Derivatization of Surfaces via Reaction of Strained Silicon–Carbon Bonds. Characterization by Photoacoustic Spectroscopy

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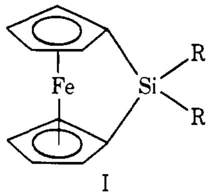
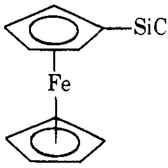
Abstract: Ferrocene-centered reagents can be bound to the surface of high surface area (400 m^2/g) silica by reaction of the silica with alkane solutions of (1,1′-ferrocenediyl)dichlorosilane (Ia), (1,1′-ferrocenediyl)dimethylsilane (Ib), or (1,1′-ferrocenediyl)diphenylsilane (Ic). Derivatization is not found when ferrocene itself is used as the derivatization reagent; ferrocene is easily washed from the silica powder by solvents which do not affect the ferrocene centers bound upon reaction of the silica with Ia–c. As determined by photoacoustic spectroscopy, derivatization with Ia–c results in ring opening of the strained C–Si–C linkage bridging the two cyclopentadienyl rings to yield a simple, monosubstituted ferrocene center attached to the surface. Surface -OH functionality apparently reacts in a manner analogous to homogeneous solution sources of -OH such as MeOH. Reaction of Ib with MeOD yields $[Fe(\eta^5\text{-}C_5H_4D)(\eta^5\text{-}C_5H_4Si(OMe)Me_2)]$. Optical absorption spectral changes accompanying reaction of Ia–c with solution sources of -OH are consistent with the differences found in the photoacoustic spectra of the pure powders of Ia–c compared to the silica powders derivatized with these reagents. Reaction of silica powders derivatized with Ia–c with acidic solutions of benzoquinone results in the oxidation of the surface-confined ferrocene centers to ferricenium centers giving photoacoustic spectra nearly the same as that from an authentic sample of a pure ferricenium salt. The surface-confined ferricenium can be used to oxidize *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) to $TMPD^{+\cdot}$ in solution; this reaction allows an estimate of the surface coverage at 10^{-11} mol/cm^2.

A number of electrode surfaces have been derivatized using (1,1′-ferrocenediyl)dichlorosilane (Ia) as a derivatizing agent.[3,5] Derivatized surfaces of Au, Pt, Si, Ge, and GaAs have been prepared using Ia and in every case it appears that attachment of polymeric quantities of electroactive material is possible when trace quantities of H_2O are present during the derivatization procedure. Qualitatively, the same results can be obtained using trichlorosilylferrocene (II) and bis(1,1′-triethoxysilyl)ferrocene (III) as derivatizing reagents.

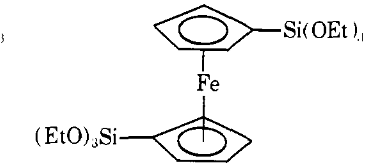


a, R = Cl
b, R = Me
c, R = Ph

I

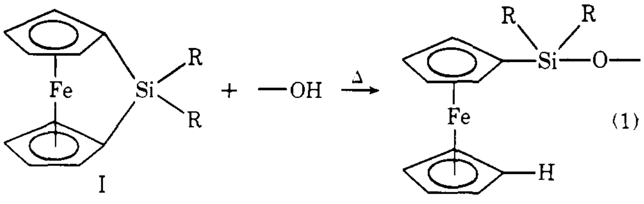


II



III

Derivatization of surfaces via reaction of surface -OH functionality with hydrolytically unstable Si–Cl or Si–OR bonds is a well-established procedure.[1-5] However, reagents Ia–c are susceptible to reaction in a way not previously exploited for molecular derivatization of surfaces. Chemistry according to eq 1 is of possible importance in the attachment of Ia to the various electrode surfaces mentioned above.[6] In this article we relate our findings concerning eq 1 using both homogeneous and surface sources of -OH functionality. Specifically, derivatization of high surface area silica is reported, and reaction of Ia–c with H_2O or MeOH in solution is described.



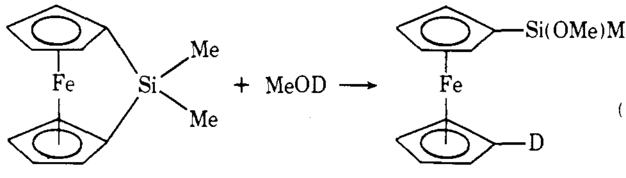
I

(1)

The optical absorption spectra of the species Ia–c are expected to be quite different from those associated with the simple substituted ring-opened product indicated in eq 1.[7] Accordingly, we have applied the technique of photoacoustic spectroscopy to determine the nature of the species on the surface of silica.[8] These studies appear to represent the first use of photoacoustic spectroscopy in monitoring the reaction of surface confined species. Reactions of Ia–c in solution were monitored by conventional ^1H NMR and UV–vis absorption techniques.

