

Mediated electrosynthesis with cerium (IV) in methanesulphonic acid

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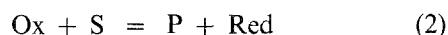
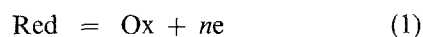
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Received 3 January 1989; revised 10 April 1989

Methanesulphonic acid has been found to solubilize the Ce(III)/Ce(IV) couple. This makes cerium mediated electrosynthesis practical for commercial production of several carbonyl compounds. Results are presented for the electrochemical generation of Ce(IV) in methanesulphonic acid and for naphthalene oxidation to 1,4-naphthoquinone using Ce(IV).

1. Introduction

Mediated electrosynthesis is a cyclic process involving electrochemical generation of a redox agent and use of that agent to effect a chemical reaction. For an oxidation reaction, the process can be represented schematically as follows



where Red represents the mediator in the reduced state, Ox represents the mediator in the oxidized state, S represents the reactant and P represents the product. Ideally, the electrochemical redox reaction is reversible and the chemical reaction highly selective. It is advantageous to carry out the electrochemical and chemical reactions in separate vessels (so-called 'ex-cell method') so that each step can be optimized independently. Several processes using this scheme have been reviewed [1, 2], as well as the chemistry of several mediators [3, 4]. Engineering design considerations for mediated electrosyntheses have been addressed by Pickett [5] and by Coeuret and Storck [6].

The use of Ce(III) as a mediator has been an area of active research because of the excellent selectivity with Ce(IV) for partial oxidations of organic compounds (for example, see Syper [7], Ho [8] or Long [9]). However, the practical realization of a cerium process has been slowed by a number of technical problems.

Ibl *et al.* [10] demonstrated an almost profitable process for making benzaldehydes using cerium in perchloric acid. However, the explosion hazard presented by mixing organics and perchloric acid has undoubtedly prevented further work on this process. Oehr [11, 12] has championed the use of cerium sulphate. However, he uses a cerium sulphate slurry to overcome the low solubility of cerium sulphate in sulphuric acid and a slurry is undesirable because of materials handling problems. Komatsu *et al.* [13] use cerium sulphate in sulphuric acid and avoid a slurry system by cycling within a narrow range of Ce(IV) concentrations. Rennie [14] solubilizes cerium in nitric

acid, but obtains significant quantities of nitrated byproducts.

We have found that methanesulphonic acid or trifluoromethanesulphonic acid solubilizes the Ce(III)/Ce(IV) couple without presenting any of the difficulties mentioned above. This discovery now makes cerium mediated electrosynthesis practical for commercial production of several carbonyl compounds. Here, results are presented for the electrochemical generation of Ce(IV) in methanesulphonic acid and for naphthalene oxidation to 1,4-naphthoquinone using Ce(IV).

2. Experimental

Solutions of cerium methanesulphonate in methanesulphonic acid were prepared by stirring cerium carbonate in water, adding concentrated methanesulphonic acid both to convert cerium carbonate to cerium methanesulphonate and to provide methanesulphonic acid and, finally, diluting with water to obtain the desired concentrations. Analysis of Ce(IV) was done by titration with ferrous ammonium sulphate using a Ferroin indicator. Analysis of Ce(III) was accomplished by oxidation to Ce(IV) using persulphate with a silver nitrate catalyst [15], followed by Ce(IV) analysis as above.

Naphthalene and 1,4-naphthoquinone were analysed by GC using dodecane as an internal standard with a capillary column (60 m fused silica column, column temperature 180°C, detector/injector temperature 260°C) and FID detector.

Three different configurations of parallel-plate cells were used. Figure 1 shows the geometries of the cells used. The cell of Fig. 1a has a flat plate anode and cathode (stainless steel cathodes were used unless otherwise noted). The Viton gaskets were 0.16 cm thick and Teflon screens were placed in the electrolyte compartments to prevent collapse of the Nafion membrane. Exposed electrode area was approximately 50 cm² (3.175 cm × 16.5 cm).

