroanisole.^[a]

Solvent	Φ_{prod}	Φ_{I^+}
MeCN	2 : 0.003	0
MeCN/H ₂ O (5:1)	2 : 0.007, 3a : 0.003	
MeOH	2 : 0.08, 3b : 0.02	0.22 ^[a]
TFE	2 : 0.038 (+0.012), ^[b] 3c : 0.02 ^[c]	
MeCN + DMB ^[d] (0.5 M)	5 : 0.07	

[a] [**1**] = 1×10^{-3} M. [b] 4-Fluoroanisole. [c] A trace of product **4** was also formed (the yield increases with a higher starting concentration, see Table 2). [d] 2,3-Dimethyl-2-butene.

Irradiation of this compound in acetonitrile, methanol, a mixture of MeCN/H₂O (5:1, v/v), and 2,2,2-trifluoroethanol (TFE) gave anisole (**2**) as the main photoproduct (the only one in MeCN) as well as products that result from the substitution of the chloro atom by the nucleophilic solvent (see Tables 1 and 2); these were 4-methoxyacetanilide (**3a**) in MeCN/H₂O, 1,4-dimethoxybenzene (**3b**) in methanol, and 4-(2,2,2-trifluoroethoxy)anisole (**3c**) in TFE. In TFE, some 4-fluoroanisole was also formed along with a concentration-dependent amount of the “self-attack” product, dimethoxybiphenyl **4**. The reaction quantum yields were measured in these solvents and are reported in Table 1. The values varied from 0.003 in MeCN to 0.08 in MeOH. Previously we have reported that irradiation in cyclohexane caused clean reduction to **2**.^[17] The reaction in C₆H₁₂ was strongly quenched in air-equilibrated solutions, whereas photodecomposition in the polar solvents mentioned above occurred to the same extent (within $\pm 5\%$) in air- and argon-saturated solutions.

Table 2. Products and yields [%] obtained by the irradiation of 4-chloroanisole (0.05 M) in neat solvent and in the presence of nucleophiles.

Solvent	Neat	DMB ^[a] (0.5 M)	1-Hexene (0.5 M)	1-Hexyne (0.5 M)	Benzene (1 M)	Thiophene (1 M)
MeCN	2: 60 ^[b]	5: 49 ^[b]	2: 5 8a: 54	2: 15 12: 30	2: 25 13: 33	2: trace
MeCN/H ₂ O (5:1)	2: 53 3a: 22	2: 10 5: 21	2: 12 8a: 30 9: 15 10: 14	2: 11 12: 53	2: 26 13: 53	2: trace 14: 65 14': 15
MeOH	2: 63 3b: 29 ^[b]	2: 22 5: 16 6a: 17 6b: 22 ^[b]	2: 13 8a: 3 8b: 42 11b: 8	2: 10 3b: 3 12: 17	2: 23 13: 15	2: 2 14: 14 14': 4
TFE	2: 24 (8) ^[c] 3c: 15 4: 20 ^[b]	2: 12 5: 21 6a: 14 6c: 17 7c: 8 ^[b]	2: 4 8a: 36 8c: 10 11c: 40	2: 6 3c: 3 12: 60	2: 6 13: 61	2: trace 14: 52 14': 5

[a] 2,3-Dimethyl-2-butene. [b] See ref. [17]. [c] 4-Fluoroanisole.

Study of the intermediates: Laser flash photolysis at 266 nm of argon-saturated solutions of **1** (ca. $1\text{--}1.5 \times 10^{-3}$ M) was performed in several solvents (measurements below 350–360 nm at short delays after the pulse were perturbed by the fluorescence of the solute). In cyclohexane an intense band with $\lambda_{\text{max}} = 335$ nm (tailing into the visible region) and a lifetime of $\tau = 220$ ns was observed after a delay of 40 ns after the end of the pulse (Figure 1A). The transient was quenched by oxygen with a rate constant $k_{\text{O}_2} = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and was assigned to the triplet **31**.^[18]

The behavior was different in polar solvents. The end-of-pulse difference spectrum recorded in MeCN showed an absorption tail in the region 350–400 nm (Figure 1B) that was attributed to the triplet based on the clear-cut peak at 350 nm at 25 ns delay. The peak disappeared with a time constant of 25 ns and a band with $\lambda_{\text{max}} = 475$ nm could be distinguished at a delay of 150 ns. In MeOH the initial triplet absorption, which tailed from 360 nm into the visible region, evolved with a time constant of $\tau \approx 30$ ns into a band with $\lambda_{\text{max}} \approx 440$ nm (see the spectrum at 70 ns delay in Figure 2A), which further shifted to 460–470 nm within 1 μ s (see the spectra at 900 ns in Figure 2A and the profile at 470 nm shown in the inset). The formation kinetics of the 460–470 nm band depended on the concentration of **1**, in accordance with a rate constant of $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Finally, in both MeCN/H₂O (5:1, v/v) and TFE an end-of-pulse absorption peak at 400 nm was observed, which evolved with a time constant of around 10 and 22 ns into spectra with $\lambda_{\text{max}} = 470$ and 420 nm, respectively (Figure 3A and Figure 4A).

In an attempt to identify one of the transients, one-electron oxidation of **1** by sulfate radicals ($\text{SO}_4^{\cdot-}$ obtained from $\text{S}_2\text{O}_8^{2-}$ by excitation at 266 nm) was carried out in an aqueous solution. The transient formed (with an absorption maximum at 460 nm) was virtually coincident with that obtained from the photolysis of **1** in methanol at 900 ns, which was thus identified as the radical cation **1**^{•+} (Figure 2C). Oxidation of **1** was assumed to be stoichiometric and gave a transient absorbance at 460 nm that increased linearly with

pulse energy.^[19a] Thus, by taking into account the fact that $\Phi(\text{S}_2\text{O}_8^{2-}) = 0.5$, $\Phi(\text{SO}_4^{\cdot-}) = 0.7$, and $\epsilon_{450} = 1600 \text{ M}^{-1} \text{ cm}^{-1}$ for $\text{SO}_4^{\cdot-}$,^[19b] an absorption coefficient of $\epsilon_{460}(\text{1}^{\cdot+}) = 7100 \text{ M}^{-1} \text{ cm}^{-1}$ was determined.^[20]

Measurements on a solution of **1** (1×10^{-3} M) in MeOH gave values of ΔA at 460 nm (measured after completion of the growing-in process) that were found to depend linearly on the laser pulse energy, which shows that a monophotonic process was occurring. By using the ϵ_{460} value determined above and by assuming that this does not depend markedly on the sol-

vent, quantum yields for the one-photon formation of **1**^{•+} were determined (see Table 1). In methanol, the value of $\Phi(\text{1}^{\cdot+})$ was 0.08 at 3×10^{-5} M and reached a limit of around 0.22 at 1×10^{-2} M. The corresponding Φ_0/Φ versus $[\text{1}]^{-1}$ plot is shown in the inset of Figure 2C.

