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Preparation and Structure of Oligomeric Iodosylbenzene Sulfate $(PhIO)_3{\cdot}SO_3$: Stable and Water-Soluble Analog of Iodosylbenzene

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New phenyliodine(III) sulfate $(PhIO)_3{\cdot}SO_3$, which has a complex polymeric structure of the trimeric iodosylbenzene units linked by sulfate anions, can be conveniently prepared by treatment of (diacetoxy)iodobenzene with sodium bisulfate in the presence of water. This sulfate can find practical application as a readily available, stable, and water-soluble hypervalent iodine reagent with a reactivity pattern similar to that of iodosylbenzene.
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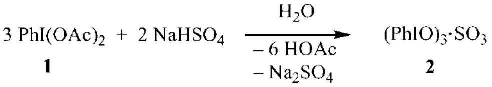
Introduction

Hypervalent aryl-λ^3-iodanes are used extensively in organic synthesis as highly selective and environmentally friendly oxidizing reagents.[1] Among these reagents, iodosylbenzene, $(PhIO)_n$, is particularly important as an oxygen-transfer agent that has found widespread application in catalytic oxygenation reactions after the discovery of its supreme efficacy as a source of oxygen atoms for oxidations catalyzed by cytochrome P-450 and by discrete transition-metal complexes.[2] However, the practical use of iodosylbenzene is hampered by its low stability and potentially explosive properties upon moderate heating and insolubility in most solvents as a result of its polymeric structure.[1a,1e,3]

In this communication we report a simple preparation, structure, and reactivity of stable, nonhygroscopic, and water-soluble oligomeric iodosylbenzene sulfate, $(PhIO)_3{\cdot}SO_3$, which can be considered as a modified, partially depolymerized, and activated form of iodosylbenzene. Several phenyliodine(III) sulfates were previously reported in the literature, but all of these are unstable and highly sensitive to moisture. In particular, the formation of a highly hygroscopic sulfate in the reaction of $PhICl_2$ and Ag_2SO_4 was briefly described by Alcock and Waddington in 1963,[4] and the unstable and extremely hygroscopic sulfates $PhIO{\cdot}SO_3$ and $(PhIO)_2{\cdot}SO_3$ were generated from PhIO and SO_3 or Me_3SiOSO_2Cl under absolutely dry conditions.[5]

Results and Discussion

We found that simple treatment of (diacetoxy)iodobenzene (**1**) with sodium bisulfate afforded, after crystallization from water, a yellow crystalline product whose analytical and spectroscopic data were in good agreement with the molecular formula $(PhIO)_3{\cdot}SO_3$ (**2**) (Scheme 1). Because of the low solubility of $NaHSO_4$ in organic solvents and the insolubility of $PhI(OAc)_2$ in water, we carried this reaction out under solvent-free conditions similarly to the recently reported synthesis of HTIB.[6] The same product, **2**, but in a lower yield, can be obtained by direct treatment of $PhI(OAc)_2$ with $NaHSO_4$ (about 1 equiv.) in water without preliminary grinding in the solid state.



$$\underset{\mathbf{1}}{3\ PhI(OAc)_2} + 2\ NaHSO_4 \xrightarrow[-\ 6\ HOAc \atop -\ Na_2SO_4]{H_2O} \underset{\mathbf{2}}{(PhIO)_3{\cdot}SO_3}$$

Scheme 1.

Single-crystal X-ray analysis of product **2** revealed a complex structure of alternating copolymers containing one $\text{-}OSO_2\text{-}$ fragment per three PhIO units in the polymeric chain (Figure 1). The X-ray structure analysis of **2** was performed at room temperature (structure **2a**) and at –100 °C (structure **2b**) because of the clearly observed phase transition. Thus, the unit cell obtained at room temperature appears to be approximately half the size of the unit cell at low temperature probably as a result of the thermal averaging observed for the phenyl rings in the pseudohelix threefold structure. Because of the large crystal decay observed at room temperature, only low-temperature structure **2b** will be discussed in detail.

