Mechanistic and Kinetic Aspects of the Direct Electrochemical Oxidation of 4-*t*-Butyltoluene[1]

Peter Loyson*, Shawn Gouws and Ben Zeelie

*Department of Chemistry, Port Elizabeth Technikon, Private Bag X6011,
Port Elizabeth 6000, South Africa.*

ABSTRACT

The direct electrochemical oxidation of 4-*t*-butyltoluene at graphite electrodes in methanol, using NaClO$_4$ as electrolyte, has been investigated in order to obtain an insight into the mechanism and kinetics of the anodic reactions taking place. It is shown that an increase in current density affects the product distribution, leading to a better yield of the target product 4-*t*-butylbenzaldehyde dimethyl acetal and a lower percentage of unknowns at the expense of an increase in electrical charge. It is suggested that oxidation takes place by two mechanisms: a direct one involving oxidation of the substrate at the electrode, and an indirect one where a pool of solvent radicals assists in the oxidation process. Further evidence is provided for reaction mechanisms in studies where the substrate loading is varied, and also where the ratio of substrate to solvent is varied; when the concentration of the substrate is high, there is evidence of the formation of dimers and other unknowns. Under certain conditions, these anodic reactions can be regarded as parallel consecutive second order reactions. The role played by the solvent is confirmed by kinetic data.

KEYWORDS

4-*t*-butyltoluene, anodic oxidation, 4-t-butylbenzaldehyde dimethylacetal, reaction mechanism, parallel consecutive 2nd order kinetics.

1. Introduction

The product 4-*t*-butylbenzaldehyde is an important industrial intermediate in the production of fragrances[1,2] and agrochemicals.[3] Typical examples of products incorporating 4-*t*-butylbenzaldehyde include 4-*t*-butyl-benzaldehyde methylcinnamaldehyde, a component in many fragrance compositions[4,5] and 3-(4-*t*-butylphenyl)-2-methylpropylamines, a class of substances with fungicidal properties.[6,7] Electrochemically, 4-*t*-butylbenzaldehyde can be made from 4-*t*-butyltoluene using either direct anodic oxidation in methanol over graphite electrodes,[8–12] or indirectly using an inorganic mediator, such as Ce^{4+} or Mn^{3+}.[13–15] Indirect procedures, however, use strong acid solutions to dissolve the inorganic oxidant and generally lead to large electrolyte volumes containing sludges (in the case of Mn^{3+}), which need to be recycled for regeneration of the mediator and often lead to complicated product isolation and purification procedures. The direct electrochemical oxidation of 4-*t*-butyltoluene in methanol over graphite electrodes offers a number of advantages, such as easy product generation, good current efficiency, high yields and environmentally friendly procedures.[16,17]

The direct electrochemical oxidation of 4-*t*-butyltoluene in methanol at graphite electrodes produces 4-*t*-butylbenzaldehyde dimethyl acetal, which is readily converted into the target 4-*t*-butylbenzaldehyde by acid hydrolysis (Scheme 1). Electrolytes offering the best yields were found to be NaBF$_4$, NaClO$_4$ and H$_2$SO$_4$.[18] Previous work on experimental design by the authors[19] showed that two mechanisms were at play when NaClO$_4$ was used as electrolyte: one at low current density and the other at high current density. It was suggested that one

mechanism involved the direct oxidation of the substrate at the anode, while the other involved oxidation of the methanol solvent to form a pool of radicals, which would then eventually react with the substrate to form the product. This work will further investigate the mechanistic and kinetic aspects of the anodic oxidation of 4-*t*-butyltoluene in methanol at graphite electrodes using NaClO$_4$ as electrolyte.
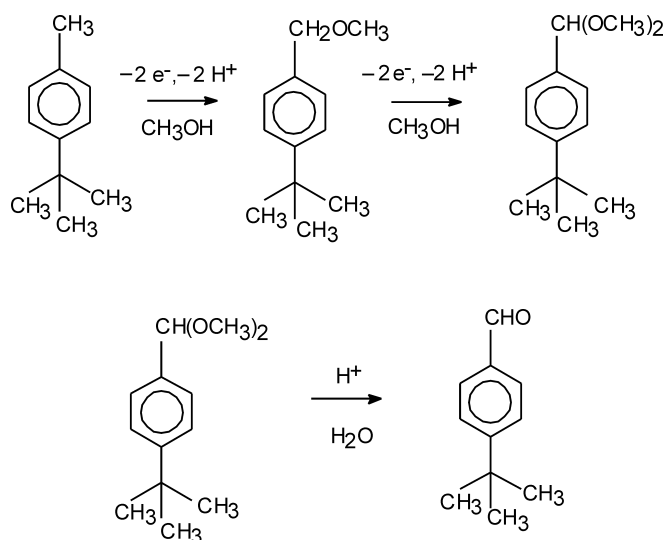
2. Experimental