Trapping experiments: The photochemistry of compound **1** was studied in the presence of various π nucleophiles, which include alkenes (a mono- and a tetra-substituted derivative), an alkyne, an aromatic, and a heteroaromatic derivative. Product studies were carried out in the same organic solvents as above with 1 M additive. Addition of 2,3-dimethylbutene (DMB) in cyclohexane led to the formation of some alkylated products along with **2**, but the differences were more marked in the other solvents, with trapping products being formed with all of the additives tested, often as the main products (see Scheme 3 and Table 2). In the case of DMB, the allylated product 4-(1,1,2-trimethyl-2-propenyl)anisole (**5**) was isolated as the only product in MeCN and along with **2** in MeCN/H₂O (5:1, v/v). In alcohols, the products **2** and **5** were accompanied by alkylanisole **6a**, as well as by the phenethyl ethers **6b** and **6c** in MeOH and TFE, respectively, and in TFE by the benzyl ether **7c**. In the presence of 1-hexene, photolysis in MeCN gave 4-(2-chlorohexyl)anisole (**8a**) in a yield of 54%. In hydroxylated solvents, ethers were again formed along with **2**, that is, 4-(2-methoxyhexyl)- (**8b**) and 4-[2-(2,2,2-trifluoroethoxy)hexyl]anisole (**8c**), but also the isomeric 1-methoxyhexyl (**11b**) and 1-(2,2,2-trifluoroethoxy)hexyl (**11c**) derivatives in MeOH and TFE, respectively. In the mixed solvent, product **8a** remained the main product, but was accompanied by alkene **9** and ketone **10**, the latter probably resulting from the oxidation of the corresponding benzylic alcohol. Further, we tested an alkyne, namely, 1-hexyne, which produced 4-(hexyn-1-yl)anisole (**12**) as the main product. With aromatic derivatives, benzene gave biphenyl **13** as the main photoproduct and thiophene formed the 2-aryl- (**14**, main product) and 3-arylthiophene (**14'**) derivatives.

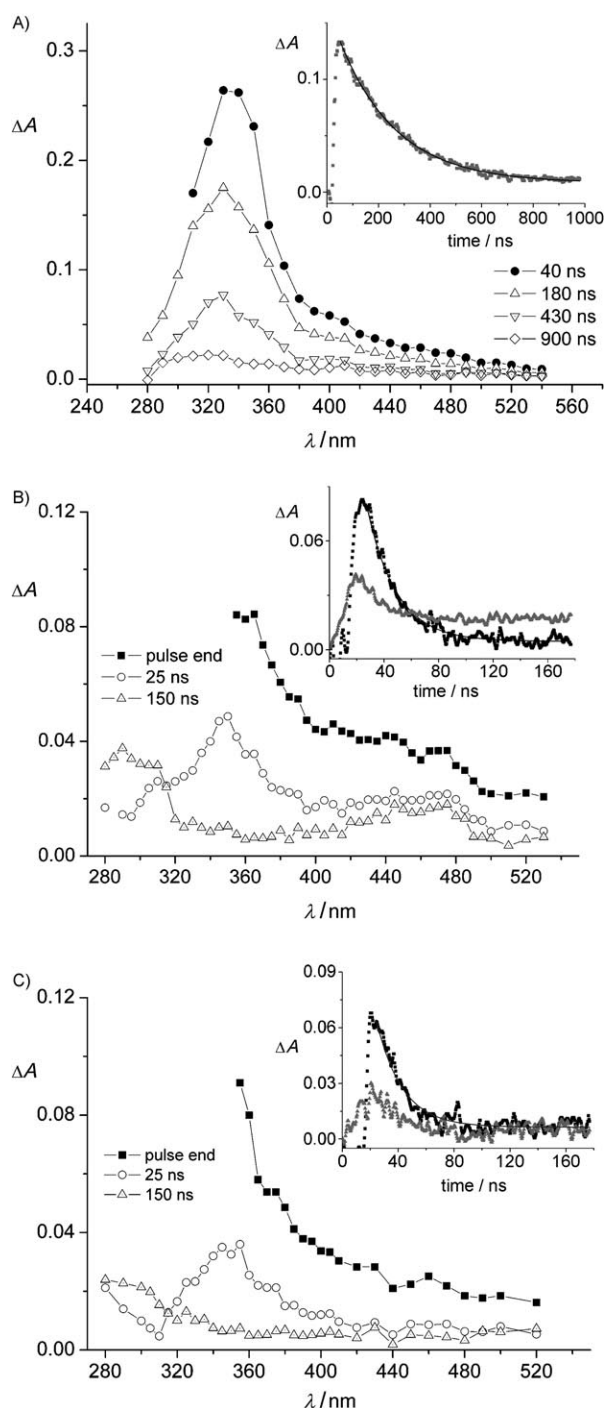


Figure 1. Difference absorption spectra of a solution of **1** (1.3×10^{-3} M) in argon-saturated C_6H_{12} (A), MeCN (B), MeCN in the presence of DMB (0.45 M) (C) at various delays from the end of a 266 nm laser pulse (4.0 mJ per pulse). Insets: zero time at pulse onset. A) (ΔA at 370 nm). B) ΔA at 370 (black) and 470 nm (gray). C) ΔA at 370 (black) and 470 nm (gray).

