Oxidation using [bis(trifluoroacetoxy)]iodobenzene: a new and potentially practical approach to detection of polychlorinated phenols

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A novel oxidation for pentachlorophenol, 2,4,6-trichlorophenol and 2,3,5,6-tetrachlorophenol using [bis(trifluoroacetoxy)]iodobenzene has been developed, and the oxidation products from pentachlorophenol and 2,3,5,6-tetrachlorophenol have been identified as tetrachloro-1,4-benzoquinone; this novel reaction can be applied in electrochemistry using glucose oxidase for sensitive determination and identification of PCP, one of the most toxic polychlorinated phenols.

Considerable effort, including time-consuming immunoassay, has been directed toward the detection and quantitation of priority chlorinated pollutants such as pentachlorophenol (PCP), 2,3,5,6-tetrachlorophenol and 2,4,6-trichlorophenol.[1,2] Although electrochemical detection has frequently been used because of its simplicity and sensitivity, the oxidation products, generally believed to be quinones or radical products, are prone to polymerization, which results in electrode surface fouling.[3] Direct electrochemical oxidation of chlorophenols also requires an overpotential of +700 to +900 mV, which is sufficiently extreme so as to introduce the possibility of electroactive interference. These drawbacks can be overcome through enzymatic oxidation of chlorophenols, followed by electrochemical reduction of the chlorinated quinones. However, the two enzymes most commonly applied to this assay, tyrosinase and laccase, have been tested and found to be effective only for catechol, hydroquinone, *p*-cresol, 4-chlorophenol and 4-amino-4-chlorophenol.[4,5]

Several chlorophenols could be oxidized by ceric sulfate or chloroperoxidase. The resulting quinones were shown to efficiently recycle glucose oxidase to the oxidized form.[6] However, the PCP oxidation with ceric sulfate or hydrogen peroxide catalysed by chloroperoxidase undergoes polymerization of the oxidation product. Photochemical oxidation with hydrogen peroxide or singlet oxygen often produces a complex mixture of products including quinones, diols and triols, and polyhydroxybiphenyls.[7,8]

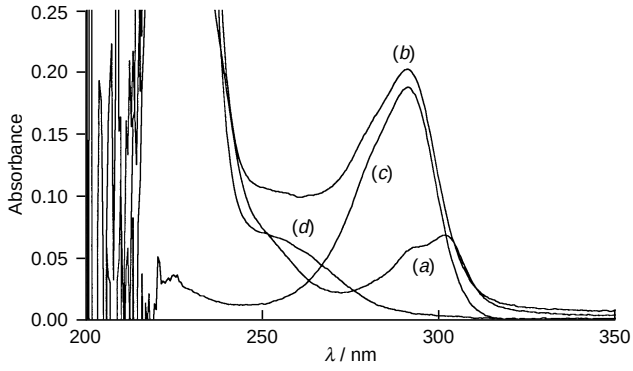


Fig. 1 UV–Visible (Beckman DU 640 spectrometer) spectrum of (*a*) pentachlorophenol (10 μM), (*b*) the oxidation product of PCP, (*c*) the standard tetrachloro 1,4-benzoquinone (10 μM) and (*d*) [bis(trifluoroacetoxy)]iodobenzene (100 μM after hydrogen peroxide addition). Measurements were performed in 0.1 M acetic buffer, pH 3. Reaction was carried out in 0.1 M acetic buffer, pH 3 for 2 h, with 10 μM pentachlorophenol and 100 μM [bis(trifluoroacetoxy)]iodobenzene. Hydrogen peroxide (88 μM) was added to stop the reaction.

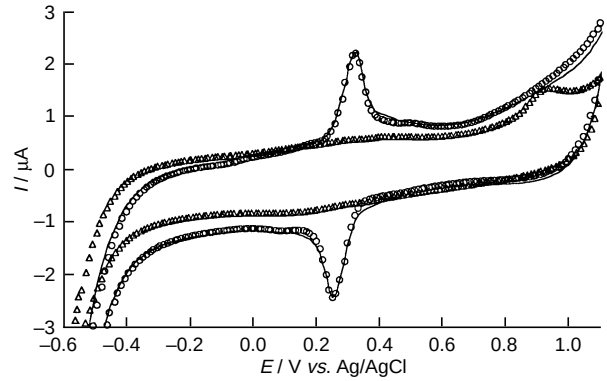
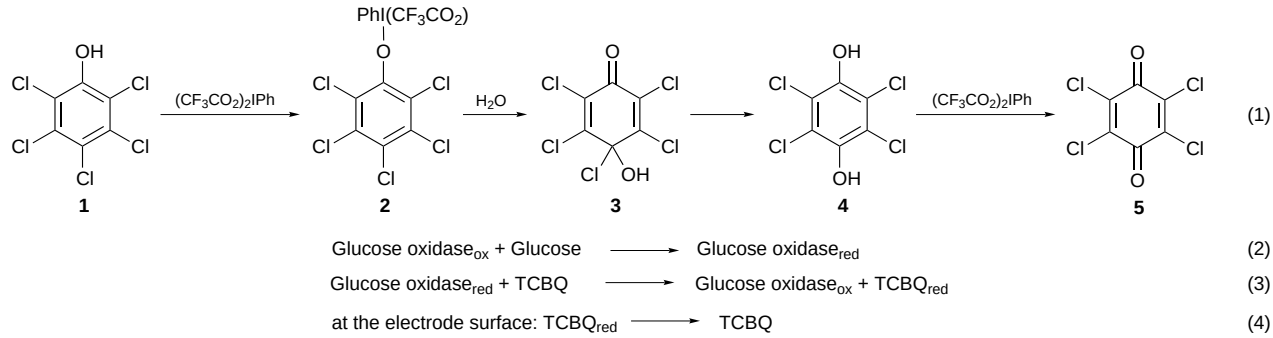


