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Regioselective Photoprotonation of 1,3-Dimethoxybenzenes in 1,1,1,3,3,3-Hexafluoroisopropyl Alcohol. H–D Isotope-Exchange and Laser Flash Photolysis Studies

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Abstract: Laser flash photolysis of 1,3-dimethoxybenzene and five substituted derivatives (2-Me, 4-Me, 5-Me, 2-MeO, 4-MeO) in 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP) results in a single transient with λ_{max} in the range 395–460 nm, dependent on the additional substituent. This transient forms in a monophotonic process, is unaffected by oxygen, but quenched by methanol and bromide, and decays by returning to the ground-state aromatic compound. These are characteristics of an intermediate cyclohexadienyl cation, produced by protonation of the aromatic excited state by the solvent. The λ_{max} values of the cyclohexadienyl cations produced by protonation of these dimethoxybenzenes in concentrated H_2SO_4 however lie in the range 315–340 nm. The 400-MHz ^1H NMR of the latter solutions reveals that the cations obtained here are 2,4-dimethoxybenzenonium ions, obtained by protonation at the 4-position. Photolysis at 254 nm in HFIP-*d* reveals that, for the four compounds that are unsubstituted at C2, there is a relatively efficient exchange of the hydrogen at this carbon; with the two compounds bearing 2-substituents there is no net photochemical reaction. Thus, the cyclohexadienyl cations observed as transient intermediates in the photochemical experiments are 2,6-dimethoxybenzenonium ions, obtained by protonation at C2 of the excited state. The change in selectivity between ground and excited states is explained by a shift of π-electron density upon excitation. The different spectra of 2,4- and 2,6-dimethoxybenzenonium ions have their origins in very different effects of *o*- and *p*-methoxy substituents, the former causing a ~40-nm bathochromic shift in a benzenonium ion and the latter a ~55-nm hypsochromic shift. Photolysis of 1-methoxynaphthalene in HFIP-*d* results in exchange at C5, and to a lesser extent at C8, as has been previously observed in acidic aqueous solutions. A transient is observed upon laser flash photolysis of this compound in HFIP with two λ_{max} at 360 and 550 nm. This transient is assigned to the cyclohexadienyl cation obtained by photoprotonation at C5.

We have recently reported an investigation of the photochemical behavior of 1,3,5-trimethoxybenzene, mesitylene, and hexamethylbenzene in 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP).[3] These compounds are protonated by this solvent upon excitation, affording cyclohexadienyl cations that were observed as transient intermediates using laser flash photolysis. Carbon protonation of aromatic compounds upon photolysis in the presence of acids has been implicated in the past through the observation of H–D exchange of ring protons[4] and has also been suggested to explain fluorescence quenching by acids[5] and as the first chemical step in the ipso photosubstitution of ortho-dialkoxyaromatics.[6a] Photoreactions proceeding by way of carbocations are well established,[7] and there have been a number of reports of the use of flash photolysis to directly observe and study the intermediate cations.[8] Our study was however the first where a cyclohexadienyl cation was characterized in this way. HFIP has several properties that make it useful for experiments involving carbocations. This solvent is polar and thus can support the formation of free cations. Relative to other alcohols, the OH group in acidic, sufficiently so to affect the protonation of excited aromatic compounds[3] and styrenes.[9] Perhaps most importantly, the solvent itself is weakly basic/nucleophilic, with the consequence that unstable cations can become quite long-lived so as to be observed with nanosecond laser flash photolysis.[9,10]

In our study of the symmetrically trisubstituted aromatics the characterization of the transients was straightforward, since there was a match with spectra reported in the literature for the same cyclohexadienyl cations obtained by thermal protonation under strongly acidic conditions.[3] We have more recently examined 1,3-dimethoxybenzenes and have found that these also produce transients upon photolysis in HFIP with the characteristics of cyclohexadienyl cations. However, the spectra are very different from those obtained in strong acids. This discrepancy has been traced through a study of H–D exchange to a different regioselectivity between the thermal and photochemical protonations, with the former favored at the 4-position while the latter proceeds, apparently exclusively, bewteen the two methoxy groups.[6b] Differential selectivity between thermal and photochemical protonations has been previously reported with 1-methoxynaphthalene.[4d,f] We have also studied this compound in HFIP, characterizing by flash photolysis a transient identified as the cyclohexadienyl cation.

Results and Discussion

Thermal Protonation of 1,3-Dimethoxybenzenes. The thermal protonation of several hydroxy- and methoxybenzenes was examined in the early seventies by Kresge and co-workers, in terms of both the kinetics of exchange in moderately concentrated acids and the equilibrium protonation in more concentrated acids.[11-13]

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[1] University of Toronto.

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[3] Steenken, S.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 9648.

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[5] (a) Brandon, W.; Pincock, A. L.; Pincock, J. A.; Redden, P.; Sehmbey, C. *J. Am. Chem. Soc.* **1987**, *109*, 2181. (b) Pincock, J. A.; Redden, P. R. *Can. J. Chem.* **1989**, *67*, 710.

[6] (a) Wan, P.; Wu, P. *J. Chem. Soc., Chem. Commun.* **1990**, 822. (b) Wan (unpublished results) has also made this observation, in his case on photolysis of 1,3-dimethoxybenzene in aqueous acids.

