Electrocatalytic debromination of open-chain and cyclic dibromides in ionic liquids with cobalt(II)salen complex as mediator

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Abstract The electrocatalytic reduction of open-chain and cyclic dibromides in ionic liquids, mediated by cobalt(II)salen, was investigated. Macro-scale constant-potential electrolysis in an undivided cell gave the corresponding debrominated products in moderate to good yields. The workup process after electrolysis proved to be much simpler in the ionic liquid than that in organic solvents. The possibility of reuse of the ionic liquid was demonstrated.

Keywords Mediator · Ionic liquid · Controlled potential electrolysis · Indirect electrolysis

Introduction

Recently, room temperature ionic liquids have attracted much attention as "green solvents" because of their low melting point, high polarity, negligible vapor pressure, non-flammability, ability to dissolve many materials, good conductivity, and reusability [1–5]. Therefore, considering their non-volatile and good conductive properties, ionic liquids seem to be ideal media for organic electrochemistry [6–14]. In fact, several papers dealing with the voltammetric study of metal complexes in ionic liquids have been reported [7].

Gaillon and Bedioui [12], Sweeny and Peters [13], and Lagunas et al. [14] reported cyclic voltammetric studies of electrocatalytic reduction in ionic liquids using Co(II)salen (N,N'-bis(salicylidene)ethylenediaminocobalt(II); Fig. 1), Ni(II)salen, and vitamin B₁₂, respectively. In these studies, they showed that the complexes operate as mediators for the cathodic reduction of various organic

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Fig. 1 Structure of cobalt(II)salen



halides. However, they did not report results on the preparative electrolysis and the reusability of ionic liquids, although reusability is a key advantage. Mellah et al. [15], Barhdadi et al. [16], and Sawamura et al. [17] have reported the use of redox mediators in ionic liquids for electrochemical organic synthesis. However, a limited number of successful examples of organic electrosynthesis in ionic liquids have yet been reported. With these facts in mind, we report herein the electrochemistry of cobalt(II)salen in a variety of ionic liquids and describe use of cobalt(II)salen as a mediator for preparative electrocatalytic reduction of dihalo compounds. We also discuss the reusability of the ionic liquids.

Experimental

Materials

All reagents and dehydrated solvents were purchased from commercial sources and used without further purification. The ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄), 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄), and 1-*n*-butyl-3-methyl-imidazolium hexafluorophosphate (BMIMPF₆) were purchased from Kanto Chemical, and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMIMTfO) was obtained from Central Glass (Chart 1).

General

All products were analyzed by ¹H NMR and ¹³C NMR spectroscopy and MS. ¹H NMR (270.05 MHz) and ¹³C NMR (67.80 MHz) spectra were acquired on a Jeol EX270 NMR spectrometer in CDCl₃ as solvent. The chemical shifts for the ¹H NMR and ¹³C NMR spectra are given in δ (ppm) downfield from an internal TMS standard. Mass spectra and high-resolution mass spectra were obtained with Shimadzu GC-MSOP-200A and Jeol JMS-700 mass spectrometers, respectively. Cyclic voltammetric measurements were obtained by use of an electrochemical analyzer (model 600A, ALS/CH Instruments). Preparative electrolysis was





performed with a potentiostat/galvanostat (Hokutodenko HA-501) and monitored with a coulomb/amperehour meter (Hokutodenko HF-201).

Preparation of the starting materials: diethyl 2,7-dibromooctanedioate and 2,3-dibromo-1,2,3,4-tetrahydronaphthalene

Diethyl 2,7-dibromooctanedioate (1)

In a three-necked flask equipped with a dropping-funnel, a double-surface condenser, and a device for absorbing evolved sulfur dioxide was placed 37.56 g (315 mmol) redistilled thionyl chloride, which was heated to boiling (76 °C). Pure suberic acid (25 g, 144 mmol) was added at such a rate that the mixture continued to boil gently under reflux for 1 h. The mixture was then heated under reflux for 0.5 h to expel any dissolved sulfur dioxide and left to cool to room temperature, before addition of 0.1 g red phosphorus. Dry bromine (55.1 g, 344 mmol) was then introduced to the gently boiling octanedioyl dichloride over a period of 2 h, and the mixture was then heated under reflux for 7 h, by which time evolution of hydrogen bromide had almost ceased. The crude 2,7-dibromooctanedionyl chloride was then added to 40 mL ethanol in a three-necked flask equipped with a mechanical stirrer and reflux condenser. The reaction was completed by heating for 4 h, during which hydrogen chloride evolved slowly. The crude ester was poured into 43 g distilled water and the oil was separated and washed successively with water and sodium hydrogen carbonate solution, and then dried under vacuum. The resulting material was subjected to silica gel column chromatography (hexane-EtOAc = 9:1) to give 41.6 g (75 % yield) pure diethyl 2,7-dibromooctanedioate (1).

