

A COMPARATIVE STUDY OF TWO STAGE ELECTROCHEMICAL OXIDATION OF TOLUENE, P-ETHOXY TOLUENE, O-CHLOROTOLUENE AND P-ISOPROPYL TOLUENE USING Ce^{4+}/Ce^{3+} REDOX SYSTEM IN METHANE SULPHONIC ACID MEDIUM

T VIJAYABARATHI, D VELAYUTHAM AND M NOEL

Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

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Two stage electrochemical oxidation of toluene, p-ethoxy toluene, o-chloro toluene and p-isopropyl toluene to their corresponding aldehydes were carried out using Ce^{4+}/Ce^{3+} redox mediator in methane sulphonic acid medium. Ceric methane sulphonate was prepared as homogeneous solution as well as yellow crystalline solid in 2 M methane sulphonic acid under optimised conditions. The order of ease of chemical oxidation of these compounds is as follows: p-Ethoxy toluene > Toluene > p-isopropyl toluene > o-chloro toluene. The duration of chemical oxidation depends on the reaction temperature and the concentration of methane sulphonic acid. Higher concentration of methane sulphonic acid decreases the duration of oxidation. The yield of p-ethoxy benzaldehyde, benzaldehyde, o-chloro benzaldehyde and p-methyl acetophenone is 95%, 93%, 70% and 37% respectively. p-Isopropyl toluene interestingly gave p-methyl acetophenone as the major product and hence the yield of corresponding aldehyde was low.

Keywords: Indirect electrochemical oxidation, toluenes, methane sulphonic acid, Ce^{4+}/Ce^{3+} mediator.

INTRODUCTION

Efforts towards production of high purity aldehydes from toluenes by electrochemical methods are noticed in the literature for quite sometime now. Both direct [1-4] and redox mediated [5-6] electrochemical oxidations have been attempted. In aqueous media, oxidation of toluene gave rise to 30% yield both in acidic and alkaline conditions [7]. Higher yields upto 70-75% was achieved for p-methoxybenzaldehyde and p-chlorobenzaldehyde from their corresponding toluenes [8]. In the direct oxidation of toluenes to benzaldehydes filming of the anode surface is a serious problem.

Mn^{3+}/Mn^{2+} redox couple has been used as the mediator for two stage oxidation of toluene [5,6]

and substituted toluenes [9,10]. An interesting single stage paired electrochemical synthesis of benzaldehyde from toluene also uses Mn^{3+}/Mn^{2+} redox mediator in the anodic compartment [11]. A detailed study of a number of toluene and substituted toluenes in different acid media indicates significant influence of acid strength on product selectivity in Mn^{3+}/Mn^{2+} as well as Co^{3+}/Co^{2+} redox mediators [12]. Cobaltic acetate is found to be a more powerful oxidising agent among redox mediators [13]. For example it is found to be efficient in oxidising p-nitrotoluene to p-nitrobenzaldehyde [14]. Comparative studies of Ce^{4+}/Ce^{3+} and Mn^{3+}/Mn^{2+} redox mediators on the oxidation of methoxy toluene [15] and Co^{3+}/Co^{2+} , Ce^{4+}/Ce^{3+} , redox couple on the oxidation of toluene are also reported.

Earlier studies relating to indirect oxidation of toluene to benzaldehyde employing $\text{Ce}^{4+}/\text{Ce}^{3+}$, redox mediator were generally carried out in sulphuric acid [16], perchloric acid [17] and acetic acid [18]. In sulphuric acid medium addition of Ag^+ ions was found to improve the overall oxidation efficiency [19]. Two stage oxidation of methoxy toluene to methoxy benzaldehyde have also been studied using this redox mediator in sulphuric acid [20,21]. In their extensive study in methane sulphonic acid, Kreh and co-workers have covered the electrochemical oxidation of toluene and a number of other substituted toluenes [22-23]. In the case of p-isopropyl toluene however the conversion efficiency was found to be poor [24]. Under nitrogen atmosphere and strong oxidation condition 40% yield of p-nitrobenzaldehyde has been achieved from p-nitrotoluene [25].