[7] (a) Cristol, S. J.; Bindel, T. H. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker, New York, 1983; Vol. 6, pp 327–415. (b) Kropp, P. J. *Acc. Chem. Res.* **1984**, *17*, 131. (c) Wan, P.; Yates, K. *Rev. Chem. Intermed.* **1984**, *5*, 157.

[8] See McClelland, R. A.; Kanagasabapathy, V. M.; Banait, N. S.; Steenken, S. *J. Am. Chem. Soc.* **1991**, *113*, 1009 and references therein.

[9] McClelland, R. A.; Chan, C.; Cozens, F.; Modro, A.; Steenken, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1337.

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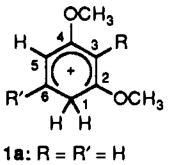
Table I. UV and NMR Spectra of Benzenonium Ions in 96% H_2SO_4 (Concentrations of Solutions Were 10^{-4} M (UV) and 10^{-1} M (NMR))

		^{1}H NMR (chem shift, ppm)					
benzenonium ion	λ_{max}, nm	H1[a,b]	H3	H5	H6[b]	OCH_3	CH_3
2,4-$(MeO)_2$	250, 317	4.04	6.58	6.99[c]	7.60[c]	4.32, 4.44	
	314[d]	4.10	6.75	7.14	7.86	4.38, 4.48	
2,4-$(MeO)_2$-3-Me	256, 340	4.03		7.35[c]	7.79[c]	4.31, 4.45	2.12
	341[d]						
2,4-$(MeO)_2$-5-Me	320, 256	3.96	6.56		7.31	4.31, 4.46	2.22
2,4-$(MeO)_2$-6-Me	326, 252	3.92	6.48	6.78		4.25, 4.40	2.42
2,3,4-$(MeO)_3$[e,f]	340, 255						
2,4,5-$(MeO)_3$[f,g]	340, 266						

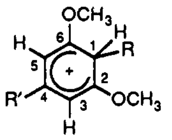
[a] Integrates as 2 H in all cases. [b] Vicinal coupling between H6 and the two hydrogens at H1 was not observed. [c] Doublets, with J = 10 Hz. [d] From ref 12. [e] Precursor was 1,2,3-trimethoxybenzene. [f] Cation was too unstable to record NMR spectrum. Assignment of structure is based on analogy with the methyl compounds. [g] Precursor was 1,2,4-trimethoxybenzene.

With 1,3-dimethoxybenzene there was a clear preference for protonation at the 4-position. The kinetic experiments showed that the rate of detritiation of 1,3-dimethoxybenzene-*4-t* in 10–50% $HClO_4$ was 5 times faster than that of 1,3-dimethoxybenzene-*2-t*,[13] while a ^{1}H NMR spectrum in 95% H_2SO_4 showed complete protonation to form the 2,4-dimethoxybenzenonium ion.[11] This same cation had been previously observed by other workers in hydrogen fluoride.[14]

The isomeric 2,6-dimethoxybenzenonium ion was apparently not observed in strong acids in amounts sufficient for this species to be detected in the NMR spectra. These experiments, however, were conducted at low field using quite high concentrations of the aromatic compound, as much as 10%,[11] and it is conceivable that some of the 2,6-isomer was present but was missed. To check this possibility, we have reinvestigated this system, as well as three methyl-substituted derivatives, using 400-MHz NMR and much lower concentrations. A typical spectrum is shown in Figure 1, with chemical shifts summarized in Table I. The pattern in each case is consistent with protonation to give a 2,4-dimethoxybenzenonium ion. For 1,3-dimethoxybenzene itself, and the 2-methyl- and 5-methyl-substituted derivatives, the key indicator is the presence of two nonequivalent methoxy signals in a 1:1 ratio. Protonation between the methoxy groups to give **2a–c** results in equivalent signals, as does protonation in the 5-position of the 1,3-dimethoxybenzene. Furthermore, the two-hydrogen singlet near 4 ppm establishes the presence of a CH_2 group ruling out protonation of a methoxy-bearing position. Hence, only structures **1a–c** remain.

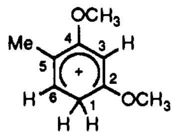


1a: R = R' = H
b: R = CH_3, R' = H
c: R = H; R' = CH_3

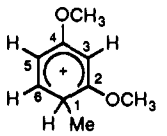


2a–c

With 2,4-dimethoxytoluene, three methoxy-stabilized cyclohexadienyl cations can form, including two 2,4-dimethoxybenzenonium ions:



1d



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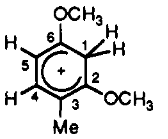

