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Electrocatalytic oxidative cleavage by electrogenerated periodate

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Abstract

An electrocatalytic method has been developed for the indirect oxidation of vicinal diols and related compounds like hydroxyketones and aminoalcohols. The oxidative cleavage has been performed in a biphase system containing a phase transfer catalyst by periodate generated from iodate at a Pb-PbO_2 electrode.
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1. Introduction

Electrogenerated reagents have been used for indirect electrooxidation [1–5]. Periodate is an example of a selective oxidising agent for reaction such as a glycol cleavage [6–8], which can be electrogenerated from iodate. The oxidative cleavage of vicinal diols and related compounds like diketones, hydroxyketones and aminoalcohols can be done with sodium periodate. For water-soluble substrates, an aqueous medium is adequate. For water insoluble substrates, a solvent such as methanol, ethanol, *t*-butanol, dioxan or acetic acid in which the substrate and the oxidising agent have reasonable solubility has to be used. Use of such solvents is not always convenient. The solubility of sodium periodate in such solvents is low, often necessitating the use of large quantity of solvent. The use of phase transfer catalysis that is ideally suited for such situations has not been extensively studied for periodate oxidations.

The iodate/periodate redox system and other systems has been extensively used for mediated electrooxidation [9–17]. In the reported procedure for the oxidation of 2,3-butanediol to acetaldehyde [10], further anodic oxidation of the aldehyde to acetic acid was encountered. This was circumvented by the use of an ex-cell process in which the electro-generated reagent (periodate) was transferred to another reactor where the organic substrate was added, and after separation of the organic products, the spent reagent was transferred back to the electrolytic cell for regeneration. It was felt that the use of a two phase anolyte where the electrogeneration of the reagent took place in the aqueous phase and the actual oxidation of the organic substrate took place in the organic phase could effectively simulate ex-cell conditions without actually transferring the oxidising agent to another reaction vessel.

A phase transfer catalyst could be used for the aqueous phase-organic phase transfer of reagents. The present study was based on this concept. Though phase transfer catalysis in connection with several electro-

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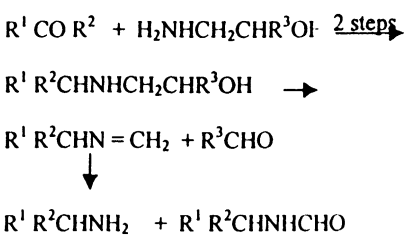
generated oxidising agents has been reported, it has not been applied to periodate.

Our interest in periodate oxidation arose from a methodology developed in our laboratory for asymmetric synthesis of amines as outlined below [18,19].



It was of interest to see whether such aminoalcohols could be cleaved by the mediated electrooxidation. In the present study, the application of phase transfer catalysis was established by the study of chemical oxidation (by periodate) of selected substrates A–G (Scheme 1). Product analysis was done by gas chromatography and after isolation, by IR and NMR spectroscopy. In a few cases GC-MS was employed.

Electrochemical oxidation of substrate A–J (Scheme 1) were done in an H-type divided cell with Pb-PbO_2 anode and lead cathode. In those experiments involving phase transfer catalysis, the anolyte consisted of, in addition to the aqueous electrolyte, dichloromethane as the lower organic phase. Tetrabutyl-ammonium hydrogen sulphate (TBHS) was used as the phase transfer catalyst. In preliminary experiments, the efficiency of formation of periodate from iodate on the anode was established by doing electrolysis without added substrate and estimating the iodate formed by conventional procedure [7,8].

2. Experimental

The *erythro*-9,10-dihydroxyocta-decanoic acid was prepared [20] from a mixture of 11.28 g (40 mmol) of oleic acid in 100 ml CH_2Cl_2 and 7.25 g (50 mmol) $KMnO_4$ in 100 ml H_2O under phase transfer conditions using 1 g of TBHS. The reaction mixture was stirred for 8 h and was filtered using suction. The residue of MnO_2 was thoroughly washed with CH_2Cl_2 and filtered again. The filterate was separated in a separating funnel. The organic layer was washed with distilled water to remove the TBHS. The separated organic layer was dried over anhydrous Na_2SO_4. The product formed was analysed by IR and NMR.

