Laser Flash Photolysis Studies of Carbocations Generated from (Naphthylmethyl)phosphonium Chlorides[1]

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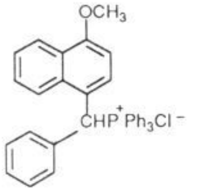
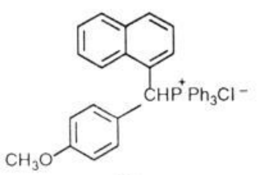
Despite the importance of carbocations as intermediates in organic chemistry, only a few recent studies have dealt with time-resolved measurements of their lifetimes and reactivity.[3-13] Laser flash photolysis studies include several diaryl- and triarylmethyl carbocations generated by heterolytic photocleavage of Ar_2CHX and Ar_3CX precursors with leaving groups such as halide, acetate, tosylate, and 4-cyanophenoxide. We report herein the first examples of time-resolved studies of carbocations containing naphthalene moieties[14] and on the use of phosphonium salts as cation precursors. We have also observed remarkable effects of lithium perchlorate on cation lifetimes and reactivities toward azide. Our studies center on the photolysis of I and II at 308 nm.



I



II

Laser excitation of 5×10^{-5} M I in either nitrogen- or oxygen-purged 2,2,2-trifluoroethanol (TFE) or acetonitrile generated a strongly absorbing transient with λ_{max} at 500 nm and with a second small band at ~360 nm (Figure 1, top).[15] The lifetime of this species was longer than we could monitor in TFE (>100 μs) and was approximately 2.5 μs in acetonitrile. In the latter, the transient decays at 500 and 360 nm yielded lifetimes that were the same within experimental error, suggesting that both bands belonged to the same species. A similar transient was observed in methanol, where the lifetime was 105 ns. Both the short lifetime in the more nucleophilic solvent, methanol, and the insensitivity to oxygen are consistent with assignment of the transient to a carbocation. Furthermore, the related methoxy-substituted diphenylmethyl carbocations absorb in the 450–500-nm region.[5] The cation assignment was further confirmed by determining the rate constants for azide and chloride (as NaN_3 and KCl) quenching; values of 1.8×10^{10} and 2.2×10^{9} M^{-1} s^{-1}, respectively, were obtained by monitoring the effect of increasing quencher concentration on the decay of the 500-nm band in 5% aqueous acetonitrile.

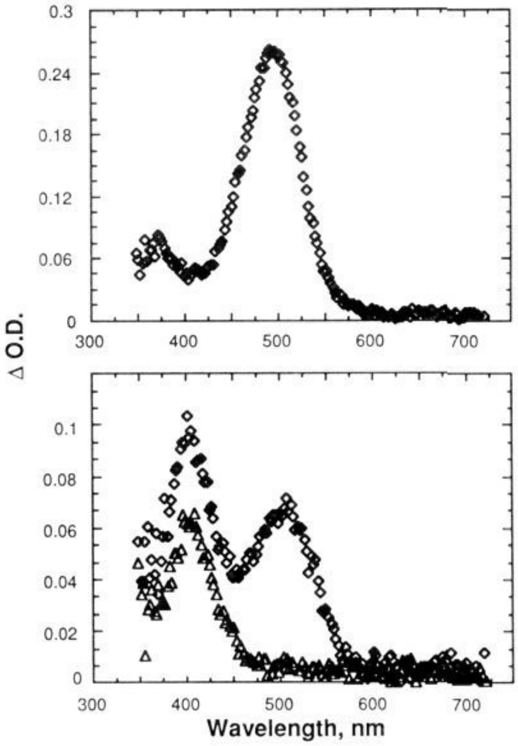


Figure 1. Transient absorption spectra produced by 308-nm excitation of I in TFE (top, 2 μs following laser excitation) and 1:4 acetonitrile/dioxane [bottom, 0.5 μs (◇) and 10 μs (△)].

Excitation of I in acetonitrile/dioxane mixtures showed the presence of an additional transient, which was longer lived than the carbocation (Figure 1, bottom). For example, the cation had a lifetime of 1.3 ± 0.2 μs in 1:9 acetonitrile/dioxane, while the 400-nm transient had a lifetime in excess of 10 μs. Two obvious candidates for the 400-nm species are triplet I and the (4-methoxy-1-naphthyl)phenylmethyl radical (III) expected from homolytic cleavage. Several experiments were done to distinguish between these two possibilities.[16] The 400-nm transient was also obtained from (4-methoxy-1-naphthyl)phenylmethyl chloride (IV) in cyclohexane.[19] In both cases, the transient was quenched by oxygen but not by 1,3-cyclohexadiene, which favors its assignment to a radical rather than a triplet. The relative yields of radical versus cation varied considerably with the solvent composition; only radical was observed between 1% and 5% acetonitrile in dioxane, whereas essentially only the cation was produced in pure acetonitrile. There was no evidence for any radical formation in TFE, and the limited solubility of I made it difficult to examine

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(14) There are several reports of product studies that have examined the competition between homolytic and heterolytic cleavage in naphthylmethyl systems: Arnold, B.; Jurgens, D. A.; Pincock, J. A. *Can. J. Chem.* **1985**, *63*, 3140–3146. Foster, B.; Gaillard, B.; Mathur, N.; Pincock, A. L.; Pincock, J. A.; Sehmbey, C. *Can. J. Chem.* **1987**, *65*, 1599–1607. Slocum, G. H.; Schuster, G. B. *J. Org. Chem.* **1984**, *49*, 2177–2185.

