Indirect electrolytic oxidation of some aromatic derivatives

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Received 12 December 1977; in revised form 29 June 1979

High current efficiencies and material yields were attained in the indirect electrochemical oxidation of toluene and chlorotoluene to the corresponding aldehyde. The oxidant used was Ce^{4+} in HClO₄, which was regenerated at platinized titanium anodes. A cost estimate showed that the electrochemical route could be economically attractive.

1. Introduction

In an indirect electrolytic synthesis the electrolysis and synthesis are separated by what has been called an 'oxygen (or hydrogen) carrier'. At the working electrode an oxidizing (or reducing) agent is generated and it is this that is reacted chemically with the feedstock, often in a separate reactor. The spent reagent is returned to the working electrode for regeneration. One thus loses the direct control of energy that is possible simply through selection of the electrode potential. In indirect synthesis the driving force for the reaction can be less conveniently varied, since this can be achieved only by modifying the redox potential through a change in the concentration or in the species of the redox system. However, the indirect procedure has a number of advantages. Two are:

(a) Since the chemical reaction takes place in a homogeneous phase (or in an emulsion) it is possible to use a sparingly soluble feedstock and still have a high concentration of the species reacting at the electrodes. This ensures a high mass transfer rate for the electrolytic regeneration.

(b) Multi-purpose reactors are popular in the fine chemicals industries (e.g. for batch processing of pharmaceuticals). Indirect electrosynthesis provides a good chance for the realization of a multipurpose electrochemical reactor since it may be possible with one (or a few) redox systems, regenerated in the same electrolytic cell, to carry out numerous syntheses. It must be verified, however, that the electrode reactions are not adversely affected by substances occurring in the chemical part of the system and dragged into the electrolytic cell. direct electro-oxidation of toluene and chlorotoluene to the corresponding aldehydes using the Ce(III)/Ce(IV) redox system and have carried out an economic evaluation of a possible industrial application.

Only a brief account is presented here. Full information including a literature survey is given in [1]. By and large, direct electrosynthesis has been more often investigated than the indirect process. A recent review of the latter has been given by Clarke, Kuhn and Okoh [2].

2. Experimental

2.1. Analysis

Product analysis was carried out mainly by gas chromatography on a Hewlett–Packard 5700 gas chromatograph. A 6ft column packed with 3 wt% Apiezon L and 1.5 wt% QF *l* on Chromosorb W 80/100 was employed. Extra verification of the product was obtained with a coupled GC–MS type Hitachi RMU 6L.

Cerium (IV) concentrations were measured by potentiometric titrations with standard Fe(II) or thiosulphate solutions.

2.2. Preparation of cerium (IV) perchlorate

Cerium (III) perchlorate can, in principle, be produced by dissolving $Ce_2(CO_3)_3 \cdot 5H_2O$ or Ce_2O_3 in perchloric acid. In practice, however, due to precipitation of polymeric cerium species or poor solubility (Ce_2O_3) this route to Ce(IV)perchlorate through electro-oxidation is unsatisfactory. Cerium (IV) perchlorate was therefore obtained by electrolysis of Ce(III) oxalate in

In the present work we have studied the in-

2.3. Oxidation of Ce(III)

The oxidation of aromatic compounds requires strong oxidizing agents of which one of the most suitable is Ce(IV). The redox potential of the Ce(III)/Ce(IV) system may be varied over a wide range by changing the electrolyte composition as is shown in Table 1. For the oxidation of toluene and chlorotoluene, redox potentials above 1.7 V (versus NHE) are required in order to achieve a useful reaction rate (see Section 2.4).

The redox system used was Ce³⁺/Ce⁴⁺ in an aqueous perchloric acid solution. The anodic reaction is:

$$Ce^{3+} \rightarrow Ce^{4+} + e$$
.

Under the very strongly acidic conditions employed and with electrode potentials close to that for oxygen evolution some difficulty was found in selecting a suitable anode material. Graphite was initially chosen on account of its low cost. A study of 17 various commercially available forms (including graphites incorporating teflon) as well as ones we specially impregnated failed to provide an anode giving a good current efficiency and sufficient corrosion resistance. However, platinum and platinum oxide on titanium gave satisfactory results. Only these ensured a sufficient corrosion resistance and current efficiency over long periods of time. The main experiments were carried out with titanium anodes coated with 5 μ m platinum.