2.1. Materials

Chemicals used in oxidation and analytical procedures were purchased from either Merck or Aldrich, and used as received. The intermediate, 4-*t*-butylbenzyl methyl ether, and 4-*t*-butylbenzaldehyde dimethyl acetal, were prepared as previously reported.[19]

2.2. Oxidation Procedures

Bench-scale oxidations were performed in the galvanostatic mode in an undivided glass cell (180 cm^3 in volume) equipped with an external heating/cooling jacket. The supporting electrolyte and substrate were weighed directly into the electrochemical cell and 150 cm^3 of methanol added. A magnetic stirrer was used to stir the contents of the cell during electrolysis and the reaction temperature was kept constant by circulating heating fluid, maintained at a constant temperature of 52 ± 0.5°C in a constant temperature bath, through the external heating/cooling jacket of the electrochemical cell. Two graphite electrodes (extruded carbon rods (>99% purity), 13 mm in diameter – Morganite Industry Carbon), positioned 1 mm apart in the centre of the cell, were used as cathode and anode. A QPS-103 Quatetron DC power supply was used to provide a constant

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* To whom correspondence should be addressed: E-mail: ployson@petech.ac.za

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Scheme 1

Figure 1 Anodic oxidation of 4-*t*-butyltoluene in methanol at low current density: relative percentage composition as a function of charge, using 2.9855 g TBT, 150 cm^3 methanol and 5.941 g NaClO$_4$, at 52°C with a current of 0.40 A (2.26 A dm^{-2}) and carbon electrodes (TBT = 4-*t*-butyltoluene, TBBME = 4-*t*-butylbenzyl methyl ether, TBBDMA = 4-*t*-butylbenzaldehyde dimethyl acetal, Sum = TBT + TBBME + TBBDMA).

current to the oxidation mixture.

In experiments where the substrate/solvent ratio was varied, the molar proportions of substrate and methanol were varied so as to cover values of 1:9, 2:8 and 3:7. When the substrate loading was investigated, increasing amounts of substrate were added to a constant volume of methanol. The current density was varied by changing the current flowing through the cell from 0.40 A (2.26 A dm^{-2}, low current density) to 1.00 A (5.66 A dm^{-2}, high current density).

Sample aliquots (0.50 cm^3) were removed from the electrochemical cell at regular intervals and diluted with 20 cm^3 of methanol, containing 1 cm^3 of 2-chlorotoluene as internal standard, and analysed by liquid chromatography as described below.

2.3. Analytical Procedures

High performance liquid chromatography analyses were performed on a Beckman System Gold HPLC system equipped with a programmable solvent module 126 and programmable detector module 166 fitted with an ultraviolet detector. Data were acquired from the detector by means of a Samsung personal computer equipped with the System Gold Data Acquisition software, Version 500. The instrumental conditions for the analysis of 4-*t*-butyltoluene and its electrochemical oxidation products were the same as reported previously.[19]

3. Results and Discussion

From the reactions shown in Scheme 1 it can be seen that 2 F of charge per mole is required to convert all 4-*t*-butyltoluene (TBT) to the intermediate ether, 4-*t*-butylbenzyl methyl ether (TBBME) and another 2 F of charge per mole is required for the further 2 electron step to 4-*t*-butylbenzaldehyde dimethyl acetal (TBBDMA). By monitoring the concentrations of the original TBT, the ether TBBME, and the dimethyl acetal TBBDMA as functions of the charge passed through the cell, one can evaluate the performance of the electrolysis. Furthermore, by plotting the sum of the amounts of TBT + TBBME + TBBDMA against the charge, it is possible to detect loss of material due to the formation of dimers, polymers and other unknowns.

In order to gain further insight into the mechanism of the anodic oxidation of 4-*t*-butyltoluene in methanol at graphite electrodes using NaClO$_4$ as electrolyte, a series of experiments was carried out on bench scale. Product distribution diagrams as a function of the charge per mole of substrate were obtained at a constant temperature of 52°C to investigate the following effects:
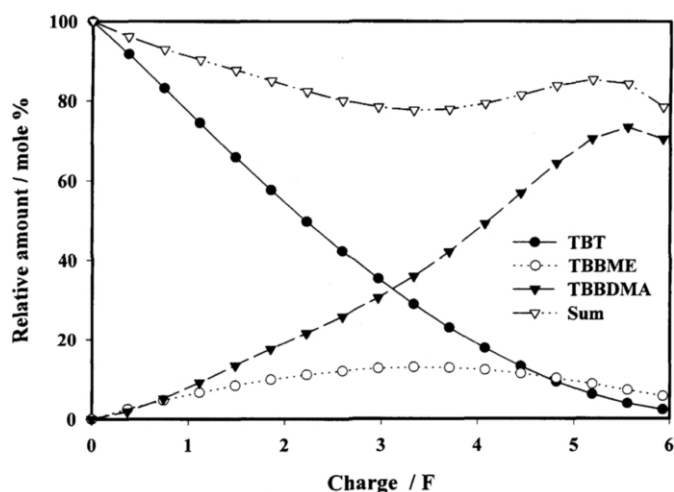
a) increase in current density,
b) increase in substrate loading, and
c) increase in substrate to solvent ratio.

