

A COMPARATIVE EVALUATION OF OPERATING CONDITIONS FOR THE ELECTROCHEMICAL BROMINATION AND CHLORINATION OF SUCCINIMIDE

S KRISHNAMOORTHY, R KANAKAM SRINIVASAN AND M NOEL

Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

[Received: 20 September 1998

Accepted: 19 September 2000]

Platinum was found to be the electrode of choice for both electrochlorination and bromination of succinimide leading to the formation of N chloro succinimide (NCS) and N bromo succinimide (NBS) respectively. Because of the competitive processes 150% and 285% of theoretical charge has to be passed for bromination and chlorination respectively. 12% (w/v) of succinimide could be used for bromination while only 2% (w/v) of this reactant is optimum for chlorination. Optimum conditions have been evaluated for the process. A maximum yield of 55% and 88% could be achieved for bromination and chlorination of succinimide respectively.

Keywords: Chlorination, bromination succinimide

INTRODUCTION

Probably because of the facile bromination [1-4] and chlorination [5-9] of succinimide (SI) by chemical means, the corresponding electrohalogenation process have not received considerable attention. A brief report on the preparation of N- bromosuccinimide (NBS) in aqueous sodium bromide solution on platinum electrode is available [10]. The electrochlorination as well as electrobromination [10] of a number of imides, including succinimide have been studied [11-12]. Fairly good yields have been reported in milligram scale experiments which however have not been confirmed by any further work. No reports on higher scales involving product isolation is available. Careful evaluation of each operating parameter for both these processes under comparable condition along with a brief cyclic voltammetric investigation to understand the basic mechanism involved were undertaken. The results are summarised in this paper.

EXPERIMENTAL

The Glassy carbon (GC) working electrode (5 mm dia Tokai GCA grade embedded in a Teflon rod), its pretreatment procedure and H type electrochemical cell used for the voltammetric measurements have been described in detail earlier [13]. Saturated calomel electrode (SCE) as a reference electrode, platinum foil counter electrode were used. All the voltammetric experiments were carried out at 298 K.

A thermostated closed glass vessel with provisions for working electrode (platinum, graphite, TSIA and GSLD) [14-15], counter electrode, platinum (4 x 3 cms) thermometer and a glass stirrer was used as the preparative cell.

After completion of electrolysis, NCS and NBS are separated by filtration and washed with a cold (275 K) saturated solution of the corresponding N-halosuccinimide. The purity of NCS and NBS was confirmed by their melting point and IR spectra. Yield and current efficiency values reported are based on the recovered products.

RESULTS AND DISCUSSION

Voltammetric studies

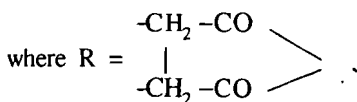
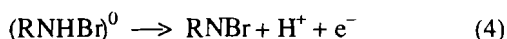
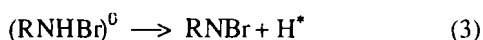
Typical cyclic voltammogram (CV) of 6 mM sodium bromide on glassy carbon in 0.1 M KClO_4 is shown in Fig. 1a. An oxidation peak around 1.3 V and a corresponding reduction peak around 0.6 V are noticed. Both the anodic and cathodic peak currents are found to increase with increase in sweep rates. However, neither the anodic peak currents nor the peak potential exhibit a sweep rate dependence corresponding to a simple 1 electron diffusion controlled process. At higher NaBr concentration the anodic peak currents become partially independent of concentration. All these observations suggest that the anodic oxidation of bromide ions proceed through adsorbed free radical intermediates on the electrode surface [16-18].

Strong adsorption and subsequent chemical reactions are probably responsible for a large peak separation of over 600 mV between the anodic and cathodic peaks and much smaller cathodic peak currents compared to the anodic peak currents.



On addition of 20, 40 and 60 mM succinimide to this solution the anodic peak current due to bromide oxidation increases slightly (Fig. 1 curves b-d) and the cathodic peak current around 0.6 V completely disappears.

Succinimide itself does not undergo any direct oxidation in this potential region. Hence, the increase in the anodic peak current noticed in the bromide oxidation region on addition of succinimide should probably due to some reactive intermediates generated during the bromination of succinimide.



