

A COMPARATIVE STUDY OF TWO STAGE ELECTROCHEMICAL OXIDATION OF ANTHRACENE, NAPHTHALENE AND BENZENE USING Ce^{4+}/Ce^{3+} REDOX SYSTEM

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Two stage electrochemical oxidation of anthracene, naphthalene and benzene were carried out to evaluate the relative ease of oxidation. Electrochemically generated Ce^{4+} species from sulphuric acid as well as methane sulphonic acid were employed to study the chemical oxidation step. The chemical step was carried out both in the absence and in presence of added solvents such as dichloromethane and dichloroethane. 2.0 M methane sulphonic acid was found to be the medium of choice for the efficient oxidation of all the three compounds. Relatively higher reaction temperatures were required for the oxidation of naphthalene and benzene when compared to anthracene. In the case of benzene excess reactant itself had to be used as a solvent. The reaction time was found to be considerably higher for benzene when compared to the other two compounds. Under optimum conditions maximum yield of anthraquinone, naphthaquinone and benzoquinone were found to be 97%, 93% and 45% respectively.

Keywords: Redox system, electrochemical oxidation, polycylindro carbons

INTRODUCTION

Ce^{4+} salts are known to be an efficient oxidising agent for the oxidation of polycyclic hydrocarbons like anthracene and naphthalene [1-5]. The two stage electrochemical oxidation of naphthalene and other hydrocarbons involving separate electrochemical regeneration step and chemical oxidation step was reported in sulphuric acid medium [6,7]. Even more advantages were noticed in methanesulphonic acid medium [8- 10]. The efficiency of overall oxidation was found to improve significantly when tetrabutyl ammonium hydroxide was employed as a surfactant [11].

The two stage electrochemical oxidation studies reported so far especially in methane sulphonic acid were mainly confined to naphthalene and substituted naphthalenes. There are only few reports on the electrochemical oxidation of anthracene. No report is available on the two stage electrochemical oxidation of benzene to quinone in such media. Hence it was felt desirable to compare the oxidation of anthracene, naphthalene and benzene in sulphuric acid as well as methane sulphonic acid media under identical experimental conditions. This was the main objective of the

present work wherever possible efforts were made to improve the yield and efficiency.

EXPERIMENTAL

The electrochemical oxidation of $Ce(III)$ to $Ce(IV)$ was carried out in a two compartment divided cell with Nafion 423 cationic membrane as diaphragm. In sulphuric acid medium lead dioxide on lead electrode was used as anode material with lead cathode at a current density of $1.0 A/dm^2$ for the generation of ceric sulphate. In methane sulphonic acid medium platinum anode and stainless steel cathodes were used at a current density of $5.0 A/dm^2$. 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 silver nitrate catalyst followed by $Ce(IV)$ analysis as above.

The chemical oxidation studies of anthracene, naphthalene and benzene were conducted in a glass reactor (500 ml capacity) using the electrogenerated ceric sulphate in aqueous sulphuric acid and ceric methane sulphonate in aqueous methane sulphonic acid medium. The aqueous ceric

TABLE I: Indirect oxidation of anthracene to anthraquinone using ceric sulphate in aqueous H_2SO_4 medium
 Reactor: 500 ml R B flask fitted with stirrer/hot plate;
 Oxidant: 200 ml of ceric sulphate (0.125 M) in 10% (1.87 M) H_2SO_4

Expt. Nos	Amount of Ce^{4+} taken for oxidation in (mM)	Amount of anthracene taken for oxidation (mM)	Temp (K)	Solvent dichloro methane used in (% v/v)	Reaction time (hrs)	Anthraquinone formed in (mM)	Purity of anthraquinone by HPLC (%)	Material yield (%)
1	24.40	4.050	333-338	-----	5 1/2	3.343	63.0	52.0
2	24.71	4.124	343-348	-----	5 1/2	3.684	84.6	75.7
3	25.50	4.225	348-353	-----	5 1/2	3.794	88.2	79.3
4	24.71	4.160	305-308	20.0	1	3.842	86.6	80.0
5	25.57	4.262	305-308	27.3	1	3.866	92.0	83.5
6	25.71	4.290	305-308	33.3	1	4.130	92.8	89.4
7	25.21	4.208	305-308	38.5	1	3.890	92.5	85.6

solutions and organic reactants were taken for oxidation in the stoichiometry of 6 moles of $Ce(IV)$ for 1 mole of aromatic hydrocarbon. The electrogenerated ceric solutions and organic reactants with solvent were taken in a chemical reactor and it was stirred vigorously by a mechanical stirrer at a particular temperature until the completion of reaction, which was found out by the absence of $Ce(IV)$ in the aqueous phase. After the completion of oxidation the aqueous phase was extracted with solvent for complete removal of organic phase and the whole organic phase was vacuum distilled to recover the solvent. The residue containing the product was analyzed by HPLC using Shimadzu LC-8A unit. After product isolation the aqueous solution was purified and it was regenerated to $Ce(IV)$ with the same efficiency.