Fig. 2 Cyclic voltammograms (0.1 M acetic acid, pH 3, 100 mV s^{-1}) of (Δ) pentachlorophenol (10 μM), (○) the oxidation product of PCP and (—) the standard solutions of tetrachloro-1,4-benzoquinone (10 μM). Reaction was carried out in 0.1 M acetic buffer, pH 3, for 1 h, with 10 μM pentachlorophenol and 500 μM [bis(trifluoroacetoxy)]iodobenzene. Hydrogen peroxide (440 μM) was added to stop the reaction. Equipment: CV-1B voltammograph (Bioanalytical Systems), platinum wire counter electrode, Ag/AgCl reference electrode and glassy carbon working electrode.

We report here a novel and simple reaction for the oxidation of pentachlorophenol into tetrachloro-1,4-benzoquinone (TCBQ) in aqueous media using [bis(trifluoroacetoxy)]-iodobenzene (BTIB). We also report the ability of TCBQ to oxidize reduced glucose oxidase. Although this hypervalent iodine agent.[9,10] has been used to oxidize various naphthols[11] into the corresponding quinone, no attempt has been made to oxidize chlorinated phenols with BTIB. Reaction of pentachlorophenol with BTIB was performed in 0.1 M acetate buffer, pH 3, at ambient temperature. A large excess of BTIB (molar ratio BTIB/PCP from 10 to 50) must be used to accelerate the reaction (2 h to 30 min). Neutralization of excess BTIB with hydrogen peroxide prevented further reaction of the initial products. Moreover, BTIB reaction by-products (iodobenzene and trifluoroacetate ion) are not electroactive species.

UV–VIS spectral, HPLC and cyclic voltammetric data obtained from the reacted solution demonstrated that the reaction product of pentachlorophenol with BTIB is tetrachloro-1,4-benzoquinone. Over the course of the reaction, the pentachlorophenol peaks at λ = 294 and 303 nm declined [Fig. 1, curve (*a*)] and a more intense absorption peak at 290 nm emerged and intensified [Fig. 1, curve (*b*)]. Both the absorbency profile and maximum wavelength of the PCP oxidation product were confirmed to be identical to those of standard tetrachloro-1,4-benzoquinone [Fig. 1, curve (*c*)]. The HPLC data also indicated that a significant portion of tetrachloro-1,4-benzoquinone was converted to tetrachloro-1,4-hydroquinone during the course of separation [HPLC column; 3.9 mm i.d. × 15 cm stainless steel packed with 10 μ C18 silica gel (μBondapak C18, Waters, Milford, MA), mobile phase: 25% pH 3.0, 0.1 M tartrate buffer + 25% water + 50% MeOH at a flow rate of 0.5 ml min^{-1}]. To facilitate the sensitive detection of tetrachloro-



1,4-benzoquinone, this oxidation product was reduced with zinc to tetrachloro-1,4-hydroquinone, which was detected by a glassy carbon electrode, +450 mV *vs.* Ag/AgCl (model LC-44 thin layer electrochemical cell connected to a model CV-1B potentiostat, Bioanalytical Systems, Lafayette, IN). The cyclic voltammogram of the product obtained from the oxidation of PCP by BTIB is identical with that of the standard tetrachloro-1,4-benzoquinone with respect to the oxidation and reduction peaks and the peak to peak separation (Fig. 2).

