Characterization of Species Present in Aqueous Solutions of [Hydroxy(mesyloxy)iodo]benzene and [Hydroxy(tosyloxy)iodo]benzene

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Abstract: Upon solution in water, both [hydroxy(mesyloxy)iodo]benzene and [hydroxy(tosyloxy)iodo]benzene undergo complete ionization to give the hydroxy(phenyl)iodonium ion (PhI^+OH) and the corresponding sulfonate ion (RSO_2O^-) as fully solvated species, i.e., "free" ions. The phenyliodonium solution species do not form ion pairs with the organosulfonate ions. The hydroxy(phenyl)iodonium ion is presumed to be ligated with at least one water molecule at an apical site of the iodine(III) atom originally occupied by the sulfonate ion. In view of the relative basicities of HO^- and H_2O, the hydroxy ligand of the [hydroxy(aquo)iodo]benzene ion ($PhI^+(OH_2)OH$) is expected to be strongly bound and the water ligand is expected to be weakly bound to the iodine(III) center. This species has a pK_A at (4.30 ± 0.05). $PhI^+(OH_2)OH$ and its conjugate base are present in equilibrium with the [hydroxy(auqo)]-μ-oxodiphenyldiiodine cation ($Ph(HO)I-O-I^+(OH_2)Ph$). This μ-oxo dimer is present at significant levels even in relatively dilute solutions as the combination equilibrium constant is (540 ± 50). This dimer can be protonated, and the pK_A of the conjugate acid is ≈ 2.5. The equilibrium constant for dimerization of [oxo(aquo)iodo]benzene ($PhI^+(OH_2)O^-$), the most important monomer in acidic solutions, is ≈ 8.6.

Introduction

[Hydroxy(mesyloxy)iodo]benzene (**1**, HMIB) and its tosyloxy analog (**2**, HTIB) are stable, crystalline organoiodine(III) compounds that can be prepared by treatment of (diacetoxy-iodo)benzene (**3**) with methanesulfonic acid and H_2O in chloroform[1] or acetonitrile,[2] or p-TsOH·H_2O in dichloroethane[3] or acetonitrile.[4] They are electrophilic at iodine and useful for the phenyliodination and/or oxysulfonylation of a range of organic substrates.[5,6] The structure of HTIB has been established by single-crystal X-ray analysis[7] and, as expected from the bonding,[8-10] possesses a T-shaped configuration in which the iodine−oxygen bonds are co-linear (O−I−O ∠ = 178.8°) and nearly orthogonal (86.0°, 92.8°) to the I−C_{Ar} bond. The I−OH bond (1.94 Å) is shorter than that predicted (1.99 Å) for covalent radii, while the I−OTs bond (2.473 Å) is much longer and partially ionic in character. The large difference in iodine−

heteroligand bond distances in HTIB is not observed with symmetrical aryl λ^3-iodanes such as $PhI(OAc)_2$[11,12] and $PhICl_2$.[13] This difference is attributed to the much greater basicity of the hydroxide ligand compared with the tosylate ligand.[8] From a structural standpoint, HTIB, and presumably HMIB, bear some resemblance to iodonium salts, e.g., $Ar_2I^+X^-$, although they are substantially more electrophilic at the iodine(III) atom. HMIB
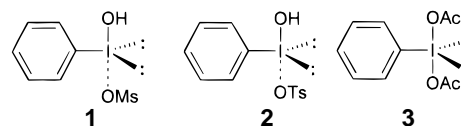
and HTIB are soluble in water at natural pH and hold promise as synthetic reagents in this medium. Not only is water an environmentally benign solvent, but it may also participate in "solvohyperiodination" reactions.[14,15] For example, while ketones are converted to α-mesylate[1,16] and α-tosylate[17] derivatives with HMIB and HTIB in organic solvents, reaction 1, they have been shown to react with HTIB in water to give α-hydroxy ketones,[18] reaction 2. A determination of the actual iodine(III)
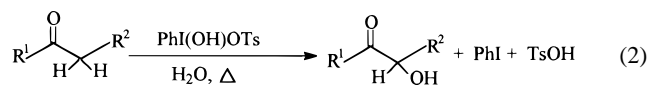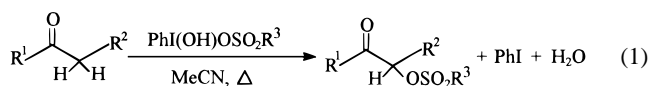
species present in aqueous solutions of HMIB and HTIB will clarify the modes of action of these compounds.

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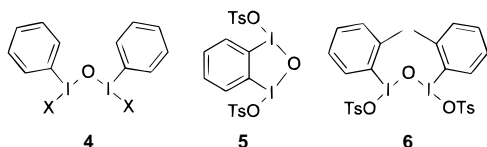(9) Varvoglis, A. *The Organic Chemistry of Polycoordinated Iodine*; VCH Publishers, Inc.: New York, 1992; see pp 4−7.
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A number of uncertainties need to be addressed. For example, do HMIB and HTIB ionize upon dissolution in H_2O to give the hydroxy(phenyl)iodonium ion (PhI^+OH) and the corresponding sulfonate ions (RSO_2O^-) and, if so, are they present as ion pairs or fully solvated ions? What are the pK_A values of the $>I-OH$ group of HMIB and HTIB in H_2O? Are they the same, as expected for fully solvated ions, or different? A variety of μ-oxodiphenyldiiodine(III) compounds of general structure **4** in which X is typically a nucleofugic group, e.g., $-OSO_2CF_3$,[19,20] $-OCOCF_3$,[21] $-OClO_3$,[19] or $-ONO_2$,[22] are now known and are formally anhydrides of the putative hydroxy-

iodanes, PhI(OH)X. Two μ-oxodiiodine ditosylates, namely, the heterocyclic species **5**[23] and *o*-tolyl analog **6**,[24] are also known and suggest that equilibrium concentrations of μ-oxodiiodine derivatives of HMIB and HTIB may be present in aqueous solution and contribute to the chemical behavior of these compounds.

In this report, we use results of UV–vis and NMR spectroscopic measurements, along with potentiometric titration data, to demonstrate the presence of these dimeric μ-oxodiiodine-(III) species in aqueous solution. We obtain the dimerization equilibrium constant and the pK_A values for the parent monomers. The data presented establish that the [hydroxy(sulfonyloxy)iodo]benzene species **1** and **2** are present in aqueous solution as fully solvated ions, an organosulfonate ion, and a free hydroxy(phenyl)iodonium ion. The hydroxy(phenyl)-iodonium ion produced is the same from either compound and is essentially hydrated iodosylbenzene in various protonated forms.

Experimental Materials and Methods

Materials. HMIB and HTIB were synthesized from (diacetoxyiodo)benzene as described in the Introduction and purified by recrystallization. All other reagents were purchased reagent grade materials and were used without further purification.

Spectroscopy and Potentiometric Titrations. UV–vis spectroscopic measurements were recorded on a Cary 17 spectrophotometer updated by OLIS, Inc., Bogart, GA, to allow digital recording of spectra. All NMR spectra were obtained on a Varian VXR 300 MHz spectrometer equipped with a broad band probe. Potentiometric titrations were done by standard methods. Solutions were open to the air.

Effects of Concentration and pH on UV–Vis Spectroscopy. For optical spectroscopic measurements, solutions containing the desired HMIB or HTIB concentration and 0.1 mol·dm^{-3} of sodium methanesulfonate were prepared. The solution temperature was regulated at (20.0 ± 0.5) °C, and the pH was adjusted by addition of 1.0 N NaOH. Quartz cells were filled with solution, and spectrophotometric readings were taken. Prior to again adjusting the stock solution pH, the solution from the sample cell was returned to the stock container. In each case,

the stock solution volume changed only 1–2% over the entire experiment so that in data fits no adjustments were made for solute concentration changes.

Equilibrium Constants. Equilibrium constant measurements were made with solutions containing 0.100 mol·dm^{-3} of sodium methanesulfonate, so that the reported equilibrium constants are concentration constants for solutions where the ionic strength was 0.1 mol·dm^{-3}. It was assumed that activity coefficients of all species participating in equilibrium were reasonably close to 1.00, since the solutions were "dilute".

Solubilities of HMIB and HTIB in Water. The solubility of HTIB in water is 0.024 g per mL (61 mmol·dm^{-3}) at 22 °C.[25] The solubility of HMIB in water was determined to be 0.71 g per mL (2.25 mol·dm^{-3}) at room temperature. The pH of a 2.25 mol·dm^{-3} HMIB solution is about 2. The solubility of HMIB at pH > 4.3 drops significantly. To obtain solutions with pH greater than this, [HMIB]$_0$ had to be kept at ≤3 mmol·dm^{-3} to prevent precipitation of iodosylbenzene. Significantly, the solubility of HMIB in 1 N NaOH is greater than that observed near pH 4.3 and under mildly alkaline conditions. The solubility of HMIB in 1 N NaOH (5.8 mmol·dm^{-3}) is about twice that under mildly alkaline conditions.