The fluorescence of **1** was found to be unaffected by the above additives (Stern–Volmer constant (K_{SV}) $< 0.1 \text{ M}^{-1}$), which indicates that the latter did not interact with the excited singlet state of the haloaromatic. Furthermore, it is important to note that, although the reactions reported above

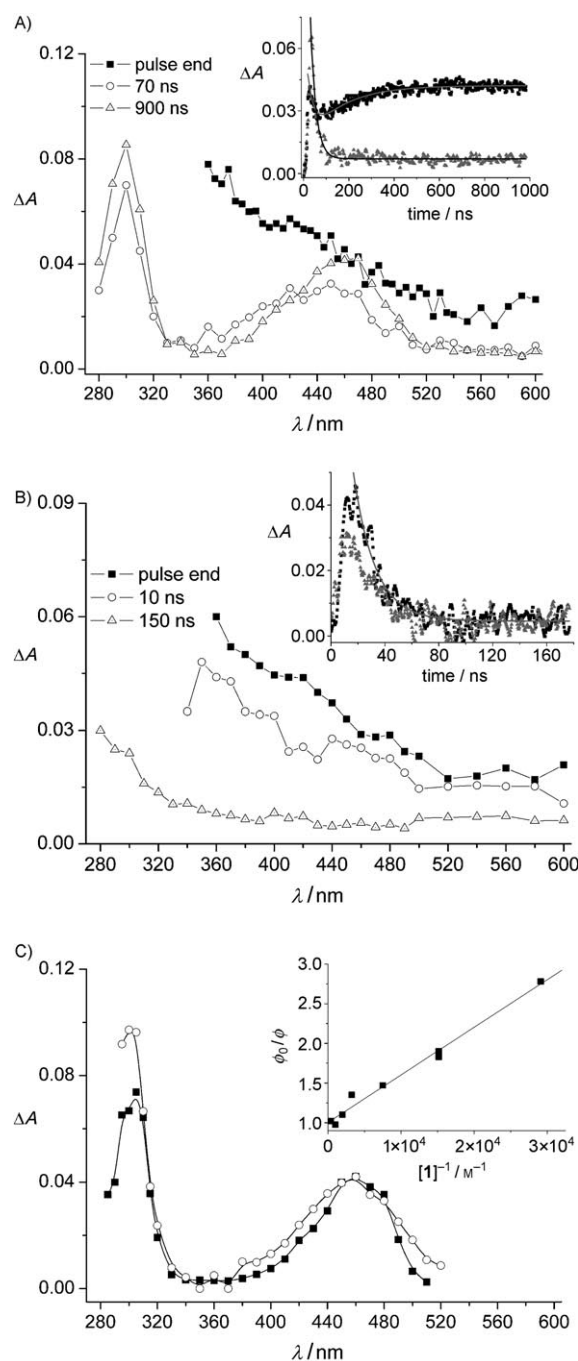
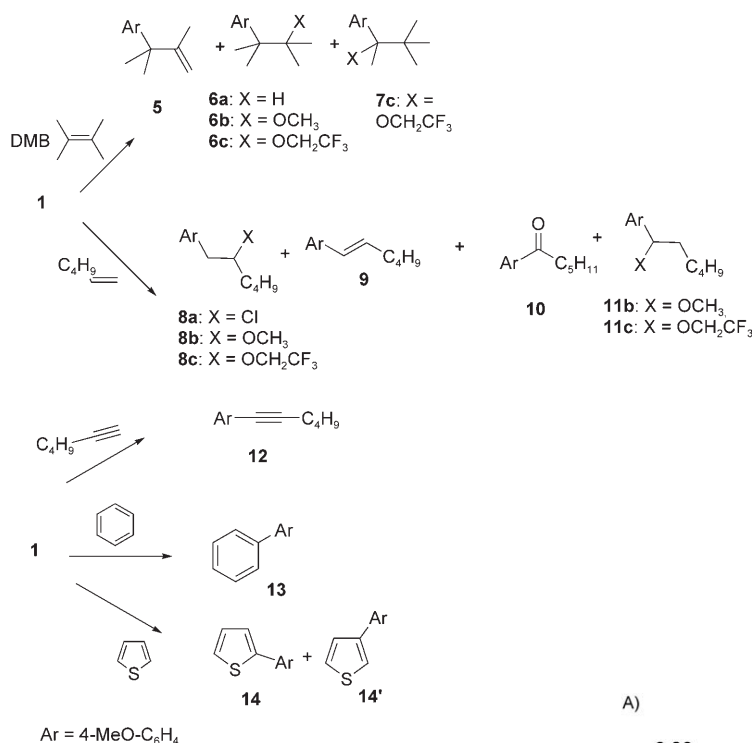


Figure 2. Difference absorption spectra of a solution of **1** (1.3×10^{-3} M) in argon-saturated MeOH at various delays from the end of a 266 nm laser pulse (4.0 mJ per pulse). Insets: zero time at pulse onset. A) No additives. Inset: (ΔA at 360 (black) and 470 nm (gray)). B) In the presence of DMB (0.2 M). Inset: ΔA at 380 (black) and 470 nm (gray). C) Solution of **1** (1×10^{-3} M) in argon-saturated MeOH at 1 μ s ($\circ$); aqueous solution of **1** (5×10^{-4} M) in the presence of $S_2O_8^{2-}$ (0.1 M, $\blacksquare$); the two spectra are normalized at 460 nm. Inset: plot of Φ_0/Φ versus $[1]^{-1}$.

were carried out in argon-saturated solutions, essentially the same results were obtained when this step was omitted.

Laser flash photolysis experiments were also performed in the presence of additives. In particular, the effect of DMB



Scheme 3. Photochemical reaction of 4-chloroanisole in the presence of various π nucleophiles.

was explored in various solvents. In cyclohexane it was found that DMB quenched the 335 nm transient ($k_{\text{DMB}} \approx 8 \times 10^7 \text{ s}^{-1} \text{ M}^{-1}$). In more polar media like MeCN, MeOH, and MeCN/H₂O (5:1, v/v), DMB had little effect on the end-of-pulse spectra, but prevented the formation of the transient absorbing around 460 nm that is otherwise observed in these solvents (see Figures 1C, 2B, and 3B).

More informative results were obtained in TFE in which the clear-cut band present in neat solvent at 400 nm was no longer observed with 0.2 M DMB and was replaced by a band at 440 nm, which had completely formed 10 ns after the pulse (Figure 4B). Concomitant with the decay of the band at 440 nm, a sharp and intense absorption grew at 320 nm in an apparently first-order process ($k \approx 5 \times 10^7 \text{ s}^{-1}$) with an isosbestic point at 390 nm. With 0.04 M DMB, the spectrum at 10 ns had a band at $\lambda_{\text{max}} = 420 \text{ nm}$, but subsequent absorbance changes and kinetics were similar. These results support the proposal that the initial transient at 400 nm (decay rate $\approx 10^8 \text{ s}^{-1}$) was partially quenched by DMB and its residual absorption at 10 ns added to the partially formed intermediate observed at 440 nm (decay rate $\approx 5 \times 10^7 \text{ s}^{-1}$). Further tests were performed at other DMB concentrations and the double reciprocal plot of the absorbance at 320 nm versus [DMB] was found to be linear (see Figure 5).