2.1. General procedure for chemical oxidation

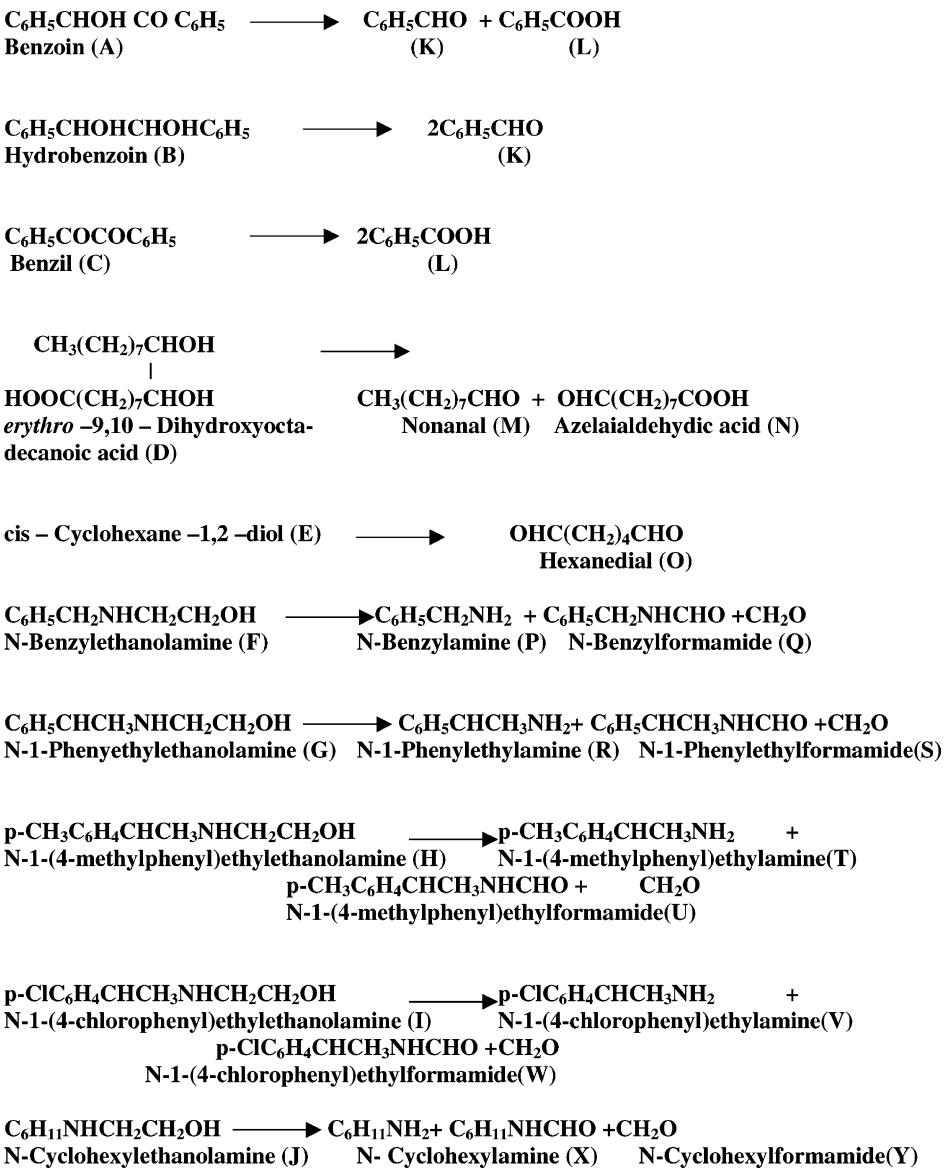
The chemical oxidations were carried out in a RB flask fitted with a stopper. The organic substrates about 1 g were dissolved in dichloromethane, the oxidising reagent dissolve in water was added to it and the mixture was stirred vigorously for about 5 h. After tested for completion of the reaction using TLC, the mixture was transferred into a separating funnel and the two layers were separated and the products were isolated.

2.2. General procedure for electrochemical oxidation

An H-type cell with a sintered glass diaphragm was used for the electrochemical studies with a lead dioxide sheet anode obtained from a lead–acid battery and lead sheet cathode. Reference electrode (SCE) was positioned near the anode. The organic substrates were dissolved in dichloromethane, which formed the lower layer in the anode compartment in the portion of H-type cell below the level of the tube connecting the two limbs, when not stirring. The aqueous layer above CH_2Cl_2 consisted of 0.5 M Na_2SO_4 with added $NaIO_3$ and TBHS. The current through the solution was maintained at 0.15–0.3 A and potential above 2.0 V. After the electrolysis the dichloromethane layer was separated, washed with water and directly analysed by GC on SE-30 column, temperature programmed at 100–200 °C.