2d

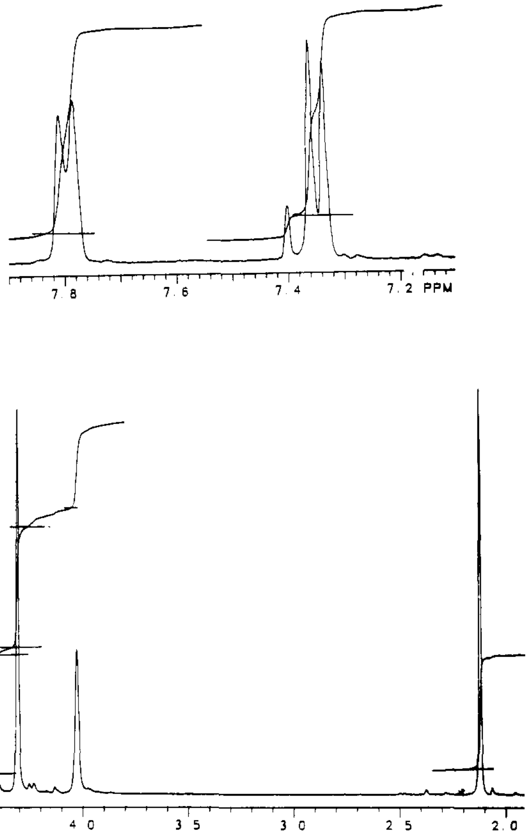

Figure 1. NMR spectrum of 2,6-dimethoxytoluene in (0.1 M) in 96% H_2SO_4. The single peak at 7.4 ppm is $CHCl_3$ contained in the $CDCl_3$ insert tube that was employed in this experiment to provide a lock. Other small peaks are unidentified.

Cation **3**, which arises from protonation at the carbon bearing the methyl group, can be ruled out since the methyl signal in the observed spectrum is a singlet, not a doublet, while the upfield signal associated with the saturated carbon integrates as two hydrogens. Protonation between the two methoxy groups can also be ruled out, principally on the basis that there is no vicinal coupling for the downfield signals at 6.56 and 7.31 ppm. In cation **2d**, these signals would correspond to H5 and H6 and would exhibit coupling, such as that observed in the spectra for **1a**,**b**. Thus, the cation that forms in this case is the 5-methyl-2,4-dimethoxybenzenonium ion **1d**.

The NMR spectra obtained with these four systems did show additional weak signals (Figure 1). Some of these grew slowly with time and therefore represent products of further reactions. It is known, for example, that 1,3-dimethoxybenzene demethylates in concentrated acids.[11] The additional signals in all cases were less than 5% of the major signals due to the 2,4-benzenonium ion. In consequence, we conclude that there is at most 5% of the 2,6-dimethoxybenzenonium ion in these solutions.

A typical UV spectrum for a 2,4-dimethoxybenzenonium ion in 96% H_2SO_4 is shown in Figure 2, with λ_{max} summarized in

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(11) Kresge, A. J.; Chiang, Y.; Hakka, L. E. *J. Am. Chem. Soc.* **1971**, *93*, 6167.

(12) Kresge, A. J.; Chen, H. J.; Hakka, L. E.; Kouba, J. E. *J. Am. Chem. Soc.* **1971**, *93*, 6174.

(13) Kresge, A. J.; Mylonakis, S. G.; Sato, Y.; Vitullo, V. P. *J. Am. Chem. Soc.* **1971**, *93*, 6181.

(14) Brouwer, D. M.; Maclean, C.; Mackor, E. L. *Discuss Faraday Soc.* **1965**, *39*, 121.

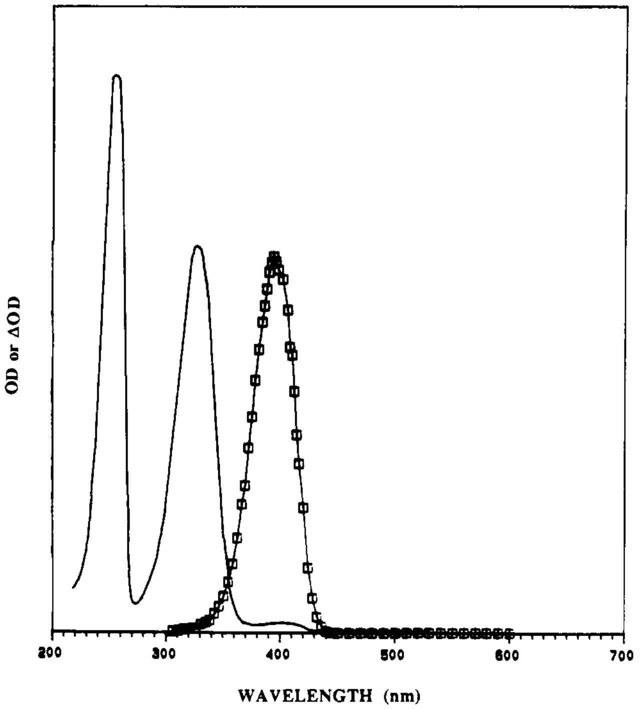

Figure 2. UV–visible spectra of the 2,4-dimethoxybenzenonium ion obtained with 3,5-dimethoxytoluene in 96% H_2SO_4 (solid line) and of the 2,6-dimethoxybenzenonium ion obtained as a transient following 248-nm photolysis of the same compound in $(CF_3)_2CHOH$ (squares). In the former case the spectrum was recorded for a 10^{-4} M solution within 5 min of preparation of the solution, since there are changes on long standing. In the latter case, the spectrum was obtained for a 10^{-3} M solution, 100 ns after the laser pulse.

Table II. UV Spectra and Lifetime of 2,6-Dimethoxybenzenonium Ions Obtained on 248-nm Flash Photolysis in HFIP (20 °C)

benzenonium ion	λ_{max}, nm	*k*(decay), s^{-1}
2,6-$(MeO)_2$	410	4.2×10^3
1-Me-2,6-$(MeO)_2$	415	1.2×10^3
3-Me-2,6-$(MeO)_2$	430	3.1×10^3
4-Me-2,6-$(MeO)_2$	395	3.1×10^2
1,2,6-$(MeO)_3$	430	4.7×10^4
2,3,6-$(MeO)_3$	460	2.6×10^4
2,4,6-$(MeO)_3$[a]	345	$<10^2$

[a] From ref 3.