Similar conditions were chosen to explore the effect of other additives (0.2 M). In the presence of 1-hexene (Figure 4C) the end-of-pulse absorption band at around 440 nm disappeared (with a time constant of ca. 10 ns) to give a

band with a maximum at 340 nm. In the presence of 1-hexyne (Figure 4D) the end-of-pulse absorption at 400–440 nm continued to grow together with the band at 340 nm and with a similar time constant. The formation of a new absorption band that peaked at 370–380 nm was observed with benzene ($5 \times 10^{-2} \text{ M}$), which was concomitant with the decay of the initial absorption tail above 400 nm (time constant ca. 20 ns, Figure 4E). In the presence of thiophene (Figure 4F), an absorption band with a maximum at 360 nm and a tail in the visible region formed with a time constant of around 13 ns in the

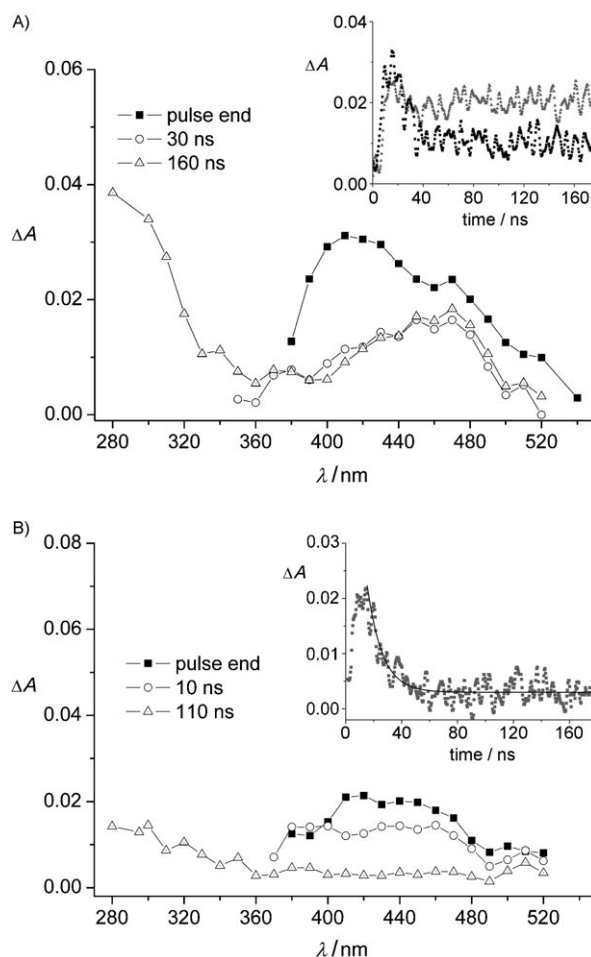


Figure 3. Difference absorption spectra of a solution of **1** ($1.3 \times 10^{-3} \text{ M}$) in argon-saturated MeCN/H₂O (5:1, v/v) at various delays from the end of a 266 nm laser pulse (4.0 mJ per pulse). Insets: zero time at pulse onset. A) No additives. Inset: ΔA at 410 (black) and 470 nm (gray). B) In the presence of DMB (0.2 M). Inset: (ΔA at 440 nm).

