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Article

The Galvanostatic Oxidation of Aldehydes to Acids on Ti/$Ru_{0.3}Ti_{0.7}O_2$ Electrodes Using a Filter-press Cell

Geoffroy R. P. Malpass and Artur J. Motheo*

Instituto de Química de São Carlos Universidade de São Paulo, CP 780, 13560-970 São Carlos - SP, Brazil

Os resultados da oxidação galvanostática de formaldeído, acetaldeído, propionaldeído e *n*-butiraldeído sobre eletrodos do tipo Ti/$Ru_{0,3}Ti_{0,7}O_2$ DSA® em H_2SO_4 0,5 mol dm^{-3}, utilizando uma célula do tipo filtro-prensa, são apresentados. Os produtos observados são os respectivos ácidos carboxílicos e CO_2. Para o formaldeído a presença adicional de CO_3^{2-} é detectada. O balanço da quantidade total de carbono decai com o tempo de eletrólise devido a liberação parcial do aldeído na forma de um gás. A liberação parcial dos gases aumenta com o comprimento da cadeia alifática e assim, a conversão de reagentes em produtos diminui. Desta forma, a eficiência do processo de eletro-oxidação diminui.

Results for the galvanostatic oxidation of formaldehyde, acetaldehyde, propionaldehyde and *n*-butyraldehyde in 0.5 mol dm^{-3} H_2SO_4 at Ti/$Ru_{0.3}Ti_{0.7}O_2$ DSA® type electrodes, using a filter-press cell, are presented. The observed products are the respective carboxylic acids and CO_2. In the case of formaldehyde the additional presence of CO_3^{2-} is detected as a product. The carbon balance is observed to decrease with electrolysis time due to the partial liberation of the aldehyde in solution as a gas. The partial liberation of aldehyde gases increases with chain length and in this way the conversion of reactants to products decreases, as does the efficiency of the electro-oxidation process.

Keywords: Dimensionally Stable Anodes, mixed Ti-Ru oxides, electrochemical oxidation, aldehydes

Introduction

Aldehydes are important industrial materials being used in a variety of applications and because of this are widely found in industrial waste discharges. As aldehydes are highly reactive chemicals and tend to polymerise in the presence of acids such as H_2SO_4 some are maintained in the presence of stabilisers.[1] This is the case for commercial formaldehyde, which is generally marketed as a 37% solution containing 8 – 15% methanol as a stabiliser.[2] The study of the electrooxidation of the lower molecular mass aldehydes can be seen to be important: formaldehyde and acetaldehyde are important intermediates in fuel-cell processes and the chemical oxidation of propionaldehyde to propionic acid is the subject of patents.[3]

In aqueous solutions aldehydes form a hydrate known as the "gem-diol" ($RC(OH)_2$).[4] Electrochemical studies of aldehydes by Sibille *et al.*[5] on Pt and Au and Fleury *et al.*[6] on Hg electrodes suggest that the electro-active species is the "gem-ol-olate" ion ($RC(OH)O^-$). A mechanism suggesting the direct oxidation of aldehydes by the elevated oxidation states of Pt was presented by Ristc *et al.*[7] to explain the observed low oxide coverage on platinum.

DSA® electrodes are promising materials for many electro-organic applications and have been classified as "active" or "non-active" depending on the electrode material.[8,9] "Active" electrodes mediate the oxidation of an organic species *via* the formation of higher oxides of the metal, (MO_{x+1}), where there is a higher oxidation state available (*e.g.* RuO_2 or IrO_2). This leads to selective oxidation. "Non-active" electrodes present no available higher oxidation state and the organic species is directly oxidized by an adsorbed hydroxyl radical – giving complete combustion (*e.g.* SnO_2 or PbO_2). In a recent paper we reported the study of the oxidation of formaldehyde at Ti/$Ru_{0.3}Ti_{0.7}O_2$ electrodes in filter-press cell and considered both the active and non-active nature of the electrode material.[10] The use of a filter-press cell enables the simulation of an industrial process on a laboratory scale, be it with a view to electro-synthesis or effluent treatment.

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* e-mail: artur@iqsc.sc.usp.br

In this way, the comparative study of the electrochemical oxidation of formaldehyde, acetaldehyde, propionaldehyde and butyraldehyde in acidic medium at a $Ti/Ru_{0.3}Ti_{0.7}O_2$ electrode is presented with the dual aim of simulating a prospective industrial treatment process and gaining understanding of the mechanistic processes involved.