Table I. As had been observed previously,[11] these cations have two peaks: one with λ_{max} near 250 nm and a second with λ_{max} in the region 315–340 nm. A reviewer has suggested the possibility that these spectra represent cation radicals forming by one-electron oxidation by sulfuric acid. This can be ruled out on the basis of the NMR spectra. Moreover, the UV–visible spectrum of the cation radical of 1,3-dimethoxybenzene is known,[15] and it is very different from that observed in the strong acid.

Flash Photolysis of 1,3-Dimethoxybenzenes in HFIP. Laser photolysis experiments were carried out with 1–5 mM solutions of the substrates in HFIP, with excitation at 248 nm. Transient spectra were obtained only above 300 nm due to the strong absorbance of the aromatic compound below this wavelength. A typical spectrum is shown in Figure 2, with λ_{max} and decay rate constants given in Table II. With each dimethoxybenzene a single peak was observed, decaying to zero with exponential kinetics with exactly the same rate at all wavelengths. This rate was unaffected by the presence of oxygen, but was significantly accelerated by the addition of small concentrations (1–10 mM) of methanol or tetrabutylammonium bromide. The initial optical density was found to vary in a linear fashion with laser dose, implying that the transient species was forming in a monophotonic process.

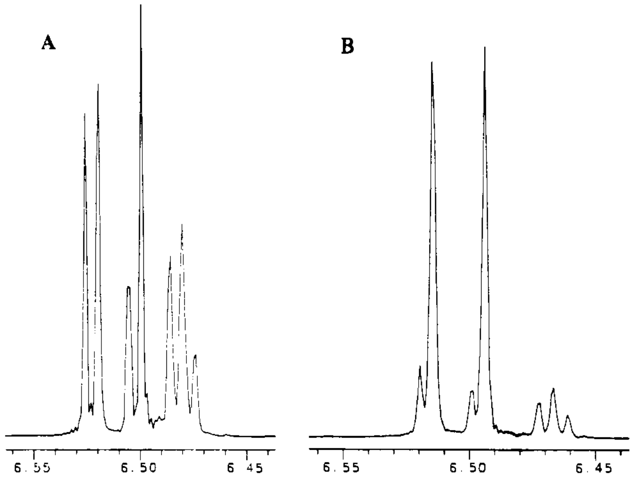

Figure 3. 400-MHz ^1H NMR signals for H2 ($\delta < 6.49$) and H4/H6 ($\delta > 6.49$) of 1,3-dimethoxybenzene in $CDCl_3$, before photolysis (A) and after 3 h of photolysis of a 10^{-3} M solution in $(CF_3)_2CHOD$ (B).

These observations are consistent with the presence of a single transient with the structure of a cyclohexadienyl cation. The accelerated decay provided by methanol is due to the presence of the much better base to remove the proton and restore aromaticity. The accelerating effect of bromide was noted in the earlier study and would appear to represent reversible nucleophilic addition to the ring.[3] The absence of an effect of oxygen rules out a triplet excited state or a radical, since these would be quenched. The dose dependence rules out the formation of cation radicals, ar least ones forming by two-photon ionization. Moreover, the spectrum of the cation radical derived from 1,3-dimethoxybenzene[15] is different from that of the transient. One further corroborating experiment involved repeated pulsing of a stationary solution, with 1 s between pulses to allow for complete decay of the transient before the next excitation. This showed no change in either the spectrum or the initial optical density of the transient even after 20 pulses, a result implying that the solution contained the same concentration of the same substrate upon each excitation. This is also consistent with the cation intermediate, since this decays by loss of a proton to the initial ground state aromatic compound.

Photochemical H–D Exchange in HFIP. As shown in Figure 2, the transients observed photochemically have spectra that are markedly different from ones obtained in concentrated acid. The NMR experiments establish that the latter correspond to 2,4-dimethoxybenzenonium ions. Thus, if the photochemical transients are cyclohexadienyl cations, they must have a different structure. To probe this, photolyses were carried out in $(CF_3)_2CHOD$ and the NMR spectra of the aromatic compounds examined for exchange of ring protons. A summary of the compounds studied and the chemical shifts in the aromatic region is given in Table III. Assignment of the signals could be made in an unambiguous manner in every case, on the basis of coupling patterns and integrations.

In the compounds not substituted at the 2-position, H2 appeared in the range 6.3–6.5 ppm, with long-range coupling to H4 and H6. On photolysis in the deuterated HFIP, it was these signals that were affected. This is illustrated for the parent compound in Figure 3. In the spectrum before photolysis, H2 appeared as a triplet at 6.48 ppm, with a doublet of doublets due to H4 and H6 at 6.5–6.52 ppm. After 3 h of photolysis the triplet was considerably reduced, the integration indicating about 85% deuterium incorporation. A further 3 h of photolysis resulted in the complete disappearance of this signal. Analysis with GC indicated that there was no chemical change over this time, the chromatogram showing a single peak for the starting substrate with the same intensity as that obtained before photolysis. This was also apparent in the NMR spectra, in that there was no change in the other signals, their integration relative to OCH_3 remaining within experimental error unchanged even on prolonged photolysis. This

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(15) O'Neill, P.; Steenken, S.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1975**, *79*, 2773.