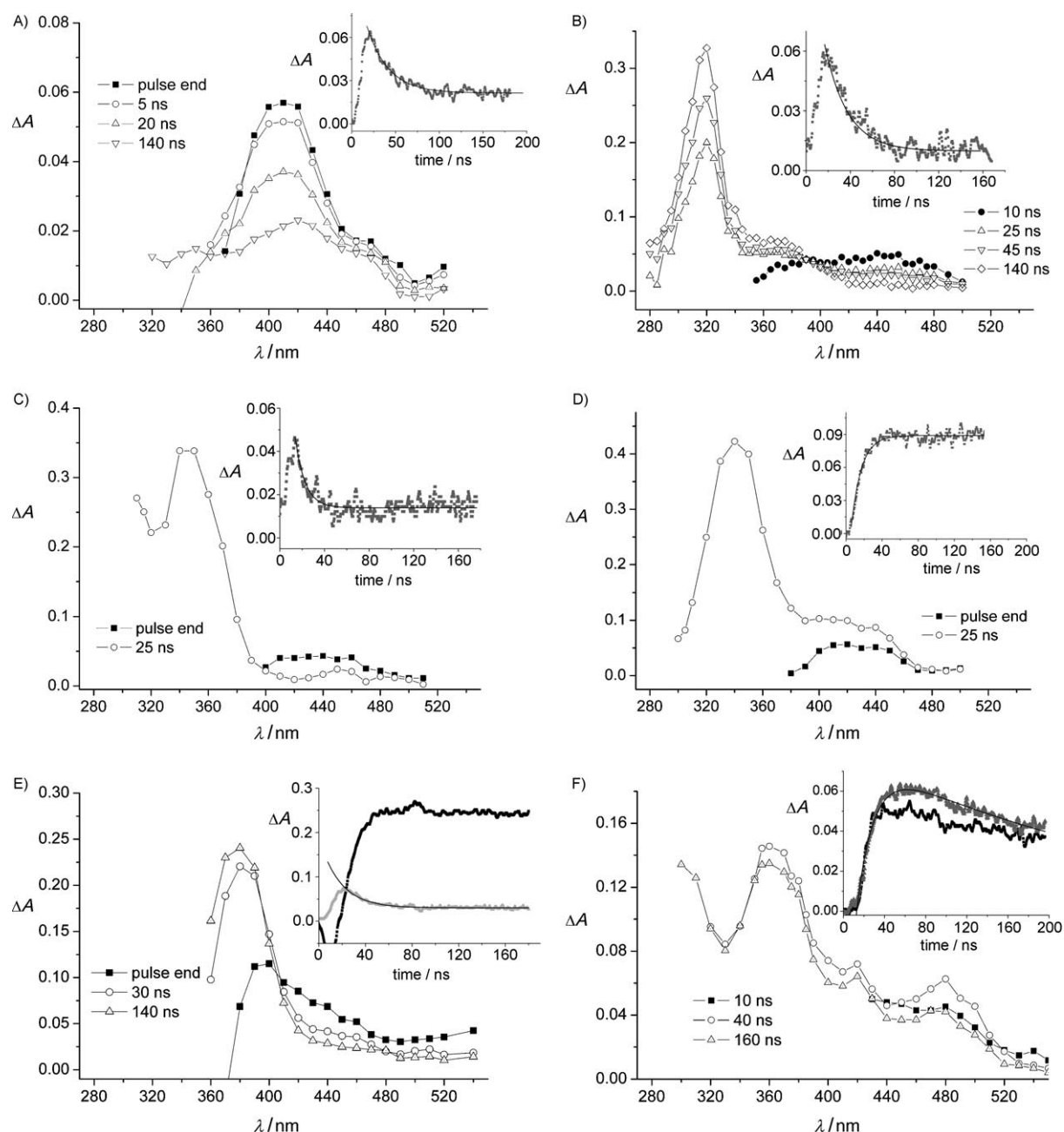


Figure 4. Difference absorption spectra from a solution of **1** (1.3×10^{-3} M) in argon-saturated TFE with various additives at various delays from the end of a 266 nm laser pulse (4.0 mJ per pulse). Insets: zero time at pulse onset. A) No additives. Inset: (ΔA at 410 nm). B) In the presence of DMB (0.2 M). Inset: (ΔA at 440 nm). C) In the presence of 1-hexene (0.2 M). Inset: (ΔA at 440 nm). D) In the presence of 1-hexyne (0.2 M). Inset: (ΔA at 440 nm). E) In the presence of benzene (0.045 M). Inset: (ΔA at 380 (black) and 440 nm (gray)). F) Solution of **1** (1.8×10^{-3} M) in the presence of thiophene (0.062 M). Inset: (ΔA at 450 (black) and 480 nm (gray)).

presence of additive (6×10^{-2} M). No concomitant decrease of the absorption in any other region of the spectrum was observed.

Calculations: The structures and energies of the singlet ($^1\mathbf{15}^+$) and triplet ($^3\mathbf{15}^+$) cations (see Scheme 4) were calculated at the UB3LYP 6-31G(d) level of theory. It was found that the singlet was stabilized by a mere $0.7 \text{ kcal mol}^{-1}$ (in MeCN bulk) with respect to the triplet (see the Supporting

Information). The potential energy surfaces (PESs) for the reactions of both cations with ethylene, acetylene, and benzene were calculated at the same level of theory and the UV spectra of the putative intermediates of the trapping processes were determined on the minima obtained by a time-dependent density functional theory (TD-DFT) method. The spectra are shown in Figure 6A–D (a fixed FWHM of 3000 cm^{-1} was assumed, see the Supporting Information) and comparisons between the experimental findings

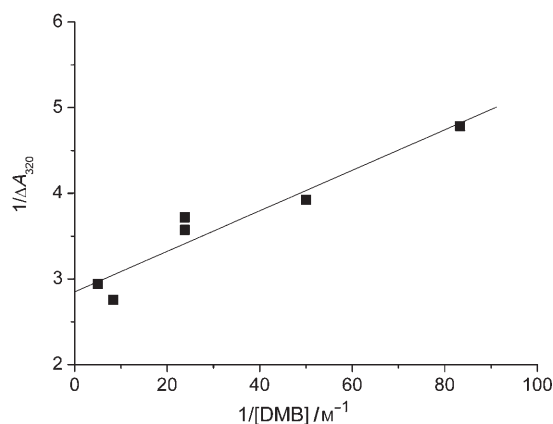


Figure 5. Double reciprocal plot of the maximum absorbance at 320 nm versus the concentration of DMB after exposing a solution of **1** (1.0×10^{-3}) in argon-saturated TFE to a 266 nm laser pulse (4.0 mJ per pulse).

and the features of the PES are discussed below. The calculated spectrum of radical cation **1**^{•+} is shown in Figure 6E.

Mechanism: A general mechanistic frame for the photochemical reactivity of phenyl halides with a strong electron-donating substituent in the *para* position has previously been presented that is based on both experiments and on DFT and CASSCF calculations of the 4-amino derivative.^[10] Thus, in polar solvents, heterolysis of the triplet state of 4-chloroaniline led to the triplet cation 4-NH₂-C₆H₄⁺, which is the lowest-energy spin state of this derivative. Contrary to the singlet cation localized at C1 ($\pi^6\sigma^0$ structure), which reacted unselectively with both π (e.g., water) and π nucleophiles (e.g., alkenes), the triplet cation had a $\pi^5\sigma^1$ structure; this gave C1 a triplet carbene character (one of the unpaired

electrons in the molecular plane, the other one delocalized in the π system) with the charge distributed over the ring. The triplet ions formed a slightly stabilized complex, but did not add to π nucleophiles (e.g., H₂O), whereas addition to π nucleophiles was predicted to occur via a diradical cation intermediate. The purpose of this study was to support this mechanism by detecting the relevant intermediates and establishing a viable kinetic scheme. For the processes discussed in the following see Scheme 4.

There is no doubt that the transient observed in cyclohexane has to be attributed to triplet **3**¹ on the basis of previous reports in the literature, the known efficient intersystem crossing (ISC) [18,21] in anisoles, and the observed oxygen quenching. The only reaction to take place under these conditions was homolysis, which finally yielded **2** via the phenyl radical. This state was liable to moderate quenching by DMB ($k \approx 8 \times 10^7 \text{ s}^{-1} \text{ M}^{-1}$), to form an exciplex. Under these conditions, a mixture of reduced **2** and alkylated products was formed, as previously determined.^[17]

In the other solvents tested, the transient absorption in the UV/Vis spectrum at the end of the pulse was much weaker and shorter-lived (rate of disappearance $\geq 3 \times 10^7 \text{ s}^{-1}$). In contrast, the fluorescence intensity did not change by more than 10% upon varying the solvent. This fact, together with the evidence that will be discussed below, such as the trapping by π nucleophiles and the minimal effect of oxygen on the photoreaction, supports the proposal that in polar solvents cleavage proceeded again from **3**¹, but by a faster process, namely, heterolysis, to yield the triplet phenylum ion **3**¹⁵⁺. In place of the 335 nm absorption, in TFE a different short-lived absorption that peaked at 400 nm was detected at the pulse-end. The same transient could also be distinguished in MeCN/H₂O (5:1, v/v), al-