Another interesting result reported here is the capability of tetrachloro-1,4-benzoquinone to reoxidize glucose oxidase in the presence of excess glucose. As shown in Fig. 3(*a*), glucose oxidase immobilized on a glassy carbon electrode was readily

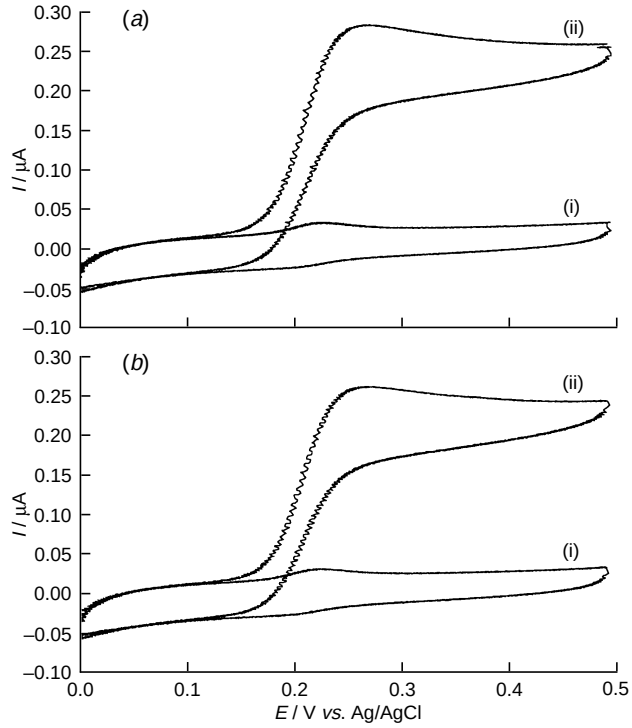


Fig. 3 (*a*) Cyclic voltammograms of the GOD electrode in 1 μM tetrachloro-1,4-benzoquinone solution [9 ml phosphate buffer (0.3 M, pH 5) and 1 ml acetic acid (0.1 M, pH 3) containing 10 μM tetrachloro-1,4-benzoquinone, 2 mV s^{-1}] (i) before and (ii) after addition of 40 mM glucose. The GOD electrode was prepared as follows. After polishing of the glassy carbon electrode, 10 μl of glucose oxidase solution (glucose oxidase: 133 U, glutaraldehyde: 2.5%, 0.1 M phosphate buffer, pH 7) was placed on the surface and covered by a dialysis membrane (MWCO 14000). After drying in water saturated atmosphere for 15 min, the electrode was rinsed with 0.1 M phosphate buffer. (*b*) Cyclic voltammograms of GOD electrode in 1 μM PCP reaction solution [9 ml phosphate buffer (0.3 M, pH 5) and 1 ml 10 μM PCP reaction solution, 2 mV s^{-1}] (i) before and (ii) after addition of 40 mM glucose. Reaction was carried out in 0.1 M acetic buffer, pH 3, for 1 h with 10 μM pentachlorophenol and 500 μM [bis(trifluoroacetoxy)]iodobenzene. Hydrogen peroxide (440 μM) was added to stop the reaction.

reduced by its substrate, glucose. TCBQ then recycled the reduced enzyme to its original active form, *i.e.* mediating the rate-limiting electron transfer from the enzyme to the electrode. The oxidation product obtained from the PCP–BTIB reaction was also able to mediate the glucose oxidase–glucose reaction [Fig. 3(*b*)]. Based on the above findings, a mechanism for the oxidation of PCP and the mediating capability of the corresponding oxidation product can be proposed [eqns. (1)–(4)].

Oxidation of phenols often produces a mixture of isomers (1,4- and 1,2-benzoquinone). However, steric hindrance by the (CF_3CO_2)IPh species could be the main reason why dechlorination occurs only in position 4. In addition to PCP, BTIB also oxidized two other important chlorophenols: 2,4,6-trichlorophenol and 2,3,5,6-tetrachlorophenol. It should be noted that the 1,4-benzoquinone structure exhibited unique symmetry, and dechlorination of chlorophenols had to occur at position 4 if it was chlorinated. In view of this, both 2,3,5,6-tetrachlorophenol and PCP must yield the same oxidation product, *i.e.* tetrachloro-1,4-benzoquinone. We confirmed that the oxidation product of 2,3,5,6-tetrachlorophenol and pentachlorophenol with BTIB exhibits identical cyclic voltammetric behaviour and similar UV–visible peaks (not shown). The oxidation products of these two chlorophenols also mediated the glucose oxidase–glucose reaction, whereas BTIB and BTIB by-products did not react with reduced glucose oxidase. The detection limit of pentachlorophenol and 2,3,5,6-tetrachlorophenol was determined to be 4 nM, whereas that of 2,4,6-trichlorophenol was 8 nM; the steady state signal was attained within 2–5 min.

We have demonstrated that highly chlorinated phenols can easily be oxidized to quinones. In combination with bioelectroanalytical chemistry, this reaction offers a sensitive method for the determination of these important pollutants.

Footnote

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