(15) All experiments were carried out by using flow samples to prevent depletion of the precursor and product buildup.

(16) Naphthalene triplets generally absorb at ~420 nm;[17] the 1-naphthylmethyl radical has λ_{max} at 365 nm[18] and would be expected to be red-shifted by phenyl substitution.

(17) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1–250.

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(19) There are problems with thermal solvolysis of this chloride in polar solvents. However, it is interesting to note that there is approximately three times more radical from this precursor than from I.

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the relative yields of cation and radical in nonpolar solvents. We note that in our transient experiments we would not observe any species that react within the initial geminate cage, so the relative yields do not necessarily coincide with those expected in product studies.

A growth was not observed for either the cation or radical signals on short time scales, indicating a short-lived excited-state precursor. In agreement with this, we observed only a very weak fluorescence from a number of naphthyl-substituted phosphonium salts, despite the strong, long-lived emission typical of naphthalenes. The observation of radical fluorescence upon excitation of chloride IV also suggests that the bond cleavage occurs within the $\sim$5-ns laser pulse.

The effect of added lithium perchlorate on the cation lifetime was examined in acetonitrile. Addition of 0.44 M salt led to a cation lifetime of $\sim$30 μs as compared to a value of 2.5 μs in the absence of lithium perchlorate and to a 70% increase in the amount of cation detected. While the effect of added salt may be anticipated in view of its known effect on ground-state solvolyses,[20] this is one of the first direct measurements of its effect on the cation lifetime.[21] Much more modest effects were observed in 4:1 TFE/water; we attribute this to the enhanced stability of the cation in this solvent as compared to acetonitrile. The cation reactivity toward nucleophiles was also modified by the presence of added salts. Thus, the rate constant for azide quenching of 1.8×10^{10} M^{-1} s^{-1} in 5% aqueous acetonitrile decreased to 3.5×10^{9} M^{-1} s^{-1} upon addition of 0.1 M LiClO$_4$, and even larger effects were observed for less reactive nucleophiles.

The lifetime of the cation decreased with increasing concentration of the phosphonium salt precursor. For example, a 3-fold increase in the concentration of I ($5-15 \times 10^{-5}$ M in 1:1 acetonitrile/dioxane) reduced the cation lifetime from 1.5 to 0.5 μs. Further, higher concentrations of I can be employed when 337-nm excitation is used; thus, 10^{-3} M I gave a 100-ns lifetime for the cation, which allows a rough estimate of $\sim 10^{10}$ M^{-1} s^{-1} for the rate constant for quenching of the cation by I in acetonitrile. This efficient quenching is largely due to chloride. Some unusual laser-dose effects may also be related to this reaction. The lifetime of the cation decreased from 1.4 to 0.7 μs in 1:1 acetonitrile/dioxane when the laser energy was attenuated to 11% of its initial value. This is the opposite effect to that expected for a second-order contribution to the transient decay. However, it is consistent with an enhanced availability of free chloride ion from the tetraphenylphosphonium salt as compared to HCl in organic solvents. Note that, at high laser doses, a significant fraction of the initial salt molecules are converted to products, which results in a lower concentration of salt (and, therefore, less "free" chloride) and a longer cation lifetime. This is consistent with the fact that the laser dose has very little effect on the cation lifetime in aqueous acetonitrile where association of chloride with either counterion is less important. The longer lifetime of the cation in aqueous acetonitrile as compared to the neat solvent is also a factor. Lifetimes of 2.5 and 7.5 μs were measured in acetonitrile and 10% aqueous acetonitrile, respectively, but only small increases were observed at higher water concentrations.

Salt II was also briefly examined. Excitation (308 nm) yielded a transient with λ_{max} at 550 nm in both TFE and acetonitrile and with lifetimes of >35 μs and 350 ns, respectively. This species could also be readily assigned to a carbocation on the basis of its characteristic quenching by azide ion and its insensitivity to oxygen.

These initial experiments have demonstrated the utility of phosphonium salts I and II as precursors for transient cations. Although the same cations can be generated from appropriate precursors in strong acids, transient techniques offer the advantage of examining these species under conditions where their reactivity can be examined. Our results also demonstrate the sensitivity of cation yields and reaction kinetics to the presence of added lithium perchlorate. Studies of such effects are of obvious importance, given the large amount of literature data based on the competition with azide ions. Further experiments aimed at examining these salt effects in more detail and quantifying the cation and radical yields as a function of solvent and precursor are in progress.

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Registry No. I, 124535-67-7; II, 124535-68-8; LiClO$_4$, 7791-03-9; azide, 14343-69-2.

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Electron Transfer Reactions between Bis(4-methoxyphenyl)methyl Cations and Triplet 1-Methoxynaphthalene[1]

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Carbocations are intermediates in a wide variety of thermal and photochemical reactions,[3,4] and their reactivity toward nucleophiles has been extensively studied by conventional competitive product studies and, more recently, by direct methods using laser flash photolysis or time resolved conductivity techniques.[5-9] Despite this wealth of information, there are very few cases in which electron-transfer reactions of these species have been examined,[10] although products resulting from electron transfer from excited singlet sensitizers to heteroatom-centered cations have been reported for a variety of sulfonium, iminium, and iodonium salts.[13] We report herein preliminary results that demonstrate that the bis(4-methoxyphenyl)methyl carbocation (I) is reduced to the corresponding radical via electron-transfer quenching of triplet

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