

Kinetic Aspects of the Direct Electrochemical Oxidation of *p*-Xylene in Methanol using Graphite Electrodes

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ABSTRACT

The kinetics of the electrochemical oxidation of *p*-xylene (A) in methanol solutions containing tetraethylammonium *p*-toluene sulphonate as supporting electrolyte using graphite electrodes were investigated. It was shown that *p*-xylene is first oxidized to the intermediate 4-methylbenzyl methyl ether (B), which is then further oxidized to the corresponding acetal, 4-methyl benzaldehyde dimethyl acetal (C). The stepwise reaction $A \rightarrow B \rightarrow C$ was first tested for first order consecutive kinetics and this approach was shown to be invalid. A model based on parallel consecutive second order kinetics was then proposed in which solvent participation assists in the electrochemical oxidation of the substrate, through free radical reactions. Using the ratios of the relevant *k* values, instead of their absolute values, the concentrations of each reactant are expressed as ratios with respect to the initial concentration of A. These are calculated using expressions based on the fraction of A remaining at a particular time. It is shown that the calculated curves agree well with those based on the observed values, indicating that the proposed kinetic model is acceptable.

KEYWORDS

p-xylene; electrochemical oxidation; parallel second order consecutive kinetics.

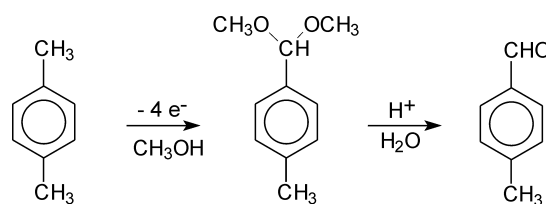
1. Introduction

p-Xylene (4-methyltoluene) is an important industrial chemical which is used as a starting material to prepare *p*-tolualdehyde (4-methylbenzaldehyde), an important intermediate, and terephthalic acid (1,4-benzene-dicarboxylic acid), used in the production of polyester fibres. These oxidations can be carried out using either a catalytic^{1–3} or an electrochemical^{4–6} route. The selective electrochemical oxidation of *p*-xylene to the corresponding aldehyde proceeds through the formation of the corresponding dimethyl acetal in the electrochemical cell, which then undergoes acid-catalysed hydrolysis to form the *p*-tolualdehyde, as shown in Scheme 1.

The selective anodic oxidation of alkyl aromatics has been studied by a number of authors^{7–9}; carbon electrodes are used in methanolic solutions of the substrate, containing a supporting electrolyte such as NaClO₄, NaBF₄, H₂SO₄ or tetraethylammonium *p*-toluene sulphonate (Et₄NOTs). The anodic oxidation proceeds through the formation of the intermediate ether, which is then further oxidized to the dimethyl acetal. The mechanism^{10,11} is shown in Scheme 2 for toluene and takes place through the initial formation of a radical cation (A), followed by generation of a free radical (B), which leads, upon further oxidation, to the benzyl cation (C). This, in the absence of other nucleophiles, undergoes nucleophilic attack by the solvent, CH₃OH, to form benzyl methyl ether (D). The sequence of reactions is repeated, finally producing the benzyl dimethyl acetal (E).

It can be seen that four electrons are removed per molecule of substrate, or that the charge per mole passed through the cell should be 4 F, if the cell is to function 100% efficiently.

In previous work¹², the effect of solution conditions for the



Scheme 1
Electrochemical route to *p*-tolualdehyde.

anodic oxidation of toluenes was examined, and the oxidation of 4-*t*-butyltoluene to 4-*t*-butylbenzaldehyde dimethyl acetal¹³ was optimized and scaled up. A further article¹⁴ explored some mechanistic and kinetic aspects of the direct electrochemical oxidation of 4-*t*-butyltoluene. This paper now deals with the kinetics of the anodic oxidation of *p*-xylene in methanol.

2. Experimental

2.1. Materials

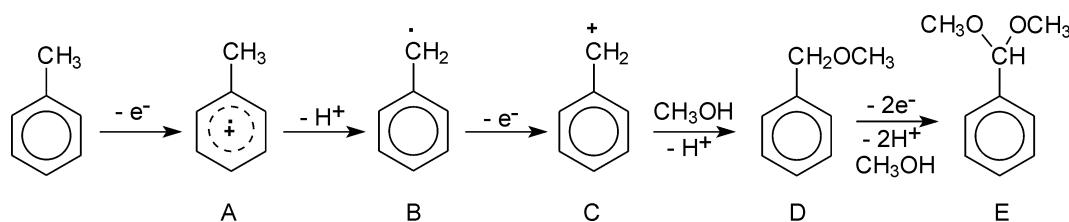
Chemicals used in the oxidation, synthetic procedures and analytical methods were purchased from either Merck or Aldrich, and were all analytical grade reagents and used as received. Methanol was of HPLC grade. Electrodes used were graphite rods of extruded carbon (>99% purity), 13 mm in diameter, obtained from Morganite Industry Carbon.