Table 1. Redox potentials of the Ce (III)/Ce (IV) system in various electrolytes

Electrolyte		E _{redox} versus NHE	
HC1	1 N	1.28	
H ₂ SO ₄	1 N	1.44	
СН,СООН	1 N	1.42	
HNO ₃	1 N	1.61	
HClO ₄	1 N	1.70	
•	2 N	1.71	
	4 N	1.75	
	6 N	1.82	
	8 N	1.87	

Care must also be taken in selecting the cathode material. In order to prevent corrosion the standard potential of the cathode must lie well anodic to the actual electrode potential. Since the strongly acidic electrolyte results in a very low cathode potential, the choice of material is severely restricted. From a consideration of the Pourbaix diagrams for several cathode materials together with the corresponding Tafel parameters for hydrogen evolution, the most suitable material (taking also cost into account) is copper. In practice copper cathodes were hardly attacked by the Ce(III)/Ce(IV) solution even in an unpolarized state! In the electrolysis cell the back reduction of Ce⁴⁺ on the cathode could be prevented by means of a diaphragm. In an industrial application this would probably be unsatisfactory because of the more complex cell construction and lack of availability of suitable diaphragms. Another possibility to minimize the cathodic reduction of Ce4+ is to use a cathode of much smaller area than the anode. This can be achieved in two ways while preserving a reasonably uniform anodic current density:

(a) with concentric electrodes, the cathode being a cylinder with a small diameter as compared to the anode;

(b) by covering the cathode with an isolating multi-aperture baffle.

Fig. 1 shows typical current efficiencies measured with a stirred cell of the first type. Ce^{4+} concentrations of 1 mole l^{-1} can be reached without impairing the current efficiency. However, the current efficiency depends strongly on the con-



Fig. 1. Current efficiency for the oxidation of Ce^{3+} in 5 M HClO₄ (CE-perchlorate 0.4 M) with a platinized titanium anode and a copper cathode without diaphragm.

Product	Yield without inert solvent	Yield with excess hexane
(a) Oxidation of O-chlorotolu [Ce (IV)/toluene = 4]	ene in 7–8 N HClO ₄ with 0.6	70.75 M cerium perchlorate
O-chlorobenzylalcohol	0.8%	$0.8\%^{*}$
O-chlorobenzaldehyde	36.0%	79.2%*
acids	4.3%	$< 1\%^{*}$
(b) Oxidation of toluene in 8.	N HClO ₄ with 0.7 M cerium p	perchlorate [Ce(IV)/toluene = 4]
benzylalcohol	0.6%	<u> † </u>
benzylaldehyde	64.2%	81.8%†
benzoic acid	8.1%	2.4%†

Table 2. Product yield (with respect to feed stock consumed) for batch oxidation of toluenes under nitrogen and with light exclusion

*with 15 times excess

[†] with 10 times excess

centration of perchloric acid (Fig. 2). It decreases markedly in the concentration range where, according to the literature [3] the activity strongly increases (from a few units to many hundreds) and where the hydrated ceric ions are progressively replaced by unhydrated particles.

As shown in Table 1 the redox potential increases sharply requiring a high oxidation potential so that a greater percentage of the current is consumed by oxygen production. Moreover, the higher redox potential of the system could lead to significant amounts of oxygen generation by oxidation of the water in the bulk solution.

2.4. Chemical oxidation

The oxidation of toluene with ceric ions has been



Fig. 2. Current efficiency as a function of perchloric acid concentration. Anodic c.d., 25 mA cm⁻². Same conditions as for Fig. 1.

discussed by many authors [4]. The main reaction is:

$$\bigcirc CH_3 + 4Ce^{4+} + H_2O \longrightarrow 4Ce^{3+} + 4H^+ + \bigcirc CHO$$