2.3. Electrooxidative cleavage of benzoin

The catholyte was made up of 3.5 g (25 mmol) of Na_2SO_4 in 50 ml H_2O and the anolyte, 10.65 g (75 mmol) of Na_2SO_4, 6.48 g (32.7 mmol) of $NaIO_3$, 100 ml H_2O, 1 g (5 mmol) of benzoin, 0.5 g (1.5 mmol) TBHS and 50 ml of CH_2Cl_2. The anolyte was agitated by a magnetic stirrer. The current through the solution was 0.15–0.30 A and the anodic potential, 3.91–4.83 V. After the electolysis, the anolyte was separated from the cell, transferred to a separating funnel, the organic layer separated, and worked up.



Scheme 1. Oxidative cleavage of diols and related compounds.

2.4. Electrooxidative cleavage of erythro-9,10-dihydroxyocta-decanoic acid (D)

The catholyte consisted of 3.5 g (25 mmol) of Na_2SO_4 in 50 ml H_2O and the anolyte was 10.65 g (75 mmol) of Na_2SO_4, 6.48 g (32.7 mmol) of $NaIO_3$, 100 ml H_2O, 1 g (3.5 mmol) of D, 0.5 g (1.5 mmol) TBHS and 50 ml of CH_2Cl_2. A magnetic stirrer agitated the anolyte. The current was about 0.15–0.30 A and the anodic potential, 3.91–4.83 V. After the electrolysis, the anolyte was separated from the cell and was transferred to a separating funnel, the organic layer was separated and treated with NaOH, two layers were separated and the aqueous alkali layer was neutralised with acid to obtain the acidic product, $CHO(CH_2)_7COOH$ (N). The organic phase

was washed with water and neutral component, $CH_3(CH_2)_7CHO$ (M) was extracted. The products were analysed using IR and NMR.

2.5. Electrooxidative cleavage of aminoalcohols

The catholyte consisted of 3.5 g (25 mmol) of Na_2SO_4 in 50 ml H_2O and the anolyte was 10.65 g (75 mmol) of Na_2SO_4, 6.48 g (32.7 mmol) of $NaIO_3$, 100 ml H_2O, 1–2 g (10 mmol) of F–J, 0.5 g (1.5 mmol) TBHS and 50 ml of CH_2Cl_2. The pH of the solution was initially adjusted to 8 by the addition of sodium hydroxide. This was done to prevent the anolyte becoming acidic which was objectionable as discussed below. The anolyte was agitated by a magnetic stirrer. The current was about 0.15–0.30 A and the anodic potential, 3.91–4.83 V. After the electolysis, the anolyte was separated from the cell and was transferred to a separating funnel, the organic layer was separated and treated with HCl, two layers were separated and the aqueous alkali layer was neutralised with acid to obtain the basic product, amine. The organic phase was washed with water and neutral component formyl derivative was extracted. The products were analysed using IR and NMR.

3. Results and discussions

The results of the periodate oxidation of substrates A–G are presented in Table 1. The oxidation proceeded smoothly in homogeneous medium (methanol). In heterogeneous medium (water–dichloromethane) in the absence of phase transfer agent (compare experiment Nos. 4–7) the conversion was low. Diketone, benzil, C (experiment Nos. 6 and 7) was oxidised at a slower rate than the diols and the hydroxyketone, benzoin. The aminoalcohols, F–G (experiment Nos. 10–13) were oxidised equally efficiently in methanol, as in the biphase system under phase transfer catalysis. Both the free amine and the formyl derivative, as already reported [19], were formed. There was no significant difference in amine selectivity between the two sets of conditions. The conclusion was that where a mutual solvent like methanol could be used, phase transfer catalysis offered no advantage other than avoiding the need to use large quantity of solvent.

