



Destruction of aniline by mediated electrochemical oxidation with Ce(IV) and Co(III) as mediators

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Abstract

Mediated electrochemical oxidation has been employed to test the feasibility of treating soluble organic wastes. We report Ce(IV)- and Co(III)-mediated electrochemical oxidation of aniline at various electrodes in acidic media as an example of organic waste. Aniline was oxidized by an electrogenerated electron transfer mediator, Ce^{4+} or Co^{3+} , in the anolyte and carbon dioxide was produced as a final oxidation product. Carbon dioxide was collected by bubbling through a barium hydroxide solution. When a powerful oxidizing agent, Ce(IV) or Co(III), was used as an electron shuttling mediator, parameters affecting the coulombic efficiency for aniline oxidation were the standard oxidation potentials of the mediators, their concentrations and the reaction temperature. Intermediate species produced during the oxidation of aniline were identified by cyclic voltammetric and absorption spectroscopic measurements.

1. Introduction

Electrochemistry offers an attractive way of treating wastewater containing solid or liquid organic wastes as it uses electrons as a reactant. Organic wastes can be treated biologically or incinerated [1]. To oxidize organic compounds more effectively, an electron transfer mediator, which oxidizes organic compounds in its oxidized state and is itself reduced, may be used. The reduced catalyst is reoxidized at the anode. This process is known as mediated electrochemical oxidation (MEO). Studies on MEO of organic compounds have been reported by a number of investigators [2–8].

Electrochemical oxidation of coal slurries mediated by Fe(III), Ce(IV), or Br_2 was reported by Park et al. [2, 3]. In Fe(III)- or Ce(IV)-MEO of coal slurries, not only were the overall reaction kinetics shown to improve but also the degree of heterogeneity was reduced for the reaction system. Anodic oxidation of aniline and phenol using a packed bed reactor of PbO_2 pellets were reported by Kirk et al. [4, 5]. Farmer et al. [6] reported oxidation of ethylene glycol and benzene using Ag(II), and destruction of chlorinated organic compounds by Co(III)-MEO [7]. Zhang and Park studied the oxidation of cellulose and its model compounds using Mn(III) as a mediator [8].

As Ce(IV) and Co(III) had been found to be very effective in oxidizing coal slurries [2, 3] and organic

alcohols [7], we used Ce(III) and Co(II) as solution catalysts for oxidation of aniline. Aniline was chosen as a model compound for two reasons. First, it is known to undergo a multielectron ($n = 28$), multistep electron transfer reaction to the final product. Secondly, it is a major pollutant in waste water from dye industries. Due to many steps and many electrons involved in aniline oxidation, it undergoes a polymerization reaction to form a fairly stable polymer, polyaniline [9–12]. For this reason, it is difficult to completely oxidize aniline to the final product, CO_2 . Also, it is reported to produce various intermediate species such as *p*-aminodiphenyl amine [11], benzidine [11], *p*-benzoquinone [12] and maleic acid [13], and further oxidation of these intermediates produces carbon dioxide as a final product. While it was reported to be oxidized to CO_2 at a PbO_2 electrode [4], the electrode itself is likely to introduce other pollutants into the environment. For these reasons, we decided to demonstrate the feasibility of oxidative destruction of aniline by means of mediated oxidation. As Ce(IV)/Ce(III) or Co(III)/Co(II) pairs have relatively high redox potentials of 1.44 and 1.80 V vs SHE in 1.0 M H_2SO_4 (1.24 and 1.60 V vs. Ag|AgCl electrode), they should be capable of oxidizing aniline rather effectively.

Ruthenium tetroxide is a versatile oxidant and has been used with a wide range of substrates including alcohols, aldehydes, ketones, ethers, amines, phos-

phines, arenes, alkenes and alkynes [14, 15]. Ayres [16] suggested that polychlorodibenzodioxins could be oxidized by catalytic amounts of ruthenium tetroxide as a primary reagent that was regenerated by a consumable secondary oxidant, such as hypochlorite. Beattie [17] reported that the ruthenium catalyst could be reoxidized at the anode and the electrocatalytic oxidation of organochlorines could be accomplished.

We carried out cyclic voltammetric and spectroscopic experiments to identify intermediate species during oxidation of aniline and also conducted exhaustive electrolyses under various conditions to study parameters affecting the coulombic efficiency for aniline oxidation. We tested two different working electrodes, platinum and RuO₂-coated titanium (dimensionally stable anode: DSA) electrodes.