RESULTS AND DISCUSSION

Oxidation of anthracene

Typical experimental results obtained during the oxidation of anthracene using ceric sulphate salt are summarised in Table I. In the absence of solvent the chemical oxidation of anthracene was indeed found to be quite difficult. Even at the reaction temperature of 348-353 K the reaction time (time required for complete removal of Ce^{4+} as indicated by colour change from yellow to colourless) for the completion of the reaction was found to be more than 5 hrs. At higher temperatures material yield efficiency of 79% could be achieved (Table I; Expts. 1-3).

Dichloromethane was found to be a good solvent for the efficient oxidation of anthracene to anthraquinone by ceric sulphate in sulphuric acid. In this medium the minimum reaction temperature of 303-308 K was found to be sufficient. The reaction time also was found to be lower at

TABLE II: Indirect oxidation of anthracene to anthraquinone using ceric methane sulphonate in aqueous CH_3SO_3H medium
 Reactor: 500 ml R B flask fitted with stirrer/hot plate;
 Oxidant: 200 ml of ceric methane sulphonate in 2.0 M in CH_3SO_3H ; Temperature: 303-308 K

Expt. Nos	Amount of Ce^{4+} taken for oxidation in (mM)	Amount of anthracene taken for oxidation (mM)	Solvent dichloro methane used in (% v/v)	Reaction time (mts)	Amount of Anthraquinone formed in (mM)	Purity of anthraquinone by HPLC (%)	Material yield (%)
1	50.00	8.248	27.3	35	7.59	98.00	90.4
2	54.57	8.971	33.3	40	8.50	98.50	93.1
3	67.86	11.220	38.5	40	10.90	99.00	96.2
4	69.30	11.220	43.0	40	10.90	99.45	96.6
5	135.70	22.440	43.0	40-50	20.08	98.00	87.2

around 1 hr. Around 30-35% of dichloromethane as solvent appears to be optimum. Material yield efficiency of over 89% could be achieved in presence of this solvent (Table I; Expts. 4-7).

Ceric methane sulphonate is found to be a more efficient oxidising agent for the oxidation of anthracene to anthraquinone. This is in addition to the advantage came by higher solubility of ceric methane sulphonate in methane sulphonic acid [8-10]. Typical experimental results of chemical oxidation of anthracene using ceric methane sulphonate in methane sulphonic acid are presented in Table II. In these experiments dichloromethane was used as the solvent throughout. The reaction temperature could be maintained at a low level of 303-308 K throughout. In most cases the yield efficiency was found to be greater than 90%. The efficiency however improves with increasing solvent content upto around 40%. In presence of 38-43% dichloromethane the yield efficiency was found to be above 96% beyond this level of solvent the efficiency decreases slightly (Table II).

Oxidation of naphthalene

Naphthalene is one of the compounds which has been extensively investigated in this two stage oxidation process in sulphuric acid [6] as well as in methanesulphonic acid [9-11]. This process has been optimised even at fairly high capacity pilot plant scales [6,11]. However, for comparative purposes under identical operating conditions a few experiments were also carried out in the present work.

Typical experimental results obtained during the chemical oxidation of naphthalene using ceric salts under different

experimental conditions are summarised in Table III. Under all the experimental conditions the reaction temperature had to be maintained at a fairly higher level of 328-333 K. Hence dichloroethane which has a relatively higher boiling point (355-357 K) when compared to that of dichloromethane (308-313 K) was employed as the solvent.

In sulphuric acid medium in the absence of solvent the total reaction time was found to be around $4\frac{1}{2}$ hrs. The material yield was found to be around 74% (Table III). The use of 20% v/v dichloroethane improves the material yield to 82%. However, even under these conditions the reaction time is found to be considerably higher (Table III; Expt. 2).

