

Oxidation of Chloroanilines at Metal Oxide Surfaces

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The oxidation reaction of chlorinated anilines by two manganese oxides, birnessite and pyrolusite, and by iron oxide has been investigated. The oxidation ability of the oxides was in the order birnessite \gg pyrolusite $>$ iron oxide. Birnessite removed 100% of chloroanilines in 30 min, whereas pyrolusite and iron oxide removed from 5 to 96% of chloroanilines in 72 h. The differences in the reactivity of chloroanilines depended on the number and the position of chloro substituents on the aromatic ring. The activity of the oxides was maximal at pH 4.0 and decreased as the pH increased. The reaction kinetics in each of the systems investigated was adequately described by a second-order rate expression. A free-radical mechanism for the oxidative coupling reaction of chlorinated anilines was suggested. Chloroazobenzene and chlorohydroxydiphenylamine dimers were detected among the oxidation products. The results obtained suggested that the oxidative mechanism occurred through a head-to-head and head-to-tail coupling of chloroanilino radicals.

Keywords: Chloroanilines; pyrolusite; birnessite; iron oxide; oxidative coupling

INTRODUCTION

The environmental behavior of organic chemicals depends on some key processes. Redox reactions involving biotic and abiotic soil components appear to be a primary route for the transformation of pollutants and for the remediation of contaminated soils.

Significant progress in understanding the oxidation reactions of aromatic reductants by soil metal oxides has been made. It has been shown that Mn and Fe oxides are effective oxidants of various di- and trichlorophenols (Stone, 1987; Pizzigallo and Ruggiero, 1992; Ukrainczyk and McBride, 1993; Pizzigallo et al., 1995).

It is likely that similar reactions can be applied to the oxidation of other chlorinated aromatic molecules of environmental importance, such as chloroanilines. Substituted chloroanilines are released in soil both by the degradation of pesticides, such as phenylcarbamates, acylanilides, phenylureas, and nitroanilines (Kaufman and Blake, 1973; Hoagland and Zablotowicz, 1995; Carey et al., 1997), and as byproducts of the industrial production of dyes. Since their persistence can cause environmental contamination (Gericke and Fisher, 1979), those factors which can reduce them are of interest. Photochemical degradation (Hwang et al., 1985), adsorption on soil colloids (Beyerle-Pfnür and Lay, 1990), and chemical and biochemical transformations (Bartha, 1971) of chloroanilines have been studied. The chloroanilines can be adsorbed by soil colloids both physically and chemically, especially by the humic substances rather than by the inorganic fractions (Hsu and Bartha, 1974; Beyerle-Pfnür and Lay, 1990; Zhang and Sparks, 1993; Weber et al., 1996). Adrian et al. (1989) studied the incorporation of 4-chloroaniline (4-CA) into a phe-

nolic monomer. They concluded that not only enzymes (tyrosinase) but also inorganic species (especially pyrolusite) catalyze the formation of covalent binding between anilines and diphenols.

Soil microorganisms and enzymes are able to affect the persistence and transformation of the chloroanilines released in soil. Kaufman et al. (1972), described the *in vivo* synthesis of 3,3',4,4'-tetrachloroxyazobenzene during the metabolism of 3,4-dichloroaniline by soil *Fusarium oxisporum* and the probable pathway of reaction, while the specificity of peroxidases as catalysts for the synthesis of chlorobenzenes from chloroanilines has been known for some time (Bartha et al., 1968; Bartha and Bordeleau, 1969). Afterward, it has also become clear that the oxidative coupling reactions are accompanied by chloride ion release through a free-radical mechanism and that the dehalogenation is a crucial step of the overall detoxification effect (Dec and Bollag, 1995).

The knowledge of the abiotic oxidative coupling process of chloroanilines is less widespread. Laha and Luthy (1990), studied the reaction of various aromatic reductants, including *p*-chloroaniline, by a manganese dioxide. The reaction rate was pH dependent and of first order with respect to both oxidant and organic compound. According to the oxidative-coupling reaction mechanism, the authors demonstrated that substituted anilines were oxidized to azobenzenes symmetrically substituted.

This investigation was aimed at comparing the oxidation power of manganese and iron oxides on mono- and dichlorinated anilines, determining the rates and kinetics of the oxidation reaction, identifying the main oxidation products, and clarifying some aspects of the oxidative coupling mechanism.