Experimental

Cell

A two-compartment filter-press cell was used with a $Ti/Ru_{0.3}Ti_{0.7}O_2$ DSA® anode (nominal area, 14 cm^2) and a stainless steel plate cathode (area 14 cm^2) and mounted using Viton® and Teflon® spacers of varying thickness, as described elsewhere.[11] Anodic and cathodic compartments were separated by an ion exchange membrane (IONAC AM 3470). The anolyte (0.5 mol dm^{-3} H_2SO_4 containing the aldehyde to be studied) and catholyte (0.5 mol dm^{-3} H_2SO_4) were pumped, from two separate electrolyte reservoirs, through the cell by a peristaltic pump at 100 rpm (32 cm^3 min^{-1}).

Electrodes

$Ti/Ru_{0.3}Ti_{0.7}O_2$ electrodes were prepared in the laboratory by the standard technique of thermal decomposition of precursor salts ($RuCl_3.nH_2O$ and $TiCl_4$) at 400 °C under a flux of oxygen (5 cm^3 min^{-1}), as described elsewhere.[12] After each addition of chloride precursors the electrode was calcinated for ten min. When the desired mass was achieved the electrode was calcinated for a further hour.

Reagents

Acetaldehyde (CH_3CHO >99%) and propionaldehyde (CH_3CH_2CHO >98%) were obtained from Merck and used without further purification. The other reagents formaldehyde (H_2CO 37% solution with 12.5% methanol), sulphuric acid (H_2SO_4 98%), barium hydroxide ($Ba(OH)_2.8H_2O$ 98.9%), barium chloride ($BaCl_2.2H_2O$ 99%), formic acid (HCOOH 94.8%), acetic acid (CH_3COOH 100%) and propionic acid (CH_3CH_2COOH 100%) were obtained from Mallinckrodt and also used without further purification.

Electrolyses

All electrolyses were carried out at a constant current density of 40 mA cm^{-2} under conditions of simultaneous oxygen evolution, as described elsewhere.[10,11] The electrolyses were performed in 0.5 mol mol dm^{-3} H_2SO_4 using a stabilised current power source (Tectrol font – TC 20-05). The gases liberated passed through two traps (250 cm^3 each) containing $Ba(OH)_2$. The reaction of CO_2 with $Ba(OH)_2$ leads to the formation of insoluble $Ba(CO_3)$. The consumption of $Ba(OH)_2$ in this reaction results in a pH change in the solution. This pH change was used to calculate the amount of CO_2 liberated.

Two concentrations, 0.10 and 0.01 mol dm^{-3} were studied for each aldehyde with the exception of *n*-butyraldehyde which is insoluble at a concentration of 0.10 mol dm^{-3}. Because of this *n*-butyraldehyde was only studied at 0.01 mol dm^{-3}.

Values for instantaneous current efficiency (ICE) and the initial electrochemical oxidation index (EOI_i) were obtained by the oxygen flow-rate method.[13]

Analysis

Analyses of the reaction products were performed using HPLC (Shimadzu LC-10AD VP) with an ion exchange column (HPX-87H, Bio-Rad). The eluent was 3.33 mmol dm^{-3} H_2SO_4. The electrolysis products were identified using an ultraviolet detector (SPD-10A VP) at $\lambda = 210$ nm in conjunction with a refractive index detector (RID-10A). The products were identified by comparing their retention times with retention times obtained for pure reference materials under the same operating conditions.

Results and Discussion

The detected products of the galvanostatic oxidation of C1, C2, C3 and C4 aldehydes at $Ti/Ru_{0.3}Ti_{0.7}O_2$ anodes were the respective carboxylic acids and CO_2. Figure 1 shows typical time-concentration profiles for the electrolysis of propionaldehyde and the simultaneous formation of propionic acid.

Carbon balance

In Figure 2 it is possible to observe that the overall yield (carbon balance) decreases with electrolysis time and this effect becomes more pronounced with increasing chain length. This apparent decrease can be explained when considering the behaviour of aldehydes in aqueous solutions. In aqueous solutions formaldehyde is present at 100% in the hydrated form, the "gem-diol" ($R(OH)_2$),[4] whereas acetaldehyde is present at approximately 58% in the hydrated form ($CH_3C(OH)_2$). The remaining