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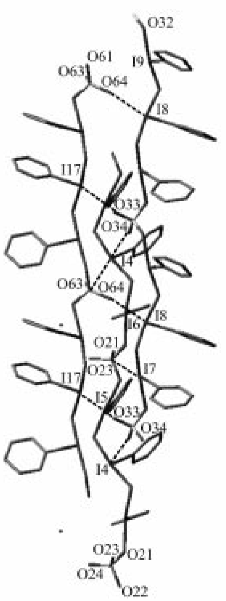


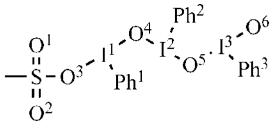
Figure 1. X-ray crystal structure of polymeric phenyliodine(III) sulfate (**2**) at –100 °C (structure **2b**).

The low-temperature X-ray structure of product **2** revealed a unique triple pseudohelix structural motif formed by three polymeric chains situated along the principle *b* axis (Figure 1). All three polymeric chains are connected by strong intermolecular interactions primarily between the oxygen atoms of the sulfate group and the hypervalent iodine centers (typical bond lengths are within a range of 2.8–3.0 Å). The pseudohelix threefold motif was found in the center of this polymer (if the phenyl groups would be eliminated). Two of these triple-helix motifs in the unit cell were found at low temperature; however, the structure obtained at room temperature reveals only one triple polymeric chain due to thermal averaging of pseudohelix polymeric chains observed in the unit cell. Each independent threefold polymeric chain is formed by three fragments of PhIO connected through μ-oxo bridging atoms and one sulfate group, which provides an alternating copolymer composition. Interestingly, the position of each sulfate group is shifted on one-third of the length relative to those on the other two subunits, which provides specific coordination within a polymer chain.

All observed intermolecular contacts with the participation of the terminal oxygen atoms in the sulfate unit are unique for each polymeric chain. For instance, both the O33 and O34 atoms form intermolecular and intramolecular contacts with I7, I16, and I17 and I4, I9, and I16, respectively. In the second sulfate unit, the O63 atom forms two intermolecular contacts and one intramolecular contact with I4, I6, and I16, whereas the O64 atom participates in four close contacts with I6, I8, I9, and I18. Finally, out of two terminal oxygen atoms in the third chain, only O23 is involved in the formation of three close contacts with I7, I8, and I18. In contrast, the nonterminal O22 atom of this group forms an additional intermolecular contact with the I7 atom, whereas the terminal O24 atom forms a strong intermolecular bond with a water molecule in the unit cell, in addition to another O62–O97 intermolecular interaction observed for the solvent water molecule. As a result of these unique intra- and intermolecular close contacts, the coordination polyhedron for each of the iodine atoms in the threefold assembly is also different. Thus, with only the short contacts taken into consideration (cf. ref.[7]), the I6, I7, and I16 atoms can be described as hexacoordinate, the I4, I5, I8, I9, and I18 atoms as pentacoordinate, and the I17 atoms are tetracoordinate centers (Figure 1).

Iodine atoms in the $(PhIO)_3$ fragment of copolymer **2** exhibit a typical trivalent iodine T-shaped intramolecular geometry with O–I–O and O–I–C bond angles close to 180° (166.54–177.99°) and 90° (79.18–92.43°), respectively. The I–O bond lengths for six independent molecules of the copolymer are listed in the Table 1 (for the sake of clarity, atomic numbering in Table 1 is different from the numbering scheme used in Figure 1).

Table 1. Intramolecular bond lengths for the six independent molecules in structure **2b**.



Bond/molecule	O3–I1	I1–O4	O4–I2	I2–O5	O5–I3	I3–O6
1	2.384	1.952	2.124	2.088	1.974	2.380
2	2.419	1.959	2.193	2.082	1.985	2.316
3	2.384	1.961	2.101	2.120	1.973	2.318
4	2.333	1.946	2.117	2.104	1.974	2.361
5	2.415	1.950	2.183	2.083	1.976	2.319
6	2.351	1.982	2.079	2.138	1.951	2.309

The analysis of the structural parameters of the $(PhIO)_3$ fragment in polymer **2** provides new insight into the structure of iodosylbenzene, which is the parent representative of λ^3-iodanes and one of the most important oxygenating reagents.[1–3] Although known for over 100 years, structural details of iodosylbenzene are still limited. On the basis of spectroscopic studies, it was suggested that in the solid state iodosylbenzene exists as a zigzag polymeric, asymmetrically bridged structure, in which monomeric units of PhIO are linked by intermolecular I···O secondary bonds (Figure 2).[8] Within the PhIO units, the I–O bond length (2.04 Å) and C–I–O bond angle near 90 ° were deduced from EXAFS analysis.[8e]

