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.

Acknowledgment. Thanks are due to S. E. Sugamori for technical assistance and to Dr. R. A. McClelland for the communication of unpublished material. E.O.A. thanks CAPES (Brazil) for a fellowship.

Registry No. I, 124535-67-7; II, 124535-68-8; $LiClO_4$, 7791-03-9; azide, 14343-69-2.

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[21] To our knowledge, the only reports are a brief mention of the effect of sodium perchlorate on the lifetime of triphenylmethyl cations in aqueous ethanol[10] and the reported 30% increase in lifetime for the triphenylmethyl cation in the presence of sodium perchlorate in aqueous acetonitrile.[3]

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

L. J. Johnston* and T. Kanigan[2]

Division of Chemistry
National Research Council of Canada
Ottawa, Ontario, Canada K1A 0R6

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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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[1] Issued as NRCC 30992.

[2] NRCC summer student.

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[9] Johnston, L. J.; Lobaugh, J.; Wintgens, V. *J. Phys. Chem.* **1989**, *93*, 7370-7374. Alonso, E. O.; Johnston, L. J.; Scaiano, J. C.; Toscano, V. G. *J. Am. Chem. Soc.*, preceding paper in this issue.

[10] To our knowledge, the observation of electron transfer processes in the photochemistry of the dianisylethyl cation[11] and of charge-transfer complexes between tropylium salts and aromatic hydrocarbons[12] are the only examples.

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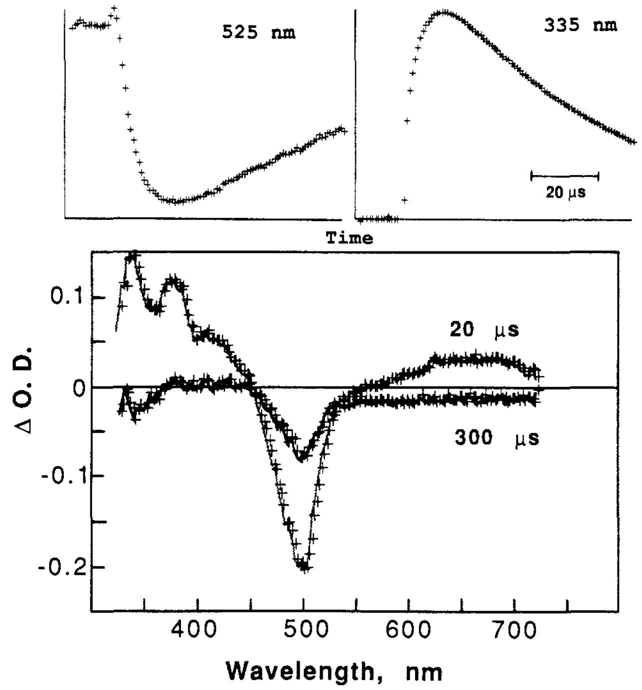
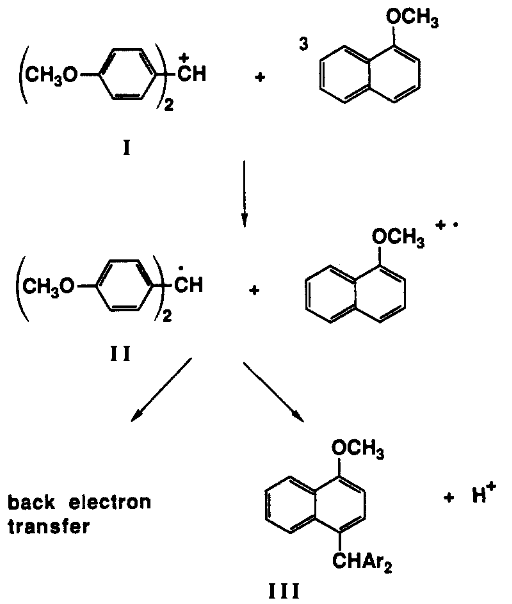


Figure 1. Top: changes in optical density recorded at 525 and 335 nm following 308-nm excitation of 1-methoxynaphthalene in the presence of 1 mM 4,4′-dimethoxybenzhydrol in TFA/TFE. Bottom: transient absorption spectra measured 20 μs (dashed line) and 300 μs (solid line) after the laser pulse for the same sample.

sensitizers. Furthermore, the final product in at least one system results from coupling of the diarylmethyl radical and the sensitizer radical cation. Although radical/radical anion coupling reactions have been observed in a number of cases,[14-16] there are, to our knowledge, few reports of products resulting from coupling of radical cations and radicals.[13,17-19]