Precipitation of Iodosylbenzene from Solutions of HMIB at pH > 4.3. We observed that the pH of HMIB solutions could not be adjusted above ≈4.3 at [HMIB]$_0$ > 3 mmol·dm^{-3} or formation of a cloudy precipitate ensued. A solution of HMIB (0.202 g, 0.64 mmol) in water (10 mL) was treated with 0.1 N NaOH, sufficient to adjust the solution to pH 5.31. The solution became cloudy, and after some time a light yellow precipitate was collected and air dried. The mp was 201–203 °C, identifying the precipitate as iodosylbenzene, PhIO.

Thermal Decomposition of Aqueous HMIB Solutions. A saturated solution of HMIB (0.7 g, 2.2 mmol) in water (1.0 mL) was prepared, sealed, and stored in the dark. After several days, white particles began to appear, and the characteristic aroma of iodobenzene was detected. After 34 days, the white solid (24.8 mg) was collected by filtration. The solid was identified as iodylbenzene on the basis of its melting point (235 °C, explosion) and its solubility in water.[26]

Aqueous Solutions of Iodylbenzene. PhIO$_2$ was prepared by oxidation of iodosylbenzene (PhIO) with hypochlorite from Chlorox. The white solid was recrystallized from water (mp 235 °C, explosion). The solubility of PhIO$_2$ in water was determined to be about 6.2 mg/mL (26 mmol·dm^{-3}). The pH of a saturated solution was 9.68, corresponding to a pK_A of 6.95 for the conjugate acid.

Results and Discussion

The reactions occuring upon dissolution of HMIB or HTIB in water are complex. The results are best understood if we first present the final picture that emerges and then discuss the results of each set of experiments and how they fit into the overall picture. The primary processes which occur when HMIB and HTIB dissolve in water are presented in Scheme 1. Both λ^3-iodanes undergo complete ionization to give the hydroxy(phenyl)iodonium ion (PhI^+OH) and the corresponding sulfonate ion (RSO_2O^-) as fully solvated species, i.e., "free" ions. PhI^+OH is presumed to be ligated with at least one water molecule at an apical site of the iodine(III) atom originally occupied by the sulfonate ion. In view of the relative basicities of HO^- and H_2O, the hydroxy ligand of the [hydroxy(aquo)-iodo]benzene ion ($PhI^+(OH_2)OH$) is expected to be strongly

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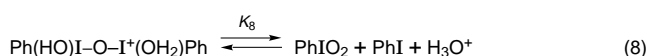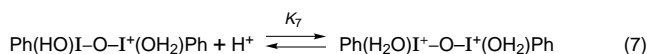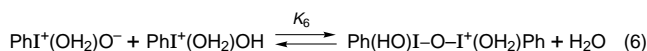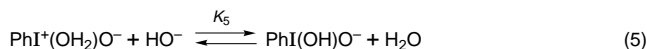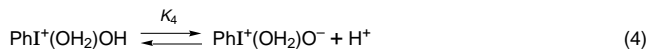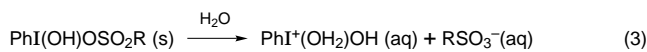(28) Perdoncin, G.; Scorrano, G. *J. Am. Chem. Soc.* **1977**, *99*, 6983.

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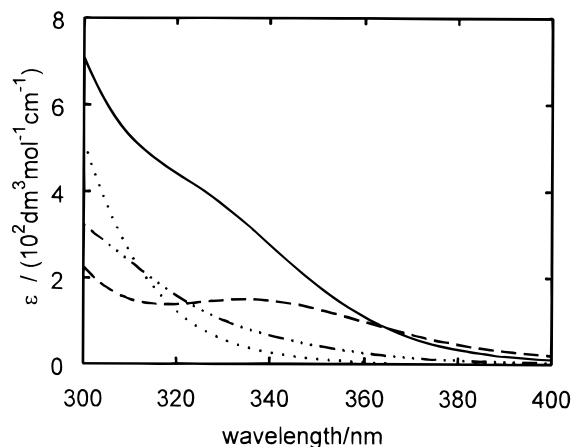(32) Schardt, B. C.; Hill, C. L. *Inorg. Chem.* **1983**, *22*, 1563–1565.

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Scheme 1

$$PhI(OH)OSO_2R \text{ (s)} \xrightarrow{H_2O} PhI^+(OH_2)OH \text{ (aq)} + RSO_3^- \text{(aq)} \qquad (3)$$

$$PhI^+(OH_2)OH \underset{K_4}{\rightleftharpoons} PhI^+(OH_2)O^- + H^+ \qquad (4)$$

$$PhI^+(OH_2)O^- + HO^- \underset{K_5}{\rightleftharpoons} PhI(OH)O^- + H_2O \qquad (5)$$

$$PhI^+(OH_2)O^- + PhI^+(OH_2)OH \underset{K_6}{\rightleftharpoons} Ph(HO)I-O-I^+(OH_2)Ph + H_2O \quad (6)$$

$$Ph(HO)I-O-I^+(OH_2)Ph + H^+ \underset{K_7}{\rightleftharpoons} Ph(H_2O)I^+-O-I^+(OH_2)Ph \qquad (7)$$

$$Ph(HO)I-O-I^+(OH_2)Ph \underset{K_8}{\rightleftharpoons} PhIO_2 + PhI + H_3O^+ \qquad (8)$$
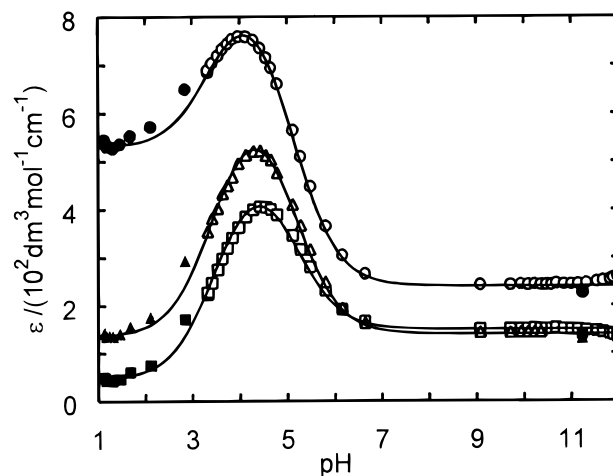
bound and the water ligand is expected to be weakly bound to the iodine(III) center.[8] Because HMIB and HTIB are largely insoluble at room temperature in nonhydroxylic solvents such as CHCl$_3$ and CH$_3$CN, their solubilities in H$_2$O and CH$_3$OH are attributed to nucleophilic assistance to ionization by solvent molecules and solvation of the resulting ions.

The dissolution of either HMIB or HTIB in water, reaction 3, Scheme 1, affords 1 molar equivalent of the same weak acid, namely, the [hydroxy(aquo)iodo]benzene ion (PhI$^+$(OH$_2$)OH), with pK_A = 4.3. The conjugate base, [oxo(aquo)iodo]benzene (PhI$^+$(OH$_2$)O$^-$), is a hydrated form of iodosylbenzene [Ph—I=O ↔ Ph—I$^+$—O$^-$) and has limited solubility in water. PhI$^+$(OH$_2$)-OH and its conjugate base (PhI$^+$(OH$_2$)O$^-$) combine, producing the [hydroxy(aquo)]-μ-oxodiphenyldiiodine cation (Ph(HO)I—O—I$^+$(OH$_2$)Ph), reaction 6. This dimer is present at significant levels even in relatively dilute solutions as K_6 = (540 ± 50). The initially formed dimer is further protonated in very acidic pH, giving the [bis(aquo)]-μ-oxodiphenyldiiodine dication (PhI-(OH$_2$)I$^+$—O—I$^+$(OH$_2$)Ph), which has pK_A ≈ 2.5, reaction 7. Thermal decomposition of solutions of HMIB is slow and produces iodylbenzene and iodobenzene. The production of these disproportionation products probably occurs *via* a concerted decomposition of Ph(HO)I—O—I$^+$(OH$_2$)Ph, reaction 8.