EXPERIMENTAL PROCEDURES

Materials. The reagent grade compounds 4-CA, 3,4-DCA, and 3,5-DCA were purchased from Sigma Chemical Co. (St.

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Louis, MO), Merck (Schuchardt, Munich, Germany), and Fluka Co. (Buchs, Switzerland), respectively, and used as received.

Pyrolusite MnO_2 was obtained from Sigma, birnessite $\delta\text{-MnO}_2$ was synthesized using KMnO_4 and HCl , according to McKenzie (1971), and iron(III) oxide (hydrated FeOOH) was purchased from Aldrich Chemical Co. (Milwaukee, WI).

Milli-Q water (Millipore Co., Milford, MA) was used in the experiments. The solvents used for chromatographic analyses were HPLC grade.

Reaction Kinetics. A weighted quantity of oxide (75 mg of pyrolusite or 75 mg of iron oxide) was combined with a 20 mL aliquot of stock solution of each chloroaniline (50 mg L^{-1}) in 0.1 M sodium acetate buffer, pH 4.0. The mixture was stirred at 25°C from 0.5 to 72 h for 4-CA and 3,5-DCA, from 0.5 to 144 h for 3,4-DCA with pyrolusite, and from 2 to 72 h with iron oxide for all the chloroanilines. Similarly, a 5 mL aliquot of stock solution of each chloroaniline (50 mg L^{-1}) was mixed with 10 mg of birnessite from 2 to 30 min. At the end of the reaction time, the supernatants were separated from the pellets by centrifugation at $31000 g$ for 30 min, filtered through $0.22 \mu\text{m}$ Millipore membrane filters, and analyzed by high-performance liquid chromatography (HPLC). The pellet of each sample was washed twice with 1 mL of acetate buffer and twice with 1 mL of ethanol. The washings of each solvent were combined and analyzed by HPLC. Control experiments without metal oxides were conducted under the same conditions. The amount of chloroanilines transformed was calculated as the difference between the chloroaniline measured in the control and that recovered in the sample. All of the experiments were performed in triplicate.

Effect of pH. To determine the influence of pH on the transformation reaction of chloroanilines, sodium acetate buffer (for values in the range of pH 4–6) and sodium borate buffer (for values in the range of pH 7–8) were used. The chloroaniline/oxide ratios were 13.3 g kg^{-1} for pyrolusite and iron(III) oxide and 25 g kg^{-1} for birnessite. The incubation times were 48 h for pyrolusite and iron(III) oxide and 10 min for birnessite. The experiments were carried out in triplicate.

Extraction and Identification of Reaction Products. The filtered solutions obtained after the reaction of the chloroanilines with inorganic oxides were acidified (by HCl to $\text{pH} < 2.0$), and the soluble products were extracted three times by partitioning techniques using dichloromethane as solvent. The organic phases were dried over anhydrous sodium sulfate and evaporated to dryness, and the products were dissolved in $100 \mu\text{L}$ of dichloromethane and analyzed by gas chromatography–mass spectrometry (GC-MS). The ethanolic washings, containing less soluble products, were injected directly in GC-MS. Blanks prepared without metal oxide were extracted in the same way and analyzed by GC-MS to assess the absence of degradation products.

Analytical Procedures. The HPLC analyses were performed with a Waters 600 S (Milford, MA) liquid chromatograph (equipped with a LCJ 90-UV detector operating at 254 nm for all of the chloroanilines and with a CC-12 computing integrator). A Supelcosil $15 \text{ cm} \times 4.6 \text{ mm i.d. LC-18-S}$ reverse phase column of 5 mm particle size was used. The mobile phase, at a flow rate of 1.0 mL min^{-1} was composed of water (with 1% acetic acid) and acetonitrile in the proportion of 40/60.

The GC-MS analyses were carried out with a 5890 Series II gas chromatograph interfaced to a 5971 quadrupole mass spectrometer (both from Hewlett-Packard, Palo Alto, CA) equipped with an electron impact ion source. The samples, typically $1 \mu\text{L}$, were injected into a split–splitless injector warmed at 250°C and then analyzed by a capillary Rtx-5 GC column of $30 \text{ m} \times 0.25 \text{ mm i.d.}$, whose temperature was kept at 40°C for 1 min, then raised at 15°C/min up to 280°C , and, finally, held at that temperature for 5 min. Electron impact mass spectra were recorded by scanning the quadrupole from mass 35 to 550 Da at 1.4 scans/s at an electron energy of 70 eV.