2.2. Synthetic Procedures

2.2.1. 4-Methyl Benzyl Methyl Ether

This compound was synthesized using a standard method¹⁵, i.e., by treating 4-methylbenzyl chloride with sodium methoxide (prepared in our laboratory) and heating the mixture under

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Scheme 2
Mechanism of anodic oxidation of toluene.

reflux. The product was purified by vacuum distillation, and its structure confirmed by means of GC/MS as well as comparison with a standard material.

2.2.2. 4-Methylbenzaldehyde Dimethyl Acetal

This compound was prepared by treating 4-methylbenzaldehyde with trimethylorthoformate in methanol according to a known procedure¹⁶. *p*-TsOH was then added and the mixture heated under reflux for 24 h. Sodium methoxide was added to neutralize the acid catalyst, and the excess methanol and trimethylorthoformate removed by distillation. Fractional distillation afforded the 4-methylbenzaldehyde dimethyl acetal, the structure of which was confirmed by means of GC-MS.

2.3. Oxidation Procedures

Bench-scale oxidations were performed in the galvanostatic mode in an undivided glass cell (100 cm³ in volume), provided with water cooling and equipped with a silica gel drying tube and thermometer. Two graphite electrodes were positioned 2 mm apart in the centre of the cell and connected to a QPS-103 Quatetron DC power supply. A magnetic stirrer was used to stir the contents of the cell during electrolysis. The supporting electrolyte, tetraethylammonium *p*-toluene sulphonate (Et₄NOTs) was vacuum-dried before use at 50°C, and weighed directly into the cell, and 80 cm³ of the appropriate solvent was added. Experiments were carried out at room temperature and a constant current of 0.32 A was used, resulting in a current density of 3.2 A dm⁻².

2.4. Analytical Procedures

For methanol as solvent, samples of 0.50 cm³ were withdrawn periodically, added to 1 cm³ of methanol containing the internal standard, chlorobenzene, and analysed by GC, using a Varian 3300 gas chromatograph and an SPB20 capillary column. GC-MS analyses were performed on a Thermo Finnigan Trace MS Plus system, containing an RX-35 MS capillary column. Data were acquired by means of a Dell computer system with Xcaliber V3 software.

2.5. Oxidation Potential Determination

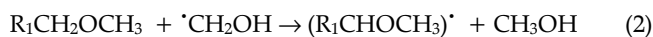
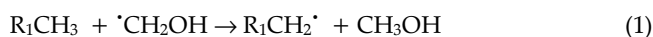
Oxidation potentials were analysed using a BAS CV-50 W system. The anodic potential was determined using linear scanning voltammetry by measuring the anodic peak of the substrate using a non-aqueous Ag/Ag⁺ reference electrode and a glassy carbon working electrode, together with a Pt auxiliary electrode. Substrates were dissolved in acetonitrile containing LiClO₄ as supporting electrolyte.

3. Results and Discussion

Figure 1 shows the results obtained for the electrochemical oxidation of *p*-xylene using methanol as solvent and Et₄NOTs as supporting electrolyte. As can be seen, the substrate leads to the formation of the ether, which subsequently undergoes further oxidation to the target compound, the acetal. The accountability

of the reaction, defined as the sum total of *p*-xylene, intermediate ether and the acetal product, is an important parameter as it can be used to indicate the formation of unwanted side products; in this case it is shown to be 100% up to 3 F, after which it slowly decreases due to the formation of other products.

