Electrochemical Incineration of 4-Chlorophenol and the Identification of Products and Intermediates by Mass Spectrometry

S T E V E   K .   J O H N S O N , [†]   L I N D A   L .   H O U K ,
J I A N R E N   F E N G ,   R .   S .   H O U K ,   A N D
D E N N I S   C .   J O H N S O N *

Ames Laboratory-U.S. Department of Energy, Microanalytical Instrumentation Center, Department of Chemistry, Iowa State University, Ames, Iowa 50011

This report summarizes results obtained as part of a larger effort to demonstrate the applicability of electrolytic procedures for the direct anodic (oxidative) degradation of toxic organic wastes. We refer to this process as "electrochemical incineration" (ECI) because the ultimate degradation products, e.g., carbon dioxide, are equivalent to those achieved by thermal incineration processes. In this work, the ECI of 4-chlorophenol is achieved in an aqueous medium using a platinum anode coated with a quaternary metal oxide film containing Ti, Ru, Sn, and Sb oxides. The electrode is stable and active when used with a solid Nafion membrane without the addition of soluble supporting electrolyte. Liquid chromatography (LC), including reverse phase and ion exchange chromatography, is coupled with electrospray mass spectrometry (ES-MS) and used, along with gas chromatography–mass spectrometry (GC-MS) and measurements of pH, chemical oxygen demand (COD), and total organic carbon (TOC), to study the reaction and identify the intermediate products from the ECI of 4-chlorophenol. Twenty-six intermediate products are identified and reported. The most abundant of these products are benzoquinone, 4-chlorocatechol, maleic acid, succinic acid, malonic acid, and the inorganic anions chloride, chlorate, and perchlorate. After 24 h of ECI, a solution that initially contained 108 ppm 4-chlorophenol yields only 1 ppm TOC with 98% of the original chlorine remaining in the specified inorganic forms. LC-ES-MS and direct infusion ES-MS detection limits are between 80 ppb and 4 ppm for these intermediate products. Elemental analysis of the electrolyzed solutions by inductively coupled plasma mass spectrometry ICP-MS showed that only trace amounts (<25 ppb) of the metallic elements comprising the metal oxide film were present in the solution.

Introduction

Chlorophenols are present in wastewater as byproducts of the pulp and paper, dyestuff, pharmaceutical, and agrochemical industries. Phenols can be readily chlorinated during treatment of wastewater and drinking water (*1, 2*).

Because these halogenated compounds are toxic and resist biodegradation, research efforts are underway to develop techniques which mineralize the carbon and chlorine atoms in chlorophenols.

Supercritical water oxidation (*3, 4*) and photocatalytic oxidation (*5, 6*) are two effective technologies used for the destruction of toxic organic waste. Supercritical water oxidation is generally done in large, chemically resistant reactors and is seldom used to remediate small waste volumes in laboratory-scale applications. A major advantage of photocatalytic oxidation is use of the sun as a possible energy source. However, photocatalytic oxidation is not suitable for solutions of high turbidity. Therefore, continued evaluation of other waste remediation processes is warranted. Electrochemical incineration (ECI) is one such waste remediation process. 4-Chlorophenol was chosen as a model compound for this study of ECI, because it is widely present in the environment, it is a priority pollutant (*7*), and its degradation has been studied previously (*1–7*).

Recent studies regarding anodic oxidation of halogenated compounds include work by Kesselman et al. (*8*) and Brillas et al. (*9*). Kesselman reported very low quantum yields for photocatalytic degradation of organics in aqueous solutions (*8*). Therefore, these scientists used Nb-doped TiO_2 electrodes for ECI to compare the effects of current density on degradation rates of organic substrates. Brillas et al. compared the degradation of 4-chlorophenol in acidic media under anodic oxidation, electro-Fenton, photoelectro-Fenton, and peroxicoagulation conditions (*9*). TOC was reduced substantially faster for the last three methods, where Fe^{2+} acted as a catalyst to produce hydroxyl radicals (OH•) from H_2O_2 that was generated at a cathode sparged with O_2(g). Vinodgopal et al. described the electrochemically assisted photocatalytic degradation of 4-chlorophenol (*10*). Haque and Rusling also studied the photocatalytic degradation of 4-chlorophenol and reported complete mineralization to CO_2 and Cl^- (*11*).

Stucki et al. reported on the performance of Sb(III)-doped SnO_2 anodes for ECI of wastewater (*12*). The oxidation of organic compounds at these anodes was five times more efficient than that observed for Pt anodes. Furthermore, the $Sb–SnO_2$ anodes produced less Cl_2 and, therefore, showed less potential to form hazardous halogenated hydrocarbons.

Kaba et al. described the ECI of human biomass containing Cl^- using Pt and PbO_2 anodes in 12 M H_2SO_4 (*13*). This group reported that the use of ultrasound and the addition of the Ce^{3+}/Ce^{4+} redox couple enhanced the rates of waste oxidation.