2. Experimental details

Cerium(III) chloride (99.9%), cobalt(II) nitrate hexahydrate (99.999%), barium hydroxide monohydrate (98%), and potassium hydrogen phthalate (all from Aldrich, 99.95%) were used as received. Aniline (Kokusan, Japan) was used after distillation. Doubly distilled water was used to prepare solutions.

The RuO₂ electrode was prepared by thermal decomposition of RuCl₃ (Aldrich) on a titanium foil (Aldrich, 99.7%, 0.0127 cm thick) [18–20]. The titanium foil was first polished with silicon carbide (600 grid), followed successively by 3 and 1 μm, washed with ethanol, acetone, and water in an ultrasonic bath. The pretreated titanium foil was dipped in an aqueous solution containing 0.10 M RuCl₃, dried at 100 °C in an oven for 10 min, and then heated under air flow at 450 °C for another 10 min. This process was repeated 10 times and then the RuO₂-coated titanium foil was annealed at 450 °C for four hours.

The electrochemical cell had two compartments separated by a glass frit. A platinum gauze electrode (~70 cm²) or an RuO₂-coated titanium electrode (~51 cm²) and a platinum spiral wire electrode were used as working and counter electrodes, respectively. A second platinum disk electrode (area ~0.3 cm²) was used as an indicator electrode for monitoring cyclic voltammograms during electrolysis. The reference electrode was a Ag|AgCl (in saturated KCl) electrode. The platinum electrodes were cleaned in concentrated nitric acid before the beginning of each experiment. Solutions containing a millimolar quantity of aniline and a few mM of cerium(III) chloride or cobalt(II) nitrate in 1.0 M H₂SO₄ were used for the electrolysis experiments. The anolyte was stirred with a magnetic stirrer and bubbled with nitrogen during electrolysis. The amount of final product, CO₂, collected in a standard barium hydroxide solution was determined by back titration with a standard potassium hydrogen phthalate solution.

An EG&G Princeton Applied Research model 273 potentiostat/galvanostat was used for bulk electrolysis and recording cyclic voltammograms at the indicator

electrode. UV–visible spectra were recorded using a SCINCO s-2030 UV–visible spectrophotometer.

3. Results and discussion

The first electrolysis experiments were carried out in solutions containing millimolar quantities of aniline with 1.0 mM Ce(III) present at a constant potential of 1.50 V. Results obtained from the constant potential electrolysis experiments are listed in Table 1. Both the fraction converted to, and the coulombic efficiency for the generation of, the final product, CO₂, increases with electrolysis time. The coulombic efficiencies for the generation of CO₂ from aniline are relatively high, although overall conversion efficiencies are relatively low. This indicates that (i) the oxidation of aniline consists of many electron transfer steps but all the intermediate species generated in the meantime must have lower oxidation potentials than that of the Ce(IV)/Ce(III) pair and (ii) competing reactions do not appear very important for oxidation of intermediate species generated during aniline oxidation. In other words, other reactions such as water oxidation do not compete with oxidation of aniline and/or intermediate to a great extent.

For Co³⁺ (Table 2) as a mediator, coulombic efficiencies for Co³⁺-mediated oxidation are much lower than those for Ce⁴⁺-mediated oxidation, while overall conversion efficiencies depend on the potential applied and electrolysis time. Two competing reactions include: direct water oxidation at the electrode surface (heterogeneous) and aniline oxidation by electrogenerated Co³⁺ in the solution (homogeneous). This is because the E⁰-value for the Co³⁺/Co²⁺ pair is well above that of water

Table 1. Results obtained from MEO of aniline by Ce⁴⁺*†

Conc. of aniline /M	Electrolysis time /h	Conversion to CO ₂ /%	Coulombic efficiency /%
0.57 × 10 ⁻³	3	1.76	29.0
0.67 × 10 ⁻³	3	4.05	63.9
0.83 × 10 ⁻³	3	2.77	56.6
1.0 × 10 ⁻³	3	3.75	84.2
1.0 × 10 ⁻³	81	18.3	71.6

* Ce⁴⁺ concentration was 1.0 mM in 1.0 M H₂SO₄

† A constant potential of 1.5 V vs Ag/AgCl was applied

Table 2. Results obtained from MEO of aniline*,† by Co³⁺

Potential /V vs Ag/AgCl	Electrolysis time /h	Conversion to CO ₂ /%	Coulombic efficiency /%
1.7	3	4.71	6.76
1.9	2	9.72	0.59
1.9	3	20.40	1.78