The figure shows that some methanol solvent is also oxidized, since the acetal maximum occurs at a charge larger than the theoretical value of 4 F. According to Ross *et al.*,¹⁷ the oxidation of methanol leads to the formation of the radical HOCH₂•, which is oxidized further to the cation, HOCH₂⁺. This cation then attacks another solvent molecule, finally leading to the product 1,1-dimethoxymethane, CH₂(OCH₃)₂. Referring to Scheme 2, which shows the typical mechanism of the electrochemical oxidation of toluene, interaction between these methanol-derived radicals and the neutral substrate or ether molecules may take place¹⁸, thereby indirectly assisting in the oxidation of the substrate. Equations 1 and 2 illustrate this action:

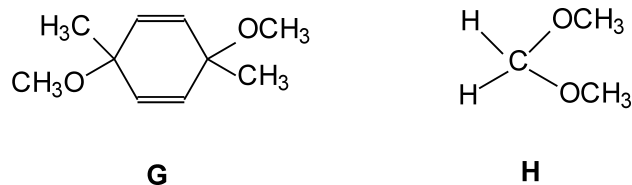


Radical-radical interactions between substrate-derived radicals can be expected to take place when the concentration of these species is high, leading to dimerization and other possible side reactions, which represent a loss in accountability. Equations 3 and 4 show two such reactions that may occur:



Formation of these dimers and other unknown side products is accompanied by a loss in accountability and leads to a drop in current efficiency, causing the acetal peak to shift to higher charge values.

Small amounts of 3,6-dimethoxy-3,6-dimethyl-1,4-cyclohexadiene (G) were detected during GC-MS analysis of the electrolysis solution, together with some 1,1-dimethoxymethane (H).



Considering the electrochemical oxidation shown in Fig. 1, the target acetal reaches a maximum of 81.4% at 5.88 F, with an accountability at that point of 84.6%. The ether maximum of 39.1% occurs at 2.24 F. Although some loss in accountability occurs in the later part of the electrolysis, the electrochemical oxidation can be regarded as an efficient method for synthesizing the target acetal compound, assuming one discontinues the electrolysis once the acetal has reached its maximum concentration.

The electrochemical conversion of *p*-xylene to the intermediate ether, and its subsequent oxidation to the acetal, can be represented kinetically by Equations 5 to 7:

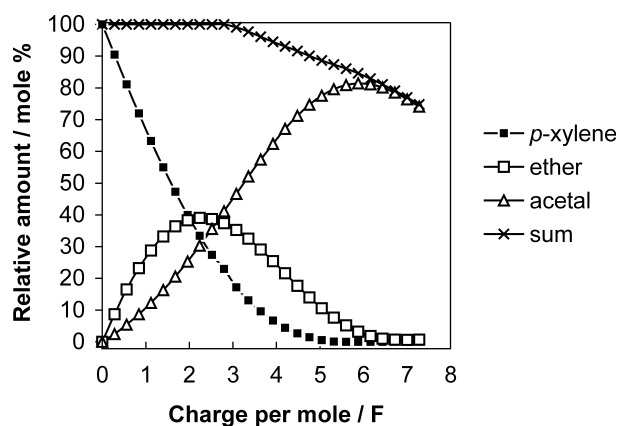
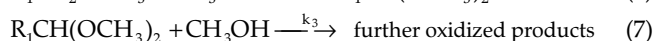
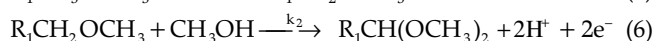


Figure 1 Electrochemical oxidation of *p*-xylene in methanol containing 2.2811 g of substrate, 80 cm³ of methanol, 3.1874 g of Et₄NOTs, with a current of 0.320 A and graphite electrodes at room temperature (ether = 4-methylbenzyl methyl ether, acetal = 4-methylbenzaldehyde dimethyl acetal, sum = *p*-xylene + ether + acetal).

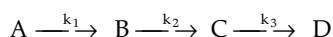


In these reactions, the further oxidized products could be the trimethyl acetal, $R_1C(OCH_3)_3$ and its decomposition products¹⁹.

The rate constants k_1 , k_2 and k_3 are related to the ease with which the particular compound is oxidized.²⁰ The lower the oxidation potential, the higher will be the k value. Table 1 shows the oxidation potentials obtained for *p*-xylene, the intermediate ether and the acetal. The substrate, *p*-xylene, has the lowest oxidation potential, followed by the ether, with the acetal having the highest potential; the acetal should therefore accumulate in the cell during the electrolysis, as is observed.

3.1. Consecutive First Order Kinetics

The conversion of the substrate to the final acetal product can be kinetically regarded as a consecutive first order reaction:



where A represents *p*-xylene, B is the ether, C the acetal and D the further oxidized products. C can be regarded as sufficiently stable in the presence of A and B, due to its high oxidation potential.

The respective k values can be obtained from the data in Fig. 1 using conventional kinetic techniques: k_1 is determined from the slope of $\ln [A]$ versus t for the early part of the electrolysis giving a value of 0.219 h⁻¹; k_2 is determined from the ether maximum, giving a value of 0.187 h⁻¹ while k_3 is obtained from the acetal maximum, giving a value of 0.00737 h⁻¹.