¹H NMR (CDCl₃) δ 1.30 (6H, t, J = 7.1 Hz), 1.42–1.54 (4H, m), 1.98–2.13 (4H, m), 4.20 (2H, t, J = 6.8 Hz), 4.23 (4H, q, J = 7.1 Hz); ¹³C NMR (CDCl₃) δ 14.0, 26.5, 34.4, 45.7, 61.9, 169.4; MS (m/z) 388 (M⁺).

2,3-Dibromo-1,2,3,4-tetrahydronaphthalene (2)

To a solution of 2.5 g (19 mmol) 1,4-dihydronaphthalene in 15 mL of carbon tetrachloride, 15 mL carbon tetrachloride containing 3.2 g (20 mmol) bromine was added dropwise slowly with stirring at 0 °C. The solvent was removed under vacuum, and the residue was recrystallized several times from ethanol to give 3.3 g (60 % yield) **2**. The structure of **2** was identified by comparison of ¹H NMR, ¹³C NMR, and MS with those of the authentic sample.

Cyclic voltammetry and electrolysis

Cyclic voltammetric measurements were obtained by use of a three-electrode setup in a two-compartment electrochemical cell. A glassy carbon (GC) disk (d = 3 mm) was used as the working electrode and a Pt plate ($0.5 \times 0.5 \text{ cm}^2$) as the counter electrode. The reference electrode was a saturated calomel electrode (SCE). The two compartments of the electrochemical cell were connected via a glass tube filled with the same ionic liquid as the cell medium.

Preparative electrolysis

Macro-electrolysis was performed with a potentiostat/galvanostat connected to a coulomb/amperehour meter. A dimensionally stable anode (DSA) electrode (RuO_2/Ti) was obtained from Permelec Electrode. The electrolytic cell was a conventional undivided cell equipped with a GC cathode ($2 \times 2 \text{ cm}^2$), an appropriate anode, as shown in Table 1, and an SCE reference electrode.

Measurements and electrolysis were performed under a nitrogen atmosphere. After electrolysis, the product in the ionic liquid was extracted three times with 10 mL diethyl ether and the extracts evaporated under vacuum to provide the product. The product was identified by comparison with an authentic sample purchased from Tokyo Kasei Kogyo. The yield of the products was estimated by ¹H NMR using phenol as internal standard. The remaining ionic liquid was dried under vacuum for more than 6 h and was reused for the next electrolysis.

Results and discussion

Cyclic voltammetry of cobalt(II)salen in different ionic liquids

Cyclic voltammetric measurements of the Co(II)salen complex were performed in four ionic liquids, EMIMBF₄, EMIMTfO, BMIMBF₄, and BMIMPF₆, using a twocompartment electrochemical cell with a GC disk (d = 3 mm) as working electrode, a Pt plate counter electrode, and an SCE reference electrode. A well-defined, reversible Co(II)/Co(I) redox couple was observed at -1.23 and -1.15 V in BMIMBF₄ (Fig. 2) and similar redox peaks were also observed at -1.18 and -1.10 V in EMIMBF₄. The peak separation was 80 mV and the redox peaks were observed in EMIMTfO and BMIMPF₆.

For a reversible system, the peak current i_p can be expressed by Eq. 1.

$$i_{\rm p} = (2.69 \times 10^5) n^{3/2} A D^{1/2} C^* v^{1/2} \tag{1}$$

where *n* is the number of electrons involved in the electrode reaction (n = 1), *A* is the area of the electrode $(A = 0.07 \text{ cm}^2)$, *D* is the diffusion coefficient of the substrate in the ionic liquid, *C** is the concentration of Co(II)salen in the ionic liquid, and *v* is the potential scan rate. Based on the plot of i_p vs. $v^{1/2}$ in Fig. 3, the $D_{\text{co(II)salen}}$ value was calculated to be $1.78 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. This value is similar to that observed for a Ni(II)salen complex in the same ionic liquid $(1.8 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1})^7$ and is approximately a factor of 100 smaller than that observed for ordinary molecular solvents.

