Electrolytically Regenerated Ceric Sulfate for the Oxidation of Organic Compounds. I. Oxidation of p-Xylene to p-Tolualdehyde

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The use of ceric sulfate as "oxygen carrier" is described in many electro-organic oxidation processes[1-3]. These carriers act as depolarizers and ceric sulfate belongs to the group of ionic oxidizing agents which act only as electron-abstracting agents[21]. The reaction of the oxidized reagent with the organic compound to give the desired product is also expected to take place. If the latter is true, it would be a most convenient and economical procedure[4] to carry out the oxidation reaction in two stages, the first stage of electrolytically oxidizing cerous sulfate into ceric sulfate and the second stage of reacting the ceric sulfate with the organic compound to obtain the desired product. The oxidation of trivalent to tetravalent ceric sulfate[5-7] at a lead dioxide anode for the use of oxidation of xylenes and the electrolytic regeneration of ceric sulfate for further use have therefore been studied. Such a two-stage process has recently been developed in this laboratory, using manganous sulfate for the oxidation of aromatic hydrocarbons[11,12].

Kinetic studies of the oxidation of organic compounds by ceric sulfate have been described in literature[8-10,20]. A kinetic study of the oxidation of *p*-xylene by manganic sulfate was reported[11], but no kinetic study of the reaction between *p*-xylene and ceric sulfate appears to have been carried out. Ceric sulfate brings about controlled oxidation of *p*-xylene to *p*-tolualdehyde and a kinetic study of this oxidation using Ce^{4+} cation in sulfuric acid is described in the present article.

Experimental

Electrolytic Cell.—A glass trough of diameter of 12 cm. and height of 6.5 cm. with a suitable perspex lid carrying four holes for the electrodes, diaphragms, and thermometer respectively was used as electrolytic cell. Cylindrical lead anode with an effective area of 40 cm² was used as rotating anode. In the case of divided cells, two ceramic diaphragms of outer diameter of 2.5 cm. and height of 10 cm. and two narrow lead strips of 2 cm. wide and 14 cm. long were used as cathodes. In the case of investigating the use of stationary electrode with the same cylindrical lead anode, a glass stirrer was used for effective agitation in the cell. The anode potential was measured by Crompton potentiometer against a saturated calomel electrode. The other experimental conditions employed are given in the tables.

Analysis.—When electrolysis was over, 5 cc. of the oxidized solution was added to a known volume (20 cc.) of N/10 ferrous sulfate solution and then the excess of ferrous sulfate was titrated with a standard permanganate solution. In the case of electrolysis in the state of suspension, a known weight of the paste was added to excess ferrous sulfate solution and titrated in the same way and the current efficiency was calculated from the titre values knowing the total weight of the paste.

Kinetic Study of the Oxidation of *p*-Xylene with Ceric Sulfate

Materials.—Distilled *p*-xylene (b. p. 138°C) was used in the study. Cerous sulfate and all other chemicals were of A. R. quality. The ceric sulfate was prepared by the anodic oxidation of cerous sulfate in sulfuric acid as described before.

Measurement of Reaction Kinetics.—Ceric sulfate solution (350 cc.) in 5% sulfuric acid was taken in a three-necked flask and maintained at a desired temperature in a thermostat. Forty cc. of *p*-xylene was added to the flask containing ceric sulfate. A blade-type stirrer with a constant r.p.m. of 200 was employed to ensure identical agitation conditions. No attempt has been made to study the reaction in the absence of air. After five minutes of starting the reaction, stirring was stopped and the emulsion allowed to clear (30 sec.)

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and an aliquot part (2 cc.) was pipetted out almost from the bottom of the flask and added to excess ferrous sulfate and then back titrated against standard potassium permanganate. Determinations were carried out at 90, 85, 80 and 75°C in the manner just described and with the experimental data curves were drawn for log *C* vs. time where *C* indicates the concentration of ceric sulfate. The slopes of all these straight lines in Fig. 1 are within experimental error. A blank was run at 90°C to make suitable corrections, but it was found that there was no appreciable decomposition of ceric sulfate during 25 min.

Reaction of *p*-Xylene with Ceric Sulfate.—Ceric sulfate solution or paste was taken in a three necked flask fitted with a mercury seal and stirrer, reflux condenser and thermometer. Required volume of *p*-xylene was added and the flask kept in the thermostat so that the oxidation could be carried out at 80°C. The contents of the flask were well agitated until the reaction was over.

Isolation of Aldehyde. — After cooling, the *p*-xylene layer was separated from the paste or solution and washed well with water to remove any sulfuric acid. Then the layer was treated with a saturated solution of sodium bisulfite to get *p*-tolualdehyde addition compound which on decomposition with soda ash and steam distillation, gave *p*-tolualdehyde.