Table III. ^{1}H NMR Chemical Shifts (ppm) and Coupling Constants (Hz) of Aromatic Protons of 1,3-Dimethoxybenzenes

substituent	H2	H4	H5	H6	$J_{2,4}$	$J_{4,5}/J_{5,6}$
1,3-(MeO)$_2$	6.48 (t)	6.51 (dd)	7.18 (t)	6.51 (dd)	2.2	8.1
1,3-(MeO)$_2$-2-Me		6.52 (d)	7.10 (t)	6.52 (d)		8.3
1,3-(MeO)$_2$-4-Me	6.42 (d)		6.38 (dd)	7.08 (d)	2.4	8.1
1,3-(MeO)$_2$-5-Me	6.27 (t)	6.32 (d)^a		6.32 (d)^a	2.3	
1,2,3-(MeO)$_3$		6.56 (d)	6.98 (t)	6.56 (d)		8.8
1,3,4-(MeO)$_3$	6.50 (d)		6.38 (dd)	7.77 (d)	2.8	8.8

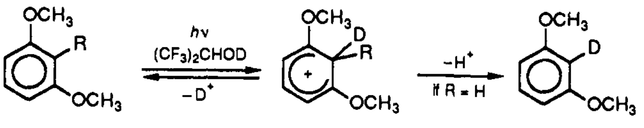
[a] Coupling with the methyl group is also observed.

was true for all of the substrates; there was also no exchange into C-Me groups in the appropriate compounds. As illustrated in Figure 3, the exchange for H2 did affect the pattern in the signals due to H4 and H6, associated with loss of coupling of these protons and H2.

The uncertainty in the NMR integration makes it difficult to rule out completely a small amount of exchange at other positions. To further investigate this possibility, ^{2}H NMR spectra were recorded on the photolyzed samples. In each case these exhibited only one signal, with a chemical shift corresponding to deuterium attached at C2. This was true even for systems that had been photolyzed to an extent where there was no residual signal for H2 in the ^{1}H NMR spectrum, i.e., complete exchange at this position. We estimate that exchange at a second position would have been observed if it were to have occurred to an extent of 5%. Thus, there is at least a 20:1 selectivity in favor of photosubstitution at the 2-position.

The two compounds that bear substituents at the 2-position, 2,6-dimethoxytoluene and 1,2,3-trimethoxybenzene, underwent no change even on prolonged photolysis. That is, there was no H–D exchange and no other chemical reaction, the latter point again verified by GC analysis. These two compounds did however produce transients in the flash photolysis experiments with characteristics similar to the ones obtained with those bearing a hydrogen at the 2-position.

The conclusion therefore is that the transients are 2,6-dimethoxybenzenonium ions obtained upon protonation between the two methoxy groups. For the compounds that start with a hydrogen at this position, exchange can obviously occur. In fact, in the experiments in HFIP-*d*, loss of the H originally attached to the ring would be favored because of the favorable isotope effect. With the compounds that bear a methyl or alkoxy substituent at C2, the H or D that was added from the solvent must obviously come off, with the result that there is no net photochemistry.



Dimethoxybenzenonium Ions. Having established that the two types of benzenonium ions have different λ_{max}, the spectra can be examined to see whether there is a sign of the other isomer present. With all of the systems investigated, the transient spectra generated photochemically appear to be due to just one cation, the 2,6-dimethoxy derivative. As illustrated in Figure 2, there is a small amount of absorbance at the lower wavelengths but this can be accounted for as the tailing end of the 400–450-nm peaks. On the basis of the NMR exchange studies, a 20:1 lower limit was established for the selectivity for photoprotonation at the 2-position. The transient spectroscopy provides strong support for this and in fact suggests that the figure may be higher, since a 5% contamination by the 2,4-dimethoxybenzenonium would probably be observed in the transient experiments.

On the other hand, the spectra obtained thermally do show that there is a small amount of the other isomer present, in that there is a definite peak with a λ_{max} in the region associated with the 2,6-dimethoxybenzenonium ion. This was observed for four of the aromatics—1,3-dimethoxybenzene itself and the 2-methyl, 5-methyl, and 2-methoxy derivatives. The spectrum for the 5-methyl compound is shown in Figure 2. With 4-methyl-1,3-dimethoxybenzene and 1,2,4-trimethoxybenzene, absorbance at the higher wavelength was negligible. With the first four, the absorbance at the higher wavelength was 1–2% that due to the major product. Thus, there is not enough of the minor isomer present for it to be unambiguously identified in the NMR experiments. As noted before, there were some extra signals, but these were very weak and could not be conclusively assigned.