Our product analysis of a hexane or pentane extract using gas chromotography was in accord with the literature findings that good yields of aldehydes may be obtained.* It turned out that the aldehyde yield was much better if the feedstock was diluted with hexane in the ratio 1:15. The improved yields with the inert organic solvent are shown in Table 2 for toluene and chlorotoluene oxidation using cerium perchlorate. They probably arise from the fact that the solvent rapidly extracts the aldehyde from the electrolyte thus minimizing further oxidation. It is easy to convert 80-90% of the toluene to the aldehyde. Highest yields were obtained when oxygen was removed from the reaction vessel and the light was excluded. However, in the case of the chlorotoluene, complications arise apparently because Cl radicals are formed which yield either chlor-

* The chlorotoluene and toluene which are only very slightly soluble in water were introduced into the oxidizing solution in the form of droplets. In order to facilitate the transfer of feed stock into the oxidant phase good stirring must be provided. This was exemplified by the higher (by a factor 3) reaction rates that were obtained by employing ultrasonic stirring (reaction vessel in an ultrasonic cleaning bath). The experiments reported here were, however, carried out with a conventional motor stirrer. Unfortunately, no measurements were taken to characterize the inter-phase mass transfer rates quantitatively.



Fig. 3. Initial rate of chemical oxidation of toluene by Ce^{4+} as a function of HClO₄ concentration. Concentration of Ce^{4+} : 0.2 M.

inated products (in the side chains and in the nucleus) or Cl-ions and chlorine.

The oxidation rate depends little on the concentration of Ce⁴⁺ but it increases strongly with increasing HClO₄ concentration (Fig. 3). However, the relative extent of the secondary reactions also increases somewhat (11 M HClO₄ itself attacks the aromatic derivative). Since the current efficiency decreases above 5 M HClO₄ (Section 2.3) it is best to use 5–6 M solutions of HClO₄. The maximum conductivity of HClO₄ also lies in this concentration range. The above conclusion concerning the optimum HClO₄ concentration is in agreement with findings of Bianchi and Faita [5].

2.5. Coupled chemical and electrochemical reactors

In preliminary experiments the chemical oxidation and the electrolytic regeneration were studied separately. In an industrial application continuous operation would be desirable. The solution leaving the chemical reactor must then be continuously stripped of organic materials in an extractor and recycled to the electrolyte cell where it is regenerated. An experimental arrangement for continuous operation was set up: it was a simplifed version of the flow sheet model of Fig. 4 which was used for the economic evaluation. To ensure high mass transfer rates the solution was pumped quickly through the electrolytic reactor and only a small fraction was bled off to the chemical reactor. The major part of the electrolyte was therefore recycled without going through the chemical reactor.

The cell used was that briefly described in Section 2.3 under (a). The electrodes were of platinized titanium and of copper.

Benzene should not be used as the solvent for the extraction (part 3 of the assembly) because it adversely affects the electrolytic regeneration.^{*} No problems were encountered with hexane or pentane. It was found that an extraction which keeps the amount of organic substances in the electrolyte circuit down to 150 mg l⁻¹ is sufficient to prevent inhibition of the electrodes. The longest experiment was run for 213 h. No deterioration of the electrodes was noticed. Table 3 shows typical results of the analysis of the products obtained. The yield with respect to Ce⁴⁺ was 80–99%.

The above results apply mainly to the case of toluene. Chlorotoluene is less suited as feed stock because various complications arise owing to the chlorine and chloro-derivatives which are generated in the process. The results of a similar continuous oxidation of chlorotoluene are shown in Table 4.

3. Economic evaluation

In the first part of this work it was shown that aromatic aldehydes such as benzaldehydes can be produced by indirect electrosynthesis with good current and material yields. In a second stage the economic aspects of a possible industrial application were considered in some detail. The cost estimate[†] was made for a plant with a yearly capacity of 2000 ton of benzaldehyde (operating

^{*} Benzene is itself oxidized by Ce(IV) perchlorate to benzoquinone. Further oxidation to polymeric species probably follows, thereby passivating the electrodes.

[†] The detailed version of this costing is given in the thesis by Kramer [1]. The prices have since been changed slightly mainly to account for the increase in the price of oil derivatives. The revised calculation can be obtained from the authors upon request.