3.1. Effect of Increasing Current Density

Figure 1 shows the distribution diagram for the anodic oxidation of 4-*t*-butyltoluene (4-TBT) using a current of 0.40 A (current density of 2.26 A dm^{-2}), while Fig. 2 displays the same results, but using a current of 1 A (current density of 5.66 A dm^{-2}), all other variables being the same as in Fig. 1. It is apparent that an increase in current density has a dramatic and beneficial effect on the oxidation of 4-TBT. In Fig. 2, the total amount remains 100% up to 6 F, while Fig. 1 shows loss of material from the start, giving a minimum in the total amount curve, indicating that some of the unknowns formed are been oxidized further to the target material.

Both figures show that some methanol solvent is also oxidized, since the acetal maxima obtained occur at a charge larger than
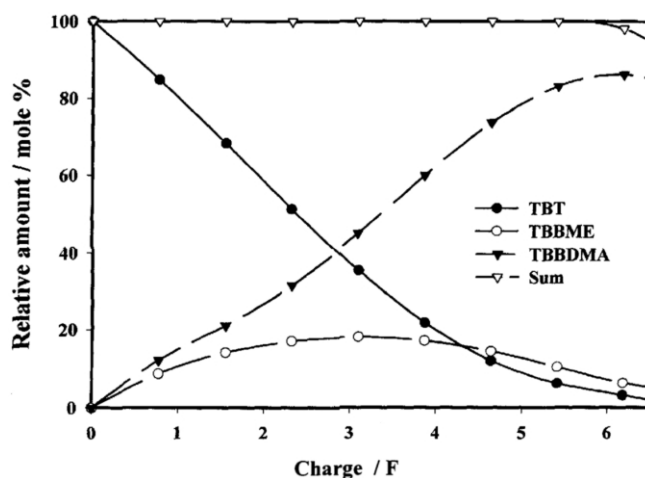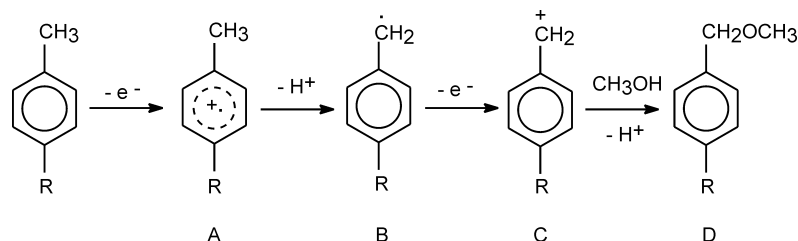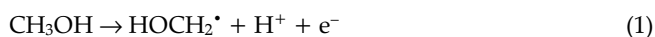

Figure 2 Anodic oxidation of 4-*t*-butyltoluene in methanol at low current density: relative percentage composition as a function of charge, using 2.9855 g TBT, 150 cm^3 methanol and 5.946 g NaClO$_4$, at 52°C with a current of 1.0 A (5.66 A dm^{-2}) and carbon electrodes (TBT = 4-*t*-butyltoluene, TBBME = 4-*t*-butylbenzyl methyl ether, TBBDMA = 4-*t*-butylbenzaldehyde dimethyl acetal, Sum = TBT + TBBME + TBBDMA).

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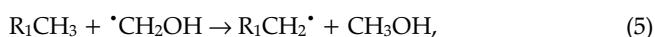<http://journals.sabinet.co.za/sajchem/>.

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Scheme 2

the theoretical value of 4 F. In Fig. 2 the acetal peaks at 6.4 F, while in Fig. 1 this maximum occurs at 5.5 F. In Fig. 2, therefore, more methanol is oxidized, due to the higher current density, than in Fig. 1. When methanol is oxidized with $NaClO_4$ as electrolyte, the following reactions take place[20]:

$$CH_3OH \rightarrow HOCH_2^{\bullet} + H^+ + e^- \qquad (1)$$

$$HOCH_2^{\bullet} \rightarrow HOCH_2^+ + e^- \qquad (2)$$

$$HOCH_2^+ + CH_3OH \rightarrow H_3COCH_2OH + H^+ \qquad (3)$$

$$H_3COCH_2OH + CH_3OH \rightarrow CH_2(OCH_3)_2 (X) + H_2O \qquad (4)$$

Ross, Finkelstein and Rudd[20] mention that 1,1-dimethoxy-methane (X) is the main product formed in the oxidation of methanol containing $NaClO_4$ as supporting electrolyte. Gas chromatographic analysis of electrolysis solutions in the authors' laboratory always showed the presence of this product.