Results and Discussion

A. Reaction of Ia–c with Solution -OH Functionality. Species Ia–c were reacted with H_2O or MeOH in solution at 25 °C, and the progress of the reactions was monitored by ^1H NMR and UV–vis spectroscopy. Reaction does occur, and the order of reactivity is Ia > Ib > Ic and H_2O > MeOH; species Ic does not appear to react with MeOH under the conditions used for Ia and Ib. The ^1H NMR spectral changes reveal that reaction occurs as indicated in eq 1, and additionally the Si–Cl bonds of Ia undergo hydrolysis. The most definitive experiment concerns treatment of Ib with MeOD, which proceeds according to eq 2; ^1H NMR and mass spectral evidence are consistent with the formation of $[Fe(\eta^5\text{-}C_5H_4D)(\eta^5\text{-}C_5H_4Si(OMe)Me_2)]$. Table I summarizes the ^1H NMR data for Ia–c and for the reaction products. These data support -OH attack of the strained C–Si–C linkage to yield monosubstituted ferrocene molecules.



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Reaction of Ia–c with H_2O yields a product containing ⪢SiOH functionality, and conversion to dinuclear ferrocenes according to either eq 3a or 3b obtains according to ^1H NMR and mass spectral evidence. For Ia formation of polymers is

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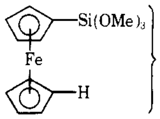
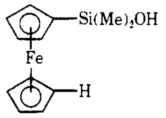
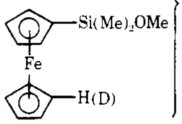
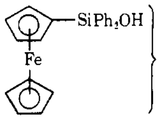
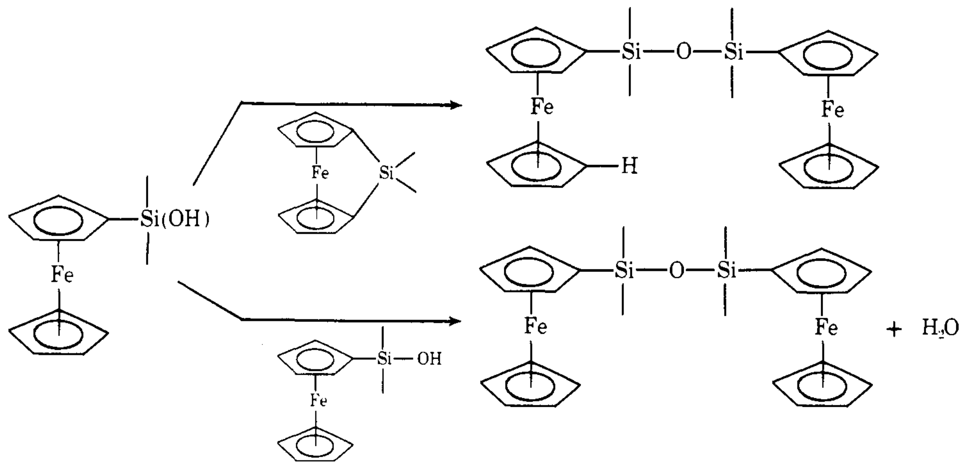
Table I. Hydrolysis Reactions Monitored by ^1H NMR[a]

starting compd	reactant	solvent	^1H NMR[b] starting	^1H NMR[b] final	product	comments
Ia	H_2O	toluene-d_8			"polymer"	not characterized
	MeOH	toluene-d_8	4.51 (t, 1) 4.14 (t, 1)	4.41 (m, 4) 4.31 (s, 5) 3.71 (s, 9)		too fast to follow
Ib	H_2O	CD_3CN	4.46 (t, 2) 4.14 (t, 2) 0.56 (s, 3)	4.39 (t, 2) 4.14 (s, t, 7) 0.34 (s, 6)		convenient rate for following by ^1H NMR
	MeOH(D)	CD_3CN	4.46 (t, 2) 4.14 (t, 2) 0.56 (s, 3)	4.46 (t, 2) 4.21 (s, t, 7) 3.43 (s, 3) 0.38 (s, 6)		
Ic	H_2O	$CDCl_3$	8.0 (m, 2) 7.5 (m, 3) 4.5 (t, 2) 4.15 (t, 2)	7.7 (m, 4) 7.3 (m, 6) 4.4 (m, 2) 4.2 (m, 2) 4.0 (s, 5)		slow reaction
	MeOH	CD_3CN				no detectable reaction

[a] All reactions carried out at 25 °C under inert atmosphere (N_2 or Ar); see Experimental Section. [b] ^1H NMR are δ ppm units relative to Me_4Si standard; t ≡ triplet; m ≡ multiplet; s ≡ singlet. Numbers following the m, s, or t in parentheses are the relative integrations.



(3a)

(3b)

possible and hydrolysis of Ia does yield uncharacterized, polymeric material.

Compared to ferrocene, or simply substituted ferrocene, Ia–c exhibit visible absorption maxima significantly to the red, Figure 1 and Table II. Upon hydrolysis with MeOH or H_2O, and independent of whether dimer (Ib, Ic) or oligomer (Ia) is formed, species Ia–c react to give visible absorption maxima which are blue shifted compared to the starting spectra. The final spectra obtained from Ia–c reveal a maximum near 440 nm in each case. Ferrocene and complexes II and III all show visible maxima at 440 nm. The red-shifted absorption maxima in Ia–c compared to ferrocene are thus due to the fact that the cyclopentadienyl rings are not parallel owing to the bridging -SiR_2 group.[7,9] Specifically, we associate the ~480 → ~440 nm shift accompanying the hydrolysis reaction of Ia–c with the attack of the -OH functionality on the strained C-SiR_2-C linkage yielding the simple, monosubstituted derivatives of ferrocene.