The cell in Fig. 1b is the commercially available MP cell (Electrocell AB); an excellent characterization of

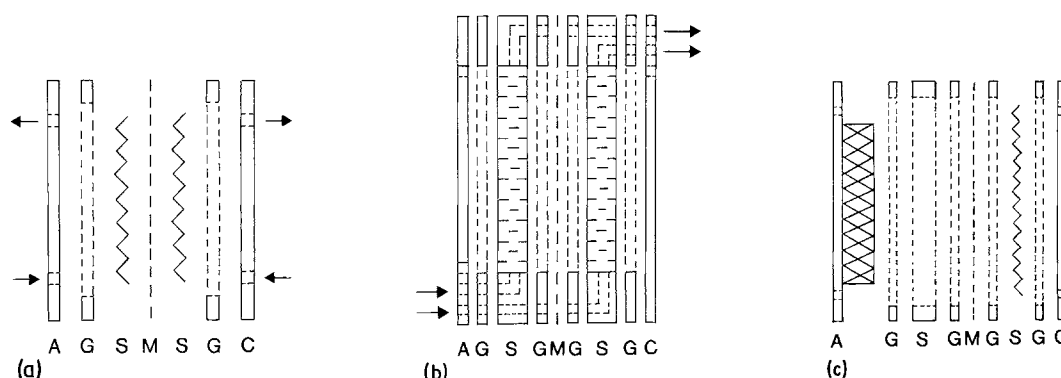


Fig. 1. Reactor geometries for Ce(IV) generation. Flat-plate steel cathodes, Viton gaskets and Nafion membranes were used in all cases. A — anode, G — gasket, S — spacer or screen, M — membrane, C — cathode. (a) Parallel flat-plate cell. (b) Parallel-plate cell with turbulence promoters (MP cell). Turbulence promoters were removed in some experiments and replaced with platinum-on-niobium expanded metal screens. (c) Electrochemical cell with flow-by anode on a titanium sheet (RETEC electrode from Eltech).

this cell is available [16]. The 6 mm thick electrolyte compartment contains turbulence promoters. For some experiments, the turbulence promoters in the anolyte compartment were removed and replaced with platinum-on-niobium expanded metal screens (Texas Instruments). The exposed area of the flat plate electrode is 100 cm^2 ($10\text{ cm} \times 10\text{ cm}$) and each screen added an additional 100 cm^2 of electrode area.

The cell in Fig. 1c is similar to that of Fig. 1a except that the anolyte compartment contains a 0.635 cm thick polyvinylidene difluoride spacer to accommodate the 0.635 cm thick porous anode. The anode consists of a piece of reticulated titanium bonded to a titanium backplate; the reticulated titanium has a TIR[®] coating and was obtained from Eltech (RETEC electrode). The dimensions of the reticulated portion are $3.175\text{ cm} \times 15.24\text{ cm} \times 0.635\text{ cm}$; the projected area of the electrode is 48 cm^2 , but the real area is unknown.

Chemical reactions between Ce(IV) and naphthalene were carried out in a 1 l jacketed baffled glass stirred-tank reactor under a nitrogen atmosphere. A 4-blade paddle stirrer with a blade diameter of 6 cm was used in the 10 cm diameter tank.

3. Results

3.1. Solubility of cerium in methanesulphonic acid

The solubility of Ce(III) in methanesulphonic acid is shown in Fig. 2, together with an estimate of the solubility of Ce(IV). In contrast to the behaviour in sulphuric acid [17], the solubility of Ce(IV) increases with increasing methanesulphonic acid concentration. But like aqueous sulphuric acid, the solubility of Ce(III) decreases with increasing methanesulphonate acid concentration. Solid Ce(III) methanesulphonate can be isolated as a white powder, $\text{Ce}(\text{CH}_3\text{SO}_3)_3 \cdot 2\text{H}_2\text{O}$ [18]. Ce(IV) precipitates from dilute methanesulphonic acid solution as a yellow powder with composition $\text{Ce}(\text{CH}_3\text{SO}_3)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$.

As a first approximation, Fig. 2 can be used to identify the concentration window where the Ce(III)/Ce(IV) couple will be soluble. The solubility of Ce(III) in the presence of Ce(IV) has not been determined;

in the case of sulphuric acid Ce(IV) apparently solubilizes Ce(III) [13].