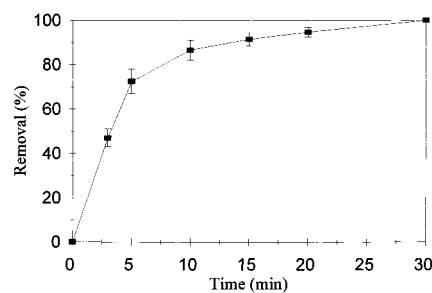


Figure 1. Kinetics of 3,5-DCA removal by birnessite.

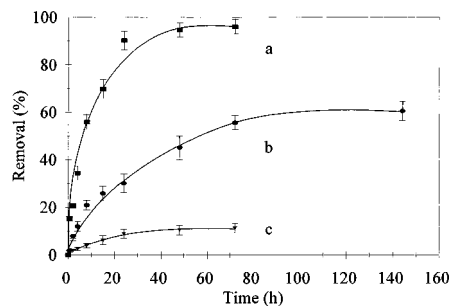


Figure 2. Kinetics of 4-CA (a), 3,4-DCA (b), and 3,5-DCA (c) removal by pyrolusite.

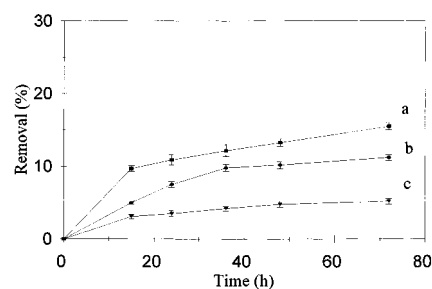


Figure 3. Kinetics of 4-CA (a), 3,4-DCA (b), and 3,5-DCA (c) removal by iron oxide.

RESULTS

The chloroanilines reacted rapidly with birnessite, developing a light red color. The results of the kinetic studies of the oxidation reaction showed that the inorganic oxides were able to transform the chloroanilines. The reaction rate was a function of the oxide used, and it was in the order birnessite \gg pyrolusite $>$ iron oxide for all of the chloroanilines investigated. At pH 4.0, the reaction of birnessite with 4-CA and 3,4-DCA was completed in such a rapid way that the reaction rate could not be measured, whereas with 3,5-DCA the reaction was relatively slower and 100% of removal was reached in 30 min (Figure 1).

The amount of chloroanilines disappearing with time by pyrolusite and iron oxide is shown in Figures 2 and 3, respectively. The comparison of the oxidation power of pyrolusite and iron oxide is significant because the same substrate/oxide ratios were used in all experiments. The removal was initially rapid and appeared to level off after variable times, as a function of oxide type, for all organic compounds. The amount removed of each chloroaniline was according to the sequence 4-CA $>$ 3,4-DCA $>$ 3,5-DCA, revealing that the extent of reaction depended on the number and position of chloro substituents on the aromatic ring. The differences in the reactivity of the chloroanilines were more evident with pyrolusite than with the iron oxide.

Since the inorganic oxide was in large excess, the reaction kinetics was studied with respect to the organic

Table 1. Kinetic and Statistical Parameters for Chloroanilines Oxidation by Birnessite, Pyrolusite, and Iron(III) Oxide

chloroaniline	metal oxide	k , ^a L mmol ⁻¹ min ⁻¹	$t_{0.5}$, ^a min	df ^a	F ^a	R^2 ^a	max removal, %
3,5-DCA	birnessite	1.17	2.5	3	7497	0.9996 ^b	100
4-CA	pyrolusite	0.006	383	6	994	0.9940 ^b	96.0
3,4-DCA	pyrolusite	0.004	1228	7	612	0.9926 ^b	65.1
3,5-DCA	pyrolusite	0.029	813	6	250	0.9766 ^c	11.5
4-CA	iron(III) oxide	0.019	746	3	274	0.9892 ^c	15.5
3,4-DCA	iron(III) oxide	0.011	1728	3	99	0.9705 ^d	11.2
3,5-DCA	iron(III) oxide	0.043	1128	3	473	0.9937 ^b	5.2

^a k = reaction rate constant; $t_{0.5}$ = half-life time; df = degrees of freedom; F = Fisher value; R^2 = correlation coefficient. ^b Significant at the 0.001 level of probability. ^c Significant at the 0.01 level of probability. ^d Significant at the 0.05 level of probability.

solute only. The rate data were tested for first- and second-order kinetics. This reaction order was also confirmed by the dependence of the $t_{0.5}$ values on the concentration of chloroaniline. The best linear plots resulted for the second-order rate equation. Table 1 shows the kinetic constants (k), the half-life times ($t_{0.5}$), the Fisher coefficients (F), the correlation coefficients (R^2), and the maximum amount of chloroanilines removed.