Carbocation I may be readily generated by addition of moderate concentrations of trifluoroacetic acid (TFA) to 4,4′-dimethoxybenzhydrol in 2,2,2-trifluoroethanol (TFE) and is stable for days under these conditions. Laser excitation (308 or 337 nm) of either anthracene or 1-methoxynaphthalene in TFE leads rapidly and efficiently to their respective triplet states, both with λ_{max} at ~420 nm. Under our conditions, both triplets have lifetimes in excess of 20–30 μs in the absence of quenchers and show mixed first- and second-order kinetics due to the occurrence of some triplet–triplet annihilation. However, when either triplet was produced in the presence of cation I, its lifetime was shortened substantially and the decay became cleanly first order. Furthermore, the decrease in the triplet lifetime was proportional to the amount of cation present. Control experiments demonstrated that the decreased triplet lifetimes did not result from quenching of the triplet by acid or by the alcohol precursor of the cation, as neither of these had any significant effect at the maximum concentration used in our experiments. A rate constant of $\sim 1 \times 10^9$ M^{-1} s^{-1} was estimated for the reaction of cation I with 1-methoxynaphthalene. Only a limited range of cation concentrations[20] was used in the transient experiments since I absorbs strongly in the visible and this prevented a more accurate determination of the quenching rate constant.

Scheme I



Monitoring of changes in the optical density of the solution in the region of the cation absorption shows that depletion of the cation absorption occurs concomitantly with the triplet decay as shown in Figure 1 for the 1-methoxynaphthalene system. Furthermore, the kinetics for the triplet decay agree well with those for the evolution of the cation depletion. These results, in combination with the fact that excitation of a solution containing cation but no sensitizer does not lead to bleaching of the cation, indicate that the sensitizer triplet is reacting with the cation. Examination of the transient absorption spectra at various times after the laser pulse shows that other transients are produced as a result of this quenching process. Thus, at early times (<1 μs), the spectrum (which records changes in optical density before and after the laser pulse) shows only the triplet–triplet absorption of the sensitizer. However, at longer delays for 1-methoxynaphthalene, there are new transients in the 650–700-nm region, at 380 nm, and at 335 nm, in addition to the bleaching of the cation absorption at 500 nm (figure 1). These may be readily assigned to the radical cation of the sensitizer (650–700 nm, 380 nm) and the bis(4-methoxyphenyl)methyl radical (II, 335 nm) on the basis of literature spectra for the radical cation[21] and a variety of diphenylmethyl radicals.[22] Further evidence for the formation of these species as a result of triplet quenching by the cation comes from the fact that the growth of the transient absorption at either 335 or 650 nm agrees well with that of the cation bleaching at 525 nm. Similar results were obtained in the anthracene system, although in this case it was more difficult to obtain convincing evidence for the radical at 335 nm since both the ground state and radical cation of the sensitizer absorb in this region.

Figure 1 also shows a spectrum measured after the radical cation and radical had completely decayed (300 μs) and indicates that a considerable fraction (~70%) of the initial cation bleaching recovers. This suggests that back electron transfer between the radical cation and the radical dominates the decay of these two species. However, the incomplete recovery also demonstrates that there is some net chemistry in this system, and accordingly we undertook a preparative irradiation to identify the products. Thus, irradiation of 1-methoxynaphthalene (5 mM) in the presence of 4 mM 4,4′-dimethoxybenzhydrol and 0.26 M TFA in TFE led to rapid disappearance of the characteristic cation absorption and the concomitant formation of longer wavelength absorptions. The longer wavelength absorption disappeared upon neutralization of

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the solution with sodium hydroxide. HPLC analysis showed loss of both the sensitizer and the cation[23] and the formation of one major new product, which, on the basis of LC/MS evidence, appeared to be an adduct (III) resulting from addition of radical II to the sensitizer (Scheme I). Isolation of the adduct by chromatography on a preparative reverse-phase column confirmed this assignment.[24,25] An additional minor product is also observed by HPLC; LC/MS data is consistent with the radical dimer.

The above results provide conclusive evidence for the electron transfer quenching of triplet 1-methoxynaphthalene by cation I (Scheme I). On the basis of the known oxidation potentials of 0.16 and 1.38 eV for the (4-methoxyphenyl)phenylmethyl radical[26] and 1-methoxynaphthalene,[27] respectively, and the triplet energy for the latter (59.7 kcal/mol),[28] we estimate that this process should be exothermic by ~31 kcal/mol.[29] The relatively efficient formation of separated radicals and radical cations is consistent with the triplet nature of the initial radical/radical ion pair, which allows cage except to compete favorably with back electron transfer. The amount of irreversible cation depletion (~30%) observed in the transient experiments demonstrates that radical/radical cation coupling competes relatively efficiently with back electron transfer, although the latter step is also highly exothermic. Further experiments aimed at measuring the quantum yields for adduct formation and investigating the generality of both the electron transfer reaction and the coupling of the radical and radical cation for a variety of sensitizers and cations are in progress. The variations in the forward and back electron transfer depending on the redox properties of the sensitizer and the cation are of particular interest.