3.2. Electrochemical generation of Ce(IV) in methanesulphonic acid

Figure 3 shows polarization curves obtained with a platinum wire in 6 M methanesulphonic acid with and without cerium present. On platinum there is a potential window between about 1350 and 1550 mV(SCE) for Ce(III) oxidation. A rotating ring-disc platinum electrode experiment was done to estimate the diffusion coefficient for Ce(III) in 6 M methanesulphonic acid: Ce(IV) generated at the disc was reduced at the ring and the reduction current used to estimate a diffusion coefficient. At ambient temperature, a value of $1.0 \times 10^{-6}\text{ cm}^2\text{ s}^{-1}$ was obtained; this low value results in part from the viscous solution (2.45 centi-stokes).

Preparative scale experiments were done using the cell geometries discussed in Section 2 above. Regardless of the reactor geometry, the following reactions

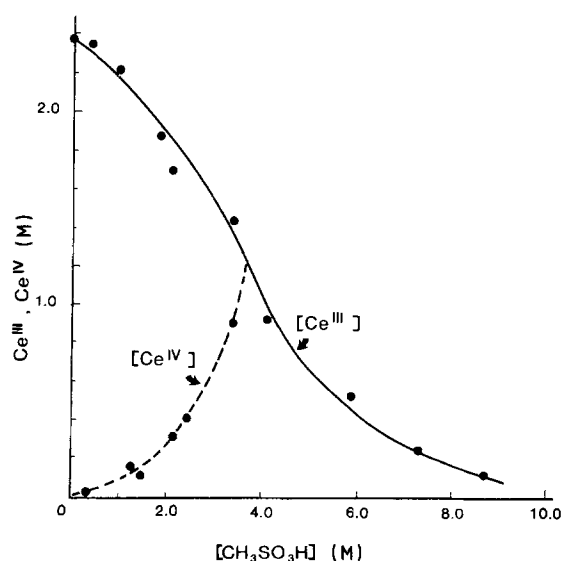


Fig. 2. Solubility of Ce(III) and Ce(IV) in methanesulphonic acid (room temperature). The Ce(III) solubility was determined by oxidizing 1.4 M $\text{Ce}(\text{CH}_3\text{SO}_3)_3$ in the stated initial acid concentration until solid Ce(IV) forms. The supernatant was analysed for Ce(IV) until equilibrium was reached (after several days).

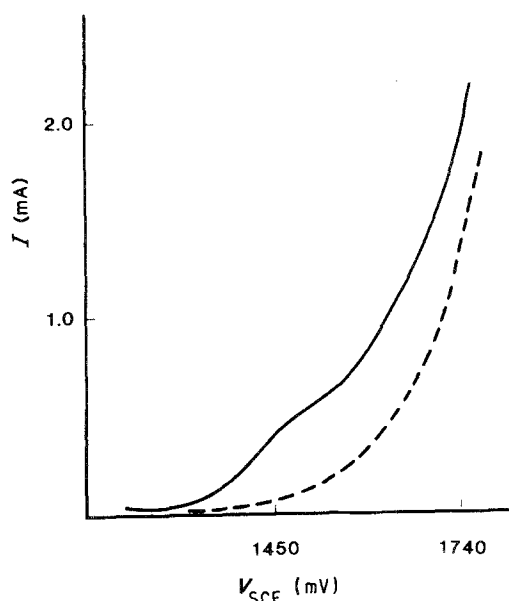
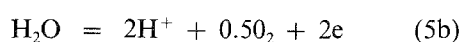
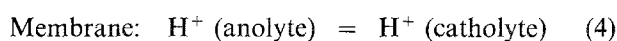
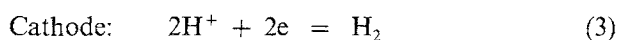


Fig. 3. Current-potential curve obtained with platinum wire in 6.0 M methanesulphonic acid: (a) without cerium (---) and (b) with 0.025 M Ce(III) (—).

take place



From the above reactions one can see that the solution becomes less acidic as the Ce(III) is oxidised; the concentration of methanesulphonic acid depends on the degree of cerium conversion. Here all acid concentrations reported correspond to zero Ce(III) conversion.