Comninellis and Nerini compared Ti/SnO_2 and Ti/IrO_2 anodes for the electrolytic degradation of phenol in the presence of NaCl (*14*). The presence of NaCl was reported to promote the rate of anodic oxidation of phenol only at Ti/IrO_2 anodes. This effect was attributed to ClO^- that was produced by oxidation of Cl^-. However, the improved efficiency obtained with use of NaCl was offset by the formation of chloroform. Therefore, our study of the ECI of 4-chlorophenol was supported by use of analytical techniques for identification and quantification of halogenated hydrocarbons that might be generated during the anodic remediation process.

Previous efforts in our laboratory have compared the activities of various pure and mixed metal oxide film electrodes for the ECI of *p*-benzoquinone (*15, 16*). For example, in a batch-type cell, the electrolysis period required to decrease by 99% the COD due to benzoquinone in an acetate buffer (pH 5) was approximately 24 h for PbO_2 and

† Present address: Department of Chemistry, West Virginia Wesleyan College, Buckhannon, WV 26201.

10 h for Fe$-$PbO$_2$ electrodes (*15*). A quaternary metal oxide electrode consisting of a SnO$_2$ film containing Ru, Ti, and Sb in unknown oxidation states ("Ru$-$Ti$-$Sb$-$SnO$_2$") required 24 h to exceed a 99% decrease in COD (*16*).

The present work focuses on the determination of ionic compounds in the electrolysis solution during the course of ECI of 4-chlorophenol. This study uses two LC-ES-MS methods to determine the components of a complex mixture without the need for chemical derivatization. Reverse phase chromatography is useful in the determination of aromatic molecules that are not easily ionized, and ion exchange chromatography separates both organic and inorganic ions. Ion exchange chromatography is used because it offers good sensitivity when coupled to ES-MS, and these combined analytical technologies enable identification and quantitation of nearly all ionic products generated during the ECI process. Xiang et al. (*17*) also have successfully coupled ion exchange chromatography with ES-MS.

Experimental Section

Reagents and Samples. 4-Chlorophenol, benzoquinone, hydroquinone, phenol, NaOH (carbonate free), NaCl, NaClO$_3$, NaClO$_4$, and methanol (HPLC grade) were obtained from Fisher Scientific. 4-Chlorocatechol was obtained from Oakwood Products (West Columbia, SC). All carboxylic acids were reagent grade (Aldrich), and water was distilled and deionized (18 MΩ cm^{-1} at 25 °C) with a Barnstead Nanopure-II system (Newton, MA). The preparation of reagents and standards has been described (*16*).

ECI Apparatus. The ECI setup and preparation of quaternary metal oxide films have been described (*16*). In this study, the film was deposited on a 22 gauge platinum wire producing an anode with an area of 5.3 cm^2 tightly coiled around a stainless steel counter electrode. The electrodes were separated by a Nafion membrane (0.25-mm thickness). The electrolysis was conducted with a constant current of 0.95 A, resulting in a current density of 0.18 A/cm^2. The cathode was 3.2-mm o.d. $\times$ 4.4-cm and was drilled with 120 holes (1-mm diameter). A cathode of this diameter permitted the use of Nafion tubing with an inner diameter of 4 mm (Perma Pure, Inc., Toms River, NJ). The volume of solution electrolyzed in this apparatus was 30 mL.

ES-MS. An API/1 (Perkin-Elmer SCIEX, Thornhill, ON, Canada) single quadrupole mass spectrometer was used. The API/1 used a curtain gas interface and has been described previously (*18, 19*). The IonSpray source of the API/1 was operated with a Perkin-Elmer SCIEX TurboIonSpray (Thornhill, ON, Canada) attachment. The TurboIonSpray forces a flow of nitrogen gas (5 L min^{-1}, 500 °C) across the aerosol stream exiting the IonSpray tube, increasing the collision and evaporation rates involved in the ionization process and allowing the use of larger liquid flow rates (1$-$2 mL min^{-1}) into the ES-MS. The detection limits and signal-to-noise ratio are improved with TurboIonSpray for many compounds when compared to similar studies in this laboratory before the addition of the TurboIonSpray (*20*). The attachment also provides much more flexibility in chromatographic flow rates and eluent compositions.

Other ES-MS conditions have been described (*20*). Horlick reported that it was necessary to compensate for the variation of electrospray signal with the total ionic composition of the sample by using an internal standard ion (*21*). In the present study, chloroacrylate and propionate were used as internal standards for quantitative measurements. In the study reported here, linear calibration curves with correlation coefficients (r^2) of 0.980$-$0.999 were compiled for analyte concentrations in the range of 0.1$-$50 ppm. Detection limits were determined as the concentration of analyte required to provide a net signal equivalent to three times the standard deviation of the blank.