Although these k values are in accordance with the trend in oxidation potentials of the relevant compounds, further testing of the experimental data for first order consecutive kinetic behaviour, using the appropriate kinetic equations^{21,22} to calculate $[A]_t$, $[B]_t$ and $[C]_t$ and comparing these calculated values

Table 1 Oxidation potentials versus non-aqueous Ag/Ag⁺ reference electrode [CH₃CN, LiClO₄ (0.1 M), AgNO₃ (0.10 M)], glassy carbon working electrode, and Pt wire as auxiliary electrode.

Compound	Potential versus Ag/Ag ⁺ /mV
<i>p</i> -xylene	1670
4-methylbenzyl methyl ether	1805
4-methylbenzaldehyde dimethyl acetal	>2200

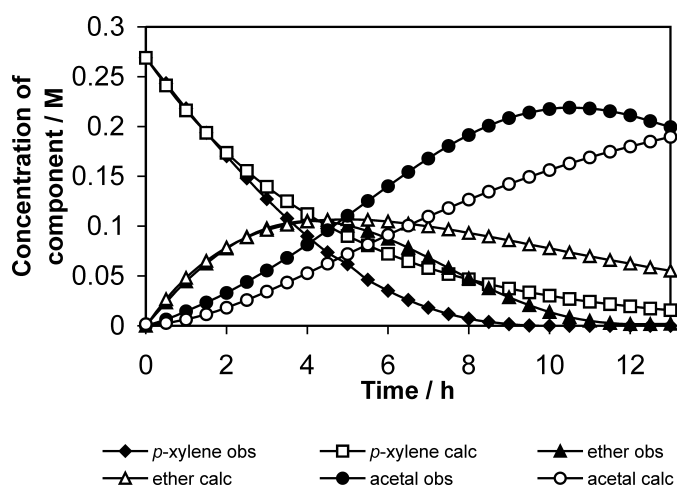


Figure 2 Calculated versus observed concentrations of *p*-xylene, ether and acetal using $k_1 = 0.219 \text{ h}^{-1}$, $k_2 = 0.187 \text{ h}^{-1}$ and $k_3 = 0.00737 \text{ h}^{-1}$. Experimental conditions are the same as those used to obtain Fig. 1.

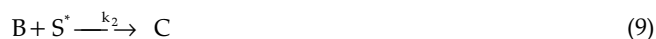
with the observed experimental values as a function of time, as is done in Fig. 2, shows clearly that the kinetic model is not acceptable, since the curves are not a good match.

The A and B curves match each other well for the first 3–4 hours, but then deviate considerably from the observed concentration curves. The calculated C curve is significantly lower than the observed C curve at all times.

The above kinetic treatment of the data is a simplification since it does not account for any solvent oxidation and any subsequent side reactions; only in the early stages of the electrolysis, when the concentration of the substrate is high, is there an indication of consecutive first order behaviour. The rate of the reaction will then depend on the rate at which the substrate can reach the electrode. As the concentration of the substrate decreases, the participation of the solvent becomes more important.

3.2. Parallel Consecutive Second Order Kinetics

The electrochemical conversion of *p*-xylene (A) to the intermediate ether (B), its further reaction to the acetal (C), and the final decomposition to unknown products (D) under the influence of solvent S can be regarded as three parallel consecutive reactions, which are each second order, as shown in Equations 8 to 10:



In these equations, S* represents some active species of the solvent, such as $\cdot CH_2OH$. This species would control the concentrations of A, B and C. Examples of parallel consecutive second order reactions of industrial importance include the reaction of benzene and methane with chlorine, and the reaction of water and ammonia with ethylene oxide²³. Reaction between benzene and chlorine leads, stepwise, to the formation of chlorobenzene, dichlorobenzene and finally trichlorobenzene. The successive replacement of hydrogen atoms in one of the methyl side chains of *p*-xylene by methoxy groups from the methanol solvent can be treated in the same way as the successive chlorination of benzene.

Since the exact values of k_1 , k_2 and k_3 are uncertain, and the concentration of the active species S* is also unknown, the treatment of the data will be limited to a knowledge of the ratios

of the rate constants, rather than their absolute values. This involves the assessment of the degree of conversion of reagent A, resulting in maximum yields of the required products B and C. In this approach, all concentrations are expressed as a ratio with respect to the initial concentration of A; in addition, this treatment will allow for the cancellation of the unknown concentration of S^* .