By comparing the half-life times of the oxidation reaction of the same chloroaniline by the two different oxides, it was observed that they were from 1.4 to 1.9 times higher with iron oxide than with pyrolusite. The values of the reaction rate constants confirmed that 3,5-DCA was the chloroaniline less susceptible to the oxidation. Its oxidation proceeded rapidly and completely by birnessite, however, always less rapidly than that of 4-CA and 3,4-DCA.

The influence of pH on the oxidation reaction of chloroanilines by metal oxides was investigated from pH 4.0 to 8.0 (Figure 4). For all chloroanilines the maximum activity of the oxides was observed at pH 4.0. With an increase in the pH, the oxide activities decreased. Already at pH 5.0, the decline in the oxidation reaction was remarkable, and pyrolusite and iron oxide did not show any activity at pH 6.0, while birnessite was inactive at pH 8.0.

The products obtained by chloroanilines oxidation by birnessite were identified by GC-MS. The only detectable products were 4,4'-dichloroazobenzene and 4-chloro-4'-hydroxydiphenylamine from 4-chloroaniline, and 3,3',4,4'-tetrachloroazobenzene and 3',4'-dichloro-3-chloro-4-hydroxydiphenylamine from 3,4-dichloroaniline. The insoluble fractions, solubilized by alcoholic washings of the pellets, showed the same reaction products as those identified in the soluble fraction of each substrate. Their quantities, however, were higher than those found in the soluble fractions. Moreover, 3,3',5,5'-tetrachloroazobenzene from 3,5-DCA was also found. An example of the GC-MS spectra obtained is shown in Figure 5.

DISCUSSION

Manganese and iron(III) oxides were effective oxidants toward chloroanilines. The extent and rate of reaction varied with the oxide and chloroaniline under investigation and with the pH values of the mixtures.

The birnessite was much more reactive than the other oxides. The reasons for this higher reactivity can be found in the structure characteristics of the birnessite. Generally speaking, the birnessite shows a varying

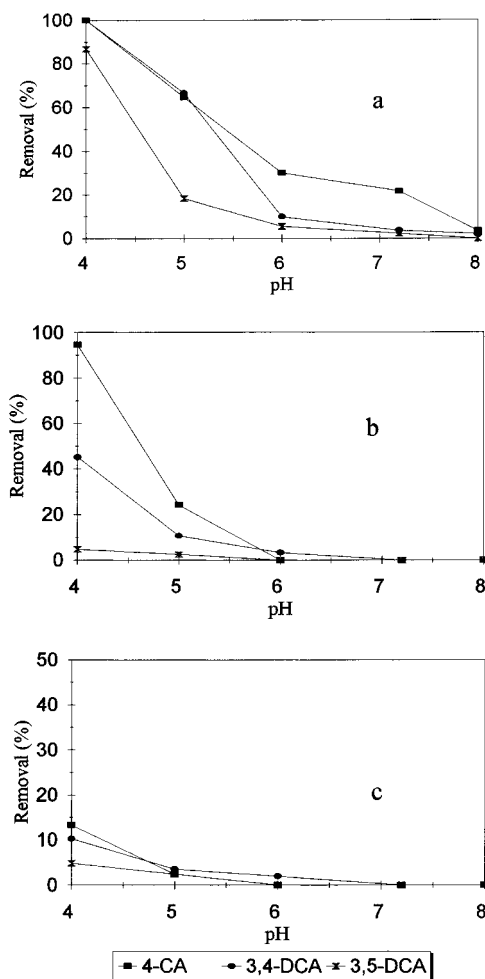


Figure 4. Effects of pH on the removal of chloroanilines by birnessite (a), pyrolusite (b), and iron oxide (c). Coefficient of variability, 0.5–5%.