The reactivity of the strained Si-C bond in Ia–c with -OH functionality is reasonable in view of the known sensitivity of strained Si-C bonds to hydrolysis.[6] While relative rate measurements have not been made, it would appear that I is significantly more reactive than silacyclobutanes.[10] Detailed structural data are not available for Ia or Ib, but Ic has been structurally characterized and the strained C-Si-C angle is 99°,[9] which is considerably greater than the 80° associated with silacyclobutane.[11] Accordingly, the release of strain energy in reactions of I is more likely associated with the nonparallel ferrocene structure than with the bonding of Si in a small ring.

B. Reaction of Ia–c with Silica. Characterization by Photoacoustic Spectroscopy. Reaction of Ia–c in the presence of solution -OH suggests an important role for chemistry according to eq 1 in attaching Ia to hydrated oxide surfaces. Further, attachment of Ib and Ic to surfaces via reaction with surface -OH functionality appears to be a viable approach to obtain monolayer or even submonolayer coverage with ferrocene centers. Reaction of Ia–c with high surface area silica does result in the persistent attachment of ferrocene centers to the surface as determined by photoacoustic spectroscopy.

Species Ia–c dissolved in dry alkane solvent were reacted with high surface area silica at 25 °C, according to the procedure outlined in the Experimental Section. The initially pristine white powders are pale yellow subsequent to reaction

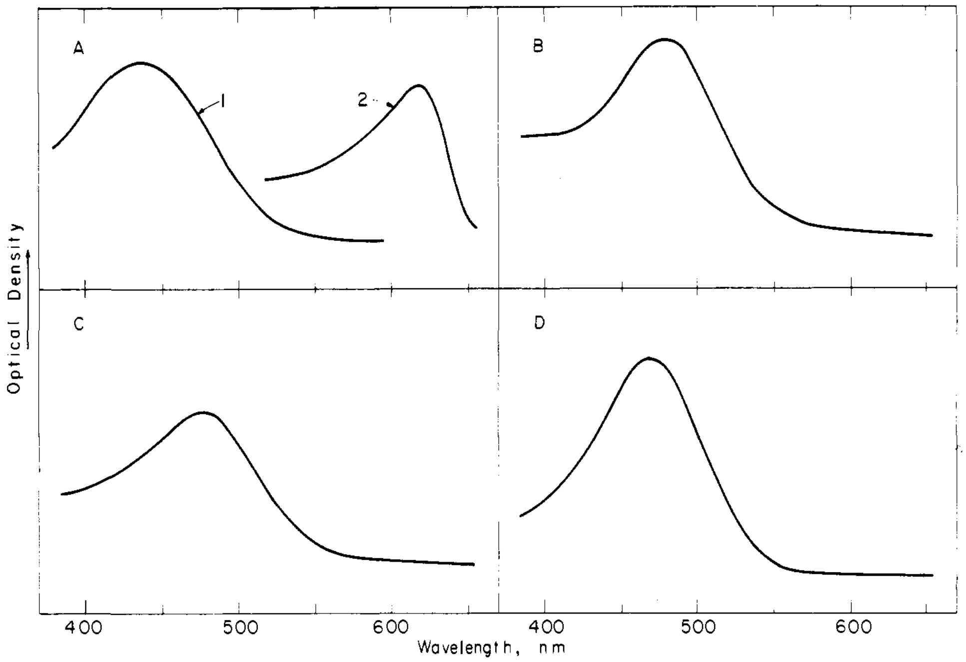


Figure 1. Solution electronic absorption spectra of ferrocene (A1), Ia (B), Ib (C), and Ic (D) all in dry hexane solvent at 25 °C. A2 shows the optical absorption for $[Fe(\eta^5\text{-}C_5H_5)_2]BF_4$ in H_2O solvent at 25 °C. Band maxima and molar absorptivities for the various species are listed in Table II.

Table II. UV-Visible Absorption and Photoacoustic Spectroscopy

compd	solvent or medium	band max, nm (ϵ or rel signal)[b]
	A. Absorption Spectroscopy[a]	
ferrocene	hexane	440 (90), 324 (50)
$[Fe(\eta^5\text{-}C_5H_5)_2]BF_4$	H_2O	618 (450), 380 (sh) (350)
Ia	hexane	470 (310), 324 (180)
Ib	hexane	478 (240), 325 (sh)
Ic	hexane	480 (270), 322 (sh) (630)
II	hexane	440 (140), 324 (110)
III	hexane	440 (120), 328 (90)
Ib + H_2O	CH_3CN	443, 325 (sh)
Ic + H_2O	CH_3CN	443
Ia + MeOH	toluene	442
Ib + MeOH	CH_3CN	438 (120), 323 (sh) (229)
	B. Photoacoustic Spectroscopy	
ferrocene	pure powder	435 (1), 327 (1)
$[Fe(\eta^5\text{-}C_2H_5)_2]BF_4$	pure powder	622 (1), 380 (sh) (0.8)
Ia	pure powder	465 (1), 335 (sh) (1)
Ib	pure powder	482 (1), 330 (0.95)
Ic	pure powder	482 (1), 330 (sh) (1.1)
Ia/silica [reduced][c]	powder	442 (1), 325 (sh) (1.2)
Ib/silica [reduced][c]	powder	442 (1), 325 (1.3)
Ic/silica [reduced][c]	powder	450 (1), 330 (sh) (1.7)
Ia/silica [oxidized][c]	powder	620 (1), 380 (sh) (1)
Ib/silica [oxidized][c]	powder	620 (1), 370 (sh) (1.5)
Ic/silica [oxidized][c]	powder	625 (1), 380 (sh) (1.3)