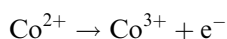
* Aniline concentration was 1.0 mM

† Co³⁺ concentration was 1.0 mM in 1.0 M H₂SO₄

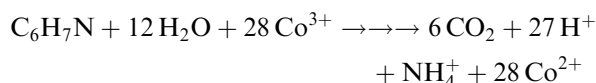
oxidation. While the conversion efficiencies increase significantly with increase in the Co^{3+} concentration (Table 3), the coulombic efficiencies remain low. At more positive applied potentials the relative conversion efficiency to CO_2 increases, but the coulombic efficiency decreases.

The results obtained from galvanostatic experiments run at 5 mA cm^{-2} in solutions containing $1.0 \times 10^{-3} \text{ M}$ aniline and various concentrations of cobalt(II) nitrate are tabulated in Table 3. We tried to avoid using the limiting current so that the mass transport would not limit the oxidation process, resulting in as high a coulombic efficiency as possible. The fraction of aniline converted to CO_2 and the coulombic efficiency increased with increase in concentrations of cobalt(III) nitrate. Thus, the efficiency for the reaction is dependent on the concentration of the solution catalysts. This arises from the higher reaction efficiencies of both homogeneous and heterogeneous reactions at higher Co^{3+} concentrations.

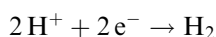
The aniline oxidation follows a catalytic reaction (EC') mechanism. At the anode,



which is followed by oxidation of aniline in the anolyte by Co^{3+} electrogenerated,



At the cathode, hydrogen evolution occurs,



From the above reactions, the catalyst concentration is expected to affect the amount of aniline converted to CO_2 . Also, the anodic oxidation of Co^{2+} should be more efficient at higher Co^{2+} concentrations than water oxidation, resulting in higher overall coulombic efficiencies. Oxygen evolution taking place during oxidation of Co^{2+} at the anode is suppressed by large amounts of Co^{2+} , leading to high current efficiencies.

Table 3. Results obtained from galvanostatic MEO of aniline*,†,‡ by Co^{3+}

Conc. of Co^{3+} /M	Conversion to CO_2 /%	Coulombic efficiency /%
1.0×10^{-3}	5.3	0.37
5.0×10^{-3}	17.90	1.26
10.0×10^{-3}	25.70	1.82
15.0×10^{-3}	26.90	1.90
20.0×10^{-3}	33.28	2.35

* Aniline concentration was 1.0 mM in 1.0 M H_2SO_4

† Electrolysis time was 3 h

‡ A constant current density of 5 mA cm^{-2} was used

To compare the performance of anode materials for oxidation of aniline, the oxidation efficiencies have been determined using platinum and $\text{RuO}_2\text{-Ti}$ electrodes. The results are summarized in Table 4. A few conclusions may be drawn from the results. First, higher overall conversion efficiencies and lower coulombic efficiencies are obtained at the platinum electrode at higher applied potentials. At more positive potentials, coulombic efficiencies become lower due to the competing reactions, although conversion efficiencies are higher as higher currents flow at more positive overpotentials. At the DSA, the same general trend is observed as that at the platinum electrode. The coulombic efficiencies are generally higher than those at the platinum electrode due to the low applied potentials. Due to a relatively low overpotential for oxygen evolution at the DSA compared to the platinum electrode, it was not possible to apply more positive potentials than 1.25 V (Figure 1). The presence of mediator ions enhances both the conversion and coulombic efficiencies at the DSA, although the applied potential, 1.20 or 1.25 V, is much lower than the oxidation potential of the catalyst itself, that is, 1.60 V (vs Ag/AgCl). The coulombic efficiency falls considerably when the potential is increased from 1.20 to 1.25 V in the presence of Ce(III) . This indicates that water oxidation competes with that of Ce(III) . It should also be noted that the reaction proceeds relatively efficiently even without the catalyst ions.

The temperature dependency of the reaction, when the $\text{Co(III)}/\text{Co(II)}$ pair is used at the platinum electrode as a solution catalyst, is shown in Figure 2. The electrolysis experiments were carried out at temperatures of 25, 50 and 70 °C with concentrations of cobalt(II) nitrate of 1.0×10^{-2} and $1.0 \times 10^{-3} \text{ M}$. Results are shown in Figure 2; both coulombic and conversion efficiencies increase with temperature, although coulombic efficiencies are still relatively low even at high temperatures. The Arrhenius plot shown in Figure 2(b) is not linear due probably to the mixed nature of the temperature effects resulting from three reactions, that is, oxidation of Co(II) , oxidation of water and MEO of aniline if not more.