Purification of used Electrolyte.—The used electrolyte was well extracted with xylene to remove all organic materials and after separation of xylene-layer the electrolyte was distilled under reduced pressure. The distillation was continued until a few cc. of water (5∼15 cc.) was collected and the electrolyte after being made up to the original strength was recycled to the cell for regeneration of ceric sulfate, thereby making the process continuous and cyclic.

Results

The relationship between current efficiency and current density using stationary anode is shown in Fig. 2. Figure 3. shows the variation of anode potential with current density. The current efficiency obtained varying the concentration of sulfuric acid is given in Table I. Table II gives the current efficiency obtained using a divided or undivided cell. Table III gives the current efficiency obtained using a suspension of cerous sulfate in the electrolyte. The influence of anode material on current efficiency and yield is given in Table IV.

Values of the rate constants obtained in the kinetic study of the oxidation of *p*-xylene are given in Table V. Similarly the results of chemical oxidation of *p*-xylene by ceric sulfate are given in Table VI. Table VII includes the

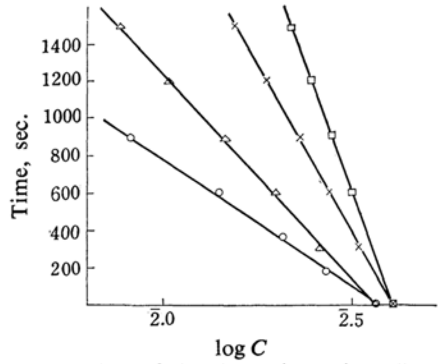

Fig. 1. Plot of log *C* against time (in sec.). ○, 90°C; △, 85°C; ×, 80°C; □, 75°C

TABLE I. INFLUENCE OF THE CONCENTRATION OF SULFURIC ACID ON THE CURRENT EFFICIENCY

Temp., 30°C; anode, PbO_2 on Pb; anolyte, 20 g. cerous sulfate in 400 cc. of sulfuric acid; catholyte, 5% sulfuric acid; cathode, lead strip; current density, 1 amp./dm^2; r. p. m. of the electrode, 3000.

Concn. of sulfuric acid %	Cell voltage V.	Current efficiency %
3	3.6	83.5
10	3.0	79.8
20	2.9	73.8
30	2.8	43.0

TABLE II. CURRENT EFFICIENCY WITH DIVIDED AND UNDIVIDED CELL

Concentration of sulfuric acid in anolyte, 10%; interelectrode distance, 3 cm.; cell voltage, 3∼3.2 V.; current density, 1 amp./dm^2; cathode current density in undivided cell, 30 amp./dm^2. All other conditions same as it Table I.

Type of cell	Motion of anode	Current efficiency, %
Undivided	Stationary	60.5
Divided	Stationary	69.9
Undivided	Rotated	69.1
Divided	Rotated	75.4

TABLE III. INFLUENCE OF SUSPENSION OF CEROUS SULFATE IN SULFURIC ACID ON THE CURRENT EFFICIENCY

Concentration of sulfuric acid, 5%; temp. 35°C; stationary anode; undivided cell; anode current density, 2 amp./dm^2; cathodic current density, 30 amp./dm^2; current strength, 3.4 amp.

Nature of electrolyte	Cell voltage V.	Current efficiency %	Duration of electrolysis hr.
100 g. cerous sulfate suspended in 250 cc. of sulfuric acid	4.0	66.1	1.03
150 g. cerous sulfate suspended in 250 cc. of sulfuric acid	4.1	59.7	1.51
200 g. cerous sulfate suspended in 250 cc. of sulfuric acid	4.2	57.3	2.06

TABLE IV. EFFECT OF ANODE MATERIAL ON THE CURRENT EFFICIENCY AND YIELD

Stationary anode; concentration of sulfuric acid, 5%; undivided cell; cell voltage, 2.9~3.0 V.; current density, 1 amp./dm².
All other conditions same as in Table I.

Anode material	Current efficiency %	Duration hr.	Yield %
Lead	67.8	1	67.8
	49.0	2	98.0
Antimonial lead	50.5	1	50.0
PbO_2 on graphite	71.6	1	71.6
	54.0	1.83	98.0
Lead	65.1*	1	65.0
Lead	62.8*	1	63.0
Lead	62.0*	1	62.0

* Results obtained in the first, second and third regeneration experiments respectively.