[a] Data recorded at 25 °C in 1.0-cm path cuvettes using a Cary 17 UV-vis-near-IR absorption spectrophotometer. Solutions of Ia-c were dry and under an inert atmosphere. [b] ϵ is molar absoptivity and applies to solution absorption measurements and rel signal refers to the relative photoacoustic signal under conditions specified in the Experimental Section; sh ≡ shoulder. [c] "Reduced" and "oxidized" refer to whether the derivatized silica was oxidized with HCl/*p*-benzoquinone; see text and Experimental Section.

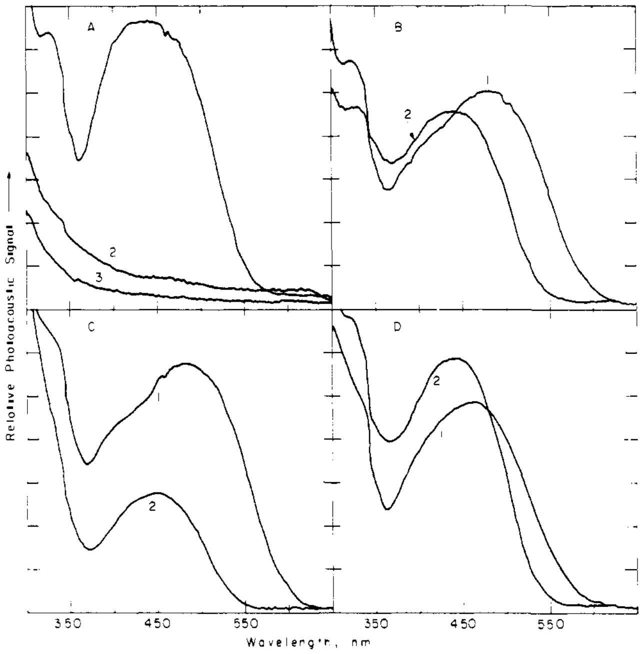


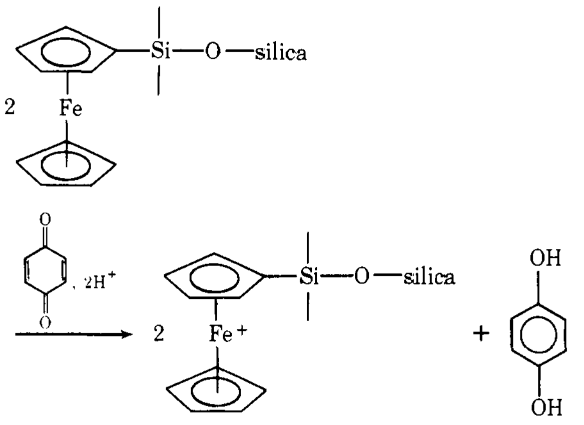
Figure 2. Photoacoustic spectra: A (1) pure ferrocene powder, (2) silica treated with ferrocene and washed with hexane, (3) silica; B (1) pure Ia powder, (2) silica treated with Ia and washed with hexane; C (1) pure Ib powder, (2) silica greated with Ib and washed with hexane; D (1) pure Ic powder, (2) silica treated with Ic and washed with hexane.

with Ia-c, whereas treatment of high surface area silica with ferrocene under the same conditions results in no change in the color of the silica powder.

The derivatized silica powder was analyzed by photoacoustic spectroscopy in the near-UV-vis region. A comparison of the photoacoustic spectra for the nonhydrolyzed pure powders of ferrocenes Ia-c and the derivatized silica is given in Figure 2. Band maxima for the photoacoustic spectra are included in Table II. The significant find is that the derivatized powders all exhibit a photoacoustic spectrum strongly resembling that for ferrocene. In particular, the derivatized silica powder exhibits a peak at ~440 nm and not the ~480 nm associated with the nonhydrolyzed materials Ia-c. We assert that the persistently attached ferrocene centers are covalently bonded via surface-Si-O-Si linkages formed by reaction of Ia-c with surface-SiOH groups. The fact that ferrocene does not bind persistently and the shift in the visible absorption maximum are consistent with the conclusion that Ia-c are covalently bonded to the surface.

The photoacoustic spectral maxima, Figure 2, for the pure powders of ferrocene and Ia-c are very similar to those found in solution absorption spectral measurements, Figure 1. This finding is consistent with a lack of intermolecular effects in the optical properties of ferrocene centers; the optical properties of single crystals of ferrocene reveal no intermolecular effects either.[12] Thus, the photoacoustic spectra logically reflect molecular properties and we assume the same to be true for the spectra obtained from the derivatized silica. The general lack of intermolecular effects on the first absorption system of ferrocene centers accords well with the fact that the absorption is associated with a ligand field, "d-d", type transition.[12]