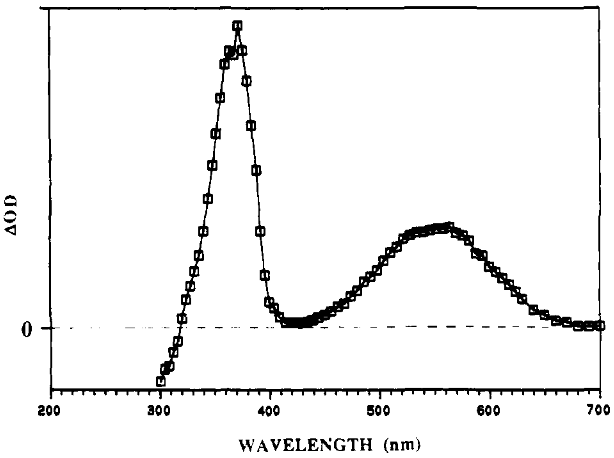


Figure 4. Transient spectrum following 248-nm photolysis of 1-methoxynaphthalene in oxygen-saturated hexafluoroisopropyl alcohol. Bleaching was observed at wavelengths below 300 nm where the precursor has strong absorbance.

It should be noted that the result in 96% H_2SO_4 represents the thermodynamic selectivity, since there is time for the two cations to equilibrate under these conditions. The exchange kinetics in more dilute acids imply that the ground-state kinetic selectivity is lower, of the order of 5:1. The photochemical selectivity obviously also has a kinetic basis.

The change in selectivity between the ground state and excited state undoubtedly has its origin in a shift of π-electron density upon excitation. This possibility was first suggested by Zimmerman and Sandel to explain the enhanced tendency of *m*-methoxy- and 3,5-dimethoxybenzyl derivatives to undergo heterolysis of the ArCH$_2$–X bond in the excited state.[16] These workers in fact gave the Huckel π-electron densities for 1,3-dimethoxybenzene as part of their arguments, and although these must oversimplify the situation, the general trend with respect to protonation is illustrated. In the ground state, the 2- and 4-positions are calculated to be the most electron rich, each with about 0.05 unit of excess charge. This predicts that these positions should be protonated thermally at similar rates, and in terms of the kinetic results, this is not too far off the mark, particularly considering that there is a statistical factor favoring protonation at the 4-position and perhaps a steric factor also. The calculation for the excited state on the other hand places 0.35 unit of extra charge at carbon 2, while carbon 4 has 0.1 unit of positive charge. On this basis it is not surprising that the photoprotonation occurs only at the former position.

Spectra of Methoxybenzenonium Ions. There has been some discussion as to the effects of substituents on the λ_{max} of benzenonium ions.[11,17] The empirical relationship of eq 1 has been

$$\lambda_{max}\ (\text{nm}) \sim 335 + \sum \Delta\lambda_i \qquad (1)$$

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(16) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963**, *85*, 915.
(17) Koptyug, V. A. *Top. Current Chem.* **1984**, *122*, 96.

Table IV. Observed and Calculated λ_{max} (nm) of Methoxy- and Methylbenzenonium Ions

substituent	solvent	λ_{max}(obs)	λ_{max}(calc)[a]	ref
2,6-$(MeO)_2$	HFIP	410	411	this work
2,6-$(MeO)_2$-1-Me	HFIP	415	421	this work
2,6-$(MeO)_2$-3-Me	HFIP	430	424	this work
2,6-$(MeO)_2$-5-Me	HFIP	395	399	this work
1,2,6-$(MeO)_3$	HFIP	430	430	this work
2,3,6-$(MeO)_3$	HFIP	460	450	this work
2,4,6-$(MeO)_3$	HFIP, $HClO_4$	345	354	3
2,4-$(MeO)_2$	H_2SO_4	317	315	this work
2,4-$(MeO)_2$-3-Me	H_2SO_4	340	328	this work
2,4-$(MeO)_2$-5-Me	H_2SO_4	320	328	this work
2,4-$(MeO)_2$-6-Me	H_2SO_4	326	331	this work
2,4,5-$(MeO)_3$	H_2SO_4	340	354	this work
2,3,4-$(MeO)_3$	H_2SO_4	340	354	this work
2-MeO-6-Me	HFIP	380	388	unpublished
4-MeO-2,6-Me_2	$HClO_4$	315	308	11
4-MeO	$HClO_4$	285	276	11
parent	HBr-n$AlBr_3$-C_6H_6	332	333	17
4-Me	HBr-n$AlBr_3$-C_6H_6	326	321	17
2,4,6-Me_3	HFIP, HF/BF_3	355	353	3
2,3,4,6-Me_4	HF/BF_3	365	366	17
2,3,4,5,6-Me_5	HF	377	379	17
1,2,3,4,5,6-Me_6	HFIP, HF	390	389	3
1,1,2,3,4,5,6-Me_7	HCl	397	399	17

[a] Calculated from eq 1 using $\Delta\lambda_i$ of +10 (ipso-Me), +16 (*o*-Me), +13 (*m*-Me), −12 (*p*-Me), +19 (ipso-MeO), +39 (*o*-MeO), +39 (*m*-MeO), and −57 (*p*-MeO).

proposed,[17] where 335 nm is the λ_{max} for the parent benzenonium ion and $\Delta\lambda_i$ are increments for whatever substituents are present. These increments can be positive or negative. An *o*-OH substituent has a bathochromic shift of about 30 nm, while a *p*-OH results in a 50-nm hypsochromic shift.[17] Methyl substituents were suggested to have effects of +5–10 (ipso), +15–20 (ortho), +10–15 (meta), and −10 (para).