TABLE V. RATE CONSTANTS EOR THE OXIDATION OF *p*-XYLENE WITH CERIC SULFATE

Temp. °C	$1/T$ °K×10³	$k\times10^4$	$\log k$
90	2.755	16.89	$\bar{3}.2276$
85	2.793	10.47	$\bar{3}.0199$
80	2.833	6.33	$\bar{4}.8016$
75	2.874	4.03	$\bar{4}.6053$

results of the effect of cathodic reduction of ceric sulfate.

Discussion

The results indicate that the anodic oxidation of cerous sulfate in sulfuric acid is dependent upon a number of factors. Figure 2 shows that high current efficiencies are obtained at low current density values. The anode potential rapidly increases with current density as seen from Fig. 3. The decrease of current efficiency with increase of current density is therefore to be attributed to simultaneous oxygen evolution taking place at higher anode potentials. Results in Table I indicate that the concentration of sulfuric acid exerts a marked influence on the current efficiency because of the above reason. The difference in current efficiency obtained with divided and undivided cells is shown in Table II. The application of the rotating anode technique gave improved current efficiency due to the decrease of polarization. In subsequent experiments only stationary anodes were employed as the results obtained were satisfactory for the present purpose. The difference in current efficiency between divided and undivided cell is not large and the use of diaphragm can therefore be avoided by employing high cathodic current density.

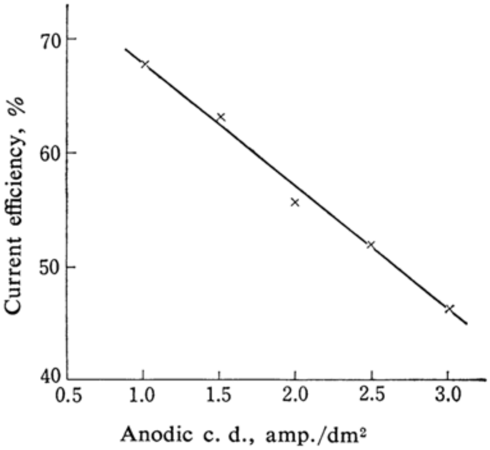

Fig. 2. Current efficiency against current density.

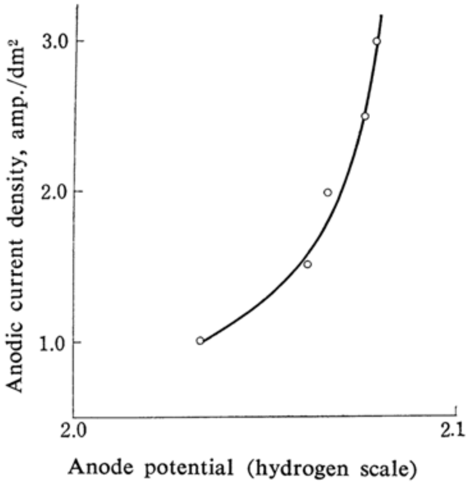

Fig. 3. Current density against anode potential (hydrogen scale).

Technique of avoiding the use of diaphragms in electrolytic cells is an important aspect to be considered on a practical scale and should lead to energy economics in addition to making cell design simple. Although this fact is known in developing practical scale production techniques, it is necessary to examine various aspects of the reaction itself. In the oxidation of manganous to manganic sulfate, evidence has been found for the existence of trivalent manganese in the complex form $H_2[Mn_2(So_4)_4]$. The reduction of the trivalent manganese in the anion $[Mn_2(So_4)_4]^{2-}$ at the cathode may be prevented especially at high current densities so that an undivided[12,13] cell can be advantageously employed. The direct reduction of the Mn^{+3} to Mn^{+2} at the cathode has thus been found to be negligible, especially when

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TABLE VI. RESULTS OF OXIDATION OF *p*-XYLENE BY CERIC SULFATE PASTE

Temp., 80°C; 40 cc. of *p*-xylene was added in each case

Strength of sulfuric acid %	Current passed amp.-hr.	Quantity of ceric sulfate g.	Current efficiency for Ce^{3+} to Ce^{4+} %	*p*-Tolualdehyde formed g.	Oxidation efficiency based on ceric sulfate used %	Overall current efficiency for aldehyde formation %
20	5.3	32.00	47.1	1.4	54.2	23.3
5	7.0	51.3	59	2.1	50.7	26.7
5	10.5	78.00	60	3.15	50.0	30.0

TABLE VII. EFFECT OF CATHODIC REDUCTION ON CERIC SULFATE

Catholyte, 4.3 g. of ceric sulfate in 300 cc. of 5% sulfuric acid; divided cell; lead electrodes, temp., 30°C

Current density amp./dm²	Current efficiency %
50	4.9
30	5.3
15	12.3
5	31.3

the ratio of anode area to cathode area is sufficiently high. In a similar manner, ceric sulfate is also known to exist as the complex[6,14)] sulfato-ceric acid, $H_4[Ce(So_4)_4]$ so that the reduction of Ce^{4+} in this anion should be prevented. The effect of cathodic reduction of ceric sulfate can be seen from Table VII and it is clear that the efficiency of reduction is very much affected, especially when the cathodic current density is above 15 amp./dm².