The consumption of bromide radical in these chemical reactions is also responsible for the disappearance of the cathodic peak in the reverse sweep.

Preparative work presented in subsequent section (3.2) indicates that the aqueous acetic acid - sodium acetate is a better medium for electrochemical chlorination. Succinimide does not undergo any direct oxidation in this medium as well. Even in the presence of 0.5 M NaCl no distinct voltammetric feature for the oxidation of Cl⁻ or succinimide is noticed (Fig. 2). In this case Cl⁻ oxidation and/or succinimide oxidation occurs along with the background oxidation namely oxidation of water leading to oxygen evolution in the same potential region.

Preparative electrolysis — Electrode material

Apart from platinum which is commonly employed in electrohalogenation reactions materials like graphite substrate lead dioxide (GSLD), titanium substrate insoluble anode (TSIA) and graphite electrodes were evaluated for their suitability in electrohalogenation reactions. The results obtained with these anode materials are shown in Table I.

Graphite electrode shows significant disintegration during the initial stages of electrobromination itself (Table I expt. no.1). When graphite substrate lead dioxide anodes (GSLD) were used the PbO₂ coating was found to peel off from the anode surface (Table I expt. no.2). Titanium substrate insoluble anode (TSIA) containing TiO₂-RuO₂ coatings was found to perform satisfactorily for a few experiments (3 to 4 experiments or 20 to 25 Ah of charge). In these experiments also the yield of N-bromo succinimide (NBS) was found to be fairly low when compared to the yield obtained on platinum electrode under identical conditions (Table I expt. nos. 3 and 4).

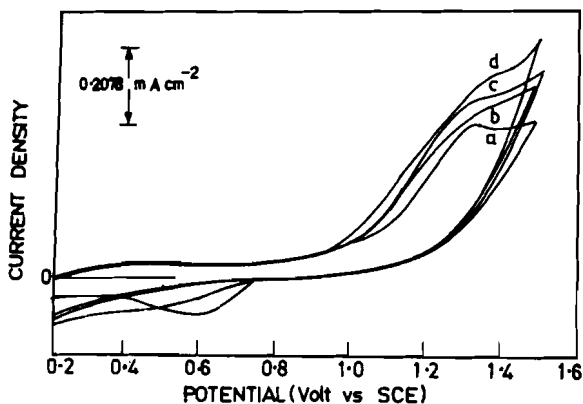


Fig. 1: C V of 0.1 M KClO₄ on glassy carbon electrode containing (a) 6 mM NaBr and a + 20 (b) a + 40 (c) and a + 60 (d) mM SI. $v = 20 \text{ mVs}^{-1}$

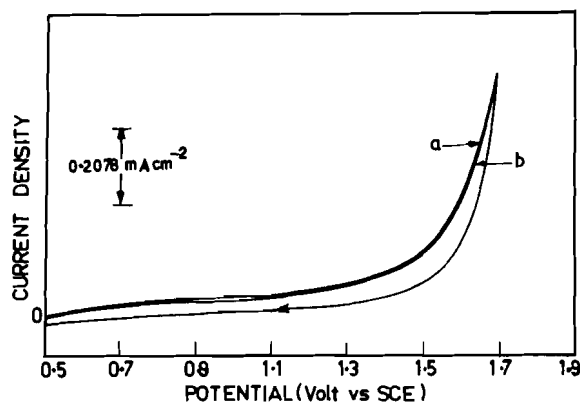


Fig. 2: C V of 60 mM succinimide containing 0.5 M sodium acetate/acetic acid buffer (a) on glassy carbon electrode; (b) a + 50 M NaCl. $v = 20 \text{ mVs}^{-1}$

Quite similar electrode effects were also observed for electrochlorination (Table I expt. nos 5 to 8). GSLD and TSIA electrodes gave better yields for this process but the electrode disintegration effects are noticed during the first preparative scale experiments itself (Table I expt nos. 6 and 7). Pt electrode showed good stability and electrochemical activity for this process as well (Table I expt no 8).

Effect of passing excess charge

In aqueous solutions oxygen evolution is closer to the bromine evolution potential (Fig. 1) the chlorine evolution occurs simultaneously with oxygen evolution (Fig. 2). Hence, the conversion efficiency was found to be below 40% when the electrolysis was stopped after just passing the theoretical quantity of charge. Some experiments were thus carried out to find out the effect of passing excess electric charge (Table II).