Fig. 4. Flow sheet of process: model for economic evaluation. 1, Electrolytic circuit heat exchanger; 2, rectifier; 3, pump for circulating the electrolyte in the cell circuit; 4, bus bars; 5, electrolytic cells; 6, chemical reactors with separator; 7, pumps for recycling of electrolyte between chemical and electrochemical units; 8, extraction column; 9, residual electrolyte stripper; 10, 11, 14, 16, 18, heat exchangers; 12, solvent extractor (heat pump principle); 13, compressor; 15, distillation column for concentrated extractant; 17, condensator (column head); 19, product distillation.

Table 3. Composition of product obtained in continuous (237h) oxidation of toluene with 5 M HClO₄ and 1 M total cerium

benzaldehyde	98.8%	
benzyl alcohol	0.1%	
benzyl benzoate	0.3%	
benzil	$\sim 0.4\%$	(uncertain)
benzoic acid	0.4%	

Table 4. Composition of product obtainedin a continuous oxidation of chlorotoluene1 M total cerium in 6 M HClO₄ *

o-chlorobenzaldehyde	83.9%
dichlorotoluol	2.5%
o-Chlorobenzylchloride	3.6%
o-Chlorobenzylalcohol	1.3%
2, 4-dichlorobenzaldehyde	4.2%
2, 6-dichlorobenzaldehyde	2.2%
o-chlorobenzoic acid	1.8%

* results here after 2 hours

8400 h per year). The calculations were based on the flow sheet of Fig. 4 which involves a two-stage recuperation of the solvent used for the extraction and a distillation to separate out the end product from the feed stock which is recycled. The benzaldehyde yield in the chemical reaction was taken to be 90%, which has been found to be easily attainable. We shall present here two cost estimates. On the basis of our results with toluene the first is very conservative. In this case the plant was dimensioned for 10% conversion (consumption) of oxidizing agent in one pass of the chemical reactors. A large safety margin is therefore incorporated. The reason for doing this was to accommodate other redox systems which have either a lower solubility or lower reaction rate with the organic compound. The second costing does not include the safety margin and is based specifically on the more favourable conditions we obtained for toluene oxidation with ceric perchlorate. It is treated in Section 4.

We start with an estimate for the electrolytic

plant, which is the same for both the aforementioned costings. Electrolytic cells with two concentric cylindrical electrodes 3 mm apart were assumed. It has been shown by Thinh [6] that the construction cost for this type of arrangement is not higher than for a cell with parallel plate electrodes. The electrolysis system was optimized with respect to current density, radius of cell R and number of cells. The overall cost as a function of the number of cells gives a flat minimum for 31 cells. The optimum conditions are obtained with cells of radius 91.4 cm, a height of 86.4 cm and a current density of 1130 A m⁻² at which the current efficiency is 88%. The solution must be pumped through the cell at a velocity of $1-2 \text{ m s}^{-1}$. The corresponding pumping power is 330 W per cell. At the above current density the total anode area needed is 269 m². The thickness of the copper electrodes was taken as 0.38 cm, that of the titanium anode as 0.29 cm, plated with platinum 5 μ m in thickness. The price for copper, titanium and platinum is 9.9, 38.5 and 30000 Sfr. kg^{-1} respectively (1 Sfr. \approx \$0.6). One thus obtains a total cell cost of 1261 000 Sfr. (4690 Sfr. m⁻² electrode area) of which 892 000 Sfr. is for the platinum and platinization alone plus 54 000 Sfr. for the special covering of the cathode (where the cost of platinization and that for the reduction of the cathode area have been taken as 100 and 200 fr. m⁻², respectively). Other investment costs associated with the electrolysis that have also been calculated are those for the heat exchangers (1), the pumps (3), the rectifiers (2), the bus bars (4), the pipes (see Fig. 4), the land (900 Sfr. m^{-2} , including foundation work), the control instrument and auxiliary equipment, the installation, the planning and other accessory expenses. The total of the investment cost C_i amounts to 608 000 Sfr. We have then to calculate the annual expense. A linear rate of amortization of 1/6 and 8% interest was taken for the investment. To the capital cost, we must add the cost of energy (at 0.05 Sfr. kWh⁻¹) consumed by the electrolysers 339 000 Sfr., by the pumps 69 000 Sfr. and the cost of cooling water, which is about 4000 Sfr. It is seen that the total expense for the electrolysis is

811 000 Sfr. (i.e. 405 Sfr. per ton of aldehyde)*.