Several electrode materials were examined for Ce(IV) generation and results are presented in Table I. The materials are listed in order of decreasing effectiveness:



Table 1. Performance of flat-plate cells for Ce(IV) generation

Anode Material	Current (A m^{-2})	Conversion (%)	Current efficiency (%)
DSA	600	6	73
DSA	600	16	62
DSA	1000	10	68
DSA	1000	33	65
TIR	600	8	92
TIR	600	23	89
TIR	1000	11	77
TIR	1000	29	69
Pt	1000	40	96
Pt	2000	29	88
Pt	3000	26	81
PbO ₂ *	1000	39	91
PbO ₂ *	2000	30	88

Conditions: 15 M Ce(III); 2 M methanesulphonic acid; 25°C.

* Screen electrode, geometric area estimated at 50 cm².

Table 2. Generation of Ce(IV) with a flat-plate electrochemical cell

Current density (A m^{-2})	Flow velocity (cm s^{-1})	Conversion Ce(III) (%)
225	1.5	95
225	5.0	94
450	3.3	85
1125	1.7	48
1125	6.7	75

Platinum sheet anode, 0.42 M Ce(III)/5.9 M MSA, 50°C. In each case, the theoretical amount of charge was passed so current efficiency and conversion are equivalent.

TIR[®] and DSA[®] electrodes are manufactured by Eltech: the TIR[®] is believed to be iridium oxide on titanium; DSA[®] is believed to be ruthenium oxide on titanium. Excluding glassy carbon, the materials are apparently ordered according to their oxygen overpotentials, lead dioxide having the highest oxygen overvoltage and DSA[®] the lowest.

The data in Table 2, obtained with a lower Ce(III) concentration, indicate that on platinum the reaction is mass-transfer controlled at higher current densities.

A commercially available reactor design (MP cell, Electrocell AB, Fig. 1b) was evaluated. Apparent mass transfer coefficients (K_a) were determined by measuring the Ce(IV) concentration-time behaviour at a current above the mass transfer limiting current density and fitting the data to the following equation

$$\ln C/C(t=0) = (Qt/V)(1 - \exp(-K_a A/Q)) \quad (6)$$

where V is the anolyte volume, 3.9 l; Q is the anolyte flowrate, 5.41 min⁻¹; A is the geometric area of separator, 100 cm²; t is the time; C is the concentration; K_a is the apparent mass-transfer coefficient in cm s⁻¹. The results are presented in Table 3. Equation 6 applies to a plug-flow reactor operating in a batch recirculating mode. The mass-transfer coefficients (see Table 3) can be used to estimate the minimum reactor area required to achieve a given conversion using Equation 6. Pickett [5] and Coeuret and Storck [6] give design equations for other reactor configurations (for example, CSTER).

To obtain high Ce(III) conversions with a starting concentration of 0.42 M Ce(III), the use of screens is mandated in order to achieve commercially viable current densities (that is, > 1000 A m⁻²).

A reticulated titanium electrode with a TIR[®] coat-

Table 3. Apparent mass-transfer coefficients for Ce(III) oxidation obtained with an MP cell

Electrode	K_a (cm s^{-1})
Flat plate	0.0014
Flat plate + 3 screens	0.009
Flat plate + 5 screens	0.0143

Conditions: 0.42 M Ce(III), 4.5 M MSA, 60°C, flowrate 5.41 min⁻¹, electrolyte volume 3.9 l.

Table 4. Oxidation of Ce(III) using RETEC electrode

Current density ($A m^{-2}$)	Conversion (%)	Current efficiency (%)
3000	100	94
4000	97	92
5000	94	89
6000	90	85

Starting Ce(III) conc. of 0.88 M, MSA conc. 4.0 M; 60°C; flow-rate of 1.29 l min⁻¹.

ing (RETEC electrode) was tested (see Fig. 1c) and some results are listed in Table 4. The RETEC electrode allows very high apparent current densities (that is, based on membrane area) to be obtained. To our knowledge, these are the highest current densities ever reported for generation of an anodic mediator. Undoubtedly, these electrodes will prove useful for the generation of other mediators (for example, Cr(VI)).