The relative concentrations of iodine(III) species present in aqueous solutions of HMIB and HTIB are highly pH dependent. In strongly acidic solutions (≤pH 1), PhI$^+$(OH$_2$)OH is the primary monomer present, while Ph(H$_2$O)I$^+$—O—I$^+$(OH$_2$)Ph is the main dimeric form. In less acidic and moderately basic

Figure 2. Dependence of the apparent molar absorbtivity of HMIB aqueous solutions on pH at (●, ○) 300 nm, (▲, △) 320 nm, and (■, □) 336 nm. Empty symbols are data for 3.0 mmol·dm^{-3} HMIB solutions, while filled symbols are for 6.0 mmol·dm^3 solutions. Lines are calculated on the basis of the proposed mechanism for 3.0 mmol·dm^{-3} solutions, as described in the text.
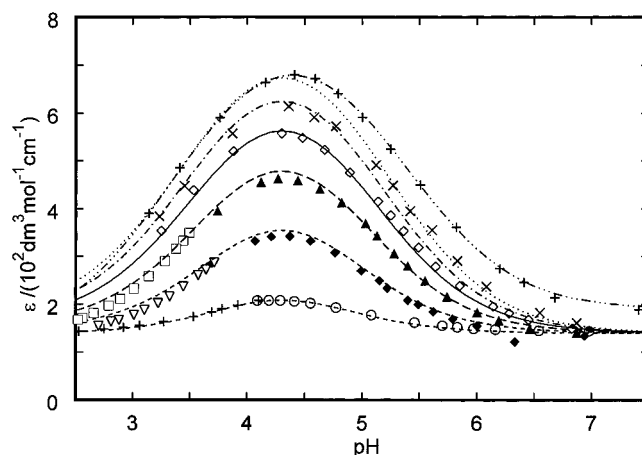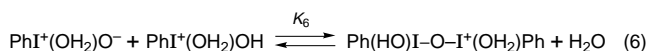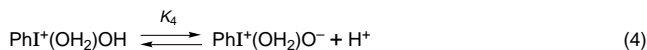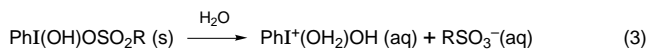

Figure 3. Dependence of apparent molar absorbtivity at 320 nm on pH in aqueous solutions for several [HMIB]$_0$ (mmol·dm^{-3}): (+, ○, - - -) 0.25; (▽, ◆, - - -) 1.0; (□, ▲, - - -) 2.0; (◇, —) 3.0; (×, •—•) 4.0; and (+, •••, ••• —) 5.0. All solutions contained 0.100 mol·dm^{-3} of NaOMs. With the exception of the 5.0 mmol·dm^{-3} data, the lines drawn through the data do not use the equilibrium constants and molar absorbtivities for the "best fits" (Table 2) but rather are derived from Scheme 3 using pK_4 = 4.30, K_6 = 540, p(1/K_7) = 2.5, and ϵ_{ih} = 135, ϵ_i = 140, ϵ_{dh} = 2860, and ϵ_{dhh} = 1530 dm^3·mol^{-1}·cm^{-1}, as discussed in the text. One of the lines (••• —) for the 5.0 mmol·dm^{-3} data uses Scheme 2 and the values in Table 2.

solutions (pH 6—11), PhI$^+$(OH$_2$)O$^-$ is the dominant monomer and ultimately separates to give solid iodosylbenzene. At even higher pH, a new species is generated, presumably PhI(OH)O$^-$, reaction 5. As expected from the dimerization reaction shown in reaction 6, [Ph(HO)I—O—I$^+$(OH$_2$)Ph] is maximized in the pH range near the pK_A of PhI$^+$(OH$_2$)OH, i.e., pH 4.3.

In the following sections, results obtained from optical and NMR spectroscopy, from concentration and pH studies, and from potentiometric titrations are presented. The supporting data for inclusion of each reaction in Scheme 1 are presented, along with arguments for exclusion of others.

Optical Absorption Spectra of Aqueous Solutions of HMIB: Dependence on pH and Concentration. The optical absorption spectra of aqueous solutions of HMIB are pH and concentration dependent, Figures 1, 2, and 3. At all pH, the significant spectral features occur in the UV, with shoulders around 275 nm and a broad plateau or slight peak near 330 nm. Only the tails of the UV peaks appear above 400 nm.

Figure 1. Optical absorption spectra of HMIB solutions at various pH: (•••) HMIB (2.0 mmol·dm^{-3}) in 1.0 mmol·dm^{-3} methanesulfonic acid; (—) HMIB (2.0 mmol·dm^{-3}) in pH 4.25 solution, adjusted by the addition of NaOH; (- - -) HMIB (2.0 mmol·dm^{-3}) in pH 9.1, adjusted by the addition of NaOH; and (•••) HMIB (4.0 mmol·dm^{-3}) dissolved in 1.0 N NaOH. All solutions, except for the solution with methanesulfonic acid, had 100 mmol·dm^{-3} of sodium methanesulfonate added. The apparent molar absorbtivity, ϵ, is the absorbance of the solution (cm^{-1}), divided by [HMIB]$_0$.

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Scheme 2

$$PhI(OH)OSO_2R \text{ (s)} \xrightarrow{H_2O} PhI^+(OH_2)OH \text{ (aq)} + RSO_3^- \text{(aq)} \quad (3)$$

$$PhI^+(OH_2)OH \underset{K_4}{\rightleftharpoons} PhI^+(OH_2)O^- + H^+ \quad (4)$$

$$PhI^+(OH_2)O^- + PhI^+(OH_2)OH \underset{K_6}{\rightleftharpoons} Ph(HO)I-O-I^+(OH_2)Ph + H_2O \quad (6)$$

The pH dependence of the apparent molar absorbtivities (ϵ) are shown in Figure 2, where ϵ is the solution absorbance (cm^{-1}) divided by [HMIB]$_0$. Two aspects of the plots at 300, 320, and 336 nm are striking: maxima appear between pH 4.0 and 4.5, and the pH at which the maximum occurs (pH$_{max}$) shifts with λ. At low pH, the ϵ appear to approach a constant value. For 7 < pH < 11, the ϵ are constant: above pH 11, the ϵ change, indicating the appearance of an additional iodine(III) species, e.g., PhI(OH)O$^-$, reaction 5. The spectrum of the iodine(III) species at pH 14 is substantially different from that at 7 < pH < 11, Figure 1. Clearly, the pK_A of PhI(OH)O$^-$ is very high.

In alkaline solutions, or in strongly acidic solution (pH 1), the ϵ are independent of concentration over a significant range, Figure 3. Thus, the ϵ are concentration and pH independent in strongly acid solution and in basic solution, at pH < 11. In contrast, the ϵ are strongly concentration dependent in the region around pH 4.3.

The wavelength dependence of pH$_{max}$, Figure 2, and the concentration dependence of ϵ, Figure 3, are consistent with a pH-dependent dimerization near 4.3. These observations can be explained with a simple mechanism which includes only reactions 3, 4, 6, and water dissociation (K_W), Scheme 2. Mass-balance and equilibrium relationships yield eqs 9 and 10:

$$\frac{2K_4K_6}{[H^+]}[PhI^+(OH_2)OH]^2 + \left(1 + \frac{K_4}{[H^+]}\right)[PhI^+(OH_2)OH] -$$
$$[HMIB]_0 = 0 \quad (9)$$

$$\frac{K_4K_6\,\epsilon_{dh}}{[H^+]}[PhI^+(OH_2)OH]^2 +$$
$$\left(\epsilon_{ih} + \frac{\epsilon_i K_4}{[H^+]}\right)[PhI^+(OH_2)OH] = A \quad (10)$$

A is the optical absorbance (cm^{-1}) of the sample at a selected wavelength, and ϵ_{ih}, ϵ_i, and ϵ_{dh} are the molar absorbtivities of PhI$^+$(OH$_2$)OH, PhI$^+$(OH$_2$)O$^-$, and Ph(HO)I$-$O$-$I$^+$(OH$_2$)Ph, respectively. Best fits of the data in Figure 2 were obtained using eqs 9 and 10. Concentrated base was used to adjust the pH so that the total volume change was only 1$-$2%, and volume corrections were unnecessary. The constants whose values must be assigned are K_4, K_6, ϵ_{ih}, ϵ_i, and ϵ_{dh}. At each pH, [PhI$^+$-(OH$_2$)OH] was calculated from eq 9. A, and hence ϵ, was calculated from eq 10.

The position of pH$_{max}$ is controlled by two factors: pK_4 and the relative values of ϵ_{ih} and ϵ_i. Experimental ϵ_{ih} and ϵ_i can be obtained from solutions at pH 1 and pH > 8, respectively, leaving only pK_4 to adjust pH$_{max}$. The K_6 and ϵ_{dh} selected control the magnitude of ϵ at pH$_{max}$, i.e., ϵ_{max}. Increasing either K_6 or ϵ_{dh} increases ϵ_{max}; however, increasing K_6 dramatically increases the peak width at half-height (PWHH), which is not true for ϵ_{dh}. Thus, by varying K_6 and ϵ_{dh}, both the experimental ϵ_{max} and PWHH can be matched. The calculated lines in Figure 2 were obtained with pK_4 = 4.30, K_6 = 670, and [HMIB]$_0$ = 3.0 mmol·dm^{-3}. ϵ_{dh} was varied to match ϵ_{max} at each wavelength, and experimental ϵ_{ih} and ϵ_i were used, Table 1. All data with [HMIB]$_0$ = 3.0 mmol·dm^{-3} were reasonably fit using the experimental ϵ_{ih} and ϵ_i, and the same pK_4 and K_6. The ϵ_{dh} giving the best fits varied with λ, as expected. The

Table 1. Molar Absorbtivities (dm^3·mol^{-1}·cm^{-1}) Used for Fits of the Data in Figure 2

nm	ϵ_{ih}	ϵ_i	ϵ_{dh}
300	530	240	2670
320	135	140	2300
336	45	150	1800

Table 2. Values of Equilibrium Constants and Molar Absorbtivities (dm^3·mol^{-1}·cm^{-1}) Giving Best Fits of the Apparent Molar Absorbtivity at 320 nm versus pH Data in Figure 3. All Measurements Were Taken at (20.0 ± 0.5) °C. All Solutions Contained 0.10 mol·dm^{-3} NaOMs

[HMIB]$_0$	pK_4	K_6	ϵ_{ih}	ϵ_i	ϵ_{dh}
0.25	4.29	590	139	143	2400
0.99	4.31	620	124	132	2420
2.0	4.30	670	125	133	2390
3.0	4.29	670	140	145	2470
4.0	4.35	690	137	145	2430
5.0	4.36	720	137	190	2465

shifts in pH$_{max}$ were well predicted, as were the peak profiles. Significantly, the 6.0 mmol·dm^{-3} data deviate from the calculated curve as pH approaches pK_4: this is consistent with Scheme 2 since the ratio of the concentrations of dimers to monomers increases as [HMIB]$_0$ increases, while the absorbtivities of the μ-oxodiphenyldiiodine species per mole of iodine-(III) are much larger than those of the monomers. Thus, Scheme 2 provides a *good approximation* of the equilibria present in aqueous HMIB solutions.