Methane sulphonic acid once again is found to be a better reaction medium for the two stage oxidation of naphthalene to naphthaquinone. At the same reaction temperature of 328-333 K the reaction time decreases considerably (Table III; Expts. 3-5). With increasing solvent content the reaction time decreases and the material yield increases upto 40% v/v of dichloroethane. A maximum material yield of 93.5% could be achieved (Table III expt. 5). In general the present experimental results are in conformity with the detailed experimental results reported in the literature for this compound.

Oxidation of benzene

Two stage electrochemical oxidation of benzene to quinone has neither been reported in sulphuric acid nor in methane sulphonic acid. Preliminary experiments also indicated that the oxidation is indeed quite difficult to achieve. Without solvent no chemical oxidation of benzene was observed even at fairly high temperature of 343-348 K with prolonged

TABLE III: Indirect oxidation of naphthalene to naphthaquinone using ceric sulphate & ceric methane sulphonate in aqueous H_2SO_4 & CH_3SO_3H medium

Reactor: 500 ml R B flask fitted with stirrer/hot plate;

Oxidant: Ceric sulphate in 1.87 M H_2SO_4 (200 ml); Ceric methane sulphonate in 2 M CH_3SO_3H (100 ml);

Temperature: 328-333 K

Expt. Nos	Amount of Ce^{4+} taken for oxidation in (mM)	Amount of naphthalene taken for oxidation (mM)	Solvent dichloro ethane used in (% v/v)	Reaction time (hrs)	Amount of naphthaquinone formed in (mM)	Purity of naphthaquinone formed by HPLC (%)	Material yield (%)
1	24.73 ^a	3.906	-----	4 1/2	3.348	86.62	74.2
2	24.73 ^a	3.930	20.0	4	3.506	91.90	82.2
3	36.07 ^b	6.250	33.3	1	5.569	96.30	87.0
4	36.36 ^b	6.310	43.0	1/2	5.696	97.50	90.0
5	36.43 ^b	6.320	50.0	1/2	6.013	100.00	93.5

a = Sulphuric acid and b = Methane sulphonic acid

ction time beyond 9 hrs. Dichloromethane as well as chloroethane were also found to be ineffective in achieving chemical oxidation of benzene to quinone.

However some success was achieved when excess benzene itself was used as a solvent. The reaction temperature was maintained around 343-348 K in these experiments. The reaction time must generally found to be greater than 9 hrs. Typical results obtained under these experimental conditions are summarised in Table IV. The oxidation efficiency of ceric for the formation of benzoquinone was found to be around 20-25% depending on the concentration of methanesulphonic acid used (Table IV; Expts. 1-3).

Benzene is known to be highly insoluble in aqueous solutions. It was hence felt that improving the miscibility of benzene with the aqueous phase using surfactants could improve the material yield in this process. Sodium lauryl sulphate (SLS) and cetyltrimethyl ammonium bromide (CTAB) were selected as the anionic and cationic surfactants respectively. 0.042 - 0.4 w% of surfactant concentration in these reaction medium were evaluated. These results are also summarised in Table IV (Expts. 4-10). In general cationic surfactant was found to be more efficient (Expts. 4, 5, 10), when compared to the anionic surfactant (Expts. 6,7). Beyond 0.4% concentration the overall yield did not improve significantly. Around 0.4% concentration level a maximum oxidation efficiency of 40-45% for formation of benzoquinone could be achieved.

Under the present experimental conditions the material yield could not be improved beyond the modest level of 45%. However, this appears to be the first report of a satisfactory yield of benzoquinone in the two stage electrochemical oxidation of benzene.

The optimum experimental conditions for the two stage oxidation of anthracene, naphthalene and benzene from the present investigations are summarised in Table V. The overall yield is found to decrease in the order

Anthraquinone > Naphthaquinone > Benzoquinone

CONCLUSION

Ce^{4+} dissolved in methane sulphonic acid medium was found to be more efficient in oxidation of the organic compound to their corresponding quinones. In the case of anthracene the yield efficiency improved from 89 to 97%. In the case of naphthalene the improvement was from 82 to 93%. Benzene which does not get oxidised to any significant extent in Ce^{4+} sulphuric acid medium, gives upto 40% oxidation efficiency for the formation of quinone in methane sulphonic acid medium.