TABLE 1. Chromatographic Components and Operating Conditions

Chromatography Components	
pump	Dionex model GMP-2 analytical pump
injection valve	Rheodyne 7010 high-pressure injector (Cotati, CA)
injection volume	50 μL
Reverse Phase Chromatography	
column	Zorbax SBC18 (25-cm length, 3.0-mm diameter)
mobile phase	50% water, 50% methanol
liquid flow rate	0.5 mL min^{-1}
Ion Exchange Chromatography	
column	Dionex IonPac AS11 (25-cm length, 4-mm diameter)
mobile phase	0.25$-$26.5 mM NaOH in 50% methanol
liquid flow rate	0.5 mL min^{-1}
suppressor column	Dionex ASRS-11 (4-mm diameter)
regenerent	25 mM sulfuric acid
regenerent flow rate	5.0 mL min^{-1}

Reverse Phase Liquid Chromatography. Electrospray ionization performs best with some organic solvent, such as methanol, in the sample flow to facilitate droplet formation and solvent evaporation. A Zorbax column (SBC18, Rockland Technologies, Chadds Ford, PA, 25-cm length, 3.0-cm diameter) was used for reverse phase LC. The Zorbax column is operated with a 1:1 methanol/water mobile phase at a flow rate of 0.5 mL min^{-1}. These eluent conditions match the appropriate ES-MS conditions, using TurboIonSpray, so the effluent of the reverse phase column can be fed directly into the ES-MS. The simplicity of the reverse phase LC-ES-MS setup and the excellent match of mobile phase composition and flow rates gave reverse phase ES-MS good detection limits and separation quality compared to other LC-ES-MS systems.

Ion Exchange Liquid Chromatography. A Dionex IonPac AS11 anion exchange column (Sunnyvale, CA) was used with a water/methanol solvent. This separation also required a strong base such as 27 mM sodium hydroxide in the mobile phase. A self-regenerating (4-mm diameter) suppressor (Dionex) was used to remove sodium cations and replace them with hydrogen ions before entering the ES-MS. The ion exchange system also included an IonPac ATC-1 anion trap (Dionex) and an IonPac AG11 guard column (Dionex). LC-ES-MS used with ion exchange chromatography can accommodate an eluent gradient, and the following program was used. Mobile phase A contained 100% water, mobile phase B was made up of 1 mM sodium hydroxide, mobile phase C was 100 mM sodium hydroxide, and mobile phase D contained 100% methanol. The gradient was held at 25% A, 25% B, and 50% D from $t = 0-2$ min, progressed linearly to 10% A, 40% B, and 50% D at $t = 5$, progressed linearly to 10% A, 15% B, 25% C, and 50% D at 15 min, and was held at that composition until the end of the separation. Note that the percentage of methanol remained constant throughout the gradient program. A small change in the concentration of methanol would have had a large effect on the ES-MS signal.

Experimental conditions for the liquid chromatography methods are shown in Table 1. The Dionex Model GPM-2 analytical pump was used for the mobile phase of each separation, and the Model AMP-1 analytical pump was used to regenerate the suppressor when using ion- exchange chromatography. A Cole-Parmer syringe pump (Nile, IL) was used for direct infusion analysis.

ICP-MS. ICP-MS measurements were taken using the apparatus, operating conditions, and semiquantitative calibration method described by Hu et al. (*22*) and Houk et al. (*16*).

GC-MS. Organic compounds in the gas escaping from the ECI cell during electrolysis were collected by a Tekmar purge trap K (Cincinnati, OH). These sorbent column traps were then analyzed by the EPA approved University of Iowa Hygienic Laboratory using a semiquantitative method based on EPA Method 8260. In this analysis, the sorbent column trap was heated and back-flushed with an inert gas to desorb purgeable compounds onto a GC column. The GC was temperature programmed, and the compounds eluted were detected with a Hewlett-Packard Model 5970B quadrupole mass spectrometer.

A liquid sample was also analyzed using EPA Method 8260 at the University of Iowa Hygienic Laboratory. For water analysis, an inert gas was bubbled through the sample to transfer purgeables to the vapor phase. This vapor was swept through a sorbent column where the purgeables were trapped. The trapped purgeables were then transferred to a GC column as described above and detected with a Hewlett-Packard Model 5972A quadrupole mass spectrometer.

Other Techniques. COD was determined by a Hach DR200 analyzer (Loveland, CO), and TOC was determined using a DC190 TOC analyzer (Dohrmann, Santa Clara, CA) at the University of Iowa's Hygienic Laboratory. Measurements of pH were made with an Orion Research Inc. Model 601A pH meter (Cambridge, MA).

Results and Discussion

Analytical Results. Figure 1 shows values of COD as a function of time during the ECI of a 30-mL solution of 4-chlorophenol at 108 ppm. The COD decreased from 140 to 10 ppm in the first 12 h of electrolysis. After 24 h of electrolysis, only 1 ppm COD remained. These data show that the ECI process is capable of degrading all organic compounds in the solution. TOC data provide similar results with a carbon concentration that decreases from 59 to 1.1 ppm carbon in 24 h. After 24 h of ECI, the electrolysis solution contained no aromatic or halogenated compounds above the detection levels of Method 8260 for wastewater analysis.

The pH of the electrolysis solution was monitored during ECI of the same solution mentioned above. The pH decreased from an initial value of 6 to a value of 2 after 4 h and then increased to 3 after 8 h of electrolysis where it remained for the duration of the procedure. The decrease in pH during the first 4 h of electrolysis is attributed to the production of carboxylic acids as intermediate products. This conclusion is in agreement with previous reports for the electrolytic degradation of benzoquinone and phenol (16, 23−25). The identities and peak concentrations of the carboxylic acids generated in this study are given below.