The electrochemical oxidation of toluene, p-ethoxy toluene, o-chloro toluene and p-isopropyl toluene using $\text{Ce}^{4+}/\text{Ce}^{3+}$, redox system in methane sulphonic acid is taken up in this study. Toluene was chosen as the compound for comparison with the earlier work. p-Ethoxy toluene was chosen with a view to select a less investigated compound

in place of well investigated p-methoxy toluene. Among the chlorotoluenes electrochemical oxidation is found to be better for o-chlorotoluene which was chosen in the present investigation. p-Isopropyl toluene has been selected for the interesting chemistry involved.

EXPERIMENTAL DETAILS

The general aspects of the experimental setup and conditions are described elsewhere [26]. Electrochemical regeneration of ceric methane sulphonate is conveniently prepared in the optimum solution of 2 M methane sulphonic acid. The higher concentration of ceric methane sulphonate beyond 0.8 M will precipitate as solid. This solid can be used for chemical oxidation with much higher concentrations of methane sulphonic acid upto 6 M. The electrolyte was purified after every chemical reaction by solvent extraction and charcoal treatment. The acid concentration and cerous methane sulphonate concentration were adjusted before electrochemical regeneration. The operating parameters for the chemical reaction were varied depending on the compound involved. In each compound however slightly modified

TABLE I: Indirect oxidation of toluene to benzaldehyde using ceric methane sulphonate in aqueous methane sulphonic acid

Volume of electrolyte: 200 ml of ceric methane sulphonate in 2 M MSA

Volume of solvent: 20% (v/v)

Expt No	Amt of Ce(IV) taken for oxidation (g)	Theoretical equivalent of toluene added (g)	Solvent	Temp (K)	Duration of reaction		Amt of benzaldehyde formed (g)	Purity of benzaldehyde by HPLC (%)	*Oxidation efficiency of ceric for benzaldehyde formed (%)
					hrs	min			
1	11.30	1.90	DCM	308-313	>4	00	Incomplete oxidation	Incomplete oxidation	—
2	12.97	2.13	DCE	328-333	>4	00	-do-	-do-	—
3	13.37	2.20	a	328-333	0	35	2.45	80.0	77.3
4	14.47	2.30	Toluene	318-323	1	40	2.30	100.0	87.0
5	14.31	2.36	-do-	328-333	0	35	2.65	95.0	93.0
6	14.94	2.46	-do-	338-343	0	12	2.80	91.0	90.0

* Oxidation efficiency since the reactant itself is the solvent a Without solvent DCE dichloroethane DCM dichloromethane

procedure for product recovery was adopted. Products were identified using HPLC, FTIR and NMR spectra. The products such as benzaldehyde, p-ethoxy benzaldehyde and o-chlorobenzaldehyde were also confirmed by making 2,4-dinitrophenyl hydrazone derivatives. The observed melting point of 2,4-dinitrophenyl hydrazones of benzaldehyde, p-ethoxy benzaldehyde and o-chlorobenzaldehyde are 238, 215 and 206°C respectively.

RESULTS AND DISCUSSION

Toluene

Kreh *et al.*, have employed either 5 *M* methane sulphonic acid or 2.6 *M* trifluoromethane sulphonic acid to achieve satisfactory oxidation of toluene to benzaldehyde. It has been observed that for electrochemical conversion of cerous to ceric, 2 *M* methanesulphonic acid is the optimum acid concentration. Hence in the present work, oxidation of toluene was attempted using electrochemically generated ceric methane sulphonate in 2 *M* methane sulphonic acid. Under normal experimental conditions using methylene chloride and ethylene chloride as solvents very little oxidation was noticed even after four hours of continuous reaction (Expt. Nos. 1 and 2 in Table I). The reaction temperature was maintained at 308-313 and 328-333 K while using

methylene chloride and ethylene chloride as solvents respectively.

The chemical oxidation was found to be reasonably efficient when theoretical equivalent of toluene alone was used without solvent (Expt. No.3 in Table I). Further improvement in conversion yield was attempted using excess toluene itself as solvent. Typical experimental results obtained under these conditions are shown in Table I. (Expt. Nos. 4-6). Using 50 ml toluene with 200 ml electrolyte the reaction time for completion of chemical reaction (as indicated by the decolourisation of ceric methane sulphonate and confirmed by test with ferroin indicator) was found to decrease with increase in temperature. However, the overall yield efficiency was found to be around 93% when the reaction temperature was maintained at 328-333K.