3.3. Chemical oxidation with Ce(IV)

Ce(IV) in methanesulphonic acid can be used to produce a wide variety of carbonyl compounds [19]. Here we report some results for oxidation of naphthalene (NA) to 1,4-naphthoquinone (NQ) in order to indicate the usefulness of this system. Conventional air oxidation of NA gives poor selectivity (less than 40%) to NQ, the major product is phthalic anhydride [20]. The use of Ce(IV) allows almost complete conversion of NA to NQ with high selectivity based on NA and Ce(IV).

Table 5. Experimental design

Experiment no.	[NA]	[Ce(IV)]	[Ce(IV)]/[NA]	Stir speed	[TBAOH]
1	-	-	-	-	+
2	+	-	-	-	-
3	-	+	-	-	-
4	+	+	-	-	+
5	-	-	+	-	-
6	+	-	+	-	+
7	-	+	+	-	+
8	+	+	+	-	-
9	-	-	-	+	-
10	+	-	-	+	+
11	-	+	-	+	+
12	+	+	-	+	-
13	-	-	+	+	+
14	+	-	+	+	-
15	-	+	+	+	-
16	+	+	+	+	+
17	0	0	0	0	0
18	0	0	0	0	0
19	0	0	0	0	0

Variables ranges: - 0 +
 [NA] (M) 0.2 0.3 0.4
 [Ce(IV)] (M) 0.4 0.55 0.7
 [Ce]/[NA] ratio 1.0 1.25 1.5
 Stir speed setting 5 7.5 10
 [TBAOH] (mM) 0 12.5 25

Design is 2⁽⁵⁻¹⁾ fractional factorial with three centrepoint replicates.

The reaction is carried out as follows. NA is dissolved in dichloroethane (0.2 to 0.3 M NA) and contacted with an aqueous cerium solution (0.37 to 0.43 M Ce(IV), 0.23 to 0.47 M Ce(III), 2.8 to 3.5 M methanesulphonic acid) in a jacketed glass stirred-tank reactor at 60°C. In some experiments a dispersion is formed at the interface between the aqueous and organic phases. The volume of this dispersed phase was measured and is reported in Table 6. A temperature of 60°C was selected as a compromise between minimizing the vapour pressure of dichloroethane and maximizing the reaction rate. Although the two phases are immiscible, the reaction is complete within 30 min when well-stirred. The two phases separate cleanly within 2 min after stirring is stopped. NQ is the major product and, under optimum conditions, the selectivity for NQ is almost 100%. However, a small amount of phthalic acid (less than 1% yield) is also produced under most conditions, and under conditions of very poor mixing binaphthalene has been identified. The distribution coefficients between the aqueous and organic phases for both NA and NQ are such that both compounds reside predominantly in the organic phase.

A fractional factorial experimental design was run in order to identify optimum operating conditions. Table 5 shows the design selected, Table 6 lists the response variables, and Table 7 lists the coefficients found to best-fit the experimental results. Selectivity and yield are defined as follows

$$NQ_{Sel} = \frac{\text{moles NQ}}{\text{moles NA}_{\text{reacted}}} \quad (7)$$

Table 6. Experimental results

Experiment no.	NQ selectivity (%)	NQ yield (%)	Reaction time (min)	Ce(IV) selectivity (%)	Dispersion (ml)
1	96.1	84.3	20	86.9	0
2	92.6	83.2	20	85.8	5
3	95.0	86.3	30	87.2	5
4	86.3	78.9	20	79.6	0
5	87.8	95.6	30	79.4	20
6	63.3	82.8	20	59.6	0
7	91.3	91.3	30	77.0	0
8	101.0	101.0	30	86.7	15
9	103.0	92.3	20	95.0	5
10	92.7	83.6	10	85.1	10
11	92.9	84.6	10	85.5	0
12	84.9	82.1	10	82.9	15
13	98.3	98.3	10	84.3	0
14	100.0	100.0	10	81.8	20
15	102.0	102.0	20	87.2	30
16	80.8	91.0	10	74.1	0
17	93.2	93.2	30	80.8	0
19	95.6	95.6	30	84.1	0
19	90.2	90.2	20	79.3	0

$$NQ_{\text{yield}} = \frac{\text{moles NA}}{\text{moles NA}_{\text{into reactor}}} \quad (8)$$

$$Ce(IV)_{\text{sel}} = \frac{\text{moles NQ} \times 4}{\text{moles Ce(IV)}_{\text{reduced}}} \quad (9)$$