With excess charge, the current efficiency continuously decreases for both the electrohalogenation reaction as one would indeed expect. However, the yield of halo succinimide improves upto a point for both the compounds. For bromination the yield improves upto 150% of theoretical charge. For chlorination this was indeed found to be 285% of the theoretical charge. Hence, these were chosen as optimum values of charge to be passed in the preparative work.

Effect of reactant concentration

Table III shows the effect of succinimide and sodium bromide concentrations on the overall yield of N-bromo succinimide and current efficiency. Under constant NaBr concentration the yield improves with increasing concentration of succinimide. In the case of electrolytes containing 6% NaBr (Table III expt nos. 1 to 3) this improvement in yield of N-bromo succinimide increases from 40% to 49%. Beyond 12% succinimide concentration the reactant itself gets precipitated on the electrode surface. Hence 12% succinimide and 12% NaBr concentrations are found to be optimum.

The high solubility of reactant succinimide (upto 14%) and fairly low solubility of N-bromosuccinimide (1.5%) is an advantageous feature of this electrobromination process. Because of the low solubility (less than 6%) NBS tends to accumulate on the anode surface itself, thus blocking the electrode surface, leading to poor yield and current efficiency. Hence, whenever the build up of NBS in the electrolyte media exceeds 6%, the electrolysis was interrupted, the product filtered before continuing further electrolysis. This procedure was also continued in all further experiments.

As in the case of electrobromination it was expected that higher reactant concentrations during electrochlorination also would lead to higher yields. In contrast, however it was found that electrochlorination proceeds only when the

TABLE I: Effect of electrode material

		Electrobromination		Electrochlorination		
C.D.		3.5 A.dm ⁻²		5 A.dm ⁻²		
pH		7 to 7.5		5.5 to 6.5		
% of charge passed		Theoretical charge		285% of theoretical charge		
Temperature		273 - 276 K		273 - 278 K		
Electrolyte		100 ml of aqueous soln. containing succinimide (SI) and NaBr 100 gl ⁻¹ each		100 ml of aqueous soln containing NaCl (60 gl ⁻¹) and SI 20 gl ⁻¹		
<i>Other experimental parameters are as in Table VIII</i>						
Expt	Type of halogenation reaction	Anode	NBS/NCS formed (g)	Yield (%)	C.E. (%)	Remarks
1.	Electrobromination	Graphite	traces	—	—	Electrode attacked
2.	"	GSLD*	< 1	—	—	PbO ₂ coating severely attacked
3.	"	TSIA**	3.5	19.5	16.3	Electrode attacked completely at 5th expt.
4.	"	Pt	6.9	38.5	20.9	Electrode stable
5.	Electrochlorination	Graphite	traces	—	—	Electrode attacked
6.	"	GSLD*	2.4	20.0	6.9	Electrode surface attacked gradually
7.	"	TSIA**	5.1	42.2	14.7	Electrode coating completely attacked at 4th expt.
8.	"	Pt	6.3	51.8	18.2	Electrode stable

* Graphite substrate lead dioxide

** Titanium substrate insoluble anode

TABLE II: Effect of percentage of theoretical charge passed

		Electrobromination	Electrochlorination		
C.D.		3.5 A.dm ⁻²	5 A.dm ⁻²		
pH		7 to 7.5	5.5 to 6.5		
Temperature		273 - 276 K	273 - 278 K		
Electrolyte		100 ml of aqueous soln. containing succinimide (SI) and NaBr 100 gl ⁻¹ each	100 ml of aqueous soln containing NaCl (60 gl ⁻¹) and SI 20 gl ⁻¹ each		
<i>Other experimental parameters are as in Table VIII</i>					
Expt	Type of electrohalogenation reaction	% of theoretical charge passed	NBS/NCS formed (g)	Yield (%)	C.E. (%)
1.	Electrobromination	100	6.90	38.5	34.3
2.	"	125	7.60	42.4	33.9
3.	"	150	8.40	46.9	31.4
4.	"	175	8.50	47.0	27.2
5.	Electrochlorination	100	4.03	33.2	33.3
6.	"	200	5.16	42.5	21.3
7.	"	285	6.30	51.8	18.2
8.	"	300	6.30	51.8	17.4