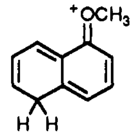
The values of λ_{max} for 17 benzenonium ions bearing methoxy and methyl substituents are summarized in Table IV. These data refer to cations obtained both as stable solutions under strongly acidic conditions and as transients generated photochemically in HFIP. As shown by the entries where the same cations have been studied in the two ways, there is little effect of solvent.[3] The values in this table were fit to eq 1 using an iterative least-squares procedure. The values of $\Delta\lambda_i$ that provide that best fit are given in the footnote; calculated λ_{max} are within an average of ±7 nm of the observed values. The $\Delta\lambda_i$ values for methyl substitution at the various positions are in agreement with ones suggested previously.[17] As with OH, there are dramatic differences between *p*- and *o*-MeO, these substituents shifting λ_{max} significantly to lower wavelengths and higher wavelengths, respectively. These combined effects are responsible for the 70–90-nm differences in the λ_{max} of 2,4-dimethoxy- and 2,6-dimethoxybenzenonium ions.

1-Methoxy- and 2-Methoxynaphthalenes. These two compounds have been previously examined in water/acetonitrile containing H_2SO_4, the 1-methoxy derivative undergoing photochemical exchange at H5 and to a smaller extent H8 (about a 10:1 ratio), while the 2-methoxy compound showed very little photoreaction.[4d] We now find that the same photochemistry occurs in HFIP-*d*. Thus, 3 h of photolysis of a 10^{-3} M solution of 1-methoxynaphthalene resulted in disappearance of the signals due to H5 and H8 in the ^{1}H NMR spectrum (see Figure 4 of ref 5 for peak positions and assignments), with the former decreasing to 10% of its initial intensity and the latter about 85%. This result was confirmed by ^{2}H NMR, which showed two signals corresponding to deuterium substitution at C5 and C8 in a 8:1 ratio. 2-Methoxynaphthalene under the same conditions showed no change.

Thermally, 1-methoxynaphthalene undergoes exchange under acidic conditions at the C2 position. The difference in selectivity was explained by the results of molecular orbital calculations, which showed that the greatest charge density is at C2 in the ground state and C5 and C8 in the excited state.[4d] The photochemistry in HFIP is clearly very similar to that in the aqueous acid. The experiments in HFIP however do not require the addition of a strong acid, since the solvent itself is sufficiently acidic to transfer a proton.

The result of laser flash photolysis of 1-methoxynaphthalene in HFIP is shown in Figure 4. Two peaks were observed, a broad peak with λ_{max} at 550 nm and a more narrow peak with λ_{max} at 360 nm. These bands are due to the same transient since the decay kinetics in each region are identical. This transient shows the various characteristics of a cyclohexadienyl cation, as described above with the 1,3-dimethoxybenzenes. In particular, excellent exponential decay was observed at all wavelengths, with *k*(decay) = 8.1×10^4 s^{-1}. Oxygen had no effect on the rate, and there was acceleration by added bromide and methanol. With the naphthalene derivative, pronounced bleaching was observed in the flash photolysis experiments below 300 nm, where the precursor absorbs strongly. This absorbance returned in an exponential fashion with the same rate constant as observed for the decay at higher wavelengths. This obviously represents the naphthalene being regenerated as the intermediate deprotonates.

We suspect that the cyclohexadienyl cation being observed in these experiments is **4** obtained by protonation at the C5 position.



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This assignment is based on the experiments in deuterated HFIP which showed that exchange at this position is the most favored. There was no sign of a second transient that could be assigned to the cation that would account for the small amount of exchange also observed at C8. This is a minor pathway, so that the absorbance of this transient could be weak. Moreover, the transient that was obtained absorbs across virtually the entire spectrum, so that a weaker signal could well be buried under this and be missed. The transient obtained in HFIP could not be detected on photolysis in aqueous acids. This however is not surprising since the lifetime of the cyclohexadienyl cation in water will be much shorter,[3] and undoubtedly the cation decays in the 20-ns laser pulse.

Experimental Section

Organic substrates were commercially available and were used as received. 1,1,1,3,3,3-Hexafluoroisopropyl alcohol-*O-d* was prepared by fractionally distilling a mixture of the alcohol and D_2O, followed by repeating the procedure with the distillate so obtained.

The photoexchange experiments were carried out by preparing 1 mM solutions in the deuterated solvent and photolysis at 254 nm in a Rayonet reactor. After the appropriate time, the solvent was evaporated under a stream of nitrogen and the residual material dissolved in $CDCl_3$. NMR spectra were recorded with a Varian 400-MHz spectrometer.

The laser flash photolysis apparatus has been described.[8]

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Facile Transformations of 12- and 13-Vertex Tungstacarborane Polyhedra: Reversible Framework Rearrangement and Acid-Induced Ejection of a Cage Vertex[1]

