248-nm Laser Flash Photoprotonation of Mesitylene, Hexamethylbenzene, and 1,3,5-Trimethoxybenzene in 1,1,1,3,3,3-Hexafluoroisopropyl Alcohol. Formation and Electrophilic Reactivities of the Cyclohexadienyl Cations

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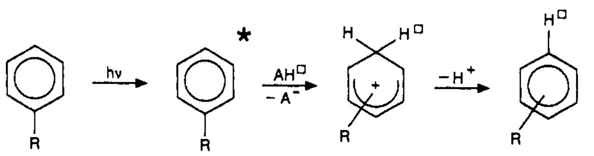
Proton exchange upon photolysis of aromatic compounds in acidic solutions suggests that the excited aromatic species is protonated to form an intermediate cyclohexadienyl cation.[2] Quenching of the fluorescence of aromatic compounds by acids[2-4] and ipso photosubstitution[3c] have been interpreted in terms of the same mechanism. Photoreactions proceeding by way of carbocations are well established,[5] and there have been a number of recent reports using flash photolysis to detect the intermediates and to study directly the kinetics of their reactions.[6] This, however, has not been done for photoprotonation of aromatics (eq 1). In fact, although cyclohexadienyl cations are well established in strong acids,[7] there is no information regarding their lifetime under solvolytic conditions (in the presence of nucleophiles), except for some highly stabilized examples.[8] We have recently found that the solvent 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP) has a dramatic kinetic stabilizing effect for the 9-fluorenyl cation.[6f] In this paper we report that this solvent has the additional property of being sufficiently acidic to effect protonation of electronically excited aromatic compounds without the need for added stronger acids. It is thus possible to produce, characterize spectroscopically, and kinetically study cyclohexadienyl cations. As examples, data on those derived from mesitylene (MES), hexamethylbenzene (HMB), and 1,3,5-trimethoxybenzene (TMB) are reported.



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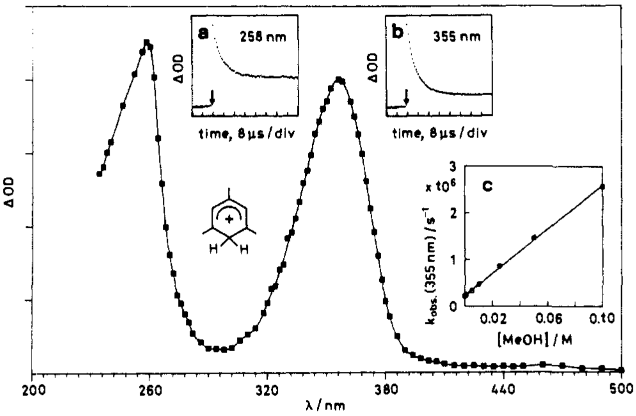

Figure 1. Absorption spectrum of MESH$^+$ produced by 248-nm photolysis of 10 mM MES in HFIP at 20 ± 1 °C and measured at 100 ns after the laser pulse. The inserts show the decay of MESH$^+$ at (a) 258 nm and (b) 355 nm and (c) the dependence on [MeOH] of k_{obsd} for decay monitored at 355 nm. The arrows show the position of the laser pulse.

The result obtained on photolysis of MES is shown in Figure 1: A transient with two absorption peaks appears within the 20-ns laser pulse and decays exponentially, with the same rates at the two wavelengths (inserts a and b). There is no difference between oxygen- and argon-saturated solutions while added bases accelerate the decay (insert c). That this transient is the cyclohexadienyl cation MESH$^+$ is seen by comparison with literature spectra obtained for MES in highly acidic solutions where the cation is stable. As shown in Table I, the peaks of the species match closely with respect to both position and relative intensity.[9] This table also shows that HMB and TMB behave in a similar manner upon photolysis in HFIP, giving the corresponding cyclohexadienyl cations HMBH$^+$ and TMBH$^+$.