Each response variable is discussed individually below:

3.3.1. *Naphthoquinone yield* was most influenced by the Ce(IV) to NA ratio. A 50% excess of Ce(IV) gave a 10% higher yield than a stoichiometric amount. Addition of 25 mM tetrabutylammonium hydroxide (TBAOH) decreased the yield by 6%. Increasing the NA concentration from 0.2 M to 0.4 M decreased NQ yield by 4%. The effect of stirring depended on the Ce(IV) concentration. At low Ce(IV) concentration, increasing the stirring speed increases yield by 7%; but at high Ce(IV) concentration, stirring had no effect on the yield, which averaged about 90% overall.

The interaction between Ce(IV) concentration and stirring can be explained by postulating the existence

of a chemical intermediate to NQ which can undergo further oxidation to form NQ or can react chemically to form a byproduct. A high Ce(IV) concentration ensures that the intermediate is oxidized to NQ. A low Ce(IV) concentration allows the concentration of Ce(IV) to become depleted at the organic-aqueous interphase, and the intermediate forms a byproduct. A high stirring speed serves to increase the selectivity. This hypothesis is consistent with the finding that NQ selectivity decreases with increasing NA concentration.

3.3.2. *Ce(IV) selectivity*. This was affected by the same variables as NQ yield and in a similar fashion. A 50% excess of Ce(IV) decreases Ce(IV) selectivity by 7%. Addition of 25 mM TBAOH decreased Ce(IV) selectivity by about 7%. Addition of 25 mM TBAOH decreased Ce(IV) selectivity by about 7% also. Doubling the NA concentration reduced Ce(IV) selectivity by about 6%. The effect of stirring depended on the Ce(IV) concentration. At low Ce(IV) concentration, doubling the stirring speed increased Ce(IV)

Table 7. Coefficients of the prediction equations* fit to experimental data

Variable	Equation term	% NQ yield	% NQ selectivity	% Ce(IV) Selectivity	Reaction time	Dispersion
Constant	b_0	90.3 ± 1.5	91.9 ± 1.5	82.2 ± 1.0	20 ± 1.3	7.1 ± 1.5
NA concentration	b_1	-2.0 ± 0.8	-4.1 ± 1.7	-2.9 ± 1.1	ns	ns
Ce(IV) concentration	b_2	-0.2 ± 0.8	0.03 ± 1.7	0.1 ± 1.1	ns	ns
[Ce(IV)]/[NA] ratio	b_3	5.4 ± 0.8	ns	-3.6 ± 1.1	ns	2.2 ± 1.7
Stir speed	b_4	1.9 ± 0.8	2.6 ± 1.7	2.1 ± 1.1	-6.2 ± 1.4	ns
TBAOH concentration	b_5	-3.0 ± 0.8	-4.0 ± 1.7	-3.4 ± 1.1	ns	-7.2 ± 1.7
[Ce(IV)] × (Stir speed)	b_{24}	-1.6 ± 0.8	-4.2 ± 1.7	-2.2 ± 1.1	ns	ns
([Ce(IV)]/[NA]) × [TBAOH]	b_{35}	ns	ns	ns	ns	-3.4 ± 1.7

* Equations have the form: Response = $b_0 + b_1 C_{NA} + b_2 C_{Ce(IV)} + \dots$

Table 8. Summary of variable levels needed to optimize responses

Var/Response	Maximum yield NQ	Maximum Selectivity Ce(IV)	Minimum reaction time	Minimum dispersion
[NA]	–	–		
[Ce(IV)]/[NA] ratio	+	–		–I
Speed	+I	+I	+	
[TBAOH]	–	–		+I
[Ce(IV)]	–I	–I		

I indicates an interaction between two variables.

selectivity by 9%; but at high Ce(IV) concentration stirring had no effect on the yield, which averaged about 83% overall.