The mechanism[21] of the direct electrochemical oxidation of alkyltoluenes at the anode is shown in Scheme 2 and proceeds 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), which in the absence of other nucleophiles undergoes nucleophilic attack by the solvent, CH_3OH, to form the respective benzyl methyl ether (D). The sequence of reactions is repeated finally to produce the respective benzaldehyde dimethyl acetal.

Interaction between the methanol-derived radicals and neutral substrate or ether molecules will take place[22] when the concentration of these radicals is high, thereby indirectly assisting in the oxidation of the substrate. Equations 5 and 6, where R_1 represents the 4-*t*-butylbenzene group, illustrate this action:

$$R_1CH_3 + {}^{\bullet}CH_2OH \rightarrow R_1CH_2^{\bullet} + CH_3OH, \qquad (5)$$

$$R_1CH_2OCH_3 + {}^{\bullet}CH_2OH > (R_1CHOCH_3)^{\bullet} + CH_3OH \qquad (6)$$

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 material. Equations 7 and 8 show two possible reactions:

$$R_1CH_2^{\bullet} + {}^{\bullet}CH_2R_1 \rightarrow R_1CH_2CH_2R_1 \qquad (7)$$

$$(R_1CHOCH_3)^{\bullet} + {}^{\bullet}CH_2R_1 \rightarrow R_1CH(CH_2R_1)OCH_3 \qquad (8)$$

Solvent oxidation forming 1,1-dimethoxymethane (equations

1–4) represents a loss in current efficiency and a consequent shifting of the acetal peak towards higher charge, while formation of dimers and other unknown side products will indicate a loss in material, together with a lower current efficiency.

Comparing Figs 1 and 2, a higher current density seems to generate a pool of methanol-derived radicals, which indirectly assists in the oxidation of the substrate, yielding a higher value of the dimethyl acetal (86% compared with 73% for Fig. 1) but at the same time resulting in a loss in current efficiency due to oxidation of the solvent, leading to a higher charge for the acetal maximum. A lower current density produces a lower concentration of methanol-derived radicals, which therefore forces the substrate to become oxidized directly at the anode. In this case, however, unknowns are formed due to dimerization of the substrate radicals; this effect increases until, at some point, the concentration of these dimers becomes large enough for some of them to be oxidized further to form either the intermediate ether or the acetal, thereby leading to the minimum in the total amount curve. Since there is an increase in the slope of the acetal curve corresponding to the minimum in the total amount curve in Fig. 1, the most probable dimer oxidized would originate from the dimerization of two $(R_1CHOCH_3)^{\bullet}$ units; oxidation of this dimer would result in the production of two dimethyl acetal molecules per molecule of dimer, causing an increase in the percentage of the acetal, superimposed on the usual production of the acetal. This is shown in the following sequence:

$$R_1CH(OCH_3)\text{-}CH(OCH_3)R_1 \rightarrow 2\,R_1CH(OCH_3)^+$$
$$\rightarrow 2R_1CH(OCH_3)_2 \qquad (9)$$
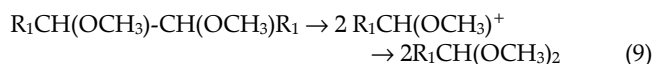
In summary, a high current density produces a better yield of TBBDMA with few or no unknowns, but at the expense of a higher charge compared with a lower current density; this can be attributed to the cooperation of methanol-derived radicals.

3.2. Effect of an Increase in Substrate Loading

Table 1 shows the data obtained from the distribution curves for the anodic oxidation of TBT using gradually increasing concentrations of substrate, under high current density conditions as used in Fig. 2, all other factors being constant.

The maximum % acetal obtained decreases with substrate loading. As the % substrate is increased, the acetal peak shifts to lower charge, indicating that less solvent is oxidized, due to the higher concentration of the substrate. The loss of material at the

Table 1 Data obtained for the anodic oxidation of TBT with an increase in substrate loading.

	2.0% TBT	4.0% TBT	10% TBT
Acetal maximum/%	85.6	84.4	71.5
Charge at acetal maximum/F	6.3	5.14	5.10
Current efficiency/%	53.5	65.6	56.7
Unknowns at acetal maximum/%	2.2	3.3	0
Ether left at acetal maximum/%	4.4	8.9	20
Ether maximum/%	18	18	29.3

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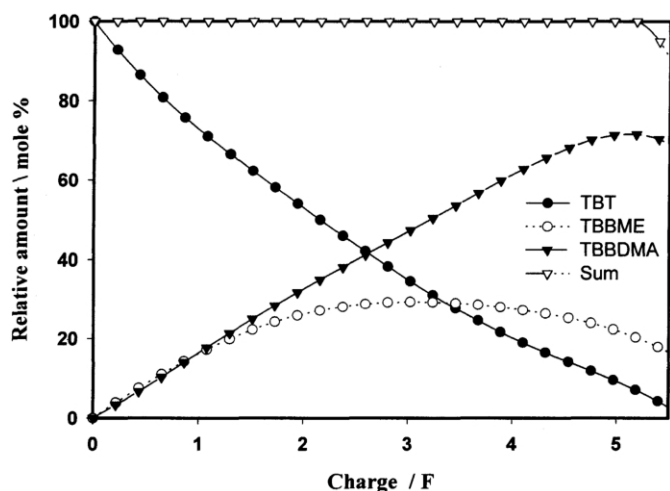<http://journals.sabinet.co.za/sajchem/>.