The next step is the evaluation of the cost connected with the chemical reaction and with the separation operations. A relatively slow reaction rate of 0.5 moles Ce(IV) $I^{-1} h^{-1}$ for the toluene oxidation was assumed (see last part of Section 4). A reactor volume of 20 m³ would thus be needed and would cost 376000 Sfr. [7]. The expense for the extraction depends on the volume of electrolyte to be treated. It was assumed that in the chemical reactors the concentration reduction of a 1 M ceric solution was 10%.⁺ The cost of the column for the extraction of the aldehyde with *n*-hexane was then calculated for five theoretical plates yielding 99.6% separation of solvent. It amounts to 140 000 Sfr. [8,9].

The two-stage evaporation and distillation of the extractant is a costly operation. To minimize this expense the estimate was made for an eva-

Table 5. Investment cost for a plant producing 2000 ton of benzaldehyde per year

Item		Investment cost (000s Sfr.)	
1	process equipment	1886	
2	piping	755	
3	steel construction	154	
4	instruments	256	
5	rectifiers and other		
	electrical equipment	350	
6	assembly	1067	
7	buildings	414	
8	indirect costs	592	
9	electrodes (platinum)	946	
10	chemicals (electrolyte,	510	
	solvent)	6930	
11	safety factor (22.66%)	1570	
12	working capital	1699	
	(stocking of feed stock and product)		
	Total	10199	

* The figure given in [1] is somewhat smaller since the energy consumed by the pumps was not included in this partial cost estimate. The interest due on the platinum has also been corrected.

[†] As mentioned previously this low conversion (concentration change 0.1 M) is very cautious. It does, however, make the costing for the operations following the chemical reactor applicable to a wider range of reagents that are much less soluble than cerium (IV) perchlorate or are unstable at high concentrations. An example that we are currently studying is Co (III) in 7 M H₂SO₄ where we can achieve a concentration of only 0.1 M Co (III).

^{*} In the absence of a diaphragm this assumes that a sufficient fraction of the area of the cathode is made inactive in order to prevent cathodic reduction (see Section 2.3).

poration with compression of the vapour and recycling of the heat of vaporization (heat pump principle). The energy cost is thus decreased but the investment for the heat exchangers, compressor and evaporator amounts to $818\ 000\ Sfr.$ for the first stage [8–10] alone.

The energy consumption for pumping, evaporation and distillation as well as the investment for the corresponding apparatus were evaluated from the actual throughput. This investment plus that for the electrolytic cells but excluding the cost of the electrodes was taken as the basis for the estimate of the additional equipment (pipes, control instruments, buildings) and indirect cost (headings 2-8 of Table 5). This estimate was made by the method of the Lang factors [11-13]. Averages of the values found in the literature were taken. Table 5 shows the breakdown of the overall investment cost (including the electrolytic part*). The heading 'process equipment' thus includes the extraction, distillation and evaporation units, as well as the electrolysis cells but minus the platinum cost which is listed separately. The high cost in heading 10 is due to the large volume of the expensive electrolyte.

Table 6 shows the main items of the production cost (referred to 1 ton of aldehyde). The figure shown under 3 (yearly payment for investment, referred to 1 ton of aldehyde) was obtained from the investment indicated in Table 5, assuming a yearly rate of 16.7% for amortization and 8% for

 Table 6. Production cost of 1 ton benzaldehyde by

 indirect electrosynthesis

Item	Total	Electrolytic part
1 raw materials (feed stock)	370.5	
2 energy	596.5	206
3 investment	941.5	333.5
4 salaries	365.5	91.5
5 maintenance	284.5	49
6 overheads	473.5	128.5
Total cost	3032	808
Processing cost	2661.5	808

* In this costing for the complete plant the electrolytic part was not treated separately. The method of Lang factors was therefore applied to the total investments (including electrolytic part) for the estimation of the costs of instruments and buildings, etc. interest[†]. The salaries were calculated on the basis of three shifts of 4 employees for the operation of the electrolysis, of the chemical reactors and of the separation operations (16.8 man hours per ton of aldehyde). The overhead was obtained by taking 30% of the salaries for the plant overhead [8] and 16% of the total of positions 1–4 of Table 6 for administration, selling and research [8].