In the case of electrooxidation (Tables 2–5) phase transfer catalysis offered distinct advantages. In the absence of phase transfer catalyst, there was very little oxidation (experiment No. 2 in Tables 2–4). With

Table 1
Chemical oxidation of diols and related compounds

Experiment No.	Substrate[a] (mmol)	Reagent $NaIO_4$ (mmol)	Solvent	PTC[b] (g)	Reaction time (h)	Yield (%)
1	A (5)	7.5	CH_3OH	None	5	87.72[c] (80.16)[d]
2	A (5)	5	CH_2Cl_2/H_2O	0.5	10	80.95[c]
3	A (5)	5	CH_2Cl_2/H_2O	0.1	10	56[c]
4	B (4.6)	4.6	CH_2Cl_2/H_2O	0.5	3	96.75[d]
5	B (4.6)	4.6	CH_2Cl_2/H_2O	None	3	33.47[d]
6	C (4.6)	4.6	CH_2Cl_2/H_2O	0.1	3	19.8[c]
7	C (4.6)	4.6	CH_2Cl_2/H_2O	None	3	2[c]
8	D (19)	28.9	CH_2Cl_2/H_2O	0.5	5	85 (76)[e]
9	E (17.2)	30	CH_2Cl_2/H_2O	0.5	5	95[f]
10	F (13)	15	CH_3OH	None	5	(74)[g] 98
11	F (13)	15	CH_2Cl_2/H_2O	0.5	5	(63)[g] 99
12	G (9)	15	CH_3OH	None	5	(63)[g] 99
13	G (9)	15	CH_2Cl_2/H_2O	0.5	5	(51)[g] 98

[a] A, benzoin (1 g); B, hydrobenzoin (1 g); C, benzil (1 g); D, *erythro*-9,10-dihydroxyocta-decanoic acid (6.1 g); E, cyclohexanediol (2 g); F, *N*-benzylethanolamine (2 g); G, *N*-phenylethylethanolamine (2 g).

[b] Tetrabutyl-ammoniumhydrogen sulphate.

[c] Benzoic acid (L).

[d] Benzaldehyde (K).

[e] Aldehydic acid, $OHC(CH_2)COOH$ (N); and aldehyde, $H_3C(CH_2)CHO$ (M).

[f] Dialdehyde, $OHC(CH_2)_4CHO$ (O).

[g] Amine selectivity (P–S).

Table 2
Electrooxidative cleavage of benzoin

Experiment No.	Anolyte composition[a]		Phase transfer catalyst, TBHS	Benzoic acid, yield (%)
	$NaIO_3$ (g, mmol)[b]	Na_2SO_4 (g, mmol)[b]		
1	Nil	10.65 (75)	None	0
2	0.212 (1)	10.65 (75)	None	5
3	6.48 (33)	10.65 (75)	0.5 (1.5)	58
4	0.212	10.65 (75)	0.5 (1.5)	48

[a] Anode, Pb-PbO_2; cathode, Pb; 2 F/mol water, 100 ml; CH_2Cl_2, 50 ml.
[b] 1 g (5 mmol).

Table 3
Electrooxidative cleavage of hydrobenzoin

Experiment No.	Anolyte composition[a]		Phase transfer catalyst, TBHS	Benzaldehyde, yield (%)
	$NaIO_3$ (g, mmol)[b]	Na_2SO_4 (g, mmol)[b]		
1	Nil	10.65 (75)	None	0
2	0.212 (1)	10.65 (75)	None	6
3	6.48 (33)	10.65 (75)	0.5 (1.5)	100
4	0.212 (1)	10.65 (75)	0.5 (1.5)	100

[a] Anode, Pb-PbO_2; cathode, Pb; 2 F/mol water, 100 ml; CH_2Cl_2, 50 ml.
[b] 1 g (4.6 mmol).

Table 4
Electrooxidative cleavage of *erythro*-9,10-dihydroxyocta-decanoic acid

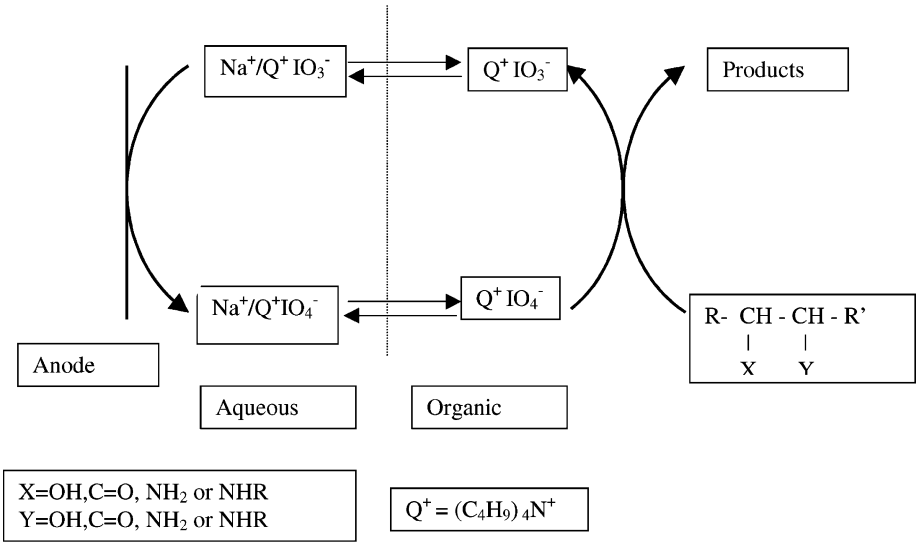
Experiment No.	Anolyte composition[a]		Phase transfer catalyst, TBHS	Conversion[b] (%)
	$NaIO_3$ (g, mmol)[c]	Na_2SO_4 (g, mmol)[c]		
1	Nil	10.65 (75)	None	0
2	0.212 (1)	10.65 (75)	None	15
3	6.48 (33)	10.65 (75)	0.5 (1.5)	95
4	0.212	10.65 (75)	0.5 (1.5)	90