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Figure 3 Anodic oxidation of 4-*t*-butyltoluene in methanol using a substrate/solvent ratio of 1:9, relative percentage composition as a function of charge, using 12.808 g TBT, 135 cm³ methanol and 5.926 g NaClO$_4$, at 52°C with a current of 1.0 A (5.66 A dm^{-2}) and carbon electrodes (TBT = 4-*t*-butyltoluene, TBBME = 4-*t*-butylbenzyl methyl ether, TBBDMA = 4-*t*-butylbenzaldehyde dimethyl acetal, Sum = TBT + TBBME + TBBDMA).

Figure 4 Anodic oxidation of 4-*t*-butyltoluene in methanol using a substrate/solvent ratio of 2:8, relative percentage composition as a function of charge, using 25.839 g TBT, 128 cm³ methanol and 5.904 g NaClO$_4$, at 52°C with a current of 1.0 A (5.66 A dm^{-2}) and carbon electrodes (TBT = 4-*t*-butyltoluene, TBBME = 4-*t*-butylbenzyl methyl ether, TBBDMA = 4-*t*-butylbenzaldehyde dimethyl acetal, Sum = TBT + TBBME + TBBDMA).

acetal maximum is surprisingly low, especially in the case of 10% TBT, where one expects considerable dimerization to take place. This must indicate that the dimers produced are re-oxidized to a large extent to the target compounds; a minimum was again observed in the total amount curve for the 4% TBT oxidation.

The relative amount of ether left over at the acetal maximum increases with substrate loading, and is shown to be proportional to the initial concentration of TBT. This illustrates a retarding effect in the conversion step from the ether to the acetal; this is also shown by the sudden increase in the maximum relative amount of ether in going from 4% to 10% TBT. Presumably fewer solvent radicals are available to assist in the oxidation of the ether according to equation 6, since more and more substrate is oxidized directly at the electrode surface.

3.3. Effect of an Increase in Substrate to Solvent Ratio

Figures 3, 4 and 5 display the distribution diagrams obtained when the ratio of substrate to solvent is varied. In these experiments the molar ratio of substrate to solvent was varied from 1:9 (Fig. 3) to 2:8 (Fig. 4) and finally to 3:7 (Fig. 5), using high current density conditions (current of 1 A) and a constant electrolyte concentration.

As the substrate/solvent ratio is increased, the maximum % acetal increases from 71.5% at 5.1 F (Fig. 3), to 72.3% at 5.9 F (Fig. 4) and finally to 76.6% at 4.9 F in Fig. 5. It is noted that Fig. 3 gives no loss of material up to the acetal maximum, but both Figs 4 and 5 give 14% and 10% loss respectively at this point.

The data can be explained in terms of more direct oxidation of the substrate at the anode with increasing concentration. In Fig. 3 the concentration of methanol is still quite high to allow methanol-derived radicals to assist in indirect oxidation of the substrate, leading to no loss of material up to the acetal maximum. As the ratio is increased, however, there is a greater danger of producing unknowns, due to the formation of dimers and other side products, some of which get oxidized further to the target compound. The higher concentration of substrate will limit oxidation of the solvent. The most efficient system is the 3:7 case, giving a current efficiency of 63%, but with the co-production of 10% unknowns. By contrast the 1:9 system
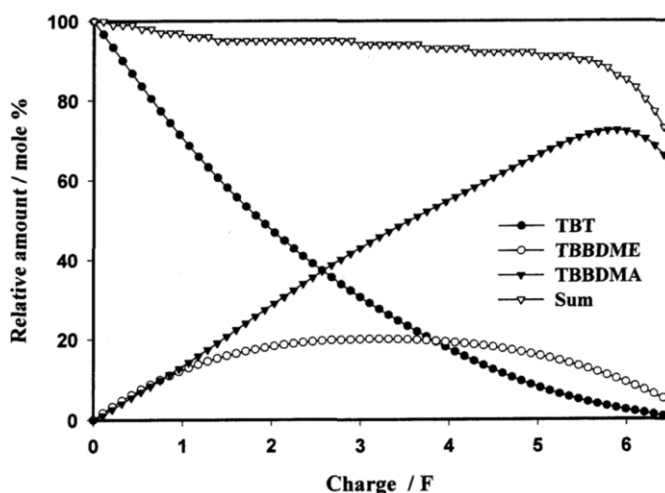
gives a cleaner oxidation, but with a current efficiency of only 57% at the acetal maximum.