Use of solvent during chemical step also has significant effect on the overall yield efficiency. In sulphuric acid medium for e.g. dichloromethane improves the yield efficiency of anthraquinone from 79 to 89%. In the case of naphthaquinone the yield efficiency once again improves

TABLE IV: Indirect oxidation of benzene to benzoquinone using ceric methane sulphonate in aqueous methane sulphonic acid

Reactor: 500 ml RB flask fitted with stirrer/hot plate; Oxidant: 200 ml of ceric methane sulphonate
Reaction time: > 9 hrs; Solvent benzene: 75.0 ml (30% v/v); Temperature: 443-448 K

Expt. Nos	Amount of Ce^{4+} taken for oxidation in (mM)	Theoretical equivalent of benzene (mM)	Acid concentration (M)	Surfactant added (% v/v)	Amount of benzoquinone formed (mM)	Purity of benzoquinone formed by HPLC (%)	Oxidation efficiency of ceric for the formation of benzoquinone (%)
1	75.21	12.53	2.0	---	3.88	72.14	22.30
2	154.40	25.70	3.0	---	7.25	93.30	26.30
3	157.10	26.21	4.0	---	6.50	85.70	21.20
4	75.14	12.52	2.0	0.400 ^a	6.00	94.19	45.00
5	75.21	12.53	2.0	0.050 ^a	5.63	94.20	42.30
6	75.21	12.53	2.0	0.400 ^b	4.21	86.40	29.00
7	177.40	29.54	3.0	0.047 ^b	10.09	82.40	28.16
8	177.40	29.54	3.0	0.040 ^a	11.68	89.00	35.20
9	150.28	25.05	3.0	0.385 ^a	10.50	94.20	39.40
10	150.28	25.05	3.0	0.437 ^a	10.54	95.95	40.30

TABLE V: Indirect oxidation of anthracene, naphthalene and benzene using ceric salts in aqueous sulphuric acid and methane sulphonic acid under optimum parameters

Optimum parameters	Aromatic hydrocarbons		
	Anthracene	Naphthalene	Benzene
Acid concentration	2.0 M CH ₃ SO ₃ H	2.0 M CH ₃ SO ₃ H	2.0 M CH ₃ SO ₃ H
Temperature	305-308 K	333 K	343-348 K
Solvent	Dichloromethane	Dichloroethane	Excess benzene
Solvent ratio (% v/v)	43	50	30
Surfactant	----	---	0.4 (% v/v) CTAB
Time taken for oxidation (hrs)	0.66	0.50	9
Yield (%)	97.0	93.5	45.0*

* Oxidation efficiency of ceric for the formation of benzoquinone

from 74 to 82%. In the case of benzene other solvents were found to be of little use. Using excess benzene itself as the reaction medium the oxidation efficiency was found to be around 26%. In the case of benzene further improvement in the oxidation efficiency was achieved when surfactants like cetyltrimethyl ammonium bromide and sodium lauryl sulphate are employed. Less than 0.5% concentration of surfactants leads to oxidation efficiency of quinone to over 40%.

Use of methane sulphonic acid and additional solvents also result in considerable decrease of reaction time. In the case of oxidation of anthracene for e.g. the reaction time decreases from 5 1/2 hrs to around 40 mts. Similar improvements are also noticed for naphthalene.

REFERENCES

1. Kozoshirai and Kiichiro Sugino, *Denki Kagaku*, **25** (1957) 284
2. M Periasamy and M V Bhatt, *Synthesis*, (1977) 330
3. M V Bhatt and M periasamy, *J Chem Soc, Perkin Trans 2* (1993) 1811
4. S krishnan, V A Vyas, M S V pathy and H V K Udupa, *J Electrochem Soc India*, **14** (1965) 32
5. Niki, Katsumi, Sekine, Taro and Sugino Kiichiro, *J Electrochem Soc Japan*, **37** (1969) 74
6. I M Dalrymple and J P Millington, *J Applied Electrochem*, **16** (1986) 885
7. Richard Alkire and Ofelia Araujo, *J Electrochem Soc*, **139** (1992) 737
8. R P Krch, R M Spotnitz and J T Lundquist, *Tetrahedron Letters*, **28** (1987) 1067
9. R P Krch, R M Spotnitz and J T Lundquist, *J Org Chem*, **54** (1989) 1526
10. P Pichaichanarang, R M Spotnitz, R P Krch, S M Goldarb and J T Lundquist, *Chem Eng Commun*, **94** (1990) 119
11. R M Spotnitz, R P Krch, J T Lundquist and P J Press, *J Applied Electrochem*, **20** (1990) 209