succinimide (SI) concentration in the electrolyte is maintained below 2% (w/v). Hence, in all subsequent experiments the electrolysis was initiated with an electrolyte solution containing 6% NaCl and 2% succinimide. The total quantity of succinimide to be electrolysed was fixed as 9 gms. Every two ampere hours passed consumes roughly 1.2 g of succinimide assuming an efficiency of 50%. Hence, 1.2 g of succinimide was

added for every 2 ampere hours passed to maintain the concentration between 2 to 3%. As depletion in concentration of Cl⁻ also occurs during electrochlorination, 0.5 g of NaCl was also added in each instalment stated above. After the passage of 8 ampere hour, the insoluble N-chlorosuccinimide was recovered by filtration. This instalment addition was found to be necessary under all the experimental conditions investigated here.

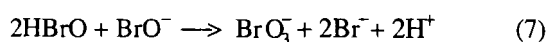
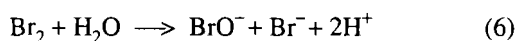
TABLE III: Effect of concentration of reactants

		Electrobromination	Electrochlorination			
C.D.		3.5 A.dm ⁻²	5 A.dm ⁻²			
Temperature		273 - 276 K	273 - 278 K			
pH		7 to 7.5	5.5 to 6.5			
<i>Other experimental parameters are as in Table VIII</i>						
Expt	Type of electrohalogenation	SI (g)	NaBr/NaCl (g)	NBS/NCS formed (g)	Yield (%)	C.E. (%)
1.	Electrobromination	6	6	3.8	35.2	23.5
2.	"	9	6	6.0	37.0	25.0
3.	"	12	6	8.5	38.8	26.0
4.	"	6	12	4.3	39.4	26.5
5.	"	9	12	7.2	44.4	29.8
6.	"	12	12	10.5	49.0	32.5
7.	Electrochlorination	9	9	traces	—	—
8.	"	9*	9	6.1	50.2	17.5

* At the start 100 ml of aqueous solution containing NaCl (60 gl⁻¹) and SI (20 gl⁻¹) was used and 7 g of SI and 3 g of NaCl added in 6 equal instalments. Total wt of SI and NaCl added 9 g each.

Effect of pH

The redox properties of bromine in different oxidation states are highly sensitive to the pH of the medium [16-18]. In acetic acid sodium acetate solutions (pH < 5) practically no electrobromination could be achieved (Table IV expt no. 3). This reaction apparently proceeds well in the pH range of 7 to 7.5 (Table IV expt nos 2a and 3). In this pH region addition of sodium acetate does not have any significant effect on the yield (Table IV expts 1 and 2). Higher pH condition also does not lead to electrobromination. Under these conditions bromate formation probably predominates over electrobromination.



Addition of sodium acetate to the electrolyte containing reactants led to noticeable improvements in the yield of N-chlorosuccinimide (Table IV expt nos. 5 and 6). Further improvements were noticed when the experiments were carried out at lower pH using sodium acetate-acetic acid buffer. The pH range of 4 to 5 was found to be optimum for this process (Table IV expt no. 7). More acidic media as well as more alkaline media were found to give poor yields. Hence during the electrolysis itself, it was found necessary to control the medium pH by adding a few drops of concentrated HCl.

Effect of temperature

The bromide radicals generated can undergo many further chemical transformations apart from brominating succinimide. These include formation of bromate and other inactive species. Escape of gaseous Br₂ from the electrolyte is another competitive process which can lower the efficiency. Hence the operating cell temperature is found to be very critical for successful electrobromination of succinimide as indicated in Table V. Lower temperature range 273 to 276 K was found to give maximum current efficiency.

The temperature could be held at much higher levels in the electrochlorination reactions (Table V). A maximum yield close to 88% was achieved in the temperature range of 293 to 298 K (Table V).

Effect of current density

Electrochemical bromination experiments were also carried out at different anode current densities (Table VI). Up to a current density of 5 A.dm⁻² the yield was found to increase with anode current density. Further increase in current density leads to slight decline in yield and current efficiency.