Table 4. Results obtained from MEO of aniline*,† by controlled potential

Electrode	Catalysts‡	Potential /V vs Ag/AgCl	Conversion to CO_2 /%	Coulombic efficiency /%
Pt	Ce(IV)	1.5	3.75	84.10
	Co(III)	1.7	4.71	6.76
	Co(III)	1.9	20.40	1.78
	none	1.5	1.04	21.07
$\text{RuO}_2\text{-Ti}$	Ce(IV)	1.2	2.59	74.80
	Ce(IV)	1.25	1.74	8.77
	Co(III)	1.2	2.10	19.55
	none	1.2	1.72	4.71

* Aniline concentration was 1.0 mM

† Electrolysis time was 3 h

‡ Catalyst concentrations were 1.0 mM in 1.0 M H_2SO_4

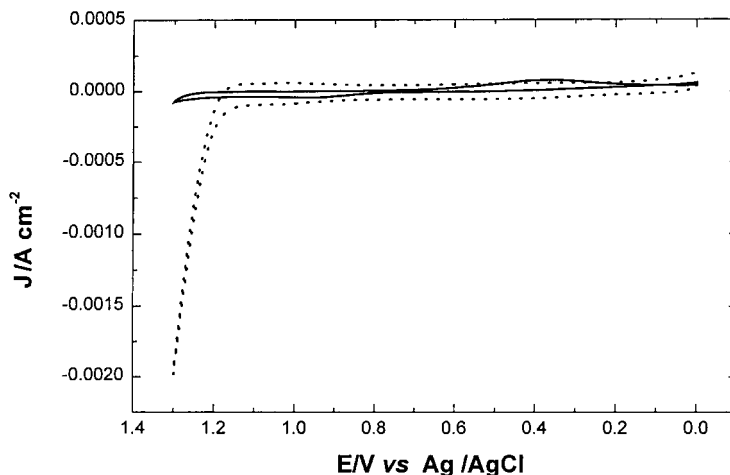
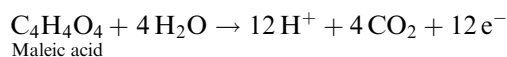
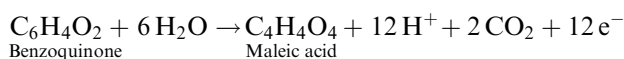
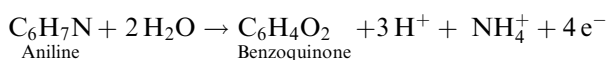


Fig. 1. Cyclic voltammograms of 1.0 M H₂SO₄ at Pt (—) and RuO₂-Ti (.....) electrodes.

A few intermediate species have been identified during the anodic oxidation of aniline in sulfuric acid at the PbO₂ electrode according to the following reactions [4]:



Three forms of dimeric species, that is, *N*-phenyl-*p*-diaminobenzene (head-to-tail), benzidine (tail-to-tail), and dihydrazobenzene (head-to-head), have also been identified in acidic media at platinum electrodes during aniline oxidation at early stages [11, 12]. To identify intermediate species, we recorded cyclic voltammograms (CVs) every 30 min. A typical CV