LC-ES-MS was used to identify and quantify compounds generated during the ECI of the 30-mL solution of 108 ppm 4-chlorophenol. Figure 1 contains a typical chromatogram obtained using ion exchange ES-MS after 2 h of electrolysis. The peaks reported correspond to the following anionic species: (a) formate, (b) chloride, (c) chlorate, (d) 2-ketoglutarate, (e) succinate, (f) malonate, (g) fumarate, (h) maleate, (i) oxalate, and (j) perchlorate. It should be noted, for these chromatographic conditions, that peaks d and e were not resolved. Fortunately, the selective detection capabilities of the mass spectrometer allowed for determination of these coeluting components. The identifications of the solution components were based on comparison of chromatographic retention times, molecular weight data, and some fragmentation data for the unknown solution components compared with that for standard compounds.

Concentrations of Intermediate Products as a Function of ECI Time. When the identity of chromatographic peaks had been made, the concentrations of these intermediate products were determined as a function of electrolysis time with calibration via standard compounds. Figure 2 shows
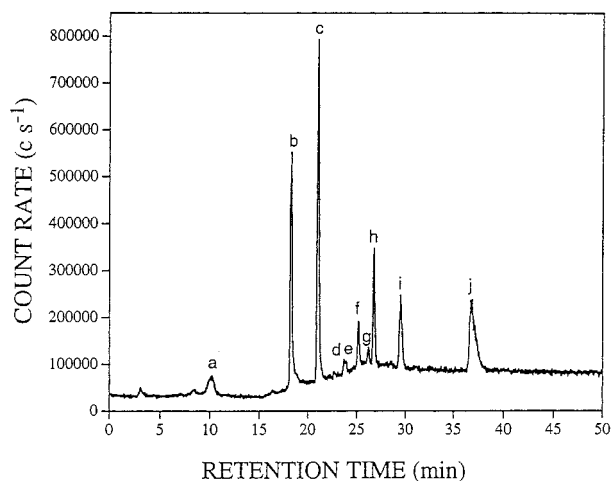

FIGURE 1. LC-ES-MS chromatogram obtained after a 2-h period of ECI of a 30-mL solution containing 108 ppm 4-chlorophenol. Peak assignments are as follows: (a) formate, (b) chloride, (c) chlorate, (d) 2-ketoglutarate, (e) succinate, (f) malonate, (g) fumarate, (h) maleate, (i) oxalate, and (j) perchlorate.
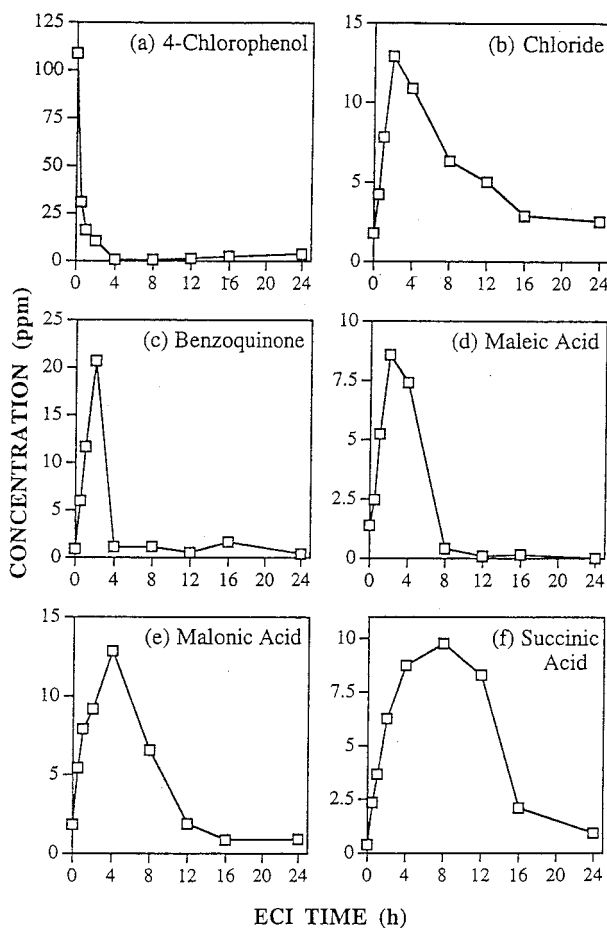

FIGURE 2. Concentration of selected compounds as a function of time. Plots are as follows: (a) 4-chlorophenol, (b) chloride, (c) benzoquinone, (d) maleic acid, (e) malonic acid, and (f) succinic acid.

the concentration of six of the prominent species as a function of time. Figure 2a demonstrates that the 4-chlorophenol concentration quickly drops from the initial value of 108 ppm to approximately 10 ppm during the first 2 h of ECI. Figure 2b reveals that the chloride ion concentration increases to its peak value of 13 ppm during this same period. Thereafter, the chloride ion concentration drops gradually