Electrocatalytic reduction of 1 using a Co(II)salen mediator in ionic liquids

On the basis of the results obtained above, we attempted to use Co(II)salen as mediator in the electrocatalytic reduction of 1 in ionic liquids. First, the reduction peak potential of 1 was measured by cyclic voltammetry in EMIMBF₄ and an

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Entry	Charge passed (F/	0% mol) Current density (mA/cm ²)	Cathodic potential (V vs. SCE)	Anode material	Yield of 4 $(\%)^a$
1	2	5	1	Pt	23
2	4	S	I	Pt	33
3	4	1	-1.30	Pt	41
4	4	1	-1.30	DSA	52
5 ^b	4	I	-1.30	DSA	0c

Table 1 Electrocatalytic reduction of 1 in the ionic liquid BMIMBF $_4$

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^c Starting material 1 was mostly recovered

^b In the absence of Co(II)salen



Fig. 3 Plot of i_p vs. $v^{1/2}$. Data were obtained from Fig. 2

irreversible first reduction peak was observed at -2.10 V vs. SCE, which was more negative than that of Co(II)salen ($E_p^{red} = -1.23$ V vs. SCE). The possibility of utilizing Co(II)salen as a mediator for cathodic reduction of **1** was suggested by the following cyclic voltammetric analysis (Fig. 4).

As shown in Fig. 4, the cathodic peak current increased substantially in the presence of 1, and the re-oxidation peak disappeared completely. This type of catalytic current suggests that reaction of electrogenerated Co(I)salen with 1 is fast and irreversible. However, in the ionic liquid EMIMBF₄, both the anodic and cathodic peak currents decreased in the presence of 1, which seems to be



attributable to the low solubility of 1 in EMIMBF_4 and adsorption of insoluble 1 on the surface of the GC electrode, suppressing the redox current.

Next, a macro-scale Co(II)salen-mediated dehalogenation reaction of **1** was performed in an undivided cell using a GC cathode at 40 °C. As shown in Table 1, cathodic reduction of **1** using the Co(II)salen mediator in BMIMBF₄ proceeded to give the corresponding debrominated product **4**. Although it has been shown that cathodic reduction of **1** in DMF gives the cyclic product **3** [18], this product was not formed in our experiment. Constant-potential electrolysis of **1** using the Co(II)salen mediator (Table 1, entry 3) gave a higher yield of **4** than constant current electrolysis (entry 2). It is noted that use of a DSA anode gave a higher yield than use of a Pt anode (entries 3 and 4). Although such an anode effect is interesting, its cause is not clear. In the absence of Co(II)salen, neither compound **3** nor **4** was detected even after a 4 F mol⁻¹ charge was passed, and the starting material was mostly recovered (entry 5).

From these results, the reaction mechanism depicted in Scheme 1 was proposed. One-electron reduction of Co(II)salen generates Co(I)salen, which reacts with starting material 1 to form the radical via elimination of bromide. Further oneelectron reduction of the radical produces anion **A**. According to a previous report [18], anion **A** can afford the cyclic product **3**. However, cyclization did not occur in the viscous ionic liquid [19, 20]. Thus anion **A** is protonated and repeated debromination occurs to provide product **4**. The proton source has not been identified but is likely to be a trace amount of water in the ionic liquid. Because a substantially enhanced catalytic reduction current was observed after addition of dibromide **1**, chemical reaction followed by electron-transfer seems to be very rapid.

In general, a divided cell has to be used for mediator systems to prevent anodic oxidation of the reduced species once generated at the cathode, which is rather inconvenient. However, in such a viscous ionic liquid, the mediator can remain in the vicinity of the cathode surface and will encounter the substrate before oxidation



Scheme 1 Proposed reaction mechanism for reduction of 1 using Co(II)salen as mediator

at the anode, enabling use of a simple undivided cell. This is a big advantage of using such an ionic liquid system.