The system is more complicated than suggested by Scheme 2. For a series of solutions with [HMIB]$_0$ from 0.25 to 5.0 mmol·dm^{-3}, ϵ_{320} was measured as a function of pH, Figure 3. The data were fit using eqs 9 and 10, much as described above, except that ϵ_{ih} and ϵ_i were not constrained to the experimental values. At each [HMIB]$_0$, after ϵ_{ih} and ϵ_i were selected, K_4 was varied to match pH$_{max}$. Finally, K_6 and ϵ_{dh} were varied to match ϵ_{max} and the PWHH. Table 2 lists the values giving best fits, which were excellent: to illustrate, the best fit line for the 5 mmol·dm^{-3} data is included in Figure 3. ϵ_{ih} for the best fits was essentially constant, and about the same as the experimental ϵ_{ih}. ϵ_{ih} most influences the fits at pH < pK_4. The best-fit ϵ_i increased somewhat with [HMIB]$_0$ but were close to the experimental value at low concentrations. ϵ_i most influences ϵ_{320} at pH > pK_4. The best-fit ϵ_{dh} were nearly constant, and at low concentrations were close to the best-fit value from Figure 2. The best-fit pK_4 increased slightly at [HMIB]$_0$ above 4.0 mmol·dm^{-3}; however, at lower concentrations, pK_4 was nearly constant and indistinguishable from the value used for Figure 2. K_6 showed the most consistent variation with [HMIB]$_0$, changing from 590 to 720 as the concentration was increased from 0.25 to 5.0 mmol·dm^{-3}. The K_6 obtained for 2$-$3 mmol·dm^{-3} solutions, i.e., 670, is the same as that obtained for 320 nm data for Figure 2, where [HMIB]$_0$ was 3.0 mmol·dm^{-1}. In summary, the best-fit constants for the data in Figure 3, based on Scheme 2 and summarized in Table 2, give the following values: at 320 nm, ϵ_{ih}, ϵ_i, and ϵ_{dh} are (135 ± 10), (140 ± 10), and (2400 ± 50) dm^3·mol^{-1}·cm^{-1}, respectively; pK_4 = (4.30 ± 0.02); and $K_6 \leq$ 590.

All of the changes in the "constants" for the best fits tabulated in Table 2 (data in Figure 3) can be attributed to changes in solution character at higher pH, resulting from increases in [PhI$^+$(OH$_2$)O$^-$], reaction 4. Iodosylbenzene is only slightly soluble in water: although supersaturated solutions apperaed to form and precipitation of the gelatinous product was slow, we observed that solutions with [HMIB]$_0$ > 3 mmol·dm^{-3} became visibly cloudy at pH > 4.7 within several minutes. The

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Scheme 3

$$PhI(OH)OSO_2R \text{ (s)} \xrightarrow{H_2O} PhI^+(OH_2)OH \text{ (aq)} + RSO_3^- \text{(aq)} \quad (3)$$

$$PhI^+(OH_2)OH \underset{}{\overset{K_4}{\rightleftharpoons}} PhI^+(OH_2)O^- + H^+ \quad (4)$$

$$PhI^+(OH_2)O^- + PhI^+(OH_2)OH \underset{}{\overset{K_6}{\rightleftharpoons}} Ph(HO)I-O-I^+(OH_2)Ph + H_2O \quad (6)$$

$$Ph(HO)I-O-I^+(OH_2)Ph + H^+ \underset{}{\overset{K_7}{\rightleftharpoons}} Ph(H_2O)I^+-O-I^+(OH_2)Ph \quad (7)$$
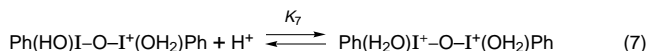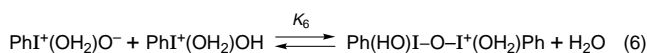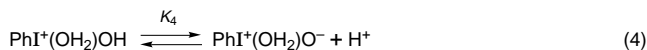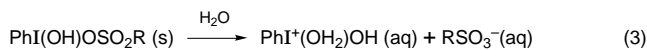
effect of the light scattering caused by the particulates is artificially high absorbances, which shift the pH_{max} to slightly higher values and broaden the peaks. Thus, artificially large K_6 and ϵ_i are needed to fit the data. As a result, the K_6 obtained at the lowest $[HMIB]_0$ is an upper limit, i.e., $K_6 \leq 590$. The effect is erratic since the degree of precipitation depends on the age of the solution, on a time scale of minutes. Thus, in Figure 2 the molar absorbtivity at pH 11 was the same at 3 and 6 mmol·dm^{-3} only because the data were taken with sufficient rapidity. Additional evidence of light scattering is seen in the data treatment described next. Please take note: with the exception of the 5.0 mmol·dm^{-3} data, the lines in Figure 3 are not best fits yielding the values in Table 2 but are derived from Scheme 3 as described later.

The data in Figure 3 define a three-dimensional surface, where the axes are pH, $[HMIB]_0$, and ϵ_{320}. Figure 3 simply shows slices through this space with $[HMIB]_0$ held constant. Using the smooth lines through the ϵ_{320} vs pH data generated using the constants in Table 2, we can take slices of pH$-[HMIB]_0-\epsilon_{320}$ space with pH held constant, giving plots of ϵ_{320} vs $[HMIB]_0$ at selected pH, Figure 4. These data cannot be collected easily in a direct fashion. The motivation for such plots is as follows. The potentiometric titration data, discussed later, suggest that protonation of Ph(HO)I$-$O$-$I$^+$(OH$_2$)Ph, reaction 7, may be important in the lower pH range of our measurements. Thus, the system is better described by Scheme 3, with K_w. Scheme 3 is the same as Scheme 2, with the addition of reaction 7. Mass-balance and equilibrium relationships give eqs 11 and 12:

$$2K_4K[PhI^+(OH_2)OH]^2 + \left(1 + \frac{K_4}{[H^+]}\right)[PhI^+(OH_2)OH] - [HMIB]_0 = 0 \quad (11)$$

$$K_4E[PhI^+(OH_2)OH]^2 + \left(\epsilon_{ih} + \epsilon_i\frac{K_4}{[H^+]}\right)[PhI^+(OH_2)OH] = A \quad (12)$$

where

$$K \equiv K_6\left(K_7 + \frac{1}{[H^+]}\right) \quad (13)$$

and

$$E \equiv K_6\left(\epsilon_{dhh}K_7 + \frac{\epsilon_{dh}}{[H^+]}\right) \quad (14)$$

ϵ_{dhh} is the molar absorbtivity of the [bis(aquo)]-μ-oxodiphenyl-diiodine dication (Ph(H$_2$O)I$^+$−O−I$^+$(OH$_2$)Ph) formed in reaction 7. Now, we have good values for pK_4, ϵ_i, and ϵ_{ih}: at each pH, we could vary K and E to obtain the best fits of the ϵ_{320} vs $[HMIB]_0$ plots. Equations 13 and 14 now provide an excellent test of Scheme 3: if the mechanism is correct, a plot of K vs $[H^+]^{-1}$ will give a *straight line*, and a plot of E vs $[H^+]^{-1}$ would *also be linear*. The K vs $[H^+]^{-1}$ plot would yield K_6 as the slope and (K_6K_7) as the intercept, allowing calculation of both K_6 and K_7: we already have a limiting value for K_6 and
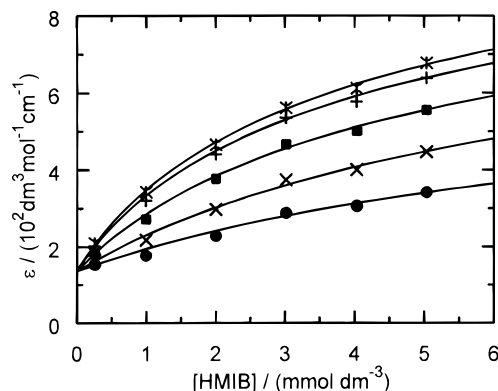
Figure 4. Dependence of ϵ_{320} on $[HMIB]_0$ at selected pH. Data points are taken from the best fits of Figure 2 at six $[HMIB]_0$. Lines are calculated fits to the data as described in the text: (●) pH 2.98; (×) pH 3.31; (■) pH 3.64; (+) pH 3.97; (top curve) pH 4.30.
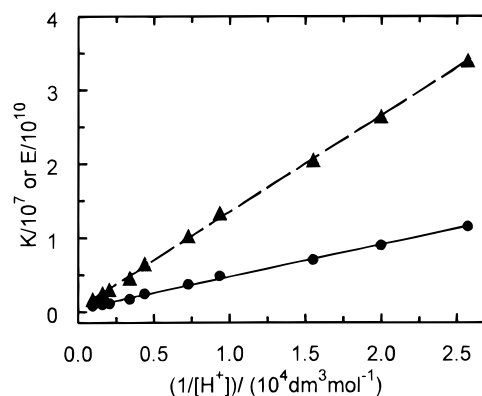
Figure 5. Dependence of K (●) and E (▲) on $[H^+]^{-1}$ for aqueous HMIB solutions.