TABLE 2. Intermediates in 4-Chlorophenol ECI Solution

compound	m/z	t_r (min)	peak conc (ppm)	peak time (h)	detectn limit (ppm)	% total C (Cl) at peak
4-chlorophenol ClC_6H_4OH	127	25	108	0	0.1	100 (100)
chloride Cl^-	35	19	13	2	0.05	(34.4)
chlorate ClO_3^-	83	22	30	16	0.1	(33.5)
perchlorate ClO_4^-	99	37	28	24	0.4	(26.2)
phenol C_6H_5OH	93	17	1	2	0.1	1.0
hydroquinone $C_6H_4(OH)_2$	109	2^a	3	2	0.04^a	2.5
benzoquinone OC_6H_4O	108	3^a	20	2	0.05^a	17.1
2-ketoglutaric acid $HO_2CCH_2CH_2COCO_2H$	145	26	4	2	0.6	2.1
malic acid $HO_2CCH_2CH(OH)CO_2H$	133	25	8	2	0.2	3.7
maleic acid $HO_2CCH=CHCO_2H$	115	27	9	2	0.08	4.8
fumaric acid $HO_2CCH=CHCO_2H$	115	26	4	2	0.1	2.1
malonic acid $HO_2CCH_2CO_2H$	103	26	13	4	0.3	5.8
oxalic acid HO_2CCO_2H	89	29	6	4	1	2.1
formic acid HCO_2H	45	11	5	4	2	1.7
succinic acid $HO_2CH_2CH_2CO_2H$	117	24	10	8	0.8	5.2
acetic acid CH_3CO_2H	59	10	2	24	0.4	3.4
4-chlorocatechol $C_6H_3(OH)_2Cl$	143	7^a	14	0.5	0.05^a	12(12)
chloromaleic acid^b $HO_2CC(Cl)=CHCO_2H$	149	32	?	4	?	?
chloroacetic acid $ClCH_2CO_2H$	93	19	1	2	2	0.3 (1.0)
dichloroacetic acid $Cl_2CH_2CO_2H$	127	23	2	4	4	0.4 (2.9)

^{a} Separated by reverse phase chromatography ES-MS. ^{b} Suspected intermediate.
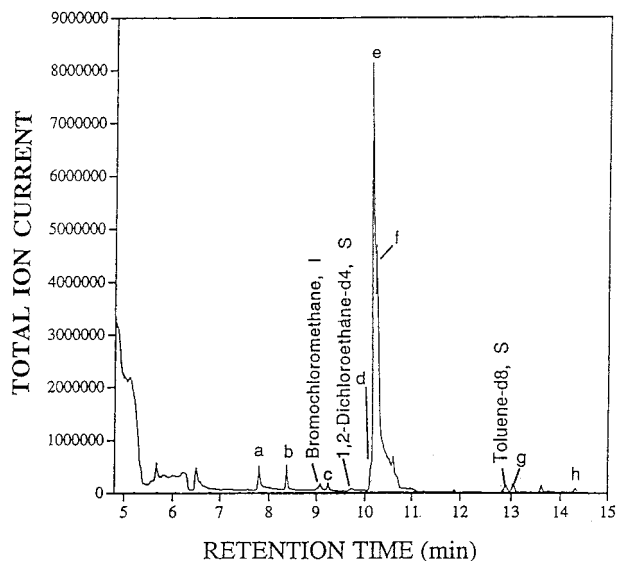

FIGURE 3. GC-MS chromatogram from a purge trap of gaseous products collected in the first 8 h during the ECI of a 30-mL solution containing 108 ppm 4-chlorophenol. Peaks are as follows: (a) cyclopentene, (b) hexane, (c) chloroform, (d) benzene, (e) cyclohexane, (f) 3-chloro-1,3-pentadiene (tentative assignment), (g) toluene, and (h) tetrachloroethene.

to 3 ppm after 24 h. Comparison of the plots for 4-chlorophenol and chloride supports the conclusion that the chlorine atom is cleaved from 4-chlorophenol early in the degradation process. Subsequent oxidation of chloride ion then produced the chlorate and perchlorate anions.

Figure 2 also contains data for benzoquinone, maleic acid, malonic acid, and succinic acid as a function of ECI time. The benzoquinone concentration rises to 20 ppm during the initial 2-h period of ECI and then drops to less than 1 ppm after 4 h. Maleic acid peaks at 9 ppm after 2 h, malonic acid peaks at 13 ppm after 4 h, and succinic acid peaks at 10 ppm after 8 h.

These data show that benzoquinone is generated very soon after removal of the chlorine atom from 4-chlorophenol. Benzoquinone is then oxidized rapidly to maleic acid and then to malonic acid. Succinic acid probably appears as a result of the reduction of some maleic acid at the cathode. It is apparent from comparison of the data in Figure 2 that anodic degradation of the aromatic 4-chlorophenol and benzoquinone to generate the carboxylic acids occurs more rapidly than the subsequent anodic degradation of these carboxylic acids. Table 2 contains chromatographic retention times for intermediate products identified in this study together with their peak concentrations and corresponding times and the percent of total carbon and chlorine present in each intermediate product at its peak concentration. These findings will be discussed more thoroughly in a latter section in conjunction with the proposed ECI mechanism.