In these experiments, it is noted that the maximum % ether decreases gradually as the amount of solvent present decreases. In this concentration range, the conversion of ether to acetal is facilitated, presumably due to more direct oxidation at the anode. There are three ways in which this conversion can take place:

a) directly at the anode, following the reaction scheme 2; this effect should increase with increasing substrate concentration,

b) indirectly due to reaction with solvent radicals, as shown in reaction 6; this effect will decrease in going from Figs 3 to 5, due to the lower concentration of solvent, and

c) due to the oxidation of ether-derived radical species, such as shown in equation 9; this effect will again increase from Figs 3 to 5, due to the higher substrate concentration.
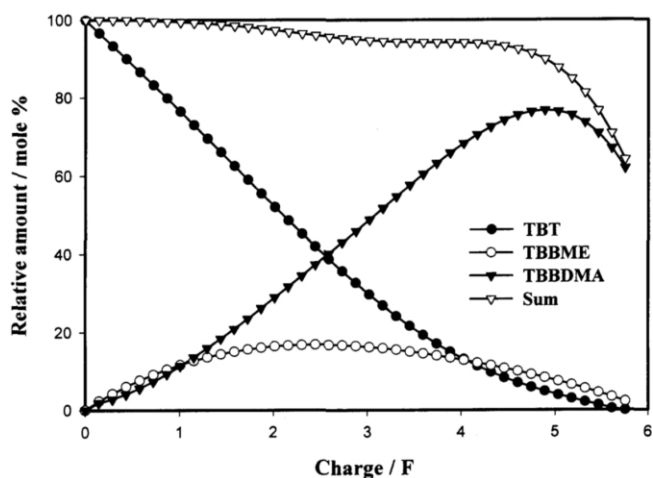

Figure 5 Anodic oxidation of 4-*t*-butyltoluene in methanol using a substrate/solvent ratio of 3:7, relative percentage composition as a function of charge, using 38.444 g TBT, 117 cm³ methanol and 5.182 g NaClO$_4$, at 52°C with a current of 1.0 A (5.66 A dm^{-2}) and carbon electrodes (TBT = 4-*t*-butyltoluene, TBBME = 4-*t*-butylbenzyl methyl ether, TBBDMA = 4-*t*-butylbenzaldehyde dimethyl acetal, Sum = TBT + TBBME + TBBDMA).

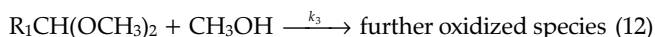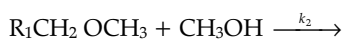**Table 2** Consecutive first order kinetic data for substrate to solvent ratio variation.
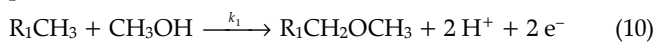
Substrate to solvent ratio	k_1/h^{-1}	k_2/h^{-1}	$t_{B\,max}/h$ (calc)	$t_{B\,max}/h$ (exp)	$B_{max}/\%$ (calc)	$B_{max}/\%$ (exp)
1:9	0.143	0.150	6.8	7.5	36	30
2:8	0.072	0.099	11.8	15.0	31	20
3:7	0.036	0.089	17.1	17.0	22	17

The combined effect of these three actions results in a gradually decreasing ether distribution profile as the substrate/solvent ratio is increased.

In summary, as the concentration of substrate increases at the expense of the solvent, direct substrate oxidation at the electrode leads to material loss.

4. Kinetic Aspects

The overall electrochemical conversion of TBT to the intermediate ether, and its subsequent further oxidation to the dimethyl acetal, TBBDMA, can be represented kinetically by equations 10 and 11, while the further oxidation of the acetal is represented by equation 12:

$$R_1CH_3 + CH_3OH \xrightarrow{k_1} R_1CH_2OCH_3 + 2\,H^+ + 2\,e^- \qquad (10)$$

$$R_1CH_2\,OCH_3 + CH_3OH \xrightarrow{k_2}$$

$$R_1CH(OCH_3)_2 + 2\,H^+ + 2\,e^- \qquad (11)$$

$$R_1CH(OCH_3)_2 + CH_3OH \xrightarrow{k_3} \text{ further oxidized species} \qquad (12)$$

The further oxidized species could be the trimethyl acetal $R_1C(OCH_3)_3$ and its decomposition products.[23] The presence of methanol-derived radicals will influence these reactions, as shown in equations 5 and 6.

The rate constants k_1, k_2 and k_3 will be related to the ease with which the particular compound is oxidized.[24] Previous work by the authors[18] has shown that the acetal obtained has a high oxidation potential compared with the toluene and the intermediate ether, and should therefore accumulate in the cell during electrolysis, as observed. The lower the oxidation potential, the higher will be the k value.