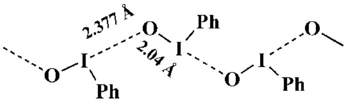
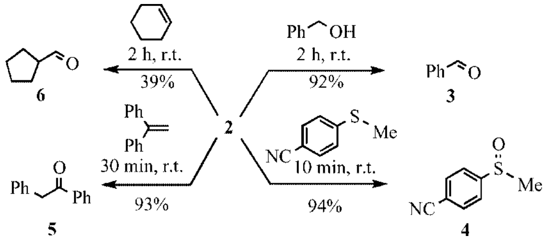


Figure 2. Zigzag structure of iodosylbenzene, $(PhIO)_n$.[8]

Our results directly confirm that iodosylbenzene does indeed have the expected T-shaped geometry around the trivalent iodine center, and that it can exist in a polymeric structure. Our analysis, however, shows significantly different O–I–O bond lengths from what was reported on the basis of EXAFS analysis of iodosobenzene. Specifically, the longer I–O bond in $(PhIO)_n$ was estimated to be 2.37 Å and the shorter one was estimated to be 2.04 Å.[8e] In polymeric structure **2**, both I–O distances around the middle I2 atom are approximately equal. The I–O bond lengths around iodine atoms I1 and I3 alternate due to the presence of the electron-withdrawing sulfate group.

The formation of polymeric sulfate **2** in the solid state can be explained by the self-assembly of species that are present in an aqueous solution of phenyliodine(III) sulfate. It was previously shown by spectroscopic measurements and potentiometric titrations that phenyliodine(III) organosulfonates upon dissolution in water undergo complete ionization to give hydroxy(phenyl)iodonium ions (PhI^+OH in the hydrated form) and the corresponding sulfonate ions.[9] The hydroxy(phenyl)iodonium ion can combine with [oxo(aquo)iodo]benzene $PhI^+(OH_2)O^-$, a hydrated form of iodosylbenzene that is also observed in the solution, producing the dimeric μ-oxodiiodine cation $Ph(HO)I–O–I^+(OH_2)Ph$ and dication $Ph(H_2O)I^+–O–I^+(OH_2)Ph$.[9] Further condensation of μ-oxodiiodine dimeric species with [oxo(aquo)iodo]benzene may produce the trimeric dicationic species observed in polymeric sulfate **2**. In agreement with this mechanistic consideration, the ESI mass spectrum of a solution of **2** in aqueous acetonitrile displayed intense peaks corresponding to the hydroxy(phenyl)iodonium ion $[PhIOH]^+$, μ-oxodiiodine cation $[Ph(HO)I–O–I^+Ph]$, and the protonated molecular ion $[M + H]^+$.

To test the reactivity pattern of phenyliodine(III) sulfate **2**, we performed a set of representative oxidation reactions that are typical of hypervalent iodine reagents: the oxidation of sulfides, alcohols, and alkenes (Scheme 2). All reactions were carried out in aqueous acetonitrile at room temperature. The final products were isolated and their spectroscopic data confirmed their identity with the known compounds. In particular, the oxidation of an aryl alkyl sulfide proceeds at room temperature within 10 min, which demonstrates the high oxidizing ability of reagent **2**. The oxidation leads to the formation of the corresponding sulfoxide (e.g. **4**) in high yield without overoxidation to sulfone. A similar oxidation with iodosylbenzene proceeds under the same conditions (water, room temperature), but only in the presence of a catalytic amount of a bromide anion, which is required for the depolymerization of $(PhIO)_n$.[10] Alcohols could also be oxidized at room temperature in short reaction times. For example, the oxidation of benzyl alcohol with reagent **2** affords benzaldehyde **3** in 92% isolated yield without overoxidation to benzoic acid. In contrast, iodosylbenzene reacts with benzyl alcohol in 30 h to give benzoic acid as the main product.[10b] The oxidation of cyclohexene with reagent **2** results in ring contraction with the formation of cyclopentanecarbaldehyde (**6**; cf. ref.[11]). Likewise, the oxidation of 1,1-diphenylethylene leads to the oxidative rearrangement to afford ketone **5** (cf. ref.[12]). This reactivity pattern is similar to the reactivity of iodosylbenzene activated by a Bronsted or Lewis acid. In particular, the reaction of $(PhIO)_n$ with cyclohexene in aqueous H_2SO_4 affords product **6** in 44% yield.[11a] Formation of the same product, **6**, in low yield was also reported for the reactions of cyclohexene with $PhIO{\cdot}SO_3$ and $PhIO{\cdot}BF_3$.[11b]



Scheme 2. Reactivity of **2** towards organic substrates (all reactions were carried out at room temperature in $MeCN/H_2O$, 5:1).