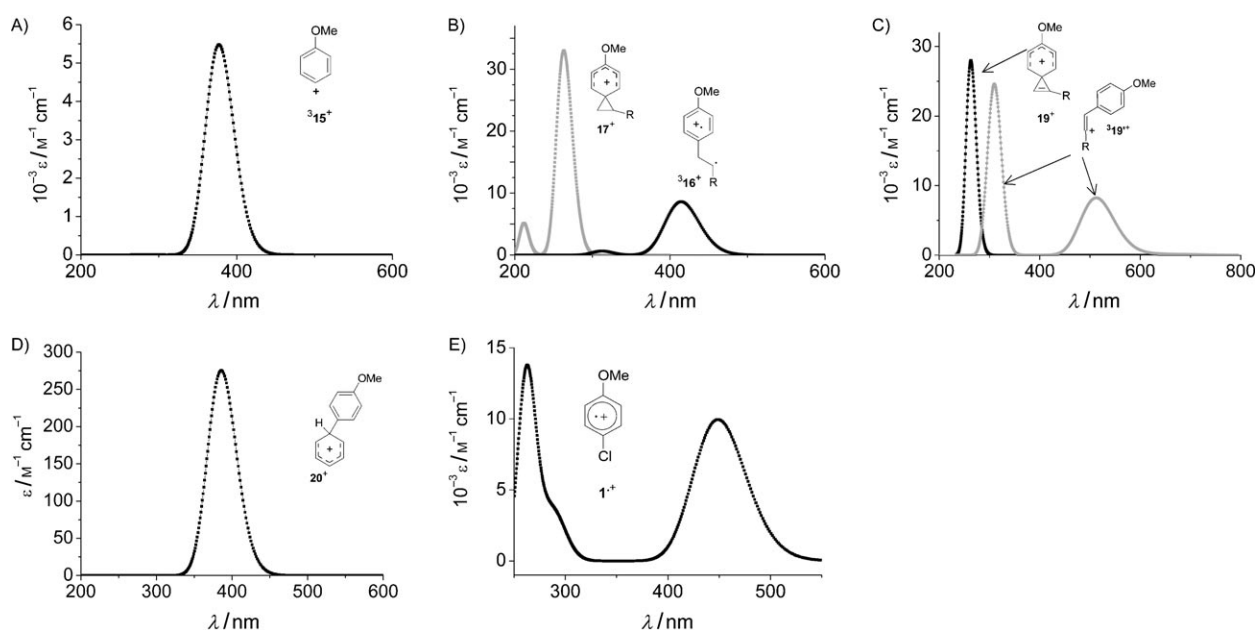
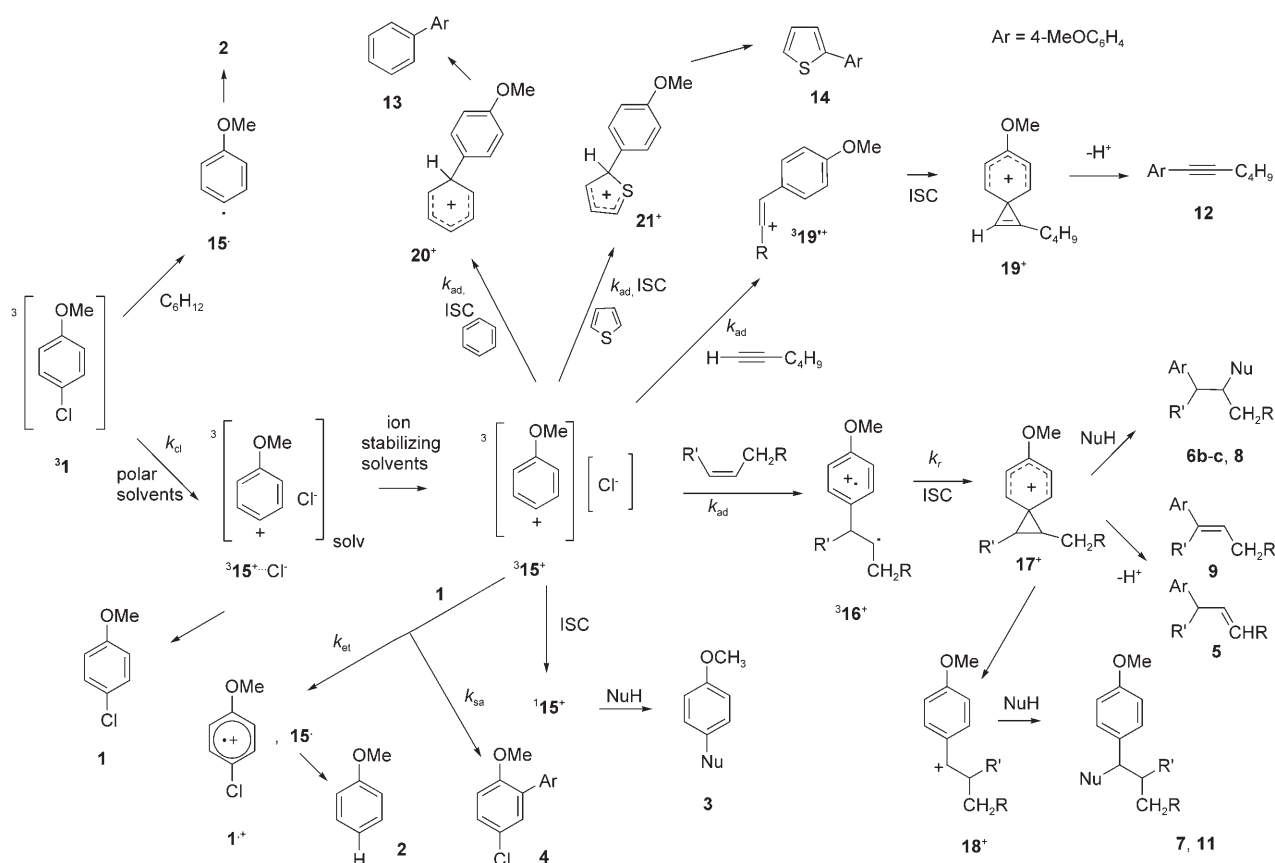


Figure 6. TD-UB3LYP 6-31G(d) calculated spectra for A) 4-methoxyphenyl cation **3**¹⁵⁺ (**1**¹⁵⁺ has a negligible absorption in this region), B) intermediates **16**⁺ (long λ) and **17**⁺ (short λ), C) intermediates **19**⁺ and **19**⁺, D) intermediate **20**⁺, and E) radical cation **1**^{•+}.