composition, various Mn oxidation states, a specific surface area ranging from 262 to 277 m² g⁻¹ (Krishnamurti and Huang, 1987), and the lowest point of zero charge (PZC) among the manganese minerals (McKenzie, 1989). Pyrolusite, the most stable form of MnO₂, is a well-ordered crystalline mineral with a much lower specific surface (8 m² g⁻¹; Oscarson et al., 1983) and a PZC higher than the birnessite's one (Shindo and Huang, 1984). The iron oxide has a lower oxidation potential than that of manganese oxides (Shindo and Huang, 1984) and a low specific surface area (from 16 to 82 m² g⁻¹; Borggaard, 1983). Chloroanilines show different pK_a values: 3.5 for 3,4-DCA and 2.7 for 3,5-DCA, determined by electrochemical method and 4.2 for 4-CA (*Handbook of Chemistry and Physics*, 1988). Their order of reactivity with metal oxides (4-CA > 3,4-DCA > 3,5-DCA) depends on the number and position of chloro substituents on the aromatic ring.

The overall results obtained support the general mechanism for a surface chemical reaction described by Stone (1987), McBride (1987), and Ulrich and Stone (1989), for the oxidation of phenols by manganese oxide. It initially implies the formation of a complex between the chloroaniline and oxide surface. Subsequently, the electron transfer forms a chloroanilino radical, which is then released into solution and further oxidized to dimers and oligomers by oxidative coupling reactions. This mechanism previously applied to the oxidation of chlorophenols by manganese and iron oxides (Pizzigallo

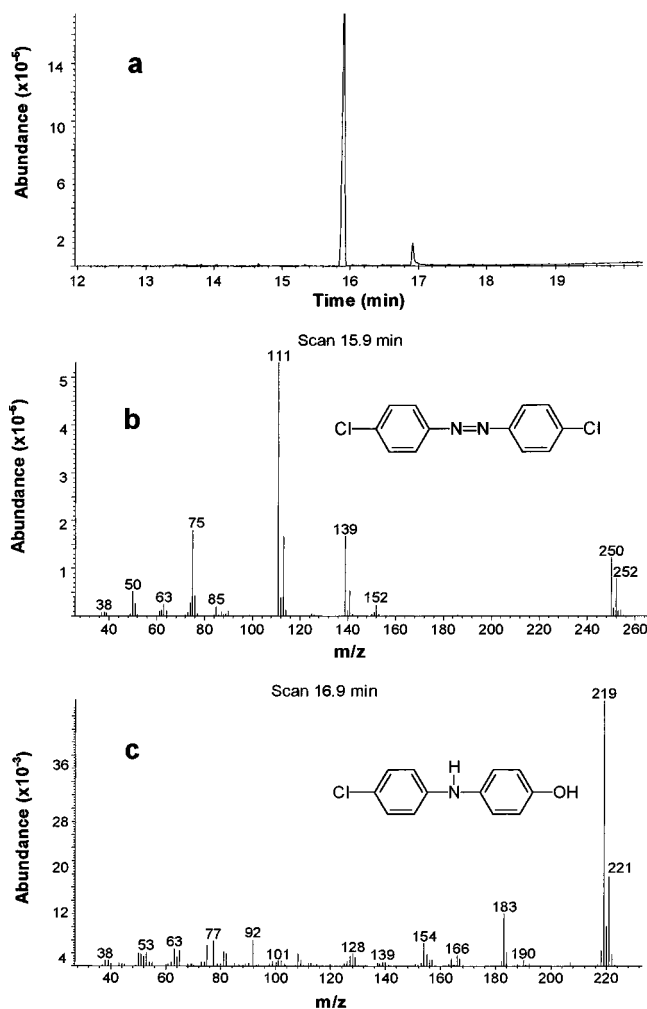


Figure 5. Chromatogram (a) and MS spectra (b, c) of the alcoholic extracts of birnessite after reacting with 4-CA.

et al., 1995) has been used to explain the results here obtained with chloroanilines.

In this context, a crucial step of the oxidation reaction is the formation of the surface complex. So, all of the reactant properties and the experimental conditions that favor the formation of metal oxide-chloroaniline complexes will promote the reaction. By considering the PZC values of the manganese and iron oxides and the pK_a values of the chloroanilines, the pH of the reaction mixture changes the charge of the pH-dependent oxide surfaces, and the concentration of neutral and protonated chloroanilines, which, in their turn, more or less likely form the complexes.