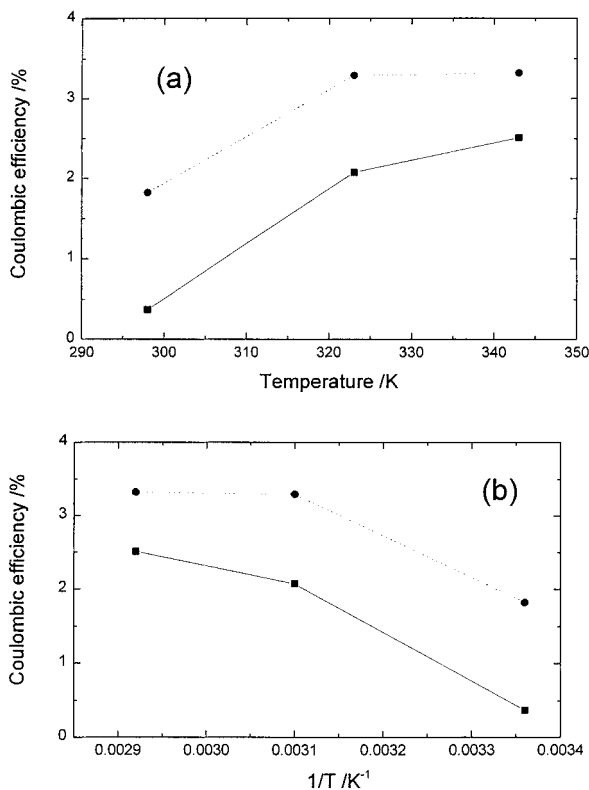


Fig. 2. Effects of temperature on the coulombic efficiency for electrolysis of 1.0 mM aniline with Co³⁺ present in 1.0 M H₂SO₄ at a current density of 5 mA cm⁻²: (a) coulombic efficiency against temperature and (b) coulombic efficiency against 1/T at a constant current density of 5 mA cm⁻². Key: (■) 1.0 mM Co³⁺ and (●) 10.0 mM Co³⁺.

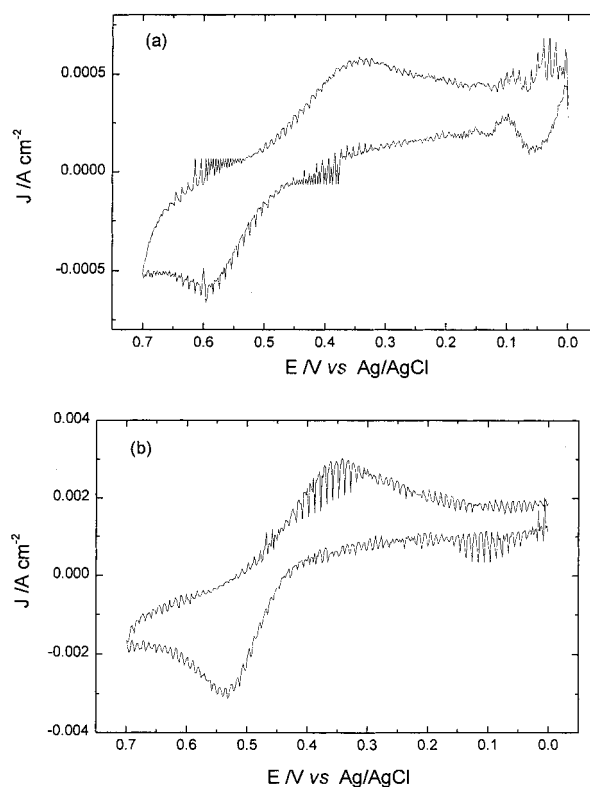


Fig. 3. Cyclic voltammograms recorded at 200 mV s⁻¹ after 0.5 h of MEO of aniline with 10.0 mM Co³⁺ present (a), and after adding benzoquinone (1.0 mM) to the Co³⁺ (1.0 mM) solution (b) in 1.0 M H₂SO₄ at a constant current density of 5 mA cm⁻².

recorded during the electrolysis experiments is shown in Figure 3(a). From the CV of authentic *p*-benzoquinone (*p*-BQ) (Figure 3(b)), we confirmed that *p*-BQ is produced as an intermediate species produced during the early phase of aniline MEO. The CV such as that shown in Figure 3(a) was not observed after 1.5 h of electrolysis, however; the higher the concentration of cobalt(II) nitrate and the higher the reaction temperature, the more rapidly *p*-BQ disappeared from the solution. *p*-BQ was the only intermediate species detected in the early stages of electrolysis by the electrochemical technique. The waves between 0 and 0.1 V must also be from some intermediate species; however, these were not identified.

To detect other intermediate species we also recorded UV-vis. spectra during electrolysis. UV-vis. spectra were recorded every 10 min and the results are presented in Figure 4. When the solution containing aniline and Co(III) was electrolysed, a weak band with a peak absorption at 417 nm shows up in the early stage of oxidation. The band disappears after about 20 min, suggesting that the species must be short-lived. The band is attributed to the oxidation product of aniline dimers such as benzidine, dihydrazobenzene, or *N*-phenyl-*p*-diaminobenzene [17]. Benzidine and/or hydrazobenzene were reported to be produced as the first dimeric products when aniline of low concentrations is electrochemically oxidized [21, 22]. Won et al. [23] reported a band at about 420 nm of low absorbance due to the formation of benzidine quinoneimine when benzidine was oxidized.