Gaseous Products. GC-MS was used to analyze the gas mixture escaping from the electrolysis vessel. Gaseous products were collected on sorbent column traps for 8-h intervals. Figure 3 contains a representative total ion chromatogram for the gas trapped during the first 8-h ECI period. Bromochloromethane and the deuterated compounds 1,2-dichloroethane-d_4 and toluene-d_8 were used as internal standards. Compounds determined to be present are as follows: (a) cyclopentene, (b) hexane, (c) chloroform, (d) benzene, (e) cyclohexane, (f) 3-chloro-1,3-pentadiene, (g) toluene, and (h) tetrachloroethene. During the first 8-h period of electrolysis, GC-MS revealed the formation of cyclohexane (120 ppb), chloroform (4.7 ppb), benzene (9.3 ppb), tetrachloroethene (0.4 ppb), and toluene (0.6 ppb). An unidentified peak at $m/z = 102$ had a fragmentation pattern consistent with 3-chloro-1,3-pentadiene. During the second 8-h ECI period, GC-MS detected chloroform (1.5 ppb), tetrachloroethene (0.2 ppb), and toluene (0.3 ppb). During the third 8-h period, only toluene (0.1 ppb) and tetrachloroethene (0.2 ppb) were detected.

Benzene- and chlorine-containing organic molecules are potentially hazardous, and the possibilities of their production and ultimate escape from the electrolysis vessel are cause for concern. Production of chloroform has been a concern common in similar remediation studies of phenols (14). It should be noted in this procedure that volatile compounds were deliberately allowed to escape for purposes of identification. However, the extent to which these gaseous intermediate products can escape is diminished by the use of a simple water-cooled condenser. This condenser returns the volatile compounds to the ECI solution where they can undergo further oxidation and be converted to less harmful products. Furthermore, an activated charcoal trap also can be used to prevent volatile compounds from escaping to the atmosphere. The ECI process used in this study produces only very low levels of chloroform, and no detectable chloroform remained in the solution after a 24-h ECI period. Ozone also was detected using capillary tubing to transfer vapor produced during ECI directly to the mass spectrometer.

Total Carbon and Chlorine Concentrations. The carbon and chlorine concentrations in the electrolysis solution were calculated from LC-ES-MS data. The total carbon concentra-
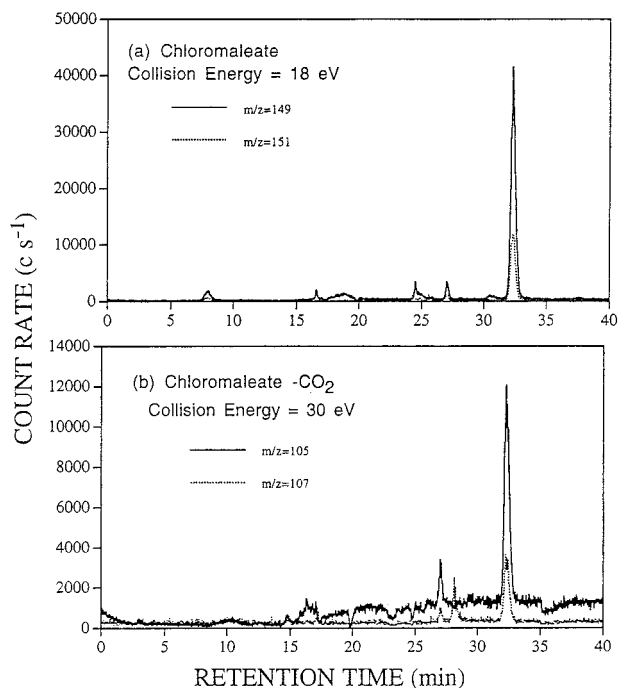
FIGURE 4. Chromatograms for suspected chloromaleate (a) and a fragment due to the loss of CO_2 and (b) after 4 h of ECI of a 30-mL solution containing 108 ppm 4-chlorophenol.

FIGURE 5. Electron impact mass spectrum from an unidentified GC-MS peak ($t_r = 10$ min) produced during the first 8-h period of ECI of a 30-mL solution containing 108 ppm 4-chlorophenol.

tion dropped from an initial value of 61 ppm to less than 20 ppm during a 4-h period with subsequent gradual decrease to 7 ppm over the remainder of the 24-h ECI period. These data are in approximate agreement with TOC data that indicated an overall decrease from 59 to 1 ppm. The total chlorine concentration decreased from an initial value of 30–23 ppm after 2 h with virtually no further decay. Based on these LC-ES-MS data, 77% of the original chlorine remained in solution after 24 h of ECI. Chlorine loss can be attributed to the escape of gaseous compounds, such as 3-chloro-1,3-pentadiene, unquantified intermediates, such as chloromaleic acid, and/or unidentified intermediate products. In other studies in this laboratory, using an electrode of similar construction with an area of 3.6 cm² and operating with a current density of 0.26 A/cm² and a condenser, 98% of the original chlorine remained in the solution as chloride, chlorate, and perchlorate anions.

Identification of Intermediate Products by Mass Spectrometry. The majority of intermediate products were identified by comparing their mass spectra and retention times with those obtained for pure standards. Two compounds were identified despite the lack of such standards. Figure 4 shows LC-ES-MS ion chromatograms that indicate the presence of an anion at $m/z = 149$ and 151 that has the 3:1 signal ratio characteristic of the presence of a chemical species containing a single Cl atom. This ion fragments under energetic extraction conditions (voltage difference between orifice plate and RF-only quadrupole = 30 V, compared to the normal use of 18 V) to lose CO_2 with retention of the Cl atom. This evidence is consistent with the conclusion that the parent ion contains two carboxylate groups (20). Therefore, the unknown species is tentatively concluded to be chloromaleic acid ($HO_2CCH=CClCO_2H$) (1). The use of ES-MS to identify the chloromaleate anion illustrates the value of this technique for charged organic ions in solution.