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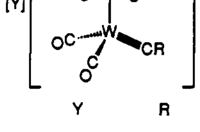
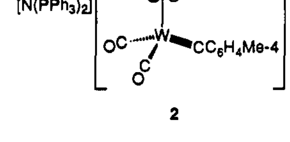
Abstract: Reactions of [Y][*closo*-1,2-Me_2-3-($\equiv$CR)-3,3-$(CO)_2$-3,1,2-$WC_2B_9H_9$] (Y = NEt_4, $N(PPh_3)_2$, PPh_4; R = Me, C_6H_4Me-4) with aqueous HX (X = Cl, I) afforded the salts [Y][*closo*-1,8-Me_2-11-(CH_2R)-2-X-2,2,2-$(CO)_3$-2,1,8-$WC_2B_9H_8$]; the structure of the product with X = Cl, Y = NEt_4, and R = C_6H_4Me-4 has been established by X-ray diffraction. A notable structural feature of the anion is that the carborane CMe groups do not occupy adjacent vertices, unlike the situation in the alkylidyne precursor complex. This observation is particularly remarkable in that the framework rearrangement occurs rapidly at temperatures as low as −78 °C. In addition, one of the boron atoms in the lower pentagonal ring of the cage carries a $CH_2C_6H_4Me$-4 substituent which evidently results from insertion of an initially formed alkylidene fragment into a cage B–H bond. Reactions between the salts [Y][*closo*-1,8-Me_2-11-(CH_2R)-2-X-2,2,2-$(CO)_3$-2,1,8-$WC_2B_9H_8$] and 1 mol equiv of $AgBF_4$ in the presence of CO gave the compounds [*closo*-1,8-Me_2-11-(CH_2R)-2,2,2,2-$(CO)_4$-2,1,8-$WC_2B_9H_8$] in which the cage CMe groups remain separated. In contrast, an excess of the reagent $AgBF_4$ afforded a 1:1 mixture of the same species and the compounds [*closo*-1,2-Me_2-8-(CH_2R)-3,3,3,3-$(CO)_4$-3,1,2-$WC_2B_9H_8$] containing adjacent CMe groups. These reactions are reversible: Addition of NEt_4Cl to tetrahydrofuran solutions of the tetracarbonyl species regenerates [NEt_4][*closo*-1,8-Me_2-11-(CH_2R)-2-Cl-2,2,2-$(CO)_3$-2,1,8-$WC_2B_9H_8$]. This is a very rare example of a reversible polytopal rearrangement of CMe groups. Reactions between [Y][*closo*-1,8-Me_2-11-($CH_2C_6H_4Me$-4)-2-X-2,2,2-$(CO)_3$-2,1,8-$WC_2B_9H_8$] and the alkynes PhC$\equiv$CR′ (R′ = Ph, Me) in the presence of $AgBF_4$ readily afforded the (alkyne)tungstacarborane complexes [*closo*-1,8-Me_2-11-($CH_2C_6H_4Me$-4)-2,2-$(CO)_2$-2-(η-PhC_2R')-2,1,8-$WC_2B_9H_8$]. An X-ray diffraction study of one of these (R′ = Me) confirmed the structure. Protonation of the salt [$N(PPh_3)_2$][*closo*-1,6-Me_2-4-($\equiv CC_6H_4Me$-4)-4,4-$(CO)_2$-4,1,6-$WC_2B_{10}H_{10}$] with HX (X = Cl, I) yielded the salts [$N(PPh_3)_2$][*closo*-1,7-Me_2-2-X-2,2,2-$(CO)_3$-2,1,7-$WC_2B_9H_9$], for which an X-ray diffraction study (X = I) revealed that a 13- to 12-vertex cage degradation had occurred, as well as loss of a CC_6H_4Me-4 fragment. This degradation is remarkable considering the acidic reaction conditions. In addition to the three X-ray diffraction studies, the new compounds were characterized by microanalysis; ^1H, ^{13}C, and ^{11}B NMR spectroscopy; and infrared spectroscopy.

Introduction

We have recently been exploring the chemistry of salts of the anionic alkylidynecarborane complexes [*closo*-1,2-Me_2-3-($\equiv$CR)-3,3-$(CO)_2$-3,1,2-$MC_2B_9H_9$]$^-$ (**1**; M = Mo, W; R = alkyl, alkynyl, aryl) and [*closo*-1,6-Me_2-4-($\equiv CC_6H_4Me$-4)-4,4-$(CO)_2$-4,1,6-$MC_2B_{10}H_{10}$]$^-$ (**2**; M = Mo, W).[3] Our initial studies concentrated on the use of these complexes for the synthesis of compounds containing metal–metal bonds, and numerous di-, tri-, and polynuclear metal species have now been prepared.[4] During this early work, the carborane cage was used as an isolobal replacement for the more widely studied cyclopentadienyl ligand. Thus, the metal atom was regarded as η^5 coordinated by the open pentagonal CCBBB face of a nido 11-vertex dianion [7,8-$C_2B_9H_9Me_2$]$^{2-}$ or η^6 coordinated by the puckered CBCBBB face of a nido 12-vertex dianion [7,9-$C_2B_{10}H_{10}Me_2$]$^{2-}$. Although the first results supported the use of this formalism, in many of these reactions the carborane ligand does not adopt a spectator role, leading to the frequent observation of exopolyhedral B–H → M or B–M (metal) bonds, or insertion of the alkylidyne ligand into a B–H bond of the cage to give a BCH_2R fragment. Consequently, we have preferred to regard anions of the salts **1** and **2**, respectively, as 12-vertex icosahedral and 13-vertex docosahedral *closo*-metallacarboranes, with the added spice of a reactive and indeed interactive alkylidyne ligand on the periphery of the cage.



	Y	R
1a	NEt_4	C_6H_4Me-4
1b	$N(PPh_3)_2$	C_6H_4Me-4
1c	PPh_4	C_6H_4Me-4
1d	NEt_4	Me



2

● CMe ○ BH

Lately we have focused upon protonation reactions of these salts. This work was prompted by our earlier observation[5] that treatment

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