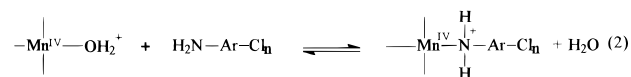
The reactive surface sites of manganese(III,IV) and iron(III) oxide surfaces are mainly associated with OH groups which are pH-dependent. With an excess of metal oxide, one chloroaniline molecule is quickly adsorbed onto surface sites forming an inner-sphere complex involving direct bonding between the metal center and organic reductant. The formation of outer-sphere complexes, in which a layer of coordinated OH groups remains intact and separates the reductant from surface metal centers, cannot be excluded. Nevertheless, the close association of the chloroaniline with the metal in the inner-sphere complexes makes the following electron transfer easier and increases the reaction rate. Moreover, the specific interactions between chloroanilines and surface metal sites are possible, and the relative affinity of the organic reductants for the sur-

faces sites produces, partly, different rates of reaction. The substrate selectivity cannot be explained by outer-sphere complex formation (Stone and Morgan, 1984; Stone, 1987). The precursor inner-sphere complex formation can be represented by a mechanism that, for birnessite at pH 4, above the PZC value, is



as, at pH 4, the product of the concentration of the reactants is highest and, for 4-CA and 3,4-DCA, $[\text{H}_3\text{N}^+-\text{Ar}-\text{Cl}_h]$ and $[\text{H}_2\text{N}-\text{Ar}-\text{Cl}_h]$ are almost equal.

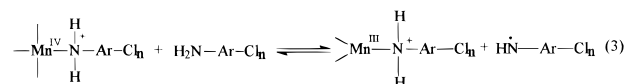
For pyrolusite (similarly for iron(III) oxide), at pH 4.0, below the PZC value, the mechanism is



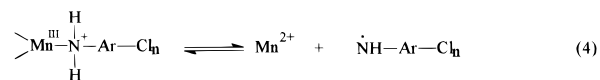
being the ligand exchange and the formation of the protonated complex, favored when unprotonated chloroaniline is considered.

On the basis of the model suggested, at pH 4.0, the maximum adsorption of chloroaniline and the highest concentration of the protonated complex are realized.

The following stage of the reaction mechanism has to be consistent with the second-order kinetics, as was also demonstrated by the dependence of half-life times on the concentration of chloroanilines. Laha and Luthy (1990), showing that 4-CA reacted rapidly with $\delta\text{-MnO}_2$, assumed a pseudo-first-order dependence for the reaction rate. The second order of the reaction rate means that another molecule of chloroaniline is involved (Pizzigallo et al., 1995). So, a second molecule is oxidized to chloroanilino radical and the metal in the complex reduced:



The complex may then release another chloroanilino radical and reduced Mn(II):



Chloroanilino radicals, by different couplings and further oxidation, will form dimers and oligomeric oxidation products.

The effective catalyst of the reaction could be the precursor complex, whose protonation increases the rates of electron transfer (Stone, 1987; Laha and Luthy, 1990). The decrease in activity of the oxides, as pH increases, can be attributed to less favorable conditions to the formation of the protonated inner-sphere complex.

The mechanism of the oxidative oligomerization of chloroanilines by oxidoreductases has been studied by some authors, who suggested reaction schemes consistent with one-electron oxidation, followed by a free-radical coupling reaction (Briggs and Ogilvie, 1971; Bordeleau et al., 1972; Iwan et al., 1976; Simmons et al., 1987).

The differences in reactivity of the three chloroanilines must be associated with the factors stabilizing the chloroanilino radical. The chlorines, independently

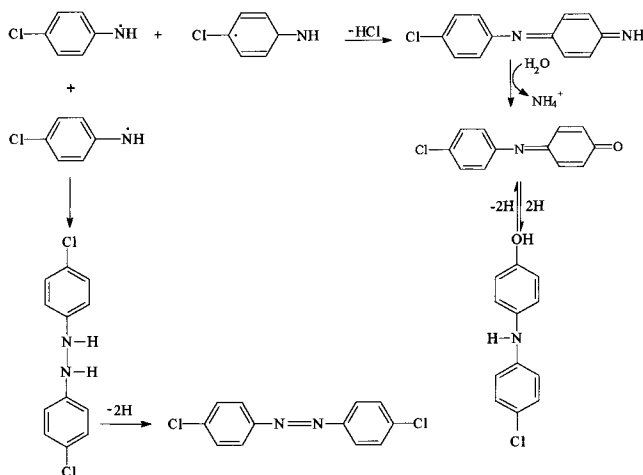


Figure 6. Proposed coupling reactions for the oxidation of 4-chloroaniline by birnessite.

of the number and position, withdraw σ -electrons, thus lowering the stability of the chloroanilino radical. Conversely, the π -electron donor effects of chloro substituents in the ortho and para positions, by increasing electron density, increase the stability of the radical intermediate. Moreover, the steric effect of chloro substituents can also affect the formation of precursor complex. Laha and Luthy (1990) investigated the reaction between δ -MnO₂ and some para-substituted anilines, including 4-chloroaniline. They found that the relative reactivity of substituted anilines depended on Hammett substituent constants; the electron-withdrawing groups made the oxidation of substituted anilines by manganese dioxide more difficult than the electron-donating groups.