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[23] Neutralization of an unirradiated sample of the cation with an equimolar amount of sodium hydroxide gives clean conversion to the corresponding trifluoromethyl ethyl ether.

[24] Physical data for the adduct was consistent with the proposed structure.

[25] The same product can be generated in a thermal reaction between the cation and 1-methoxynaphthalene when the sensitizer and cation are present in much higher concentrations (>0.05 M); an analogous reaction has been reported between the dianisylethyl cation and 1,2,4-trimethoxybenzene.[12]

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Prediction by AM1 of More Reasonable Geometries for 1,2-Diphenylcycloalkenes Than by Other Semiempirical MO Methods

Martin Müller and Georg Hohlneicher*

Lehrstuhl für Theoretische Chemie
Universität zu Köln, Greinstrasse 4
D-5000 Köln 41, Federal Republic of Germany

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In a recent publication,[1] we discussed the geometric and electronic structures of 1,2-diphenylcycloalkenes with $n = 0$–4, where $n = 0$ refers to *cis*-stilbene (see Figure 1).

In that paper, we stated that none of the frequently successfully applied semiempirical MO methods such as MNDO[2] or MINDO[3] were able to predict a reasonable structure for these sterically hindered molecules (see Table I). The steric hindrance caused primarily by H-H interactions completely overrides the π-interaction that tends to stabilize more planar structures of the conjugated system. In contrast, force-field methods such as MMP2[4] or QCFF/PI[5] provide structures that are in good agreement with the results derived from a variety of experimental methods.[1] We now have applied AM1[6] to the same problem and found that the torsion angles Ω and θ predicted by this method are in much better accordance with those obtained from force-field methods. The main change in AM1 compared to some earlier semiempirical methods is the reparametrization of the nuclear repulsion integrals.[7]

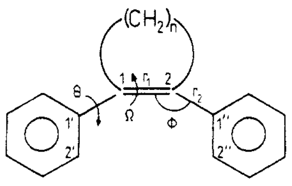

Figure 1.

Table I. Optimized Geometries Derived from Three Different Semiempirical MO Methods and from the Force-Field Method QCFF/PI[a]

n	method	r_1	r_2	ϕ, deg	θ, deg	Ω, deg
0	exptl	1.34	1.49	129	43	
	QCFF/PI	1.35	1.49	127	35	9
	MINDO/3	1.34	1.50	135	90	0
	MNDO	1.35	1.48	129	75	0
	AM1	1.34	1.46	128	47	1
1	exptl					
	QCFF/PI	1.34	1.42	151	7	4
	MINDO/3	1.35	1.48	152	79	1.5
	MNDO	1.34	1.44	152	26	2.7
	AM1	1.33	1.42	152	2	0.3
2	exptl	1.35	1.47	137	16/26	10
	QCFF/PI	1.36	1.46	136	23	9
	MINDO/3	1.38	1.50	138	83	1.5
	MNDO	1.38	1.47	136	65	1.5
	AM1	1.38	1.44	138	27	1.7
3	exptl	1.34	1.48	125	44/48	8
	QCFF/PI	1.36	1.49	128	36	10
	MINDO/3	1.38	1.51	130	90	1
	MNDO	1.36	1.48	128	84	0.5
	AM1	1.36	1.45	129	50	2
4	exptl	1.33	1.49	125	40/55	7
	QCFF/PI	1.36	1.51	122	50	10
	MINDO/3	1.38	1.53	126	90	0.9
	MNDO	1.36	1.50	123	88	0
	AM1	1.33	1.47	124	63	2.7

[a] The experimental geometries are the same as those discussed in ref 6.

Examining the results in somewhat more detail, we find two trends that are worth mentioning (see Table I): (i) The angle Ω describing the torsion of the central double bond is predicted as fairly rigid in AM1. The force-field methods predict a somewhat higher flexibility, in better agreement with the experimental findings. (ii) The length of the single bond that connects the phenyl rings to the double bond is predicted as a little too short by AM1. MNDO seems to yield the best average results with respect to this bond length.

In comparing theoretical and experimental values of the torsion angle θ, we have to be aware that the torsional potential is flat and very anharmonic.[1] The thermal average of θ is therefore always larger than the value corresponding to the minimum of the potential. Since it is this latter value that is obtained from calculations, we expect the theoretical values to be somewhat smaller than the observed ones.[8] This is the case with the

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