The conversion of the original toluene to the final acetal product can be regarded as a first order consecutive reaction: $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, where A, B and C represent the toluene, ether and acetal respectively. C can be considered to be sufficiently stable in the presence of A and B, due to its high oxidation potential.

It can be shown[25] that the following equations are valid for first order consecutive reactions:

$$\ln\frac{[A_0]}{[A]} = kt \qquad (13)$$

$$t_{B_{max}} = \frac{\ln(k_2/k_1)}{k_2 - k_1} \qquad (14)$$

$$\frac{[B_{max}]}{[A_0]} = \frac{k_1\left[\frac{k_2}{k_2-k_1}\right]}{k_2} \qquad (15)$$

In these equations $[A_0]$ = the initial concentration of A, while $[A]$ and $[B]$ represent the concentrations of A and B at time t; $t_{B\,max}$ = the time required for B to reach its maximum concentration, while $[B_{max}]$ = the maximum concentration of B.

The data obtained from the substrate/solvent ratio variation (Figs 3, 4 and 5) can now be tested for first order consecutive kinetics. The k_1 values are obtained from equation 13, by plotting the logarithm of the ratio $[A_0]/[A]$ versus time and determining the slope of the line. In all three cases it was found that straight lines were obtained for the early part of the electrolysis. As the substrate/solvent ratio increased, the linearity increased, from 2 hours of electrolysis time for 1:9 to 4 hours for 3:7. The k_2 values were obtained by determining $[A]$ and $[B]$ at the ether maximum, and using equation 16.

$$k_1\,[A] = k_2\,[B] \qquad (16)$$

Table 2 shows the calculated values of k_1, k_2, $t_{B\,max}$ and $[B_{max}]$ (expressed as a relative percentage of $[B]/[A_0]$); also shown are the experimentally determined values for $t_{B\,max}$ and $[B_{max}]$. In all three cases $k_1 < k_2$, suggesting that the toluene has a higher oxidation potential than the ether, as observed in previous work.[18] The k values decrease with an increase in substrate to solvent ratio, due to the increased amount of substrate used; t_{Bmax} values agree poorly, except for the ratio 3:7, while the % B_{max} values generally also agree poorly.

The above treatment, which assumes no side reactions, shows that the kinetics of the oxidation of TBT do not conform to first order consecutive reaction kinetics. Only in the early stages of the electrolysis, when the concentration of the substrate is high (especially in the 3:7 case), is there an indication of first order consecutive behaviour. The rate of the reaction will then depend on the rate at which the substrate can get to the electrode. As the ratio of the substrate to solvent decreases, however, the participation of the solvent becomes more important.

4.1. Parallel Consecutive Second Order Kinetics

The electrochemical conversion of TBT (A) to the intermediate ether (B), its further reaction to the acetal (C), and final decomposition to unknown products (D) under the influence of the solvent S can be regarded as three parallel consecutive reactions, which are each second order, as shown in equations 17 to 19:

$$A + S^* \xrightarrow{k_1} B \qquad (17)$$

$$B + S^* \xrightarrow{k_2} C \qquad (18)$$

$$C + S^* \xrightarrow{k_3} D \qquad (19)$$
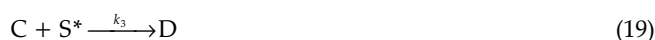
In these equations S* represents some active species of the solvent, such as $^\bullet CH_2OH$. This species would control the concentrations of A, B and C. Examples of parallel consecutive second order reactions of industrial importance include the reaction of benzene with chlorine to form, step-wise, monochlorobenzene, dichloro-benzene and finally trichlorobenzene.[26] The successive replacement of hydrogen atoms in the 4-*t*-butyltoluene molecule 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 unknown, and the concentration of the active species S* is also unknown, the treatment 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
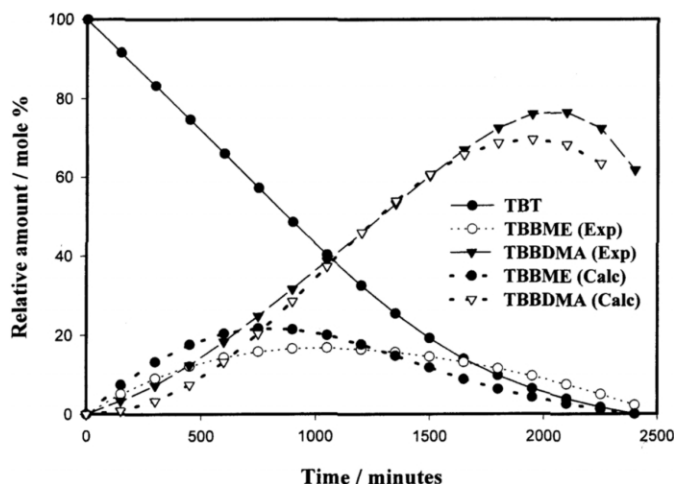
Figure 6 Parallel consecutive second order kinetics treatment for the anodic oxidation of 4-*t*-butyltoluene in methanol for the 3:7 substrate/solvent ratio: calculated and experimental values for the relative amounts (mol%) of TBBME and TBBDMA as functions of the disappearance of substrate TBT with time. Experimental conditions the same as for Fig. 5 (TBT = 4-*t*-butyltoluene, TBBME = 4-*t*-butylbenzyl methyl ether, TBBDMA = 4-*t*-butylbenzaldehyde dimethyl acetal, Sum = TBT + TBBME + TBBDMA).