agreement of the values will provide strong support for the mechanism. The E vs $[H^+]^{-1}$ plot will give $(K_6\epsilon_{dh})$ as the slope and $(K_6K_7\epsilon_{dhh})$ as the intercept, yielding ϵ_{dh} and ϵ_{dhh}: we have a value for ϵ_{dh} from other data sets, providing a further test of the mechanism.

Figure 4 plots were fit as follows. For a selected pH, [PhI$^+$-(OH$_2$)OH] was calculated from eq 11 for a series of $[HMIB]_0$. At each $[HMIB]_0$, A was calculated using eq 12, yielding ϵ_{320} at that $[HMIB]_0$. Experimental ϵ_{ih} and ϵ_i were used, Table 1. The pK_4 obtained from the fits of the ϵ vs pH data at low $[HMIB]_0$ in Figures 2 and 3 was used (4.30). At each pH, K and E were varied to obtain the best fit of the ϵ_{320} vs $[HMIB]_0$ data for that pH. K determines the curvature of the initial portion of the curve, while E determines the slope at higher concentrations. Excellent fits were obtained with this model, Figure 4. As seen in Figure 5, the K vs $[H^+]^{-1}$ and E vs $[H^+]^{-1}$ plots *were straight lines* for data from pH 3.0 to 4.6, a change in $[H^+]$ by a factor of almost 50. The linearity of these two plots lends considerable support to the equilibria in Scheme 3.

A linear regression fit of the K vs $[H^+]^{-1}$ plot gives $K_6 = (434 \pm 7)$ and $(1/K_7) = (1.2 \pm 0.3) \times 10^{-3}$. Significantly, this value of K_6 is not very different from that obtained from Figure 2 ($K_6 = 670$) using Scheme 2, or the K_6 from Figure 3 ($K_6 \leq 590$) using Scheme 2. Using the K_6 and K_7 obtained here, a linear regression fit of the E vs $[H^+]^{-1}$ data give ϵ_{dh} and ϵ_{dhh} equal to (3000 ± 70) and (1500 ± 700) dm^3·mol^{-1}·cm^{-1}, respectively. The ϵ_{dh} obtained is slightly higher than that obtained from fits of Figures 2 and 3 using Scheme 2, i.e., 2400 and 2300 dm^3·mol^{-1}·cm^{-1}, respectively. The deviations in K_6 and ϵ_{dh} are not so large when we consider the large difference in the way the values were obtained.

It is significant to note that when K and E at pH > 4.6 are included, the plot of K vs $[H^+]^{-1}$ curves downward, while the

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plot of E vs $[H^+]^{-1}$ curves upward. Both trends result from precipitation of iodosylbenzene and the consequent light scattering. This curvature probably also affects the equilibrium constants and molar absorptivities obtained. For example, when K vs $[H^+]^{-1}$ was fit for pH 3.0−4.0, the K_6 obtained was (487 ± 14), closer to the value of ≤590 obtained from Figure 3. We can reasonably conclude that the actual K_6 lies somewhere between these, i.e., $K_6 = 540 \pm 50$. For p(1/K_7), 2.5 was found vs 2.9 for $3.0 \leq$ pH ≤ 4.6. In this smaller pH range, E vs $[H^+]^{-1}$ gave $\epsilon_{dh} = 2860$ dm^3·mol^{-1}·cm^{-1}, closer to those obtained from fits of Figures 2 and 3. ϵ_{dhh} was 1530 dm^3·mol^{-1}·cm^{-1}.

To evaluate the consistency of the data fits, theoretical lines based on the above model were calculated for Figure 3: the best fits of the data sets in this figure were used to generate the three-dimensional surface yielding Figure 4. The theoretical lines were calculated using a single set of equilibrium constants and molar absorptivities: p$K_4 = 4.30$, $K_6 = 540$, p(1/K_7) = 2.5, and $\epsilon_{ih} = 135$, $\epsilon_i = 140$, $\epsilon_{dh} = 2860$, and $\epsilon_{dhh} = 1530$ dm^3·mol^{-1}·cm^{-1}. Good agreement is seen between the theoretical lines and the data, Figure 3, except at higher pH and higher $[HMIB]_0$, where precipitation of iodosylbenzene produces deviations.

Spectra of HMIB and HTIB solutions in the visible region showed only the trailing edge of the UV absorptions. HMIB in 1 mol·dm^{-3} methanesulfonic acid produced no visible color, even at concentrations as high as 120 mmol·dm^{-3}. At natural pH, a 64 mmol·dm^{-3} HMIB solution was light yellow, with the corresponding increased molar absorptivity relative to the acid solution in the range from 450 to 550 nm. When NaOH was added to the natural pH HMIB solution in a 1:2 molar ratio (NaOH:HMIB), the yellow color of the solution visibly intensified, as reflected by strongly increased molar absorptivities. Moderately alkaline (pH 8−9) or strongly alkaline (1 N NaOH) solutions were colorless. In virtually every respect, equivalent solutions of HMIB or HTIB gave identical results.

Spectrum of the Dimeric [Hydroxy(aquo)-μ-oxodiphenyldiiodine Cation. The optical absorption spectrum of Ph(HO)I−O−I$^+$(OH$_2$)Ph was calculated from spectra of HMIB solutions at pH 1, pH 9.6, and pH 4.25. The mechanism predicts that for a 2 mmol·dm^{-3} solution at pH 1 or 9.6 the spectrum is due almost entirely to PhI$^+$(OH$_2$)OH or PhI$^+$(OH$_2$)O$^-$, respectively. The spectrum at pH 4.25 given in Figure 1 was obtained from a 2.00 mmol·dm^{-3} solution. Using eqs 11 and 13, based on Scheme 3, the concentrations of PhI$^+$(OH$_2$)OH, PhI$^+$(OH$_2$)O$^-$, Ph(HO)I−O−I$^+$(OH$_2$)Ph, and Ph(H$_2$O)I$^+$−O−I$^+$(OH$_2$)Ph can be calculated for this pH and $[HMIB]_0$. Using p$K_4 = 4.30$, $K_6 = 540$, and p(1/K_7) = 2.5, the respective concentrations of the iodonium species are 0.762, 0.679, 0.280, and 0.005 mmol·dm^{-3}. About 28.5% of the total iodine(III) species are present in dimeric form. Then, to a good approximation, the molar absorptivity at a given wavelength of Ph(HO)I−O−I$^+$(OH$_2$)Ph is

$$\epsilon_{dh} = 2\left(\frac{\epsilon - 0.381\epsilon_{ih} - 0.340\epsilon_i}{0.285}\right) \quad (15)$$

The calculated spectrum is given in Figure 6, along with the spectra of PhI$^+$(OH$_2$)OH and PhI$^+$(OH$_2$)O$^-$. The molar absorptivities of the dimer in the region from 300 to 400 nm are dramatically larger than those of the monomers, consistent with assertions that the yellow color of aqueous solutions of a number of iodine(III) species results from the −I−O−I− unit of the μ-oxodiphenyldiiodine dimer.[33] The calculated value of ϵ_{dh} at 320 nm is 2485 dm^3·mol^{-1}·cm^{-1}, in reasonable agreement with