Electrocatalytic reduction of 2 using a Co(II)salen mediator in the ionic liquid $BMIMBF_4$

Although reductive cyclization cannot be achieved, as demonstrated above, debromination proceeds well with Co(II)salen as mediator in the ionic liquid BMIMBF₄. With this in mind, macro-scale electrocatalytic reduction of **2** using the Co(II)salen mediator was also investigated in BMIMBF₄. First, cyclic voltammetry measurements of **2** were carried out separately in DMF and BMIMBF₄. The reduction peaks were observed at -2.05 and -1.91 V vs. SCE, respectively. The reduction peak potential in BMIMBF₄ thus obtained was more negative than that of Co(II)salen ($E_p^{red} = -1.23$ V vs. SCE).

Figure 5 shows the cyclic voltammograms of Co(II)salen with (curve b) and without (curve a) **2** in the ionic liquid BMIMBF₄. The cathodic peak current of Co(II)salen increased markedly after addition of **2**, whereas the re-oxidation peak disappeared completely. Because the reduction potential (E_p^{red}) of **2** is -1.91 V vs. SCE in BMIMBF₄, the enhanced cathodic current of Co(II)salen seems to be a typical catalytic current.

Hence, constant-potential electrolysis of 2 was carried out using the Co(II)salen complex as mediator in BMIMBF₄ at -1.30 V vs. SCE, at which potential 2 cannot be reduced. Furthermore, the effects of anode materials on the yield of the cathodic reduction product of 2 were investigated. The electrolytic results are shown in Table 2. When a platinum plate was used as anode, the reduction product 1,4-dihydronaphthalene (5), only, was formed in 38 % yield (Table 2, entry 1). Use of a sacrificial aluminium anode resulted in yields comparable with those obtained with a Pt anode (Table 2, entry 2). When an iron (Fe) plate was used as a sacrificial anode, the yield of 5 increased to 53 % (entry 3). However, in this case, the



Table 2 Effect of anode materials on electrocatalytic reduction of 2 in ionic liquid

2	$\int_{H}^{Br} \frac{+ ne}{GC \text{ cathode}}$			
Entry	Anode material	Yield of 5 (%) ^a		
1	Pt	38		
2	Al	40		
3	Fe	53		
4	DSA	68		
5 ^b	DSA	73		

Electrolytic conditions: substrate **2**, 0.5 mmol in 10 mL BMIMBF₄; Co(II)salen, 0.05 eq; electrolysis potential, -1.30 V vs. SCE; charge passed, 4 F mol⁻¹

^a According to ¹H NMR

^b Electrolysis in 0.1 M Bu₄NBF₄/DMF

Table 3 Reuse of Co(II)salenand ionic liquid BMIMBF4 for	Cycle	Yield of 5 (%)
4 F mol ⁻¹ charge was passed	1st	68
	2nd	52
	3rd	37
^a 0.05 eq fresh Co(II)salen was added	4th	69 ^a

electrolyte became very dark and viscous after electrolysis, and unidentified precipitates were observed. When DSA was used as an anode, the yield of **5** increased to approximately 70 % (entry 4). Similar anode effects on product yield



Scheme 2 Proposed reaction mechanism for the reduction of 2 using Co(II)salen mediator

were observed for **1**. For comparison, electrolysis was also performed in DMF using n-Bu₄NBF₄ as supporting electrolyte. Although the yield of **5** obtained in DMF (Table 2, entry 5) was slightly higher than that in the ionic liquid (entry 4), the workup process after electrolysis of **2** proved difficult. That is, both the product **5** and the Co(II)salen complex were extracted with a non-polar organic solvent from the DMF solution. In contrast, with the ionic liquid, the product could be extracted conveniently with diethyl ether and the Co(II)salen mediator remained in the ionic liquid phase. The remaining mediator could be reused for subsequent electrocatalytic debromination of **2**.