From the present investigations it is apparent that oxidation of toluene to benzaldehyde may be achieved with good efficiency using 2 *M* methane sulphonic acid itself by employing excess toluene and carrying out the reaction at 328-333K.

p-Ethoxy toluene

p-methoxy toluene has been found to undergo efficient oxidation in ceric methane sulphonate [24]. It was expected that ethoxy toluene would

TABLE II: Indirect oxidation of p-ethoxy toluene using $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox system in aqueous methane sulphonic acid
Volume of electrolyte: 100 ml of 2 *M* MSA Purity of p-ethoxytoluene: 95.5% by HPLC
Volume of solvent: 33.3% (v/v)

Expt No	Amt of Ce(IV) taken for oxidation (g)	Amt of p-ethoxy toluene taken for oxidation (g)	Solvent	Temp (K)	Duration of oxidation (min.)	Amt. of product formed (g)	Purity of product by HPLC (%)	Material yield (%)
1	11.4	2.77	Without solvent	313-323	15	2.90	39.9	40.4
2	11.4	2.70	Dichloromethane	308-313	65	2.96	72.0	75.0
3	14.0	3.15	Dichloroethane	318-323	20	3.36	93.3	94.5
4	11.4	2.78	-do-	328-333	10	3.50	70.0	83.7
5	11.4	2.76	-do-	338-343	10	3.75	64.5	77.7

also respond quite similarly under the same set of experimental conditions. Indeed similarity was observed between the voltammetric responses of methoxy toluene reported in the literature and ethoxy toluene presented earlier in this work [27]. Experimental results obtained during the chemical oxidation of p-ethoxy toluene using electrochemically generated ceric methane sulphonate are summarised in Table II.

In the absence of solvent, chemical oxidation of p-ethoxy toluene was found to be less efficient. A material yield of 40% alone could be achieved (Expt. No.7 in Table II). Use of methylene chloride as solvent at a lower possible reaction temperature 308- 313K led to some improvement in the yield. The yield was indeed found to be 75% (Table II Expt. No.2) Dichloroethane was used as the solvent for carrying out the chemical reactions at higher temperature. In this solvent at the reaction temperature of 313- 323K maximum yield close to 90% was achieved (Expt. No.3, Table II). In this case further increase in the

reaction temperature was indeed found to decrease the overall yield efficiency (Expt. Nos. 4 & 5 in Table II).

Since the chemical conversion was quite facile and efficient some further experiments were carried out at optimum experimental conditions to study the reuse of cerous/ceric electrolyte solution and its influence on the overall yield and current efficiency of regeneration of ceric methane sulphonate. These results are summarised in Table III. The same electrolyte was reused five times after adjusting the concentration of methanesulphonic acid and Ce^{4+} ions. The overall current efficiency could be comfortably maintained at the same level of above 80%. The material yield of p-ethoxy benzaldehyde in all these experiments was found to be 91-95%, since ethoxy toluene is slightly water soluble it is not expected to block the electrode surface as a carryover impurity during electrolyte recycling. This is indeed the reason for fairly high efficiency of the two stage electrochemical process.

TABLE III: Indirect oxidation of p-ethoxy toluene (p-ET) using Ce^{4+}/Ce^{3+} redox system in methane sulphononic acid, regeneration and reuse of ceric solutions

Anode : Platinum Cathode : Stainless steel Anolyte : 100 ml of cerous methane sulphonate in 2 M MSA Catholyte : 100 ml of 2 M methane sulphononic acid Cell voltage : 2.5 to 3 V Temp. of electrolytic cell : 305-308 K				Vol. of electrolyte taken for chemical oxidation : 100 ml contg. 11.3 g ceric Amount of (p-ET) taken for oxidation : 2.745 g (95.5% pure) Duration of chemical oxidation : 20 min Chemical reactor temperature : 318-323 K		
Expt Nos	Amt of $Ce(III)$ taken (g)	Amt. of $Ce(IV)$ formed (g)	Current efficiency (%)	Amt. of product formed (g)	Purity of p-ethoxy benzaldehyde by HPLC (%)	Material yield (%)
1	11.5	9.7	84.3	2.96	92.1	94.0
2	11.5	9.2	80.0	3.40	79.2	95.0
3	11.3	9.3	82.0	3.36	80.0	93.0
4	11.5	9.6	83.5	3.16	84.0	91.8
5	11.3	9.0	80.0	3.20	83.0	92.0
6	11.0	9.1	82.7	3.10	85.0	91.2