The results given in Table III are quite interesting and reveal the fact that the current efficiency remains more or less the same even when a cerous sulfate suspension in sulfuric acid is used for the oxidation. The portion of cerous sulfate in solution gets oxidized to ceric sulfate and a corresponding amount of the former dissolves in the electrolyte from the suspended state. However, when the solution becomes saturated with ceric sulfate, further formation of the same leads to a separation of the salt giving finally a suspension of ceric sulfate in the electrolyte. The effect of anode material on the current efficiency is shown in Table IV and it indicates that either lead dioxide electrodeposited on graphite[15)] or lead dioxide on lead electrode can be used. By passing excess current, the yields obtained are almost theoretical even though the current efficiency bared on the ceric sulfate is somewhat lowered.

The electrochemical oxidation of *p*-xylene[16-19)] in a single stage process using ceric sulfate as oxygen carrier has been reported to give very poor current efficiency. The oxidation carried out in two stages gives overall current efficiency of 23 to 30% as seen from Table VI, even though the efficiency of the oxidation of *p*-xylene with reference to ceric sulfate is more than 50%.

Energy of Activation for the Oxidation of *p*-Xylene by Ceric Sulfate

The reaction appears to be essentially homogenous, the dissolved *p*-xylene mainly taking part in the reaction. The efficient agitation was helpful in maintaining the solution saturated with *p*-xylene.

Figure 4 shows plot of log *k* against $1/T$ (°K). From the slope, the calculated apparent energy of activation is 23840 cal./mol., which would be inclusive of the effect of change of solubility of *p*-xylene in the medium with temperature.

Oxidation of hydrocarbons generally requires severe conditions and is usually retarded by bases, but is catalyzed by acids. The mechanism appears to be a single electron transfer reaction

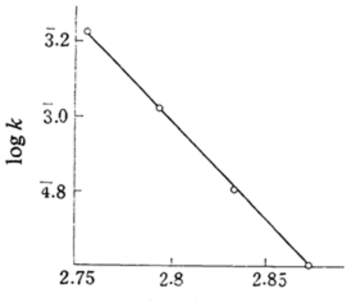

Fig. 4. Plot of log k against $1/T\times10^3$.

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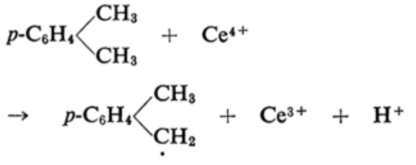
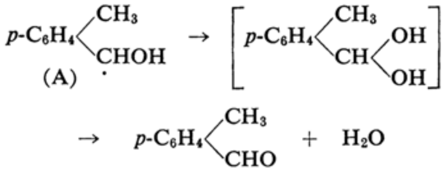
and by the action of tetravalent ceric ion, exclusive oxidation of one of the methyl groups takes place and the initial attack may occur by hydrogen abstraction according to the reaction 1 given below:



$$p\text{-}C_6H_4\begin{cases}CH_3\\CH_3\end{cases} + Ce^{4+} \rightarrow p\text{-}C_6H_4\begin{cases}CH_3\\\dot{C}H_2\end{cases} + Ce^{3+} + H^+ \quad (1)$$

The reaction of the substituted benzyl radical then takes place to yield tolylcarbinol which again reacts with Ce^{4+} to give the radical A which immediately reacts to give p-tolualdehyde as in Eq. 2.



$$\underset{(A)}{p\text{-}C_6H_4\begin{cases}CH_3\\\dot{C}HOH\end{cases}} \rightarrow \left[p\text{-}C_6H_4\begin{cases}CH_3\\CH\begin{cases}OH\\OH\end{cases}\end{cases}\right] \rightarrow p\text{-}C_6H_4\begin{cases}CH_3\\CHO\end{cases} + H_2O \quad (2)$$

Summary

1. The current efficiency for the oxidation of cerous sulfate in sulfuric acid at a lead dioxide in an undivided cell was generally found to be 70%.

2. By using a paste of cerous sulfate in sulfuric acid, ceric sulfate reagent is obtained in a concentrated form.

3. A kinetic study of the oxidation of p-xylene by ceric sulfate is described and apparent energy of activation is calculated.

4. The process of oxidation of p-xylene to p-tolualdehyde is made cyclic and continuous by regeneration of ceric sulfate at a lead dioxide anode.

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