Table II lists the quantum yields for the formation of the cyclohexadienyl cations and rate constants for their decay. The former were determined as previously described,[6b] with the photoionization of iodide in water as actinometer, and using values reported in highly acidic media for the extinction coefficients of the cations.[9] Quantum yields measured at the two maxima are in good agreement in each case. Rate constants for decay of cation for replicate measurements with the same solution were reproducible to ±3%. However, for MESH$^+$ and HMBH$^+$, decay rates for different solutions showed larger deviations (±30%), and there was an effect of dose, rate constants being slightly higher at very high laser intensities with a poorer obeyance to first-order decay. Both these observations were made previously with 9-fluorenyl cation.[6f] The former can be attributed to varying amounts of trace water in HFIP (see rate constants in Table III), the latter to reaction with the hexafluoroisopropoxide ion which must also form in the photoprotonation so that its initial concentration increases with laser dose. TMBH$^+$ is extremely long-lived in the solvent HFIP, with little decay in 10 ms. This cation is also observed in trifluoroethanol (TFE) and even water (with 20% acetonitrile (AN)), although the quantum yields for its formation are an order of magnitude lower. The amount formed was increased by adding $HClO_4$, although even 3 M acid did not give as much cation as in HFIP. There was no cation signal for MES in any of these other solvents, including 5 M $HClO_4$ in 20% AN.

As expected, added bases/nucleophiles accelerate the decay of the cyclohexadienyl cations. Table III lists some preliminary

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[9] With both MESH$^+$ and TMBH$^+$, the optical density does not decay to zero at either λ_{max} (see inserts a and b to Figure 1), due to the presence of other, as yet unidentified, photoproducts. The optical densities employed in the comparisons at the two wavelengths and in the quantum yield measurements were calculated from differences between the initial value and the value after decay of the cation, using the ϵ values at λ_1 and λ_2 for MESH$^+$ and HMBH$^+$ and that at λ_1 for TMBH$^+$. Due to the assumptions involved in the ϵ values of the cations in HFIP, the error in the quantum yields for cation formation is estimated as ±20%.

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Table I. UV Spectra of Cyclohexadienyl Cations

cation	solvent	λ_1(max)	ϵ_1, M^{-1}, cm^{-1}	λ_2(max)	ϵ_2, M^{-1}, cm^{-1}	OD(λ_1)/OD(λ_2)
$MESH^+$	HFIP[a]	355		260		1.27[b]
	HF/BF_3[c]	355	11 000	254	8700	1.26
	$HCl/AlCl_3$/ImCl[d]	360	10 700	262	10 200	1.05
	CF_3SO_3H[e]	358				
$HMBH^+$	HFIP[a]	390		275		1.51[b]
	$HCl/AlCl_3$/ImCl[d]	396	9880	285	6700	1.47
	98% H_2SO_4[f]	395	≈10 000	283	7240	1.38
$TMBH^+$	HFIP[a]	345		250		0.58[b]
	65% $HClO_4$[g]	346	10 000	251	15 000	0.65

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Table II. Quantum Yields for Formation of Cyclohexadienyl Cations and Rate Constants for Decay at 20 ± 1 °C

cation	solvent	Φ[a]	k(decay), s^{-1}
$MESH^+$	HFIP	0.08	1×10^5
$HMBH^+$	HFIP	0.04	7×10^3
$TMBH^+$	HFIP	0.06	$<1 \times 10^2$
$TMBH^+$	TFE	~0.006	7×10^2
$TMBH^+$	1:4 AN:H_2O	~0.003	5.8×10^5
$TMBH^+$	0.4 M $HClO_4$ (20% AN)	0.01	3.2×10^5
$TMBH^+$	3 M $HClO_4$ (20% AN)	0.03	6.3×10^4

[a] See footnote 9.