[a] Anode, Pb-PbO_2; cathode, Pb; 2 F/mol water, 100 ml; CH_2Cl_2, 50 ml.
[b] Based on GC analysis.
[c] 1 g (4.6 mmol).

Table 5
Oxidative cleavage of aminoalcohols

Experiment No.	Substrate[a] (mmol)	Anolyte composition[b]		Time (h)	Conversion[c]	Amine selectivity
		$NaIO_3$ (mmol)	Na_2SO_4 M			
1	F (10)	28	0.5	10	93	58
2	F (10)	14	0.5	10	98	88
3	G (9)	25	0.5	10	71	65
4	H (10)	25	0.5	10	75	68
5	I (10)	25	0.5	10	74	70
6	J (10)	25	0.5	10	72	66

[a] F, *N*-benzylethanolamine; G, *N*-1-phenylethylethanolamine; H, *N*-cyclohexyethanolamine; I, *p*-$CH_3C_4H_4CH(NHCH_2CH_2OH)CH_3$; J, *p*-$ClC_4H_4CH(NHCH_2CH_2OH)CH_3$.
[b] pH of the solution was adjusted to 8 by the addition of NaOH; PTC, tetrabutyl-ammonium hydrogen sulphate; 0.5 g 2 F/mol water, 100 ml; CH_2Cl_2, 50 ml.
[c] Based on GC analysis: includes amine and other products like formyl derivative hydrolysable to amine (P–S).



Scheme 2. Mediated biphase oxidation.

iodate as the redox reagent and phase transfer catalyst, conversions were quite high (experiment Nos. 3 and 4 in Tables 2–4). Initial experiments were done with excess iodate in the anolate (experiment No. 3 in Tables 2–4). Subsequent studies with substoichiometric quantity of iodate gave equally satisfactory results (experiment No. 4 in Tables 2–4). Iodate, converted to periodate in the aqueous phase at the anode got extracted into the organic phase as ion pair with tetrabutyl-ammonium cation. After oxidation periodate was regenerated in the aqueous phase, completing the catalytic cycle. Effectively, dichloromethane layer in the anolyte had simulated ex-cell conditions (Scheme 2).

The results of the oxidation of aminoalcohols are presented in Table 5. The situation with aminoalcohols was different from that with the other substrates. During electrolysis, the anode compartment became acidic. Hence, in principle there was no need to use a biphase system. However aminoalcohols gave intraceable products in acidic medium. Hence it was necessary to control the pH of the anolyte at neutral or slightly alkaline. This was done by the addition of alkali as required to maintain the pH at about 8. Because of the alkaline pH, tetrabutyl-ammonium ion underwent Hofmann degradation to some extent and tributylamine was detected as a product. Periodate oxidation of aminoalcohols gave, in addition to the amine, the *N*-formyl derivative of the amine as already reported [19].

4. Conclusion

The oxidative cleavage of compounds such ketoalcohol, diol and aminoalcohol by electrogenerated periodate utilising IO_4^-/IO_3^- redox mediator in a biphase system at the PbO_2/Pb electrode was shown to be successful for water insoluble susbstrates. Under these conditions the IO_4^- generated at the anode was transferred to the organic phase by the phase transfer agent, where the oxidation took place and the iodate formed in this step was transferred back to the aqueous phase where it got reoxidised to periodate at the anode, completing the catalytic cycle. Thus the “ex-cell” methodology was simulated within the cell itself, overcoming the solubility limitations and preventing further oxidation of the product formed.

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