Conclusions

We reported a simple preparation of phenyliodine(III) sulfate **2**, which has a complex polymeric structure of the oligomeric iodosylbenzene units linked by sulfate anions. Sulfate **2** can find practical application as a readily available, stable, and water-soluble reagent with a reactivity pattern similar to that of activated iodosylbenzene.

Experimental Section

Synthesis and Characterization of $(PhIO)_3{\cdot}SO_3$ (2)

Method A: Solid (diacetoxy)iodobenzene (322 mg, 1.00 mmol) was added to $NaHSO_4{\cdot}H_2O$ (142 mg, 1.03 mmol) in an agate mortar. The mixture was ground for 5 min, and the resulting yellowish mass was transferred to a beaker and mixed with water (3 mL). A clear yellow solution was formed after 1 min of stirring and then yellow crystals started to precipitate. After 1 h, the precipitate was filtered, washed with cold water, and dried to afford 127 mg of a yellow crystalline solid. Additional product (71 mg) was obtained by slow evaporation of the mother liquor. Overall combined yield: 198 mg (80%). M.p. 143–145 °C. ^1H NMR (300 MHz, D_2O): δ = 8.18 (d, J = 8.4 Hz, 2 H), 7.7 (t, J = 7.5 Hz, 1 H), 7.57 (t, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, D_2O): δ = 135.26, 134.49, 134.22, 133.84, 133.12, 132.78, 132.02, 131.62, 130.88 ppm. HRMS (ESI): m/z (%) = 740.8025 (10) $[M + H]^+$, 440.8806 (30) $[Ph(HO)IOIPh]^+$, 220.9424 (100) $[PhIOH]^+$. $C_{18}H_{15}I_3O_6S$ (740.09): calcd. C 29.21, H 2.04, I 51.44, S 4.33; found C 29.22, H 2.08, I 51.06, S 4.32.

Method B: Solid (diacetoxy)iodobenzene (161 mg, 0.50 mmol) was mixed with $NaHSO_4{\cdot}H_2O$ (71 mg, 0.51 mmol) in water (1 mL) whilst stirring at r.t. The mixture was stirred overnight, and the resulting yellow precipitate was filtered, washed with cold water (2 × 5 mL), and dried in vacuo to afford 69 mg (56%) of product **2** as a yellow crystalline solid.

X-ray Crystal Structure Analysis of 2: Single crystals of product **2** suitable for X-ray crystallographic analysis were obtained by slow evaporation of an aqueous solution of **2**. X-ray diffraction data were collected at room temperature (structure **2a**) and at 173 K (structure **2b**).

Structure 2a: X-ray diffraction data were collected with a Rigacu AFC-7R diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 293 K. ψ-Scan absorption corrections were applied to the data by using the TeXsan 10.3b program (Rigaku Inc. 1997). The structure was solved by direct methods (SIR-92) and refined by full-matrix least-squares refinement on F^2 with the Crystals for Windows program. Crystal data for **2a**: $C_{18}H_{15}I_3O_6S$: M = 740.09, triclinic, space group P1, a = 12.436(3) Å, b = 12.537(3) Å, c = 13.454(3) Å, α = 112.10(3)°, β = 95.91(3)°, γ = 116.69(3)°, V = 1640.2(6) Å^3, Z = 3, μ = 4.414 mm^{-1}, 4273 reflections measured, 4072 unique; final R_1 = 0.0501, R_w = 0.1282.

Structure 2b: X-ray diffraction data were collected with a Bruker SMART CCD system by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 173 K. The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares refinement on F^2 with SHELXTL. Crystal data for **2b**: $C_{18}H_{15}I_3O_6S$: M = 740.09, triclinic, space group P1, a = 12.939(3) Å, b = 13.438(3) Å, c = 21.379(4) Å, α = 79.50(3)°, β = 89.50(3)°, γ = 62.50(3)°, V = 3229.9(12) Å^3, Z = 6, μ = 4.484 mm^{-1}, 28011 reflections measured, 24327 unique; final R_1 = 0.0395, R_w = 0.0652.

CCDC-654601 and -654602 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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