(33) Dasent, W. E.; Waddington, T. C. *Proc. Chem. Soc.* **1960**, 71.
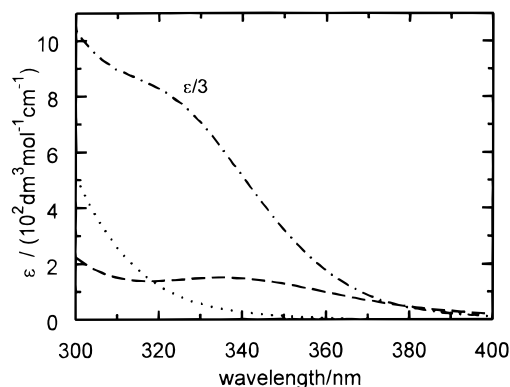
Figure 6. Optical absorption spectrum of Ph(HO)I−O−I$^+$(OH$_2$)Ph, calculated as described in the the text (·−·): the values plotted are $\epsilon_{dh} \div 3$. Spectra of the pH 1 (···) and pH 9 (- - -) monomers, from Figure 1, are included for comparison.
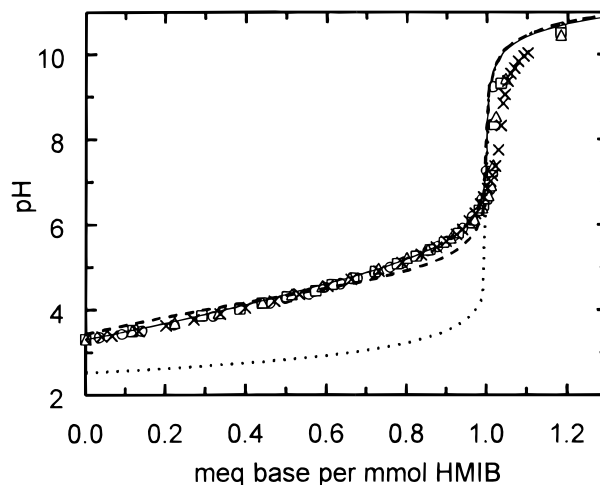
Figure 7. Potentiometric titrations of HMIB aqueous solutions: (—) calculated curve based on Scheme 3 and values for the K's given in the text; (···) calculated curve based on 1 mol of strong acid per mole of HMIB; (- - -) calculated curve based on 1 mol of weak acid per mole of HMIB with p$K_A = 4.3$. 3 mmol·dm^{-3} HMIB with (○) 0 mmol·dm^{-3} NaOMs, (□) 100 mmol·dm^{-3} NaOMs, (△), or 200 mmol·dm^{-3} NaOMs. (×) HTIB, 3 mmol·dm^{-3} in water with no other additives.

the value of 2860 dm^3·mol^{-1}cm^{-1} obtained from the series of data fits described previously.
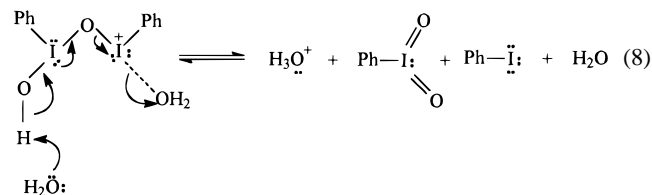
Potentiometric Titrations of Aqueous HMIB Solutions. Potentiometric titrations of HMIB solutions showed the presence of 1 equiv of titratable protons per mole of HMIB. The shape of the titrations curves does not conform to that of a strong acid, nor to that of a simple monoprotic weak acid. The addition of dimer formation to the solution dynamics, reaction 6, accounts for the large slopes seen in the titration curves, Figure 7. The difference between the potentiometric titration curves of strong acids, weak acids, and weak acids with a dimerization equilibrium in the region of the pK_A is dramatic, so that it is clear which type of species is present. The large slope in the pK_A region of the titration curve can be considered a "fingerprint" for the presence of PhI$^+$(OH$_2$)OH and related species. Initial fits using a model including only reactions 3, 4, 6, and K_W, i.e., Scheme 2, showed that the pK_A was near 4.3. Using a model including reactions 3, 4, 6, 7, and K_W, i.e., Scheme 3, the potentiometric titration data were very well fit, Figure 7. The data fits were substantially improved by inclusion of the protonation equilibrium for the initially formed dimer, reaction 7. In the fits of the titration data, the value chosen for K_4, the K_A of PhI$^+$(OH$_2$)OH, essentially varies the y-axis offset and hence the y-axis intercept of the curve. The value chosen for

K_6, the dimerization equilibrium constant, increases the slope by dropping the initial points in the titration and raising the later points, with a "pivot point" near 0.5 mequiv of base per mmol of HMIB. The solid line in Figure 7 was calculated using $pK_4 = 4.30$, $K_6 = 540$, and $p(1/K_7) = 2.5$, values obtained from the treatments of the dependence of *optical molar absorbtivity* on pH. The essential agreement of the data with the calculated line, based on equilibrium constants obtained from optical measurements, substantiates the proposed mechanism and solution species.

For illustrative purposes, the potentiometric titration curves expected for production of 1 mol of strong acid per mole of HMIB, and for 1 mol of weak acid with $pK_A = 4.30$ per mole of HMIB, are included in Figure 7. These visually demonstrate how different the behavior of HMIB solutions are from those of simple strong or weak acids. The clear deviation of the potentiometric titration curves from the simple cases eliminates some possible reactions following dissolution of HMIB. For example, it is *not possible* that the $PhI^+(OH_2)OH$ formed in reaction 3 immediately and completely deprotonates, giving $PhI^+(OH_2)O^-$. If this were so, then addition of HMIB to water would produce 1 equiv of strong acid (H^+) and 1 mol of a weak acid with a pK_A of 4.3, $PhI^+(OH_2)O^-$, per mole of HMIB, and this was *not* observed. We can conclude that pK_A observed at 4.3 is *not* that of $PhI^+(OH_2)O^-$. Thus, the titration results support a mechanism in which the species exhibiting a pK_A at 4.3 is the initially formed [hydroxy(aquo)iodo]benzene cation.

The three sets of data plotted in Figure 7 are for different concentrations of added sodium methanesulfonate (0, 0.100, and 0.200 mol·dm^{-3}). The coincidence of the plots shows a virtual lack of dependence of the system on ionic strength, and lack of dependence on $[MsO^-]$, in the range examined. The lack of dependence on $[MsO^-]$ implies that the equilibrium constant for formation of ion pairs between MsO^- and $PhI^+(OH_2)OH$ is either very large (essentially complete ion-pairing at a one-to-one concentration ratio) or very small (not detectable with $[MsO^-] = 0.200$ mol·dm^{-3}). The absence of a large equilibrium constant for ion-pairing is seen from the following experiment. When an aqueous solution of 3.00 mM HTIB in water was titrated in the same manner as the HMIB solutions at 20 °C, virtually identical results were obtained as with HMIB solutions, Figure 7. This is consistent with a model in which HMIB and HTIB both dissolve in water to give organosulfonate ions and identical aqueous iodine(III) species.

Thermal Stability of HMIB Solutions. The observed products of the thermal decomposition of HMIB in H_2O are the disproportionation products iodylbenzene and iodobenzene. Disproportionation of HMIB most likely occurs via heterolysis of a *μ*-oxodiphenyldiiodine species such as $Ph(HO)I-O-I^+-(OH_2)Ph$, where decomposition is initiated by deprotonation of the hydroxy group, reaction 8:

The only significant divergence between the calculated and measured data in the potentiometric titrations occurred beyond the point where 1.00 equiv of base per mole of HMIB had been added. It was regularly observed that if the titrations were done within 30−60 min after solution preparation, then 1.00 ± 0.01 equiv of acid was obtained per equivalent of HO^-; however, if some time elapsed from solution preparation to titration, then

Table 3. ^{1}H Chemical Shifts of the Phenyl and Methyl Protons of HMIB, HTIB, and NaOMs in D_2O at Natural pH

	ortho-^{1}H	para-^{1}H	meta-^{1}H	methyl-^{1}H
HMIB	8.192	7.751	7.593	2.785
HTIB	8.163	7.725	7.566	2.357
NaOMs				2.795

slightly more than 1 equiv of neutralizable protons was obtained. Although the number of equivalents of neutralizable protons per mole of HMIB in the potentiometric titrations was very nearly equal to one, in many titrations this number was significantly greater than one: values as high as 1.07 were obtained. Clearly, the production of "extra" acid is related to the thermal decomposition of HMIB since prompt titrations after solution preparation gave 1.00 ± 0.01 equiv per mole. Since $PhIO_2$ itself is a weak base (the conjugate acid has a pK_A of 6.95), and since we expect that PhI would be neutral in its reaction with water, it would seem that the "extra acid" in aged solutions arises from an interaction of products and reactants not heretofore recognized.
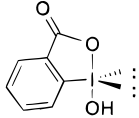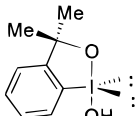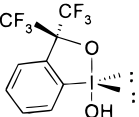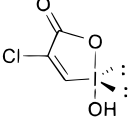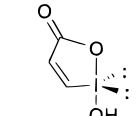
NMR Spectroscopy of HMIB and HTIB Solutions. Potentiometric titrations of aqueous HMIB and HTIB solutions indicate that identical aqueous species are produced from these iodine(III) compounds. ^{1}H NMR spectra in D_2O support this conclusion. At natural pH, the peaks due to the ortho-, meta-, and para-hydrogens of the iodine(III)-bound phenyl group of HMIB and HTIB occur at the same positions, Table 3. Furthermore, the methyl protons of the methanesulfonate species in HMIB solutions give chemical shifts identical to those seen in D_2O solutions of sodium methanesulfonate, a result expected only if the methanesulfonate ions in the HMIB solutions are free from the iodine(III) species.