Referring to Fig. 1, one can determine the ratio k_2/k_1 from the ether (B) maximum. Since $d[B]/dt = k_1[A][S^*] - k_2[B][S^*]$, it follows that $k_2/k_1 = \alpha_2 = [A]/[B]$. Similarly the ratio k_3/k_1 can be obtained from the acetal (C) maximum. Since $k_2[B][S^*] = k_3[C][S^*]$, it follows that $k_3/k_1 = \alpha_3 = \alpha_2[B]/[C]$. It can be shown²⁴ that the ratio of [B] to the initial concentration of A, $[A_0]$, can be expressed as a function of γ , the fraction of A remaining at that time; this is given by Equation 11:

$$\frac{[B]}{[A_0]} = \frac{1}{\alpha_2 - 1}(\gamma - \gamma^{\alpha_2}) \quad (11)$$

Similarly, it can be shown that the ratio $[C]/[A_0]$ can be expressed in terms of γ , as shown in Equation 12:

$$\frac{[C]}{[A_0]} = \alpha_2 \left[\frac{\gamma}{(1 - \alpha_2)(1 - \alpha_3)} + \frac{\gamma^{\alpha_2}}{(\alpha_2 - 1)(\alpha_2 - \alpha_3)} + \frac{\gamma^{\alpha_3}}{(1 - \alpha_3)(\alpha_2 - \alpha_3)} \right] \quad (12)$$

The value of α_2 was calculated from the concentrations of A and B at the ether maximum and found to be 0.854, while α_3 was calculated from the concentrations of B and C at the acetal maximum and found to be 0.0337. The concentration ratio of $[A]/[A_0]$ was calculated from the data, while the ratios $[B]/[A_0]$ and $[C]/[A_0]$ were obtained using equations 11 and 12, respectively. These two ratios can be compared as a function of time with the observed ratios $[B]_{\text{obs}}/[A_0]$ and $[C]_{\text{obs}}/[A_0]$. Figure 3 displays the curves that were thus obtained.

It can be seen from Fig. 3 that the data for the anodic oxidation of *p*-xylene satisfy the kinetic model of parallel consecutive second order reactions: an excellent fit is obtained between the predicted and observed concentrations of the intermediate ether, B; also, the acetal curves match well. Unfortunately

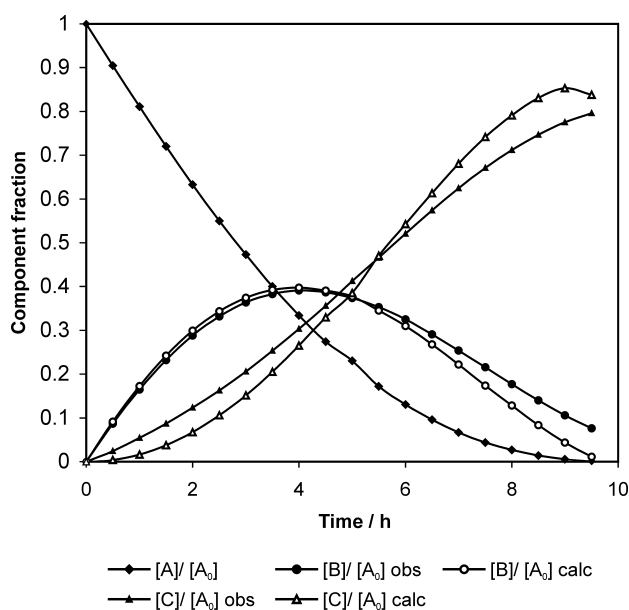


Figure 3 Calculated concentrations $[B]/[A_0]$ and $[C]/[A_0]$ and observed ratios $[A]/[A_0]$, $[B]/[A_0]$ and $[C]/[A_0]$ for the anodic oxidation of *p*-xylene (A).

the calculations cannot be extended to the later stages of the electrolysis, when the substrate has completely disappeared. Slight deviations of the calculated curves, especially towards the end of the electrolysis, must be due to the formation of unknowns, which causes a decrease in the sum of $A + B + C$ (see also Fig. 1).

4. Conclusion

It has been shown that the anodic oxidation of *p*-xylene using graphite electrodes, in methanol solutions containing tetraethylammonium *p*-toluene sulphonate as supporting electrolyte, conforms to parallel second order consecutive reactions. This illustrates the important role played by the solvent during the electrolysis: if neutral solvent molecules were to react with the substrate, the reaction would conform to pseudo-first order kinetics, since the methanol reagent is present in large excess. However, this has been shown not to be the case, and therefore the methanol reagent is partly oxidized at the anode to some active species, which then assists in the oxidation of the substrate.

Acknowledgements

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