The GC-MS measurements also indicated the presence of a compound at $t_r = 10.3$ min whose electron impact mass spectrum is shown in Figure 5. The presence of peaks at $m/z = 102$ and 104 with a 3:1 signal ratio again indicates that the parent ion contains one Cl atom. The fragments at $m/z =$
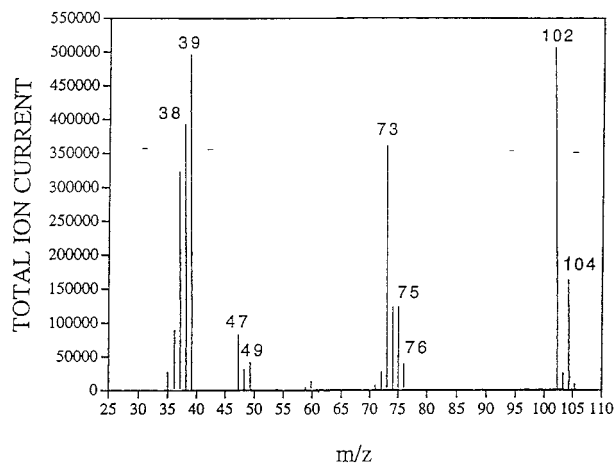
74 and 76 indicate loss of C_2H_4 due to the presence of a $-CH=CH_2$ group in the parent molecule. Likewise, the peaks at $m/z = 73$ and 75 represent loss of C_2H_5 from a $=CHCH_3$ group. The Cl atom is retained on each of these pairs of ions. Peaks from CCl^+ also appear at $m/z = 47$ and 49. Hence, this molecule is 3-chloro-1,3-pentadiene, $CH_3CH=CClCH=CH_2$. Surprisingly, the mass spectrum for this compound does not appear in either the NIST or Wiley compilations. This compound likely forms when the aromatic ring of 4-chlorophenol is broken at the phenolic carbon during ECI.
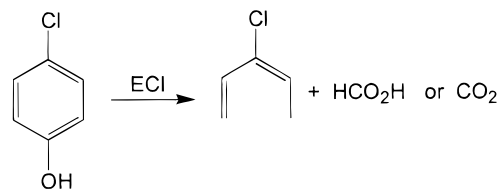
Both the chloromaleic acid and 3-chloro-1,3-pentadiene were detected only during the first 8-h period of ECI. These compounds could not be quantified because of the absence of standards and, therefore, were not included in the calculation of total chlorine referred to above.

Mechanism of Electrochemical Incineration. Figure 6 presents possible pathways for the ECI of 4-chlorophenol to form carbon dioxide as the ultimate degradation product. Figure 2 shows that the chlorine atom is removed from 4-chlorophenol early in the incineration process, and benzoquinone is then produced upon further oxidation. The results presented in Table 2 and Figure 2 are consistent with this pathway. Benzoquinone is oxidized to produce maleic or fumaric acids whose subsequent oxidization produces malonic acid followed by acetic acid and, finally, carbon dioxide. This proposed pathway agrees with that proposed by Kuo and Huang on the basis of ozonation techniques (1). Maleic acid can also be reduced at the cathode to form succinic acid, as reported by Kanakum et al. (26). It has been shown in our laboratory that electrolysis of succinic acid results in the production of malonic and acetic acids, which again leads to CO_2.