Scheme 4. Overall mechanism for the photochemical reaction of 4-chloroanisole.

though it was partially superimposed on another signal (at 460–470 nm, Figure 3A) and was likely to contribute to the absorbance changes observed at 70 ns in MeOH (Figure 2A, see below). This band was thus attributed to the triplet cation and indeed fitted well the calculated spectrum of $^3\mathbf{15}^+$ ($\lambda_{\text{max}}(\text{calcd})=377$ nm; see Figure 6A); note that singlet $^1\mathbf{15}^+$ had no significant absorption in the near-UV region (see the Supporting Information). The lifetime of the transient ($\tau \approx 20$ ns) was appropriate for a cation in a non-nucleophilic, ion-stabilizing solvent, such as TFE (relevant solvent parameter $Y=1.04$, to be compared with $Y=-0.5$ evaluated for MeCN/H₂O (5:1, v/v) and $Y=-1.09$ for MeOH).^[22]

In TFE the free cation was formed and reacted within around 50 ns. In a less ion-stabilizing solvent, such as methanol, cage escape and reaction occurred on a somewhat longer time scale (ca. 300 ns) with the band of triplet $^3\mathbf{15}^+$ less clearly discerned in the initial phase and that of the radical cation $\mathbf{1}^+$ (maximum at 460–470 nm, as proven by its generation by $\text{SO}_4^{\cdot-}$ oxidation and calculations) emerging later (see inset of Figure 2A). This revealed (one of) the reduction mechanism(s), namely, the electron-transfer process [Eq. (1), Scheme 4].

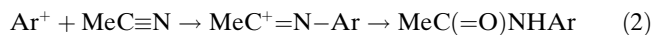


The reaction rate depended on the starting concentration of **1** with a bimolecular rate constant of $k_{\text{et}} \cong 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

Radical cation $\mathbf{1}^+$ was apparent in MeOH because this solvent rapidly reduces $\mathbf{15}^\bullet$ to anisole ($\mathbf{2}$) and prevents back-electron transfer [reverse of Eq. (1)]. However, this is probably a general mechanism, although the amount of intermediates accumulated depended on the medium. The results in MeCN/H₂O were intermediate between those obtained in TFE and MeOH, as one may expect from the intermediate value of Y , with both $^3\mathbf{15}^+$ and $\mathbf{1}^+$ detectable, although with less intense signals than in TFE and MeOH, respectively. This is not surprising, as in poorly ion-stabilizing MeCN ($Y = -3.45$), the quantum yield of the reaction was low and the transients almost undetected.

Most of the end-products observed were those expected from cation **315⁺** by reaction with the starting material or with the solvent. The reaction with **1** gave either reduced **2** (by electron transfer) or self-attack diphenyldiamine **4** (by addition, see Scheme 4). Competition between the two processes ($k_{\text{et}}/k_{\text{sa}}$) depended on the medium and addition was important in an ion-stabilizing, less nucleophilic solvent, such as TFE (see Table 2). Reactions with the solvent involve fluoride abstraction from TFE (a process previously observed on decomposition of benzenediazonium salts in this solvent)^[23] and solvolysis. The latter reaction was that expected of singlet **115⁺** and gave products **3a–c**. However, these were not formed in the presence of π nucleophiles; arylated products, diagnostic of the triplet cation, formed instead. Clearly, **315⁺** was generated as the first intermediate

by photoheterolysis of $^3\mathbf{1}$, but in the absence of a convenient trap, intersystem crossing to the almost isoenergetic singlet (calculated $\Delta G_{\text{ST}} = 0.7 \text{ kcal mol}^{-1}$) occurred. Singlet $^1\mathbf{15}^+$ is an unselective electrophile and gave ethers $\mathbf{3b}$ and $\mathbf{3c}$ with MeOH and TFE, respectively. In MeCN/H₂O addition to the solvent gave $\mathbf{3a}$ [Ritter reaction, see Eq. (2)].



The formation of such products allowed us to assess the singlet reaction path, even though $^1\mathbf{15}^+$ did not absorb in the accessible λ window, and their absence when triplet diagnostic products were formed allowed the chemistry of the two spin states to be distinguished.

Trapping by π nucleophiles was best followed in TFE in which the formation of the phenylum ion was conspicuous. Calculation of the PES for the reaction of the triplet cation with ethylene supported the proposal that addition to alkenes led to a single-bonded triplet diradical as the first intermediate. Formation of a second C–C bond and intersystem crossing led to the strongly stabilized (singlet) phenonium ion.^[10] This mechanism fitted nicely with the sequence of events observed in the flash photolysis experiments performed in the presence of DMB (0.2 M). Thus, complete quenching of $^3\mathbf{15}^+$ within the laser pulse was accompanied by the appearance of a new transient ($\lambda_{\text{max}} = 440 \text{ nm}$), which in turn converted ($k \approx 5 \times 10^7 \text{ s}^{-1}$) into a longer-lived species ($\lambda_{\text{max}} = 320 \text{ nm}$). These intermediates were identified as the open-chain cation $^3\mathbf{16}^+$ and phenonium ion $\mathbf{17}^+$, respectively, and indeed the experimental spectra closely corresponded to those calculated for these species ($\lambda_{\text{max}}(\text{calcd}) = 414$ and 272 nm , respectively, see Figures 4B and 6B). Also, the rate constant measured for the formation of $\mathbf{17}^+$ is consistent with the occurrence of a spin-forbidden process. The trapping of triplet $^3\mathbf{15}^+$ by DMB was efficient and the yield of adduct cation $\mathbf{17}^+$ reached a plateau at a DMB concentration of $\approx 0.1 \text{ M}$. The double reciprocal plot in Figure 5 shows a linear fit in agreement with Equation (3):

$$\frac{1}{\epsilon_{320}[\mathbf{17}^+]} = \frac{1}{\epsilon_{320}\eta} \left(1 + \frac{k_d}{k_{\text{ad}}[\text{DMB}]} \right) \quad (3)$$

in which ϵ_{320} is the molar absorption coefficient (optical path 1 cm), η is the overall yield of $\mathbf{17}^+$, k_d is the rate constant for decay of the phenylum cation in the absence of trap, and k_{ad} is the bimolecular rate constant for the addition reaction. From the intercept/slope ratio, the value $k_{\text{ad}}/k_d = 120 \text{ M}^{-1}$ was extracted, which indicates that quenching of $^3\mathbf{15}^+$ by DMB occurs with a rate constant close to diffusion control ($k_{\text{ad}} \approx 6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), on the basis that $k_d \approx 5 \times 10^7 \text{ s}^{-1}$. In turn, the final products were obtained from adduct cation $\mathbf{17}^+$ either by deprotonation or by nucleophile addition, although with the additional complication that a Wagner–Meerwein shift of a methyl group (R') to form a benzylic cation ($\mathbf{18}^+$) might precede the final step (as shown by the formation of product $\mathbf{7}$ and analogously the formation of $\mathbf{11}$

from 1-hexene by a hydride shift). Such a rearrangement was expected and is diagnostic of a carbocation, but again had been previously reported to occur from the phenonium ion only under strongly acidic conditions.^[13]