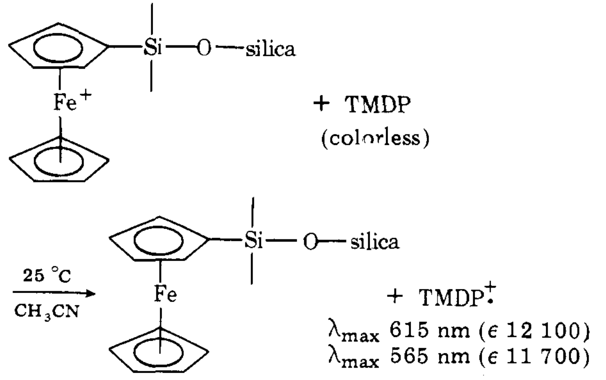
Silica powders derivatized by reaction with Ia-c are fairly rugged. For example, reaction of the derivatized powders with acidic solutions of benzoquinone proceeds according to eq 4



(4)

to yield pale baby blue powders.[13] That the chemistry does correspond to the generation of surface-confined ferricenium centers is established by the photoacoustic spectra of the "oxidized" powders, Figure 3 and Table II. For comparison, Figure 3 includes the photoacoustic spectrum obtained from an authentic sample of ferricenium, $[Fe(\eta^5\text{-}C_5H_5)_2]BF_4$. As can be seen the pure powder of the ferricenium salt gives essentially the same visible spectral maximum as obtained from oxidized powders derivatized with Ia-c. Further, the optical absorption maximum, Figure 1, for ferricenium is very close to that found from the photoacoustic spectra, Figure 3.

Derivatized powders oxidized with HCl/benzoquinone are reducible with solution species. For example, *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) reacts with suspensions of the silica/ferricenium powder to give $TMPD^{+\cdot}$ on the time scale of mixing, eq 5. The structured, intense, visible



(5)

absorption of $TMPD^{+\cdot}$[14] provides a measurable, molecular specific spectroscopic feature, and the formal potentials $E°$(ferricenium/ferrocene) = +0.40 V vs. SCE[15] and $E°(TMPD^{+\cdot}/TMPD)$ = +0.10 V vs. SCE[16] indicate that the reaction represented by eq 5 should proceed completely. Interestingly, such chemistry allows the determination of the number of oxidizing equivalents confined to the surface of the silica. Assuming the surface area to be 400 m^2/g, we find $\sim 10^{-11}$ mol of ferricenium/cm^2 when either Ia or Ib is used as the derivatizing reagent. Thus, the reactive Si-Cl bonds of Ia do not lead to significantly greater coverage under the conditions used here than when only Si-C bonds are involved in derivatization. The value of 10^{-11} mol/cm^2 is significantly below monolayer coverage and may reflect the initial coverage of -OH functionality. The particular process represented by eq 5 has been carried out by photogenerated ferricenium confined to the surface of a silicon photoelectrode,[3] and studies of derivatized high surface area silica may allow screening of potentially useful photoelectrode catalyst systems.

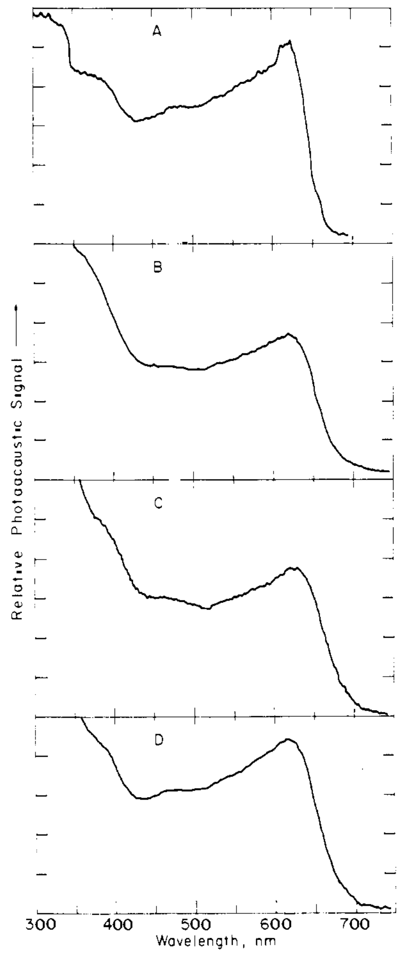


Figure 3. Photoacoustic spectra of $[Fe(\eta^5\text{-}C_5H_5)_2]BF_4$ (A) and silica treated with Ia (B), Ib (C), and Ic (D) after oxidation with *p*-benzoquinone.

C. Use of Photoacoustic Spectroscopy. Photoacoustic spectroscopy has been used here to make measurements having molecular specificity for species confined to a surface in submonolayer quantities. The spectral maxima obtained allow the unequivocal conclusion that ferricenium/ferrocene centers are attached to the surface, and the shift in the visible maxima from ~480 nm for the pure powders of Ia-c to ~440 nm allows the conclusion that reaction with surface-OH is involved in the derivatization. Photoacoustic spectroscopy is of considerable value here; the material confined to the surface has modest absorptivity ($\sim 10^2$ M^{-1} cm^{-1}) in solution but the silica is high surface area providing derivatized surfaces which are even visibly colored to the naked eye. Transmission UV-vis spectroscopy is of course not possible here and reflectance spectra are often inconvenient and dependent on the sample preparation. Interestingly, the signal-to-noise for the photoacoustic spectra of derivatized powders is about the same as for the pure ferrocenes. However, these high surface area samples are not a good test of the sensitivity of the photoacoustic spectroscopy. Future studies will be concerned with elaborating this point.