The presence of the various equilibria shown in Scheme 1 are manifest in the NMR spectra. Solutions of iodobenzene in CD_3OD show well-developed fine structure in the peaks for its aromatic protons, while the corresponding ^{1}H peaks for HMIB in D_2O or CD_3OD appear virtually as two simple broadened triplets and a broadened doublet (iodobenzene is insoluble in water). The proton of the hydroxy ligand initially present in HMIB and HTIB clearly is exchanged to the HDO pool, i.e., there is no proton signal corresponding to an $-OH$ group other than HDO.

Monomeric Species. Optical spectroscopy and potentiometric titrations of aqueous solutions of HMIB or of HTIB establish that between pH 1 and 10 there are two monomeric iodine(III) species present, i.e., the [hydroxy(aquo)iodo]benzene ion and its conjugate base. Identical solution species are produced from the two compounds. Optical absorbance results for solutions above pH 11 show that a new species appears there.

The initially formed monomer is the [hydroxy(aquo)iodo]benzene cation ($PhI^+(OH_2)OH$) formed when the organosulfonato ligand is displaced by a water molecule. In this species, the H_2O ligand is loosely bound to the iodine(III) center,[8] while the hydroxide ligand is covalently bound. The lack of significant covalent character in the water−iodine(III) bond is rationalized as follows. If the bond were purely covalent, the positive charge would reside on the oxygen atom, and the species would be a strong acid. Witness the pK_A values of other tricovalent oxygen-centered compounds: the pK_A of H_3O^+ is -1.74,[27] while the pK_A of protonated dimethyl ether, $(CH_3)_2O^+-H$ is -2.5.[28] Thus, a species in which the water ligand is covalently bound to the iodine(III) would be very acidic, with a pK_A many units below 4.3. This would result in the production of 1 mol of strong acid and 1 mol of weak acid ($pK_A = 4.3$) per mole of HMIB dissolved, and this was not the case. Thus, we conclude that the water ligand(s) is (are) weakly bound to the iodine-

Characterization of Species in Aqueous Solutions

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Table 4. pK_A Values for Heterocyclic Hydroxy(aryl)iodanes with Internal Carboxylate and Alkoxide Ligands

Hydroxyiodane		pK_A (H$_2$O, 25 °C)
	7	7.25[29]
	8	> 11[30]
	9	7.75[30]
	10	7.45[30]
	11	7.78[30]

(III), with a bond order significantly less than one. Single-crystal X-ray analysis of HTIB[7] shows that the HO–I bond length is 1.94 Å, consistent with a covalent bond between the iodine-(III) atom and oxygen, while the TsO–I bond length is 2.47 Å, indicating significant ionic character in this iodine–oxygen bond. Thus, both solution and solid state data suggest that the

$$\text{Ph}-\overset{O^-}{\underset{}{I^+}}$$

structure forms a stabilized unit with any additional ligands exhibiting low bond order.

The hydroxide ligand in PhI$^+$(OH$_2$)OH is a very weak base, i.e., the conjugate acid formed in reaction 16, PhI$^+$(OH$_2$)$_2$, is a strong acid. Were this not the case, the natural pH of HMIB/HTIB solutions would be alkaline, whereas they are acidic. In

$$\text{PhI}^+(\text{OH}_2)\text{OH} + \text{H}_2\text{O} \rightleftarrows \text{PhI}^{2+}(\text{OH}_2)_2 + \text{HO}^- \quad (16)$$
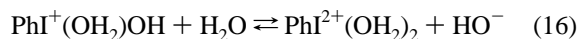
the pH range of our experiments, we could not discern the effects of the putative PhI^{2+}(OH$_2$)$_2$ dication. In summary, it is PhI$^+$-(OH$_2$)OH which has an acid dissociation constant with pK_A = 4.3. Given that H$_2$O is loosely bound, and that HO$^-$ is tightly bound, what can we say about the deprotonation that results in the observed pK_A at 4.3?

pK_A measurements of acyclic hydroxy(aryl)-λ^3-iodanes have not been reported. In contrast, heterocyclic hydroxy(aryl)-iodanes with internal carboxylate and alkoxide ligands are known, and pK_A values for a few of them have been reported,[29,30] Table 4. It is noteworthy that the acidity of the >I–O–H moiety in these hydroxyiodanes is inversely related to the basicity of the second heteroligand. For example, the benziodoxolone **7** is at least 5600 times more acidic than the dimethylbenziodoxole **8** and manifests the lower basicity of an internal carboxylate ligand compared to that of an internal alkoxide ligand. Presumably, ionic structures of ArIOHB contribute *less* to the hybrid as the basicity of B:$^-$ increases, i.e.,
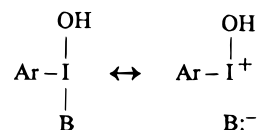

This lowers the degree of positive charge at iodine and decreases the acidity of the hydroxyl function. The greater acidity of the bis(trifluoromethyl)benziodoxole **9** compared to **8** and the greater acidity of **10** compared with **11** is consistent with this logic. Even if the iodanes **7** and **8** ionize in H$_2$O and are ligated with one or more water molecules they would not give free ions, since the anions would be held in close proximity to the iodonium centers, reaction 17. Both HMIB and HTIB give the

$$(17)$$
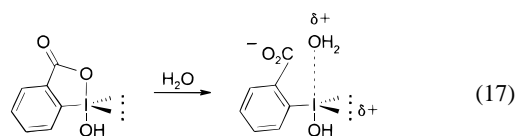
free [hydroxy(aquo)iodo]benzene cation, PhI$^+$(OH$_2$)OH, upon dissolution in aqueous solution. The high acidity of this species (pK_A = 4.3) is understandable if it is the hydroxy ligand and not the water ligand, which deprotonates. The water ligand is a much weaker base than either the carboxylate and alkoxide ligands in **7** and **8**, respectively, so that we would expect a pK_A substantially below 7, such as 4.3.

What is necessary to obtain [hydroxy(B)iodo]arenes in which the B:$^-$ ligand is covalently bound to the iodine(III)? The discussion in the preceding paragraph provides insight. The observed trend is that an increase in the basicity of B:$^-$ lowers the acidity of the proton in >I–O–H; this is because the >I–B bond is less ionic in character. The least basic of the B:$^-$ ligands in Table 4 is in compound **7**, which has the most acidic –OH group. The conjugate acid of a typical carboxylate ion has a pK_A of about 4.8. Bases whose conjugate acids have pK_A values greater than this should be able to form covalent bonds in [hydroxy(B)iodo]arenes. The conjugate acid of H$_2$O is H$_3$O$^+$, which has a pK_A of −1.74.[31] H$_2$O is a very weak base relative to the bases known to form covalent bonds: it should be no surprise that the bond with H$_2$O in PhI$^+$(OH$_2$)OH is of a very low order. Clearly, there is an upper limit to the basicity of B:$^-$ which can be tolerated by the [3c-4e] bond, which must be polar with significant electron density residing on the axial ligands. For example, [hydroxy(methoxy)iodo]benzene has not been isolated; the pK_A of CH$_3$OH is 15.2.[31] [Bis(methoxy)-iodo]benzene has been isolated, but it decomposes explosively.[32]

Thus, we see that a pK_A of 4.3 is not unreasonable for deprotonation of the hydroxy ligand. Now consider the relative stabilities of the possible conjugate bases of PhI$^+$(OH$_2$)OH, i.e., PhI$^+$(OH$_2$)O$^-$ and PhI(OH)$_2$. Just as [hydroxy(methoxy)iodo]-benzene cannot be isolated due to instability resulting from the very high basicity of the two axial ligands, we would expect PhI(OH)$_2$ to be of a low stability. In contrast, PhI$^+$(OH$_2$)O$^-$ is a hydrate of PhIO, iodosylbenzene, a very stable molecule. Thus, it is highly unlikely that PhI(OH)$_2$ is the conjugate base of PhI$^+$-(OH$_2$)OH. The structural considerations discussed all support the assignment of PhI$^+$(OH$_2$)O$^-$ as the conjugate base, while the water ligand remains very loosely bound. The probable identity of the high pH monomeric species is PhI(OH)O$^-$:

$$\text{PhI}^+(\text{OH}_2)\text{O}^- + \text{HO}^- \rightleftarrows \text{PhI(OH)O}^- + \text{H}_2\text{O} \quad (5)$$
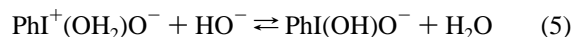
In the above discussion, we examined the results and theoretical arguments, reaching the conclusion that the three monomeric forms of aqueous iodosylbenzene are PhI$^+$(OH$_2$)-OH, PhI$^+$(OH$_2$)O$^-$, and PhI(OH)O$^-$. HMIB is extremely water

soluble (0.71 g/mL, 2.25 mol·dm^{-3}) because the MsO$^-$ ligand is highly water soluble. HTIB is less soluble (0.024 g/mL, 0.061 mol·dm^{-3})[25] due to the lesser solubility of TsO$^-$ (relative to MsO$^-$) resulting from the aromatic ring in this anion. Thus, HMIB solutions (and the MsO$^-$ counterion) provide greater insight into the solubilities of the three monomers. If the pH is <2.3, then >99% of the monomer present is PhI$^+$(OH$_2$)OH. Thus, the "solubility of HMIB at natural pH" gives a lower limit on the solubility of PhI$^+$(OH$_2$)OH: it is *very soluble*, >2.25 mol·dm^{-3}. This solubility is consistent with an ionic species that is easily solvated. At pH >5.3 through mildly alkaline conditions, >90% of the monomer is PhI$^+$(OH$_2$)O$^-$: this monomer is soluble only to the extent of about 3 mmol·dm^{-3}. Such low solubility is consistent with the zwitterionic character of this species, and with the observation that dehydration produces PhIO, a highly stable uncharged molecule. In highly alkaline pH, PhI$^+$(OH$_2$)O$^-$ deprotonates to PhI(OH)O$^-$. This species is more soluble than PhI$^+$(OH$_2$)O$^-$ and dissolved at about 6 mmol·dm^{-3} at the highest pH tested.