In the case of electrochlorination significantly higher current densities could be employed. A current density of 10.5 A.dm⁻² was found to be optimum (Table VI).

Reuse of electrolyte

As mentioned earlier (section 3.2.3) the solubility of the product N-bromo succinimide (NBS) was fairly low (less than 1.5%). Hence the electrolysis was stopped at regular

TABLE IV: Effect of pH

Expt	Type of electrohalogenation reaction	Constituents of the medium	pH	Electrochlorination		
				NBS/NCS formed (g)	Yield (%)	C.E. (%)
				C.D. 5 A.dm ⁻² Temperature 273 - 276 K <i>Other experimental parameters are as in Table VIII</i>		
				Electrochlorination 5 A.dm ⁻² 273 - 278 K		
1.	Electrobromination	Electrolyte (a)	7-7.5	11.9	55.0	36.8
2.	"	(a) + 2.5 g of SA	6.5-8	7.0	32.4	20.6
3.	"	(a) + AA (3 ml) + SA (5 g)	4.4-5.5	Nil	—	—
4.	"	(a) + conc. NaOH solution in drops	8-8.5	Nil	—	—
5.	Electrochlorination	Electrolyte (b)	5.5-6.5	3.3	27.0	9.5
6.	"	(b) + SA (5 g)	5-8	4.8	29.5	14.2
7.	"	(b) + glacial AA (3 ml) + SA (5 g)	4.5-5.5	6.3	52.0	18.2
8.	"	(b) + conc. NaOH solution in drops	8-8.5	Nil	—	—

SA = Sodium acetate and AA = Acetic acid

TABLE V: Effect of temperature of electrolysis
Other experimental parameters are as in Table VIII

Expt	Type of electrohalogenation reaction	Temp (K)	NBS/NCS formed (g)	Yield (%)	C.E. (%)
1.	Electrobromination	273-276	11.9	55.0	36.8
2.	"	280-283	3.0	13.8	9.2
3.	"	285-288	traces	—	—
4.	Electrochlorination	273-278	7.0	57.5	19.4
5.	"	283-288	9.0	74.0	25.9
6.	"	293-298	10.7	87.9	30.8
7.	"	298-303	5.4	44.4	15.6

intervals the product filtered out and the electrolysis continued again. Care was taken to carry out all these operations around 273 to 276 K. The results obtained under these conditions are summarised in Table VII. These results suggest that the electrolysis can be continuously carried out and the yield could be maintained above 50% with a current efficiency of over 30%.

Continuous electrolysis with intermittent product isolation was attempted in the case of electrochlorination also. The results obtained from these experiments are summarised in Table VII. By filtering out the N-chlorosuccinimide formed at regular intervals the electrolysis could be continued with the same electrolyte for atleast four times. The overall yield could still be maintained around 87% with the average current efficiency of over 30%.

The optimum experimental operating conditions and the best yield and efficiency achievable under these conditions for electrobromination and chlorination reactions are summarised in Table VIII.

CONCLUSION

The present study reveals that electrochemical chlorination as well as bromination could be carried out in laboratory

scale under fairly similar conditions, but with some critical modifications. Pt was found to be the only electrode of choice for both these processes. Higher concentration of succinimide is favourable for electrobromination while lower concentration is favourable for electrochlorination. Unbuffered electrolytes give better yields of N-bromosuccinimide while acetic acid-sodium acetate buffer was found to be better for higher yields of N-chlorosuccinimide. For electrochlorination in buffered solutions higher current densities upto 10 A.dm⁻² could also be employed. Under optimum conditions, the electrolyte could be reused after filtering the halogenated product. The maximum yield obtained for N-bromosuccinimide was 55% while this was as high as 88% for N-chlorosuccinimide. This is inspite of the fact that bromide ions are easily oxidisable when compared to chloride ions as revealed by cyclic voltammetry. This is probably due to much faster competitive chemical reactions for electrochemically generated bromine radical. The current efficiency in both the cases is around 30%. This is also due to competitive chemical processes and simultaneous oxygen evolution reaction. The reactant

TABLE VI: Effect of current density
Other experimental parameters are as in Table VIII