4. Discussion

According to Table 6 the production cost is 3032 Sfr. per ton of aldehyde and the processing cost (i.e., total cost minus the expense for the raw material) is 2661 Sfr. This is five times more than the value obtained by Bianchi and Faita [5]. There are several reasons for this discrepancy. Among others, these authors have not included salaries and overheads. However, the main difference is that they have assumed the overall investment cost to be the same as in chlorine electrolysis (i.e. 2000 m^{-2} electrode area) whereas in the present work a detailed evaluation was made (including all the separation operations) which leads to an overall investment of 31 600 Sfr. (\$19 000) m⁻².

Indeed, the separation operations which involve large quantities of liquids, are very costly, A striking feature of the cost structure shown in Table 6 is the small share of the electrolytic part of the process in the total cost and this in spite of the very expensive platinum electrode. It is seen that the electrolysis (including auxiliary equipment, rectifiers, etc.) is responsible for only 30% of the overall processing cost. This is similar to the general experience of chemical engineering at large, namely that the chemical reactor itself contributes only 10-20% to the total expense, the major share being taken by the preceding or following separation and purification operations. It is likely that the situation is similar in organic electrochemical systems with respect to the electrolytic cell. It is thus probable that the breakdown of electrolytic and non-electrolytic expenses shown in Table 6 is typical for many cases of organic electro-

[†] The calculation here differs slightly from that previously given [1] in that the cost contribution due to the platinum is now included in the capital cost and not partly under the maintenance cost.

synthesis (including direct electrochemical oxidation and reductions). An interesting conclusion may be drawn from this which is applicable to research in industrial organic electrochemistry.

It is important to cut down the cost of the electrolysis but it is even more important to design the electrochemical reaction in such a way that the following or preceding separation operations are made very economic. If one succeeds in, say, halving the cost of these operations the competitiveness of the process will be improved more than through a halving of the expense connected with the electrolysis. If the latter leads to an increase in the cost of the separation operations the whole advantage may even be lost completely.

From the viewpoint of the separation operations the situation is less favourable for organic electrochemical systems than for non-electrochemical ones because one is often dealing (especially in the case of an aqueous phase) with dilute solutions, so that large quantities of liquids have to be treated. Let us illustrate the influence of such effects with the present example of aldehyde synthesis. We have assumed a chemical reaction rate of 0.5 mole Γ^{1} h⁻¹ and a concentration reduction of 10% of the ceric ions in the chemical reactors. These somewhat pessimistic assumptions were made in order to get an evaluation for a multi-purpose system which could also be used for similar syntheses of other aromatic aldehvdes or with other redox systems. However, in the case of the oxidation of toluene reaction rates of 2 mole l^{-1} h⁻¹ are easily realizable and with a decrease of concentration of Ce4+ -ions to virtually zero aldehyde yields of 80% were observed. With an excess of feed stock yields of 90% can be expected. It would therefore be possible to work with a very large conversion of Ce(IV) to Ce(III) in the chemical reactor, say 90%. This would simply be achieved by reducing the rate of feed of electrolyte to the reactor by a factor 10. The following extraction processes therefore have to deal with much lower through-puts. The expense for the chemical reactor and more particularly that connected with the separation and the recuperation of the extractant are thus strongly reduced: the overall expenses for energy and for investment are decreased

by almost one half. The production cost for 1 ton of benzaldehyde thus falls to 2160 Sfr.,* which illustrates well the aforementioned great impact on the overall cost of the operation of the chemical part of the process. The market price is 4500 Sfr. The electrochemical route could thus possibly be attractive for the synthesis of benzaldehyde. However, the use of perchloric acid solution is not desirable owing to safety aspects. The use of redox systems other than the one described here has also been investigated in our laboratory [14].

Acknowledgement

We wish to thank Ciba Geigy AG (Basle, Switzerland) for the financial support of this work.

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* This figure has been calculated in a more quantitative way by scaling-down the equipment associated with the product work-up.