Note: (a) Fresh electrolyte was used in expt No. 1

(b) Purified used electrolyte was used in expts 2 to 6

o-Chloro toluene

Kreh *et al.*, [24] have studied the two stage oxidation of *o*-chlorotoluene to *o*-chloro benzaldehyde. They have employed 8 *M* MSA to achieve 92% conversion and 73% selectivity. No further work on the oxidation of this compound is reported. Initial experiments on the oxidation of *o*-chlorotoluene using ceric methane sulphonate in 2 *M* methane sulphonic acid indeed showed very little yields of *o*-chloro benzaldehyde. Use of methylene chloride solvent and correspondingly lower reaction temperatures did not show any conversion of *o*-chlorotoluene. In 2 *M* methane sulphonic acid when the reaction was carried out in ethylene chloride solvent at reasonably high temperature of 333-338K some conversion with 11% yield of *o*-chloro benzaldehyde was noticed. Even in this case the reaction time was found to be around 14 hrs. In this medium the reaction time was substantially reduced to 5 hrs when the chemical reaction was carried out without solvent.

However, the yield of *o*-chloro benzaldehyde increased only slightly to 18% (Expt. No.5 in Table IV). These observations led to the conclusion that increasing the acid concentration was indeed necessary.

Typical experimental results obtained in different methane sulphonic acid concentration in presence of ethylene chloride solvent are presented in Table IV (Expt. Nos. 3-5). The yield of *o*-chloro benzaldehyde increases with the increasing methane sulphonic acid concentration. Further improvement in the yield of *o*-chloro benzaldehyde was noticed in 6 *M* methane sulphonic acid. The yield efficiency was around 70% (Expt. No.6 in Table IV). In all these cases however, the reaction time was found to be substantially higher at around 12 hrs. In 6 *M* methane sulphonic acid the reaction time could once again be decreased to 1 hour in the absence of solvent (Expt. No.7 In Table IV). However the yield of *o*-chloro benzaldehyde decreased.

TABLE IV: Indirect oxidation of *o*-chloro toluene using ceric methane sulphonate in aqueous methane sulphonic acid

Volume of electrolyte : 200 ml of ceric methane sulphonate Temp : 333-338 K						Solvent : 26% (v/v) DCE		
Expt No	Amt. of Ce(IV) taken for oxidation (g)	Concn of MSA (M)	Amt. of o-chloro- toluene taken for oxidation (g)	Duration of reaction		Amt of product formed (g)	Purity of o-chloro- benzaldehyde HPLC (%)	Material yield (%)
				hrs	min			
1	8.5	2.0	2.0	>14	00	0.98	25.0	11.0
2*	8.3	2.0	1.85	5	00	1.50	25.0	18.3
3	9.4	3.0	2.10	>12	00	2.10	40.0	36.0
4	11.2	4.0	2.50	>12	00	2.65	62.2	59.4
5	8.9	5.0	2.00	>12	00	1.85	81.8	68.0
6	11.3	6.0	2.47	>12	00	2.50	77.2	70.4
7*	8.2	6.0	1.82	1	20	2.00	65.3	64.5
8	11.6	8.0	2.54	7	00	2.00	78.3	55.5
9*	11.2	8.0	2.40	1	10	2.30	62.2	53.7

* Expt Nos 2, 7 & 9 were carried out without solvent. All other experiments were carried out using DCE as solvent

TABLE V: Indirect oxidation of p-isopropyl toluene using ceric methane sulphonate in aqueous methane sulphonic acid medium

Volume of electrolyte : 200 ml of ceric methane sulphonate					Amount of solvent : 26% (v/v)				
Expt No	Amt of Ce(IV) taken for oxidation (g)	Conc of MSA (M)	Amt of isopropyl toluene taken for oxidation (g)	Solvent	Temp (K)	Duration of oxidation		Amt. of methyl acetophenone formed* (g)	Yield of p-methyl acetophenone (%)
						hrs	min		
1	9.3	2.0	2.16	**	333-338	1	10	0.449	20.8
2	8.6	3.0	2.05	-do-	-do-	0	55	0.525	25.6
3	9.0	4.0	2.06	-do-	-do-	0	22	0.510	24.8
4	9.0	5.0	2.07	-do-	-do-	0	13	0.700	33.8
5	9.6	6.0	2.30	-do-	-do-	0	07	0.547	23.8
6	9.0	4.0	2.07	DCE	-do-	6	20	0.621	30.0
7	9.0	5.0	2.05	-do-	-do-	3	20	0.765	37.3
8	9.5	5.0	2.16	-do-	323-328	5	10	0.499	23.1
9	9.5	5.0	2.19	-do-	343-348	3	00	0.491	22.4
10	9.5	5.0	2.25	DCM	308-313	5	30	0.520	23.1