Table III. Rate Constants, k_{Nu} for the Reaction of Bases/Nucleophiles Nu with $MESH^+$, $HMBH^+$, and $TMBH^+$ in HFIP at 20 ± 1 °C

	k_{Nu},[a] M^{-1} s^{-1}		
Nu	$MESH^+$[b]	$HMBH^+$[c]	$TMBH^+$[d]
H_2O	8.8×10^6	2.7×10^5	<10
MeOH	2.4×10^7	1.5×10^6	$<10^2$
EtOH	1.7×10^7	8.2×10^5	$<10^2$
i-PrOH	2.0×10^7	8.1×10^5	$<10^2$
t-BuOH	1.2×10^7	8.7×10^5	$<10^2$
tetrahydrofuran	2.0×10^7	2.1×10^6	34
1,4-dioxane	5.4×10^6	1.3×10^5	
$C_2H_5OCH{=}CH_2$	$\approx 2.2 \times 10^6$	$\approx 1.6 \times 10^5$	
$\overline{CH_2(CH_2)_2CH{=}CHO}$	5.6×10^6	3.0×10^5	
$\overline{CH_2(CH_2)_3CH{=}C}(Me)$	$\approx 9 \times 10^6$	$\approx 9 \times 10^5$	
Cl^-[e]	2.4×10^9	4.3×10^8[f]	$\leq 5 \times 10^2$[f]
Br^-[e]	3.7×10^9	6.3×10^8[f]	$\leq 10^3$[f]
I^-[e]	3.8×10^9	1.1×10^9[f]	
NO_3^-[e]	1.4×10^9	1.7×10^8[f]	

[a] Error limits typically ±10%. [b] Monitored at 355 nm. [c] Monitored at 390 nm. [d] Monitored at 345 nm. [e] Counterion is $(n\text{-}Bu)_4N^+$. [f] Reaction is possibly reversible. If this is the case, the measured k_{Nu} is *not* identical with the rate constant for ion combination.

results, e.g., the second-order rate constants for the reaction of $MESH^+$ and $HMBH^+$ in HFIP with alcohols, ethers, and halides. With the series of alcohols there is obviously very little steric effect, even for *t*-BuOH. Since the basicities of these compounds are similar, it is this factor that determines reactivity. This also explains why tetrahydrofuran, which has similar basicity, reacts at a rate similar to the alcohols, while 1,4-dioxane, which is less basic due to the inductive (−*I*) effect of the additional oxygen, is less reactive. In comparison, the very high reactivity of the three halides and of NO_3^- suggests that these do not react as bases, but rather by nucleophilic combination with the cyclohexadienyl cations.[10] With all the bases/nucleophiles, $HMBH^+$ reacts considerably slower than does $MESH^+$, which is obviously due to the higher degree of stabilization and steric demand of $HMBH^+$. As seen from column 4 of Table III, $TMBH^+$ has an astounding lack of reactivity in HFIP toward bases/nucleophiles.

Detailed studies of the reactivities with additional reagents, as well as extensions to other aromatic systems, are currently in progress. The present study demonstrates that the solvent HFIP has the remarkable properties of a very weak basicity/nucleophilicity combined with good photoprotonating capabilities. Thus the photolysis of aromatic compounds in this solvent provides an excellent method for generating and observing unstable cyclohexadienyl cations. Moreover the reactivities of the so-formed cations with the solvent and with added bases/nucleophiles can be directly examined.

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(10) See note *f* in Table III.

Picosecond Flash Photolysis of Carboxy Horseradish Peroxidase: Rapid Geminate Recombination in the Presence of Benzohydroxamic Acid

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Photolysis of heme–CO bonds occurs on the femtosecond time scale.[1] Photolysis quantum yields (Φ) of less than 1, as measured on micro- or millisecond time scales, have been ascribed to fast geminate recombination of CO with the heme.[2] In sperm whale myoglobin (Mb), most of the CO molecules pass through the protein matrix into the solvent at room temperature[3] and Φ is very near unity,[4,5] but for ferrohorseradish peroxidase (HRP), a Φ of less than 1 has been reported.[5] A smaller Φ for HRP compared to Mb is consistent with the proposed lower barrier for CO binding to the heme in the peroxidase,[6] since this would allow rapid

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