Reuse of Co(II)salen and ionic liquid BMIMBF $_4$ for electrocatalytic reduction of **2**

To demonstrate the advantages of using an ionic liquid, we examined the possibility of reusing both the Co(II)salen mediator and the ionic liquid. After electrolysis of **2** in BMIMBF₄, the ionic liquid was readily recovered simply by extracting **5** with diethyl ether. The recovered ionic liquid was then dried under vacuum for 6 h to remove any remaining ether or moisture and was reused for subsequent electrolysis. The second electrolysis was performed in the recovered ionic liquid with addition of **2**. The experimental results are listed in Table **3**. The yield decreased from the first cycle (68 %) to the third cycle (37 %). Because the amount of Co(II)salen lost during workup can be disregarded, the sharp decrease in yield seems to be attributable to deactivation and/or decomposition of Co(II)salen during electrolysis. However, when 0.05 equiv fresh Co(II)salen was added with **2** before the fourth cycle, the yield of **5** increased to 69 %. This clearly suggests that the ionic liquid is reusable although maintaining the activity of the mediator remains an issue.

Taking into account the reported mechanism of electrocatalytic reduction of organic halides with similar complexes [12] we propose the reaction mechanism shown in Scheme 2. First, one-electron reduction of Co(II)salen generates Co(I)salen, which reacts with the starting dibromide 2 to form radical **B** and a bromide ion. Next, **B** reacts with electrogenerated Co(I)salen to provide 5.

Conclusions

In summary, we have successfully performed electroreductive debromination in several ionic liquids, including BMIMBF₄, using a Co(II)salen complex as mediator. The catalytic effect of the Co(II)salen mediator on the reduction of open-chain and cyclic dibromides in ionic liquids was investigated by cyclic voltammetry. Macro-scale controlled potential electrolysis gave the corresponding debrominated product in moderate to good yields. The workup after electrolysis proved to be much simpler for the ionic liquid than that for conventional organic solvents. The possibility of the reuse of the ionic liquid was demonstrated to some extent. Further efforts to enable reuse of the ionic liquid and mediator are now in progress.

References

- 1. A.E. Visser, R.P. Swatloski, R.D. Rogers, Green Chem. 2, 1 (2001)
- 2. T. Welton, Chem. Rev. 99, 2071 (1999)
- 3. P. Wassersheid, W. Keim, Angew. Chem. Int. Ed. 39, 3772 (2000)
- R.D. Rogers, K.R. Seddon, S. Volkov (eds.), Green Industrial Applications of Ionic liquids (Kluwer, Dordrecht, 2002)
- R.D. Rogers, K.R. Seddon (eds.), *Ionic liquids as Green Solvents, Progress and Prospects* (American Chemical Society, Washington, DC, 2003)
- T. Fuchigami, S. Inagi, in *Electrochemical Aspects of Ionic Liquids*, 2nd edn., ed. by H. Ohno (Wiley, New Jersey, 2011), Chap. 8, pp. 101–127
- 7. P. Hapiot, C. Lagrost, Chem. Rev. 108, 2238 (2008)
- 8. J. Yoshida, K. Kataoka, R. Horcajada, A. Nagaki, Chem. Rev. 108, 2265 (2008)
- 9. M.C. Buzzeo, R.G. Evans, R.G. Compton, ChemPhysChem 5, 1106 (2004)
- 10. D.S. Silvester, R.G. Compton, Z. Phys. Chem. 220, 1247 (2006)
- 11. A.J. Fry, J. Electroanal. Chem. 546, 35 (2003)
- 12. L. Gaillon, F. Bedioui, J. Mol. Catal. A 214, 91 (2004)
- 13. B.K. Sweeny, D.G. Peters, Electrochem. Commun. 3, 712 (2001)
- 14. M.C. Lagunas, D.S. Silvester, L. Aldous, R.G. Compton, Electroanalysis 18, 2263 (2006)
- 15. M. Mellah, S. Gmouh, M. Vaultier, V. Jouikov, Electrochem. Commun. 5, 591 (2003)
- R. Barhdadi, C. Comminges, A.P. Doherty, J.Y. Nédélec, S. O'Toole, M. Troupel, J. Appl. Electrochem. 37, 723 (2007)
- 17. T. Sawamura, S. Kuribayashi, S. Inagi, T. Fuchigami, Org. Lett. 12, 644 (2010)
- 18. M. Tokuda, A. Hayashi, H. Suginome, Bull. Chem. Soc. Jpn. 64, 2590 (1991)
- 19. P. Hapiot, D. Lorcy, A. Tallec, R. Carlier, A. Robert, J. Phys. Chem. 100, 14823 (1996)
- 20. C. Lagrost, D. Carrie, M. Vaultier, P. Hapiot, J. Phys. Chem. A 107, 745 (2003)