* p-MA = p-Methylacetophenone formed calculated based on NMR results

** Oxidation carried out without solvent DCE = dichloroethane DCM = dichloromethane

Further increase in methane sulphonic acid concentration actually led to decrease in conversion yield (Expts. 8,9 in Table IV). All these results suggest that chemical oxidation using ceric methane sulphonate in 6 M methane sulphonic acid with ethylenechloride solvent at 333-338K is the optimum experimental condition for o-chloro benzaldehyde. The reaction time inevitably is still as high as 12 hrs.

p-Isopropyl toluene

Product identification after chemical oxidation of p-Isopropyl toluene posed some difficulty in 70:30 and 100% methanol. Hence the product distribution obtained by the reaction of p-isopropyl toluene with ceric methane sulphonate was analysed using primarily NMR data. These results are summarised in Table V. In general the

concentration of reactant after the chemical step was found to be greater than 50% under all the experimental conditions. The yield of p-isopropyl benzaldehyde was found to be around 5%. Hence the optimisation studies were mainly confined to the formation of p-methyl acetophenone which is the main product from this chemical reaction. This conclusion has also been reached by the earlier report [24] which has indicated a maximum of 20% conversion of p-isopropyl toluene to p-methyl acetophenone.

Some further experiments were carried out in the present work to study the effect of operating parameters on the overall yield of p-methyl acetophenone. Initial experiments were carried out without using any solvent (Table V, Expt. Nos. 1-5). Acid strength was found to have a significant effect on the overall yield of p-methyl

TABLE VI: Indirect oxidation of toluene, p-ethoxytoluene, o-chlorotoluene and p-isopropyltoluene using Ce^{4+}/Ce^{3+} redox system in aqueous methane sulphonic acid under optimum parameters

Optimum parameters	Toluenes			
	Toluene	p-ethoxy toluene	o-chloro toluene	p-isopropyl toluene
Concn of MSA (M)	2.0	2.0	6.0	5.0
Temperature (K)	328-333	318-323	333-338	333-338
Solvent	Excess toluene	Dichloroethane	Dichloroethane	Dichloroethane
Solvent ratio (% v/v)	20	33	26	26
Duration of oxidation (hrs)	0.58	0.33	> 12	3.33
Yield aldehyde (%)	93.0*	95.0	70.4	37.3

* Oxidation efficiency of ceric for the formation of benzaldehyde

acetophenone. 5 M MSA was found to be optimum (33.8% yield, Expt. No.5). Use of dichloroethane as the solvent during the chemical oxidation of p-isopropyl toluene also had some effect on the overall yield of p-methyl acetophenone. Dichloroethane was found to be a better solvent when compared to dichloromethane (compare Expt. No. 10 with Expt. Nos. 6-9). 333K - 338K of reaction temperature was found to be optimum (Expt. No. 7). The chemical conversion of p-isopropyl toluene to p-methyl acetophenone was found to be around 37% in 5 M methane sulphonic acid using dichloroethane as the solvent and carrying out the reaction at 333-338K. (Expt. No. 7 in Table V).

CONCLUSION

Optimum experimental conditions and yields obtained during the chemical oxidation of toluene and substituted toluenes namely p-ethoxy toluene, o-chlorotoluene and p-isopropyl toluene using electrogenerated ceric methane sulphonate are summarised in Table VI. Toluene and p-ethoxy toluene gave a fairly high yield of over 90% under optimum experimental conditions. o-Chlorotoluene gave a lower yield of around 70% even under optimum experimental conditions. Reaction time for this compound was also found to be substantially higher. p-Isopropyl toluene led to the

formation of p-methyl acetophenone. The reaction pathway appears to involve the preferential oxidation at the tertiary carbon of iso-propyl group. The yield was also found to be only around 37%. These results once again confirm the earlier view that chemical oxidation of different starting materials depend significantly on the operating parameters. Hence study of individual organic compounds becomes necessary.

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