Expt	Type of electrohalogenation reaction	C.D. (A.dm ⁻²)	NBS/NCS formed (g)	Yield (%)	C.E. (%)
1.	Electrobromination	3.5	10.5	48.6	32.5
2.	"	5.0	11.9	55.0	36.8
3.	"	7.0	10.8	50.0	32.9
4.	"	8.0	7.5	34.7	22.8
5.	Electrochlorination	5.0	6.3	51.6	18.2
6.	"	8.5	7.8	64.1	22.4
7.	"	10.5	9.0	74.0	26.0
8.	"	13.5	7.0	57.5	20.2

TABLE VII: Reuse of electrolyte
Other experimental parameters are as in Table VIII

Expt	Type of electrohalogenation reaction	Fresh/reuse of electrolyte	SI added for replenishment	NaBr/NaCl added (g)	NBS/NCS formed (g)	Yield (%)	C.E. (%)
1.	Electrobromination	Fresh	—	—	11.5	53.2	35.6
2.	"	Reuse 1	4	6	10.2	47.2	31.5
3.	"	Reuse 2	4	6	11.0	50.0	34.0
4.	"	Reuse 3	4	6	10.6	49.0	32.8
5.	Electrochlorination	Fresh	5	—	5.9	87.2	29.8
6.	"	Reuse 1	4	—	4.8	88.8	32.4
7.	"	Reuse 2	4	—	4.6	85.2	31.1
8.	"	Reuse 3	4	—	4.9	90.7	33.1

TABLE VIII: Optimum conditions for the electrobromination and electrochlorination of succinimide

Experimental conditions	Electrobromination	Electrochlorination
Anode	Pt	Pt
Cathode	Pt	Pt
% of charge	150% of theoretical charge	285% of theoretical charge
Conc of reactants for 100 ml of electrolyte	12 g (w/v) of SI and NaBr each	2 g of SI and 6 g of NaCl (w/v) each at the start, instalment addition of the reactants
pH	7 to 7.5	4.5 to 5.5
C.D. (A.dm ⁻²)	5	10.5
Temp (K)	273 to 276	293 to 298
Reuse of electrolyte with intermittent isolation of the products	Possible	Possible
Max. yield (%)	55.0	87.9
Max C.E. (%)	36.8	30.8

concentration may be around 12% for electrobromination whereas it should be around 2% for electrochlorination.

Acknowledgment: The authors wish to thank Director, Central Electrochemical Research Institute, Karaikudi, India for his kind permission to publish this work.

REFERENCES

- Y Pasternak and J C Traynard, *Bull Soc Chim, France* (1960) 23
- T D Waugh and R C Waugh, *U S Patent 2,971,959* (1961); *Chem Abst*, **55** (1961) 14483
- T D Waugh and R C Waugh, *Brit Patent 933,531, US Patent, 3,120,715* (1964); *Chem Abst*, **60** (1964) 12021
- S Kajigashi, T Nakagawa, S Fujisaki and A Nishida, *Bull Chem Soc Jpn*, **58** (1985) 769
- W C Arson, *U S Patent, 2,472,369* (1949); *Chem Abst*, **43** (1949) 75177
- L F Audrieth and H Zimmer, *J Amer Chem Soc*, **76** (1954) 3586
- Y Corvea, *Chem Abst*, **85** (1976) 159873
- Ger Offen, 2,721,738 (1977); *Chem Abst*, **88** (1978) 50527
- A C Dynamit Nobel, Netherlands, *Chem Abst*, **63** (1965) 8383
- M Lamchen, *J Chem Soc*, (1950) 747
- H Miyazaki, *Denki Kagaku Oyobikogyo Butsuri Kagaku*, **45** (1977) 475
- H Miyazaki, *Denki Kagaku Oyobikogyo Butsuri Kagaku*, **45** (1977) 553
- M Noel and P N Anantharaman, *The Analyst (London)*, **110** (1985) 1095
- R Thangappan, H V K Udupa, B R Yadav and P Subbiah, *Indian Patent*, **134** (1972) 375
- K C Narasimham and H V K Udupa, *J Electrochem Soc*, **123** (1976) 1294
- E L Littauer and L L Shrein, *Electrochim Acta*, **11** (1966) 527
- J Liopis and M Vazquez, *Electrochim Acta*, **6** (1962) 167
- J Liopis and M Vazquez, *Electrochim Acta*, **6** (1962) 177