3.3.3. Reaction time. This was significantly affected only by stirring speed. Doubling the stirring speed halved the average reaction time (from 25 to 12.5 min).

3.3.4. Dispersion formation. This depended on TBAOH addition. Addition of TBAOH eliminated the dispersion in seven of eight experiments. When TBAOH was not present, the Ce(IV) to NA ratio appeared to determine the amount of dispersion. Experiments with excess Ce(IV) produced an average of 21 ml of dispersion, whereas experiments with stoichiometric Ce(IV) produced an average of 10 ml of dispersion. This result suggests that dispersion formation maybe due to over-oxidation of naphthalene. Note that TBAOH effectively eliminated dispersion even at a concentration of 12.5 mM (experiments to 17–19).

Table 8 summarizes the levels of the variables which optimize each response. Clearly, high speed stirring is desirable. Decreasing NA concentration or Ce(IV) concentration increases NQ yield and Ce(IV) selectivity, but increases reaction time. Addition of TBAOH eliminates the dispersion problem, but at the cost of reduced NQ yield and Ce(IV) selectivity. Excess Ce(IV) increases NQ yield but decreases Ce(IV) selectivity.

Based on these results, the following conditions were selected: 0.2 M NA, high speed stirring, 0.4 M Ce(IV), 12.5 mM TBAOH, and 50% excess Ce(IV). Table 9 lists the results for two replicate experiments done under these conditions; clearly, these conditions

allow very high NQ yields to be obtained. The yields for the first of these replicates are very close to those predicted by the model. The justification for these conditions is as follows. In order to separate cleanly the aqueous and organic phases at the end of the reaction, it is essential that TBAOH be present to prevent dispersion formation. Naphthalene and cerium concentrations are kept low in order to maximize NQ yield and Ce(IV) selectivity; stirring speed is kept high for these reasons also. An excess of Ce(IV) is used to maximize NQ yield (at the expense of Ce(IV) selectivity) in turn to minimize downstream separation problems.

After the chemical reaction has been achieved the two phases are separated. NQ crystals can be recovered from the organic phase by evaporating off the dichloroethane. The aqueous phase consists of spent cerium solution and is electrochemically regenerated. Regeneration of a spent cerium solution at 60°C takes place with good current efficiency, but the effectiveness of the solution for carrying out another reaction is diminished; that is, the NQ yield based on cerium decreases. However, if the cerium solution is extracted with fresh dichloroethane before being regenerated, the solution shows no affect of prior use. The effect of prolonged recycling of the mediator has yet to be examined.

6. Conclusions

The following conclusions can be drawn from the above work:

- (1) Methanesulphonic acid allows relatively high cerium(IV) concentrations to be used in a fluid system.
- (2) Cerium(IV) can be electrolytically generated in methanesulphonic acid with good current efficiency.
- (3) Organic oxidations with cerium(IV) take place with good selectivity, high conversion and do not give rise to unwanted byproducts.
- (4) Solutions used for organic oxidations can be easily regenerated.

Economic analysis indicates that cerium-mediated electrosynthesis is a superior technology to conventional routes (for example, air oxidation) to carbonyl compounds because of the high selectivity and conversion of the chemical reaction, simple product recovery, easy regeneration of Ce(IV) solution, and mild conditions of the cerium process.

Table 9. Experimental results under optimized conditions

Experiment no.	NQ conversion	NQ yield	Ce(IV) selectivity	Dispersion
20	100	99	83	0
21	100	95	78	0

3.5 M MSA; 0.43 M Ce(IV); 0.47 M Ce(III); 0.2 M NA; Ce(IV)/NA = 1.5; stirring speed = 10; 12.5 mM TBAOH; reaction time = 30 min.

Acknowledgements

We thank M. Anderman for his assistance in carrying out the rotating ring-disc experiments, and J. Ambrose-Ritchey, W. Henry, V. Hoover and D. McFarland for carrying out many of the experiments reported here.

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