Summing up, DMB efficiently quenched $^3\mathbf{15}^+$ to form, as predicted by calculations, diradical adduct $^3\mathbf{16}^+$ and closed-shell $\mathbf{17}^+$, and the course of the reaction could be followed step-by-step by flash photolysis. A similar course was followed with 1-hexene, with the first intermediate barely distinguishable by a decreasing absorbance at 440 nm , but a strongly absorbing phenonium ion was observed ($\mathbf{17}^+$, $\lambda_{\text{max}} = 340 \text{ nm}$, Figure 4C).

With alkynes, calculation of the PES predicted the formation of an open-chain triplet cation $^3\mathbf{19}^+$ as the first intermediate, which then collapsed (upon ISC) to the ring-closed vinylphenonium $\mathbf{19}^+$.^[15a,b,24] In the experiment with 1-hexyne a conspicuous transient was detected ($\lambda_{\text{max}} = 340 \text{ nm}$, Figure 4D) although the final spectrum retained a shoulder at $400\text{--}440 \text{ nm}$. The observed transient corresponded to that of $^3\mathbf{19}^+$ ($\lambda_{\text{max}}(\text{calcd}) = 310 \text{ nm}$), whereas isomeric $\mathbf{19}^+$ was less easily observed because of the blueshifted spectrum ($\lambda_{\text{max}}(\text{calcd}) = 262 \text{ nm}$, see Figure 4D and Figure 6C). Reduction of these high-energy ions to give $\mathbf{12}$ as the end-product is in accordance with previous findings.^[25]

With benzene as the trap, an open-chain triplet adduct was not markedly stabilized and a single transient (strong absorption with $\lambda_{\text{max}} = 380 \text{ nm}$) could be observed by flash photolysis. This was attributed with confidence to benzenium cation $\mathbf{20}^+$ on the basis of its closeness to the calculated band at 385 nm (see Figure 6D). This transient absorption was identical to that observed by Steenken, McClelland and co-workers by photolysis of phenyldiazonium tetrafluoroborate in the presence of triisopropylbenzene.^[7] Note, however, that photolysis of the diazonium salt yielded the singlet cation as a nonselective intermediate. Indeed, these authors were able to observe cation $\mathbf{20}^+$ only in an extremely non-nucleophilic solvent, such as 1,1,1,3,3,3-hexafluoroisopropyl alcohol.^[26] In our case, photolysis of 4-chloroanisole yielded triplet cation $^3\mathbf{15}^+$, which reacted preferentially with π nucleophiles. The cationic adduct with benzene (at the same concentration) was clearly detected in TFE and also in the other polar solvents tested, although it was less clear-cut in some cases. A heteroaromatic molecule, such as thiophene, also gave a transient at $\lambda_{\text{max}} = 360 \text{ nm}$, which was attributed to the analogous cation $\mathbf{21}^+$.

The overall mechanism proposed for the photochemical reactions of $\mathbf{1}$ is presented in Scheme 4.

Conclusion

Conditions for observing a phenylum ion in solution have been found for the first time, the role of this species in reactions has been demonstrated, and the assignment is supported by calculations. The agreement between predicted and observed chemistry, as well as between the calculated and observed spectra of the intermediates, has demonstrated the

spin-dependent chemistry of the phenylium ion first suggested by Schuster and co-workers in 1995.^[2f] In accordance with previous reports,^[6] we have shown by calculation that singlet phenylium has no convenient absorption window and may escape detection, but calculations and product studies have demonstrated that it does play a role to play. In contrast to the singlet state, triplet phenylium is a synthetically useful intermediate owing to its selective reactions with π nucleophiles, which have been characterized in detail. As an example, addition to an alkene is calculated to yield an open-chain cation adduct that then converts by intersystem crossing into the phenonium cation ($^3\mathbf{15}^+ \rightarrow ^3\mathbf{16}^+ \rightarrow ^1\mathbf{17}^+$) and in fact three spectra (very similar to those calculated) can be observed that have an isosbestic point (Figure 4B) and rate constants that fit expectation. Under such conditions, none of the products expected from the singlet is observed, thus excluding its formation as the primary intermediate upon dechlorination, although they are found in the absence of traps, which indicates that ISC to the singlet can occur as a secondary step.

Photoheterolysis of phenyl halides in the presence of suitable traps under neutral, mild conditions, has thus allowed us to obtain cationic adducts by C–C bond formation, namely, phenonium ions with alkenes, phenylvinyl cations (or vinylenphenonium ions) with alkynes, and a benzenium ion from benzene. The ions have been identified under the same (and very mild) conditions and full agreement between experimental data and calculations was observed. These intermediates have been the object of intense investigation and in some cases have previously been characterized, although generally under acidic conditions. The development of a mild method for their generation greatly enlarges the choice of conditions available for their exploitation, and thus, the control over the final outcome, which hopefully will allow the use of these versatile intermediates for preparative purposes.^[10]

Experimental Section

The photochemical reactions were performed by using nitrogen-purged solutions in quartz tubes in a multilamp reactor fitted with six 15 W phosphor-coated lamps (maximum emission = 310 nm) for irradiation. The photoproducts were isolated by chromatography and compared with authentic samples or identified by chemical and spectroscopic analysis. Nanosecond laser flash photolysis experiments were carried out by using a JK-Laser Nd-YAG laser operated at $\lambda = 266$ nm and pulse FWHM = 20 ns; the minimum response time of the detection system was around 2 ns (see the Supporting Information). The structures and energies of the singlet and triplet 4-methoxyphenylium ions and the PES for the reactions with ethylene, acetylene, and benzene were calculated at the UB3LYP/6-31G(d) level of theory by using the Gaussian 03 package^[27] (see the Supporting Information). The spectra of transients were calculated by the TD-DFT method (see the Supporting Information).

Acknowledgements

We thank Dr. Francesco Manoli for technical support and the MIUR for partial support of this work.

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Received: July 6, 2007

Published online: November 14, 2007