The chloroanilino radical, released by the surface complex, is stabilized by extensive resonance, with the lone electron delocalized at the N, para, and ortho positions; it can enter in oxidative coupling reactions.

Dimeric intermediates may be formed by N–N, N–para, and N–ortho radical couplings. The predominance of any dimer depends on the extent of the radical coupling type, that is, on the degree of the lone electron localization in the N, para, and ortho positions. The N–N and N–para radical couplings are expected to be favored, even if substituents in the para position, when present, may limit the amount of para coupling by steric hindrance.

By considering the structures of the soluble dimers identified as reaction products, the possible combinations involving free radicals are presented in Figure 6.

N–N coupling of 4-CA forms a substituted hydroazobenzene which will be dehydrogenated to the 4,4'-dichloroazobenzene. N–para coupling forms a monoimine intermediate which, at low pH, is hydrolyzed to substituted benzoquinone monoimine (Simmons et al., 1987), which can be reduced to hydroxydiphenylamine. Identical mechanisms can be proposed for 3,4- and 3,5-DCA. The symmetrical coupling of substituted anilines might be favored because of blocking at the para position. In fact, when the impaired electron of the free radical is located at the chlorine-substituted aromatic carbon, a preliminary dehalogenation takes place before a head–tail coupling. The release of chloride ions during oxidative coupling of mono-chlorinated anilines has been recently well-discussed by Dec and Bollag (1995). When the para position is free, as in the oxidation of 3,5-DCA, the only product found by GC-

MS analysis was the corresponding azobenzene. The lack of hydroxydiphenylamine formation may result from steric hindrance of the chlorine atoms next to the unpaired electron (Dec and Bollag, 1995). Laha and Luthy (1990) showed that the main oxidation products of aniline and *p*-toluidine by MnO₂ in aqueous buffer solution at pH 4 were azobenzene and 4,4'-dimethylazobenzene, respectively. It is known that the coupling of chlorinated anilines can also be obtained in the presence of biotic catalysts. Bordeleau et al. (1972) proposed a pathway involving transformation of the chloroanilines by peroxidases and H₂O₂ to chlorophenylhydroxylamines with or without involvement of free chloroanilino radicals. Simmons et al. (1987) presented a reaction scheme for the oxidative oligomerization of 4-CA by peroxidase and laccase. Both enzymes catalyzed a free-radical coupling reaction with production of three dimers which formed trimers and tetramers by a nonenzymatic reaction. Evidence of this kind of enzymatic activity was obtained also by Hoff et al. (1985). The common steps of the enzymatic and chemical oxidation are the production of an anilino-free radical and chloroazobenzene formation, but other dimeric and trimeric products by enzymatic oxidation were also found (Corke et al., 1979; Hoff et al., 1985; Simmons et al., 1987).

In conclusion, the results presented in this paper show that the oxidation of chloroanilines by manganese oxides, in particular birnessite, and iron oxides is an important reaction in moderately acidic environments. This might be the preferential pathway for eliminating these aromatic pollutants, particularly when the conditions for microbial life are unfavorable. The physicochemical properties of the oxides and aromatic amines are useful for predicting rates and mechanisms of oxidative coupling reaction. Nevertheless, the reaction products might be more undesirable than the initial compounds. Substituted azobenzenes, owing to their high toxicity (Allison and Morita, 1995), may cause environmental contamination problems. A further transformation of dimers in less soluble oligomeric products is important in preventing or reducing their potential hazard in natural environments.

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Received for review September 15, 1997. Revised manuscript received February 16, 1998. Accepted February 19, 1998. This research was supported in part by Ministero dell'Università e della Ricerca Scientifica e Tecnologica-Progetti Nazionali and in part by Consiglio Nazionale delle Ricerche.

JF9707905