D. Implications for Electrode Derivatization Using Ia. The data reported here, both in solutions and for surfaces, reveal that derivatization of electrode surfaces with Ia likely involves both hydrolysis of the Si–Cl bonds and reaction according to eq 1.[3,5] This is especially certain when oligomeric quantities of ferrocene material are found on the electrode, since the oligomerization requires H_2O. Further, the ability to oxidize and reduce redox reagents confined to the surface of silica is consistent with the ability to effect mediated redox processes involving ferrocene centers confined to the surface of silicon photoelectrodes.[3] Experiments are underway to examine derivatized photoelectrodes by photoacoustic spectroscopy, to provide molecular specific information concerning the cyclical oxidation and reduction of redox reagents confined to the surface of the electrode.

Experimental Section

Preparation of Compounds. The preparation of 1,1′-dilithioferrocene TMEDA and 1,1′-ferrocenediyldichlorosilane followed established procedures.[5] The procedure used for the preparation of Ic is a modification of a synthesis in the literature.[17] The details of the preparation of Ib and Ic appear below.

Hexane was distilled from sodium benzophenone ketyl under argon. Dimethyldichlorosilane and diphenyldichlorosilane were distilled from activated 3 Å molecular sieves immediately before use. All the reactions and handling procedures, unless otherwise specified, were carried out under N_2 or Ar using standard Schlenk techniques or in a Vacuum Atmospheres drybox.

1,1′-Ferrocenediyldiphenylsilane. 1,1′-Dilithioferrocene·TMEDA (5.0 g, 0.016 mol) was added to 100 mL of hexane in a round-bottom flask and stirred to form a slurry. The mixture was heated to a gentle reflux and 3.0 mL (0.019 mol) of diphenyldichlorosilane in 50 mL of hexane was added dropwise over 2 h to the refluxing slurry. The mixture was allowed to reflux overnight. The mixture was then filtered to remove LiCl and any unreacted starting material and the filtrate was reduced in volume under vacuum. The resulting precipitate was collected and washed three times with hexane before being dried under vacuum.

Yield was 20% of a light orange powder: λ_{max} (hexane) 480 nm (ϵ 270); NMR ($CDCl_3$) δ 8.0 (m, 2), 7.5 (m, 3), 4.5 (t, 2), 4.15 (t, 2); mass spectral analyses yielded the molecular ion (*m/z* 366) as the parent peak (100% rel abundance).

1,1′-Ferrocenediyldimethylsilane. 1,1′-Dilithioferrocene·TMEDA (8.0 g, 0.025 mol) in a slurry with 20 mL of hexane was added over 1 h to 3.1 mL (0.026 mol) of dimethyldichlorosilane in 100 mL of hexane. The reaction mixture was allowed to stir overnight. Hexane and excess silane were removed under vacuum and the solids were taken up in hexane and filtered to remove LiCl. The solvent was again stripped under vacuum and the product was extracted from the residue by vacuum sublimation (0.01 mm, 40 °C), forming orange platelets. The yield was 60% with mp 72–75 °C: λ_{max} (hexane) 478 nm (ϵ 240); NMR (CD_3CN) δ 4.46 (t, 2), 4.14 (t, 2), 0.56 (s, 3); mass spectral analysis yielded the molecular ion (*m/z* 242) as the parent peak (91% rel abundance).

Preparation of Derivatized SiO_2 Powders. SiO_2 catalyst support with a surface area of 400 m^2/g was used both as received from Alfa and also dried by heating to 150 °C under vacuum (10^{-2} mm) for 2 h with similar results. Preparations were carried out in a Vacuum Atmospheres drybox.

In parallel fashion $\sim$0.05 g of ferrocene, Ia, Ib, and Ic were added to $\sim$0.1 g of SiO_2 in round-bottom flasks, and 10 mL of hexane was added to each of the four flasks after which they were sealed and allowed to stir overnight. The resulting slurries were filtered and washed four times with 5-mL portions of hexane. The last two washings in all cases were colorless. The powders, white for the ferrocene treated and shades of light yellow for the other three, were dried under vacuum and examined by photoacoustic spectroscopy. The yellow portions were sensitive to air oxidation to a bluish, ferricenium coated form.

For spectroscopic examination of the powders with the surface ferrocene in the oxidized ferricenium form slurries of the treated SiO_2 were reacted with *p*-benzoquinone. To slurries of the yellow powders in 5% HCl, a small amount of a dilute solution of *p*-benzoquinone, also in 5% HCl, was added with the characteristic blue color of ferricenium appearing immediately. The oxidized powders were washed four times with 5% HCl and dried under vacuum. The last two washings were clear and all four washings showed no trace of ferrocene or ferricenium under UV–vis spectroscopic examination. The bluish, oxidized powders were quite stable and were handled in air without special care.

Solution Reactions. Concentrated solutions of Ia–c were prepared and placed in NMR tubes fitted with septum stoppers. The septum permitted the use of a microsyringe for the introduction of the reagent being used and permitted the removal of a small aliquot of the NMR mixture for dilution and examination by UV–vis spectroscopy before and after reaction.