Another possible pathway presented in Figure 6 involves the hydroxylation of 4-chlorophenol to form 4-chlorocatechol, which we believe is oxidized to oxalic acid and chloromaleic acid. Chloromaleic acid probably can be oxidized to produce chloroacetic acid and dichloroacetic acid. Both of these products then oxidize further to eventually produce acetic acid and carbon dioxide. Kurien and Robins (27) reported that 1,2,4-trihydroxybenzene is formed as an
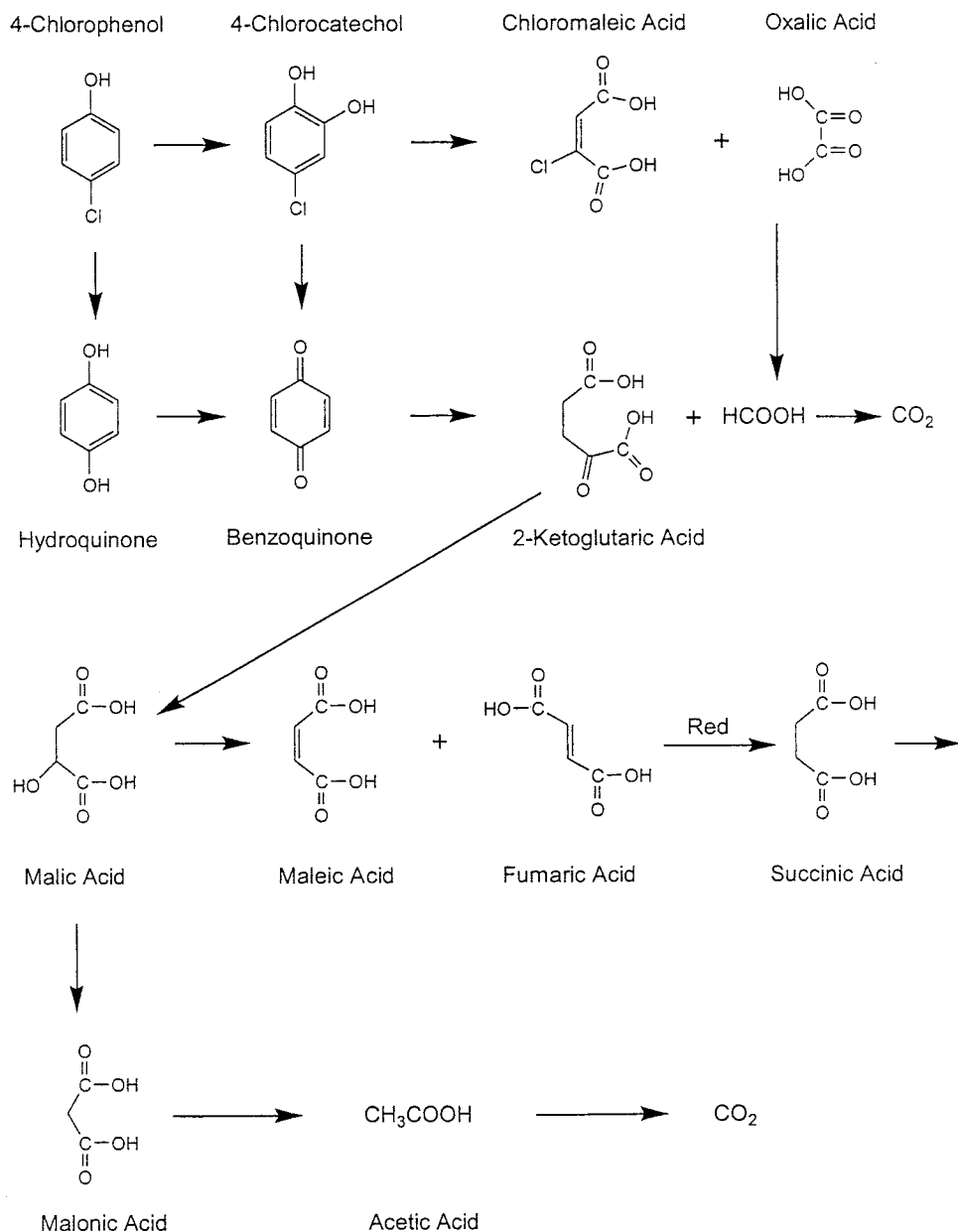
FIGURE 6. Proposed pathways for the ECI of 4-chlorophenol.

intermediate product during the oxidation of benzoquinone. Though this particular compound was not detected in our work, it could also form from the oxidation of 4-chlorocat-echol by exchange of a hydroxyl radical for a chlorine atom on the aromatic ring. This compound would then be oxidized to the carboxylic acids reported in Figure 6.

From Table 2, the peak molar concentration of 4-chlo-rocatechol at 30 min is roughly half that of benzoquinone. This suggests that formation of 4-chlorocatechol is another important pathway in the oxidation of 4-chlorophenol. Kesselman et al. (*8*) reported that 4-chlorocatechol is oxidized directly at a Nb-doped TiO_2 surface. That report is consistent with our observation that 4-chlorocatechol does not persist in the electrolysis solution.

According to data in Table 2, phenol is also produced within the first 2 h of ECI. The pathway for phenol production is uncertain; however, reactions at the cathode are suspected to result in generation of some phenol. It has been shown previously that phenol is oxidized to form hydroquinone and benzoquinone (*28*), which would suggest that degradation of phenol follows the benzoquinone pathway.

Elemental Analysis for Electrode Materials in Solution. When metal oxide films are considered for the remediation of organic waste, the possibility of dissolution of these electrode materials becomes a matter of concern. Therefore, the elemental content of the ECI solution was determined by ICP-MS after the electrolysis process. The measured concentrations (ppb) of the eight elements detected are as follows: Ti = 5.3, Zn = 5.4, Ru = 22, Sn = 10, Sb = 25, Ba = 0.2, Pt = 8.0, and Pb = 0.6. The concentrations determined after electrolysis using a newly prepared electrode ranged from 10 to 100 times larger than those reported here for a well-used electrode. Therefore, a fresh electrode should be conditioned before long-term operation to avoid dissolution of metals into subsequent ECI product solutions.

Prospectus. Electrochemical incineration as a remediation technology is imminently logical for application to small volumes of toxic organic waste. As illustrated in this study, the time periods required for complete remediation are too long. This is a consequence of (i) slow electrode kinetics and (ii) inefficient cell design. The former issue is expected to be mitigated by the continued search for improved electro-

catalytic materials. The latter issue has already been solved by well-engineered flow-through systems of the type already applied in various electrosynthetic industries (*29−31*).

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