Unfortunately, the information available from Figure 4 is very limited due to overlapping spectral bands. We thus present the spectra in a slightly different format in Figure 5, that is, by subtracting the spectrum of Co³⁺ recorded before addition of aniline. As soon as aniline is added, the bands at about 233 nm and 215 nm undergo reduction in intensity and a new band at 417 nm emerges (Figure 5(a)). We believe that the disappeared bands are $\pi-\pi^*$ and $n-\pi^*$ transitions of aniline, while the new band is from the oxidized form of the aniline

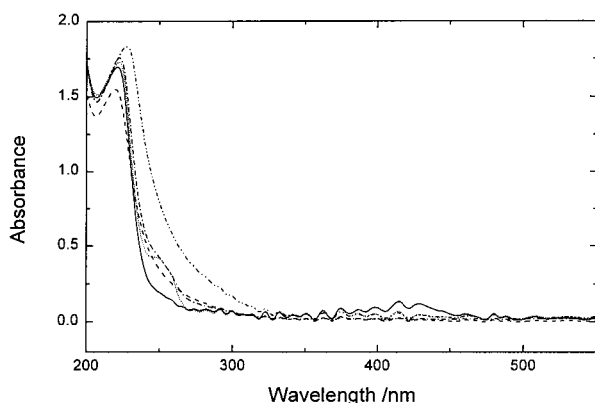


Fig. 4. UV spectra recorded: (—) after adding aniline (1.0 mM) to the Co³⁺ (10.0 mM) solution, and after (.....) 10 min, (- - - -) 2 h, and (- · - · - ·) 3 h of MEO.

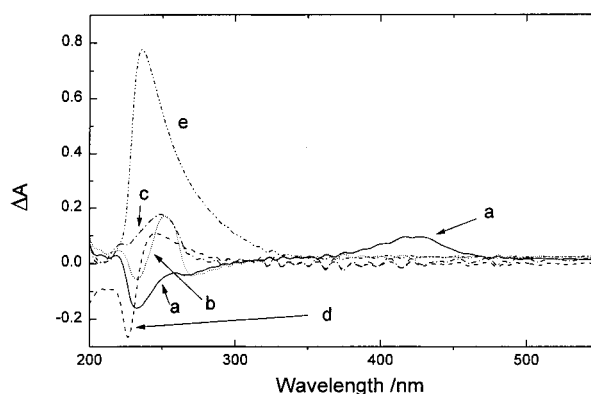
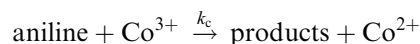


Fig. 5. Difference spectra obtained by subtracting the initial spectrum recorded from Co³⁺ before the addition of aniline. Key: (a) —; (b); (c) - - - -; (d) - · - · - ·; (e) - · - · - ·.

dimers. Thus, the dimers are formed immediately upon addition of aniline to the Co³⁺ solution. After 10 min electrolysis (Figure 5(b)), a reduction in the band intensity occurs at 219 nm; the band with maximum intensity at about 251 nm remained more or less the same. This is probably due to the decrease in aniline concentration and increase in another band from *p*-BQ absorbing at about the same wavelengths. In about an hour of electrolysis (Figure 5(c)), only the band at about 250 nm remained. Another weak band of *p*-BQ at about 405 nm is not seen here as it is too weak. After two hours (Figure 5(d)), part of this band became less intense (~225 nm) with a new band emerging at about 250 nm. With further electrolysis (Figure 5(e)), a strong band peaking at about 236 nm was observed. This is due to maleic acid and maleic anhydride.

The series of reactions observed here are the same as those reported for anodic oxidation of aniline at platinum or PbO₂ electrodes. All the intermediate species identified in previous studies are confirmed in our MEO of aniline. Thus, the reaction path may not be fundamentally different, with only the electrolysis efficiencies improved (Table 4).