Samples of degassed H_2O and MeOH were added to the NMR tubes in a slight excess based on the amount of silane present as determined by use of an internal standard. The subsequent reactions were monitored by NMR. Reaction of Ia with H_2O and MeOH proceeded very rapidly while for Ib the reactions proceeded slowly enough for progress to be conveniently followed. Reaction of Ic with H_2O was very slow, requiring hours to approach completion, and almost no reaction occurred with MeOH. The products of the reaction of Ia–c with H_2O were subject to dimerization while the product of reactions with MeOH and Ia and Ib persisted for accurate assignment of the NMR spectra. Ib was reacted with MeOD and mass spectral analysis of the product isolated from the NMR mixture had the molecular ion as parent peak (*m/z* 275). Concomitant with the changes in the NMR spectra associated with the reactions were the shifts of λ_{max} in the UV–vis spectra to $\sim$440 nm characteristic of a simple substituted ferrocene.

Reaction of Silica/Ferricenium with *N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine (TMPD). Silica/ferricenium powders from reaction of HCl/benzoquinone from Ia or Ib as the initial derivatizing reagent were reacted with freshly sublimed TMPD (Aldrich). A slurry of a preweighed amount ($\sim$40 mg) of silica/ferricenium was prepared by addition of a known volume (3.0 mL) of dry, deoxygenated CH_3CN to the powder contained in a septum covered test tube under N_2. Then a known volume (1.0 mL) of CH_3CN/0.1 M TMPD solution was added and the solution turned purple instantly. UV–vis absorption of the solution following centrifugation of the suspension revealed that $TMPD^{+\cdot}$ formed, and the $TMPD^{+\cdot}$ concentration was determined quantitatively from the known absorptivity.[14] Control reaction of nonderivatized powder treated in parallel gave $TMPD^{+\cdot}$ in amounts less than 10% of that found using the ferrocene derivatized powders. The small amount of $TMPD^{+\cdot}$ formed with the control may be a consequence of O_2 or other adventitious oxidants adsorbed to the surface of silica. The ferricenium powder after reaction with TMPD appears to adsorb some $TMPD^{+\cdot}$, and the amount is significant. Under the conditions used, we find that $\sim$40 mg of nonderivatized silica powder will adsorb $\sim$50% of the $TMPD^{+\cdot}$ from a 4.0-mL CH_3CN solution of 0.0025 M $TMPD^{+\cdot}$ in the presence of 0.0025 M ferrocene and 0.02 M TMPD.

Photoacoustic Spectroscopy. The photoacoustic spectra were taken using a modified Princeton Applied Research Model 6001 photoacoustic spectrometer which employed three gratings and order filters under microprocessor control to cover the 200–1600-nm wavelength range. A beam splitter just before the sample cell reflects part of the light into a pyroelectric detector to provide continuous compensation for light intensity variation. A cell was built at MIT that allows control of the gas composition in contact with the sample. In addition, the sample chamber can be completely sealed and loaded in a drybox. The cell consists of two stainless steel blocks, one for the sample chamber and one for the microphone chamber. The sample is placed on the upper side of a plunger which is inserted from the front to a position below a Suprasil II window. The sides of the sample chamber contain two Nupro Model SS2H2 bellows valves which connect to a gas manifold on one side and an exhaust line on the other. A third bellows valve with a 0.25 in. stainless steel tube welded to one end is connected to the back of the chamber. This tube is connected to the microphone chamber using a Cajon Ultra-Torr fitting. The microphone chamber has a bellows valve that connects to the exhaust line. A Bruel and Kjaer Model 4166 condenser microphone, Model 2619 1X gain preamp combination is sealed into the block from the back with an O-ring. The sensitivity of the cell is 0.25 V/W measured at the output of the preamp for a modulation frequency of 40 Hz with a lock-in time constant of 1 s. This compares to a sensitivity of 1.0 V/W for the original Model 6001 cell. The light source is a 1-kW xenon arc lamp.

All of the samples with the exception of the ferrocene and ferricenium tetrafluoroborate were loaded into the cell in a drybox under N_2. The sample and microphone chambers were flushed with at least 20 times their volumes of dry N_2. All of the spectra were corrected for the nonidealities of the optical system by dividing the spectra by a carbon black reference. The resolution for the ferricenium salt spectrum is 16 nm. All of the other spectra have a resolution of 8 nm. The pure powder spectra were taken at a modulation frequency of 400 Hz in order to avoid signal saturation. The ferricenium salt was run at 2 kHz to reduce saturation effects due to the strong absorption of this pure sample. The samples on the silica were run at 80 Hz.

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References and Notes

(1) (a) Moses, P. R.; Wier, L.; Murray, R. W. *Anal. Chem.* **1975**, *47*, 1882. (b) Watkins, B. F.; Behling, J. R.; Kariv, E.; Miller, L. L. *J. Am. Chem. Soc.* **1975**, *97*, 3549. (c) Brown, A. P.; Koval, C.; Anson, F. C. *J. Electroanal. Chem.* **1976**, *72*, 379. (d) Lane, R. F.; Hubbard, R. T. *J. Phys. Chem.* **1973**, *77*, 1401, 1411.

(2) (a) Ed. Grushka, E., "Bonded Stationary Phases", Ann Arbor Science Publishers: Ann Arbor, Mich., 1974. (b) Wheetall, H. H. *Science* **1969**, *166*, 615.