Figure 7 Parallel consecutive second order kinetics treatment for the anodic oxidation of 4-*t*-butyltoluene in methanol for the 1:9 substrate/solvent ratio: calculated and experimental values for the relative amounts (mol%) of TBBME and TBBDMA as functions of the disappearance of substrate TBT with time. Experimental conditions the same as for Fig. 3 (TBT = 4-*t*-butyltoluene, TBBME = 4-*t*-butylbenzyl methyl ether, TBBDMA = 4-*t*-butylbenzaldehyde dimethyl acetal, Sum = TBT + TBBME + TBBDMA).

approach all concentrations are expressed as a ratio with respect to the initial concentration of reagent A, and the time variable can be eliminated by taking ratios of concentrations. In addition, this treatment will allow for the cancellation of the unknown concentration of S*.

Referring to the distribution diagrams dealing with varying substrate/solvent ratios, 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 shown[27] 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; this is given by equation 20:

$$\frac{[B]}{[A_0]} = \frac{1}{\alpha_2 - 1}(\gamma - \gamma^{\alpha_2}) \qquad (20)$$

Similarly it can be shown that the ratio $[C]/[A_0]$ can be expressed in terms of γ, as shown by equation 21:

$$\frac{[C]}{[A_0]} = \alpha_2\left[\frac{\gamma}{(1-\alpha_2)(1-\alpha_3)} + \frac{\gamma^{\alpha_2}}{(\alpha_2-1)(\alpha_2-\alpha_3)} + \frac{\gamma^{\alpha_3}}{(1-\alpha_3)(\alpha_2-\alpha_3)}\right] \quad (21)$$

Using these equations one can calculate the theoretical ratios of $[B]/[A_0]$ and $[C]/[A_0]$ as functions of γ, and compare these with the experimentally obtained values. Instead of plotting these values against γ, one can also determine γ experimentally as a function of time, and hence plot the calculated ratios against time. Figs 6 and 7 show these plots for the 3:7 and 1:9 substrate/solvent ratios respectively and also show the experimentally obtained curves. The behaviour of the 2:8 system lies between those of the other two systems.

The following observations can be made for the 3:7 ratio experiment: there is generally good agreement between the calculated and experimental curves for both the ether and acetal;
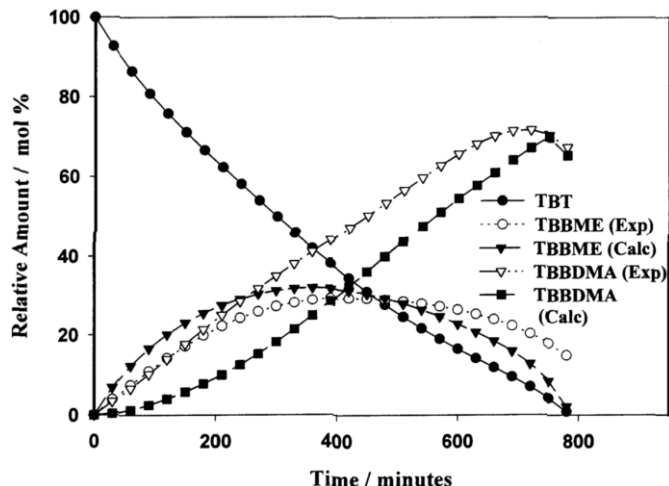
the small deviations could be attributed to side reactions leading to a loss of material and interactions between methanol radicals, the formation of which is not taken into account in this theoretical treatment. For the 1:9 case, however, the ether curves match well, but the acetal curves compare poorly; the experimental acetal values are considerably higher than the calculated ones, indicating that the ether to acetal step takes place more readily than expected, hinting at increased solvent interaction with the ether due to the higher solvent concentration.

This treatment therefore shows evidence that solvent interaction with the substrate plays a vital role in the oxidation. The 3:7 case conforms best to parallel consecutive second order kinetics. As the concentration of the methanol is increased, however, large deviations, especially in the ether to acetal step, are apparent, indicating that the interaction between solvent species and substrate during the oxidation is more complex.

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