Finally, we determined the catalytic rate constants for MEO of aniline at both the platinum electrode and DSA. The catalytic rate constants for the reaction,



can be determined by assuming that the rate of anodic oxidation of the catalyst ion, Co²⁺, at the electrode surfaces is faster than that (k_c) for mediated oxidation of aniline in solution. The rate constants are computed from steady-state currents observed at a constant potential under convective conditions. With continuous regeneration of catalyst, the current decays to a steady-state value from an initial current observed when the potential step is made. Figure 6 shows the currents observed during MEO of aniline with Ce⁴⁺ and Co³⁺ at Pt and RuO₂-Ti electrodes. From the initial slope of each curve, an empirical parameter, p , related to the

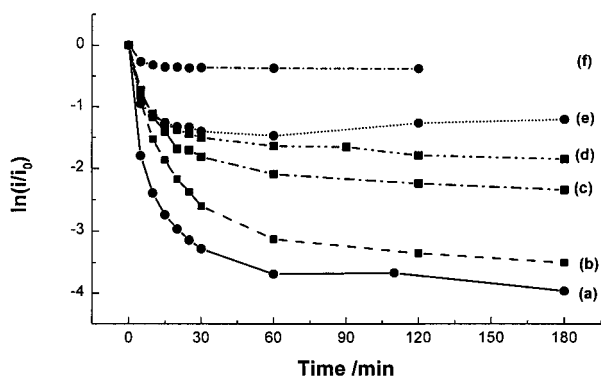


Fig. 6. Controlled potential electrolysis of aniline (1.0 mM) at Pt (●) and RuO₂-Ti (■) electrodes with 1.0 mM Ce⁴⁺ (a, b, d) and 1.0 mM Co³⁺ (c, e, f) at 1.2 V (b, e), 1.25 V (d), 1.5 V (a), 1.7 V (e), and 1.9 V (f) vs Ag/AgCl.

mass transport, is obtained under a given experimental condition from the equation,

$$i(t) = i_0 \exp(-pt)$$

where i_0 is an initial current observed upon stepping the potential, and $i(t)$ is the current observed at time, t , before it reaches a steady state value. With p known, the catalytic rate constant can be calculated from the steady-state current using the equation [24],

$$\frac{i_{ss}}{i(t=0)} = \frac{\gamma}{1 + \gamma}$$

where $\gamma = k_c/p$ and i_{ss} is the steady state current. The rate constants are listed in Table 5.

The results indicate that the rate constant is dependent on the potential applied, and the kind and concentration of catalyst ions. For example, the catalytic rate constant for Co³⁺ at 1.7 V is about five times of that for Ce⁴⁺, while it is about one-third of that at 1.9 V. The rate constants obtained at the DSA show an unusual trend. The rate constant for Ce⁴⁺ determined at 1.25 V is about four times larger than that at 1.20 V, while the rate constants for Ce⁴⁺ and Co³⁺ are about the same, although the potentials for these two measurements are different. This is perhaps because many reactions including oxidation of catalyst ions, aniline, and water take place at the potential applied.

Table 5. Rate constants for MEO of aniline*

Electrodes	Catalysts [†]	Potential /V vs Ag/AgCl	Rate constant, k_c /s ⁻¹
Pt	Ce(IV)	1.5	7.70×10^{-5}
	Co(III)	1.7	4.29×10^{-4}
	Co(III)	1.9	1.14×10^{-3}
RuO ₂ -Ti	Ce(IV)	1.2	8.16×10^{-5}
	Ce(IV)	1.25	3.45×10^{-4}
	Co(III)	1.2	2.11×10^{-4}

* Aniline concentration was 1.0 mM

[†] Catalyst concentration was 1.0 mM in 1.0 M H₂SO₄

4. Conclusion

When aniline was treated by Ce(IV) and Co(III) mediated electrochemical oxidation, the kinds and concentrations of solution catalyst ions, as well as reaction temperature, affected the coulombic efficiencies. The temperature effect appears to result from composite reactions, that is, anodic oxidation of water, aniline and catalyst ions as well as catalytic oxidation of aniline and water by electrogenerated catalyst ions. As a result, a clear trend was not seen in the Arrhenius plot. The catalytic rate constants are also shown to depend on the kind of catalyst ions and potentials applied.

The intermediate species identified confirm that the reaction mechanism is not basically different from the direct anodic oxidation of aniline. By using MEO, the overall reaction rate is much improved. In conclusion, the mediator ion, whose oxidation potential is reasonably high and yet whose redox reaction is reversible, would give good coulombic and conversion efficiencies. In the present case, the Ce⁴⁺/Ce³⁺ pair would be better than the Co³⁺/Co²⁺ pair in terms of cost per given amount of aniline treated. Studies on other experimental parameters affecting efficiencies of this process including pH, current density, aniline and catalyst concentrations, agitation rates etc. are under way in this laboratory.

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