Dimerization in Acidic Media. The equilibrium constant for dimerization of PhI$^+$(OH$_2$)OH to produce the [bis(aquo)]-μ-oxodiphenyldiiodine dication (Ph(H$_2$O)I$^+$−O−I$^+$(OH$_2$)Ph), reaction 18, can be calculated since this reaction is the sum of

$$2PhI^+(OH_2)OH \rightleftharpoons Ph(H_2O)I^+-O-I^+(OH_2)Ph + H_2O \quad (18)$$
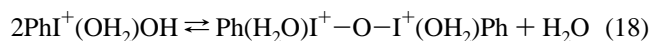
reactions 4, 6, and 7. Thus, $K_{18} = K_4K_6K_7$ and $K_{18} \approx 8.6$. HMIB is very soluble in water at natural pH (2.25 mmol/mL). At pH ≈ 1, PhI$^+$(OH$_2$)OH is the primary monomer: at 0.1 mol·dm^{-3}, about 50% of the iodine(III) species will be present as Ph(H$_2$O)-I$^+$−O−I$^+$(OH$_2$)Ph. Such concentrations of the [hydroxy-(aquo)]-μ-oxodiphenyldiiodine cation cannot be achieved since this dimer forms primarily near pH 4.3 (i.e., pK_4) where [PhI$^+$(OH$_2$)O$^-$] become significant, and the solubility of PhI$^+$(OH$_2$)O$^-$ is only ≈ 3 mmol·dm^{-3}.

Acyclic Hydroxy(aryl)-λ^3-iodanes, Their Anhydrides, and Aqueous Solutions of [Hydroxy(sulfonyloxy)iodo]arenes. Apart from the [hydroxy(sulfonyloxy)iodo]arenes **12**, acyclic hydroxy(aryl)-λ^3-iodanes are rare. For example, stable acyclic hydroxyiodanes such as **13** and **14**, containing carboxylate or nitrate ligands, have not been isolated. However, dimeric μ-oxodiphenyldiiodine species such as [bis(acetato-*O*)]-μ-oxo-diphenyldiiodine (**15**), formally anhydrides of these putative hydroxyiodanes, have been isolated.
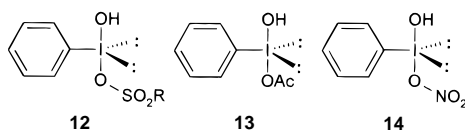
Dasent and Waddington[33] obtained **15** by treatment of (diacetoxyiodo)benzene with nitric acid. (Diacetoxyiodo)-benzene is substantially soluble in nitric acid, while crystals of **15** slowly precipitate from solution. Willgerodt,[26] as later shown by Dasent and Waddington,[33] obtained [bis(nitrato-*O*)]-μ-oxodiphenyldiiodine (**16**), upon treatment of iodosylbenzene with *nitric acid*. On the other hand, when aqueous solutions of HTIB were treated with *sodium nitrate* solutions, [hydroxy-(nitrato-*O*)]-μ-oxodiphenyldiiodine (**17**) was obtained by Wettach.[25] The absence of hydroxyiodanes, PhI(OH)X, corresponding to these dimers and the pH dependence of the dimeric

(34) Zhdankin, V. V.; Tykwinski, R.; Caple, R.; Berglund, B.; Koz'min, A. S.; Zefirov, S. S. *Tetrahedron Lett.* **1988**, *29*, 3717.

(35) Zhdankin, V. V.; Tykwinski, R.; Berglund, B.; Mullikin, M.; Caple, R.; Zefirov, N. S.; Koz'min, A. S. *J. Org. Chem.* **1989**, *54*, 2609.

(36) Carmalt, C. J.; Crossley, J. G.; Knight, J. G.; Lightfoot, P.; Martin, A.; Muldowney, M. P.; Norman, N. C.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1994**, 2367.

structures suggest that they are formed via interactions of the anions with dimeric species already present in solution. In moderately acid solution, Ph(HO)I−O−I$^+$(OH$_2$)Ph is the main dimer: anions such as nitrate can displace the water ligand and **17** precipitates:

$$Ph(HO)I-O-I^+(OH_2)Ph + NO_3^- \rightarrow$$
$$Ph(HO)I-O-I(NO_3)Ph \downarrow + H_2O \quad (19)$$
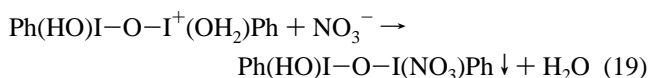
In very acidic solution, the bis(aquo) dimer, Ph(H$_2$O)I$^+$−O−I$^+$(OH$_2$)Ph, predominates: nitrate can replace both water ligands, and **16** is obtained:

$$Ph(H_2O)I^+-O-I^+(OH_2)Ph + 2NO_3^- \rightarrow$$
$$Ph(NO_3)I-O-I(NO_3)Ph \downarrow + 2H_2O \quad (20)$$
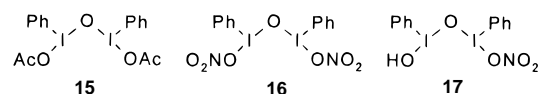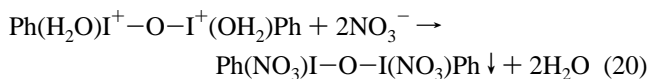
Zhdankin and co-workers[34,35] prepared the tetrafluoroborate, hexafluoroantimonate, and hexafluorophosphate disalts of oxybis[phenyliodonium], **18a−c**, by treating chloroform solutions of (diacetoxyiodo)benzene with aqueous solutions of the corresponding acids at room temperature. Oxybis[phenyl-, bis-(tetrafluoroborate(1−))] iodonium (**18a**) was obtained (70%) from reaction of (diacetoxyiodo)benzene with aqueous HBF$_4$ and was the first such salt reported.[34] Hydroxy-μ-oxodiphe-nyldiiodine(1+), tetrafluoroborate(1−) (**19**) was obtained when **18a** was treated with water for 2−3 h. In summary, synthetic results support our conclusions regarding the presence of dimeric iodine(III) species in solution and the presence of more than one protonated form.
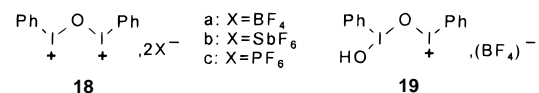
Iodosylbenzene in the solid state is an amorphous powder, where in the PhIO units form polymeric chains.[36] Probably, each chain contains one water of hydration so that the *polymer* has HO endcaps, i.e.,
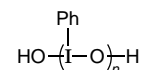
From this point of view, [bis(aquo)]-μ-oxodiphenyldiiodine is the diprotonated *dimer* of iodosylbenzene, while [hydroxy-(aquo)]-μ-oxodiphenyldiiodine is the monoprotonated dimer of iodosylbenzene. One or both of the HO endcaps can be replaced by various anions, such as nitrate, producing [bis(nitrato-*O*)]-μ-oxodiphenyldiiodine or [hydroxy(nitrato-*O*)]-μ-oxodiphenyl-diiodine, respectively. From this same point of view, we can consider HMIB to be an adduct of methanesulfonic acid with the monomeric PhIO. We can consider

a *special unit* of exceptional stability.

Conclusions

The primary processes which occur when HMIB and HTIB dissolve in water are presented in Scheme 1. Both λ^3-iodanes undergo complete ionization to give the hydroxy(phenyl)iodonium ion (PhI$^+$OH) and the corresponding sulfonate ion (RSO$_2$O$^-$) as fully solvated species, i.e., "free" ions. PhI$^+$OH

is presumed to be ligated with at least one water molecule at an apical site of the iodine(III) originally occupied by the sulfonate ion, and this water molecule is loosely bound. Solution behavior is strongly influenced by the presence of μ-oxodiphenyldiiodine dimeric species. The monomeric solution species from HMIB and HTIB are simply various protonated states of hydrates of iodosylbenzene. Many of the reactions described herein will also be important in solutions in organic solvents in which water has not been rigorously excluded.

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