(3) (a) Bolts, J. M.; Bocarsly, A. B.; Palazzotto, M. C.; Walton, E. C.; Lewis, N. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 378, and references cited therein. (b) Bolts, J. M.; Wrighton, M. S., *J. Am. Chem. Soc.* **1979**, *101*, 6179. (c) Bocarsly, A. B.; Walton, E. G.; Bradley, M. G.; Wrighton, M. S. *J. Electroanal. Chem.*, **1979**, *100*, 283.

(4) Allum, K. G.; Hancock, R. D.; Howell, I. V.; McKenzie, S.; Pitkethly, R. C.; Robinson, P. J. *J. Organomet. Chem.* **1975**, *87*, 203; **1976**, *107*, 393.

(5) (a) Wrighton, M. S.; Palazzotto, M. C.; Bocarsly, A. B.; Bolts, J. M.; Fischer, A. B.; Nadjo, L. *J. Am. Chem. Soc.* **1978**, *100*, 7264. (b) Wrighton, M. S.; Austin, R. G.; Bocarsly, A. B.; Bolts, J. M.; Haas, O.; Legg, K. D.; Nadjo, L.; Palazzotto, M. C. *J. Electroanal. Chem.* **1978**, *87*, 429.

(6) Earborn, C.; Bott, R. W. In "Organometallic Compounds of the Group IV Elements", Vol. I, Part I, "The Bond to Carbon"; MacDiarmid, A. G., Ed.; Marcel Dekker: New York, 1968.

(7) Bark, T. H.; Watts, W. E. *J. Organomet. Chem.* **1968**, *15*, 177.

(8) (a) Rosencwaig, A. *Anal. Chem.* **1975**, *47*, 592A. (b) Rosencwaig, A.; Gersho, A. *J. Appl. Phys.* **1976**, *47*, 64.

(9) Evans, H. S.; Osborne, A. G.; Whiteley, R. H. *Helv. Chim. Acta* **1976**, *59*, 2402.

(10) Damrauer, R. *Organomet. Chem. Rev., Sect. A* **1972**, *8*, 67.

(11) Vilkov, L. V.; Mastyryukov, V. S.; Baurova, Y. V.; Vdovin, J. M.; Grinberg, P. L. *Dokl. Akad. Nauk SSSR* **1967**, *177*, 1084.

(12) Sohn, Y. S.; Hendrickson, D. N.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3603.

(13) (a) Hendrickson, D. N.; Sohn, Y. S.; Gray, H. B. *Inorg. Chem.* **1971**, *10*, 1559. (b) Rudie, A., Ph.D. Thesis, Massachusetts Institute of Technology, 1978.

(14) Michaelis, L.; Schubert, M. P.; Gramick, S. *J. Am. Chem. Soc.* **1939**, *61*, 1981.

(15) Janz, G. J.; Tomkin, R. P. T. "Nonaqueous Electrolyte Handbook", Vol. II; Academic Press: New York, 1973.

(16) Yao, T.; Musha, S.; Munemori, M. *Chem. Lett.* **1974**, 939.

(17) Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1975**, *101*, C27.

Photodissociation Spectroscopy of Halogen-Substituted Benzene Ions

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Abstract: Photodissociation spectra of the four halobenzene gas-phase parent ions are presented, obtained by a combination of one-photon and two-photon photodissociation. The spectra are compared with the corresponding halotoluene ion spectra, with the photoelectron spectra of neutrals, and with theory. The close similarity of halobenzene and halotoluene spectra indicates a minor perturbing role for the methyl group. It is concluded from the analysis that the fluorine substituent has little or no spectroscopic manifestation but that, in the other halobenzene ions, the halogen substituent plays an important spectroscopic role, in particular contributing a prominent spectral feature having halogen-to-ring charge transfer character. Comparison of peak positions in the photodissociation and photoelectron spectra in the bromobenzene and iodobenzene cases suggests that the ion ground state is substantially distorted relative to the neutral molecule.

Introduction

The photodissociation spectrum of a gas-phase ion is the wavelength dependence of the rate of photodecomposition of the ion. As has been shown in numerous cases,[1d] such a spectrum is a valuable source of information about the position of optical absorption features for the ion, and, since direct optical absorption spectra of most gas-phase ions are currently not obtainable, photodissociation spectra have been interpreted and used for their optical spectroscopic value.

It is thus beginning to be possible to map out systematically the spectroscopy of gas-phase cations, and, just as with neutral-molecule spectroscopy, the aromatics constitute an exceptionally interesting group among larger polyatomics. The spectroscopy of benzene cation and its methyl derivatives has moved some distance toward a satisfactory understanding,[2] but less attention has gone to developing systematic understanding of resonance-interacting substituents on benzene cation. For the halogen substituents treated here, the substituent plays an important role in determining the qualitative features of the spectroscopy, in contrast to the neutral molecules in which the spectroscopic role of the halogen is hardly observable. We believe that a coherent interpretation of the halobenzene ion spectra is now feasible.

Spectra of a number of halotoluene ions were reported some time ago,[3,4] but there are several drawbacks to basing an analysis on these alone: the possible effect of the methyl substituent is unknown; the π and σ electronic systems are not fully separated so that calculations are not convenient; and the photoelectron spectra of these molecules do not show the sharp peaks needed for quantitative comparisons.

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