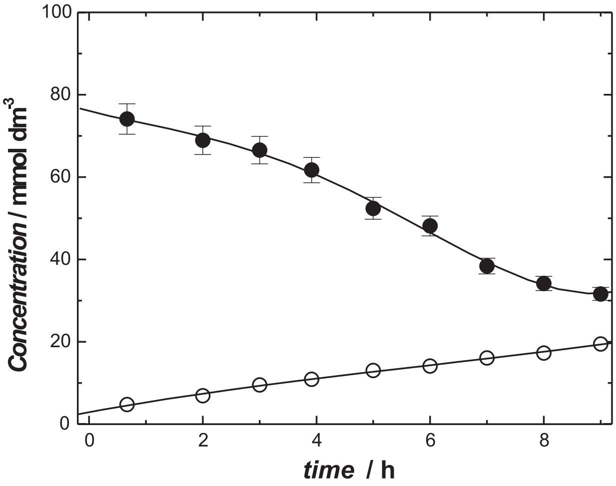

Figure 1. Dependence of the concentration of reactants with the electrolysis time for the oxidation of 0.1 mol dm^{-3} propionaldehyde in 0.5 mol dm^{-3} H_2SO_4 at 40 mA cm^{-2}; (●) propionaldehyde and (○) propionic acid.

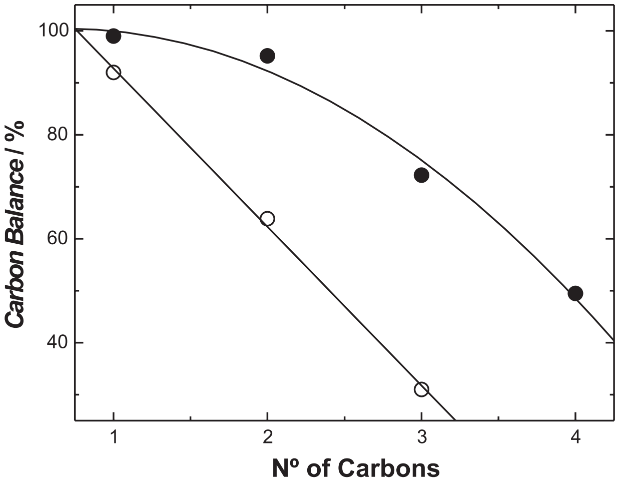

Figure 2. Dependence of the carbon balance with the length of the aliphatic chain during the electrolysis of aldehydes in 0.5 mol dm^{-3} H_2SO_4 at 40 mA cm^{-2}; (●) 0.10 mol dm^{-3} and (○) 0.01 mol dm^{-3}.

acetaldehyde is present in the form of a true solution of monomeric acetaldehyde gas (CH_3CHO). Propionaldehyde and *n*-butyraldehyde exist in solution in equal amounts of hydrated and non-hydrated aldehyde.[4] In non-polar solvents formaldehyde exists only in the non-hydrated form, which is liberated from solution when left to stand. In this way it is reasonable to assume that the acetaldehyde, propionaldehyde and *n*-butyraldehyde present as gases in solution are partially liberated during the experiment. As the electrolyses were performed under conditions of simultaneous oxygen evolution, the removal of aldehyde would be increased by the evolution of oxygen at the electrode surface. To verify this proposal a solution of 0.10 mol dm^{-3} acetaldehyde was subjected to a flow of N_2 over a period of 7 h, during which time the concentration was monitored. Figure 3 shows the variation of the concentration of acetaldehyde, under a flow of N_2, with time. From Figure 3 it can be seen that the acetaldehyde concentration decreases rapidly with time.

Another possible reason for the decrease in the carbon balance could be the formation of a cyclic trimer, which was not quantified in this study and therefore does not form part of the calculation of the overall carbon balance. The formation of the trimer is catalysed in the presence of acids such as H_2SO_4. However, as can be seen from Figure 3, when a solution of 0.10 mol dm^{-3} acetaldehyde in 0.5 mol dm^{-3} H_2SO_4 was left to stand for 7 h the concentration was not observed to vary significantly. Small quantities of trimer were observed by HPLC for both of the solutions presented in Figure 3. Although the pH of the solution is decreased by the production of H^+ at the anode during the processes leading to the oxygen evolution reaction, the reaction mixture employed in this study was already at pH ≈ 0.30. By calculating the quantity of H^+ produced during electrolysis, the *maximum* pH change (considering the absence of organic interaction at the electrode surface) is to take the bulk pH to –0.1 (9 h). However, when considering the average Instantaneous Current Efficiency (ICE) over the electrolysis time the maximum effect is to take the pH to –0.01 (9 h). For electrolysis of 0.01 mol dm^{-3} aldehyde the calculated pH falls from 0.30 to about 0.09 (4 h) in all cases.

The local pH at the electrode surface may vary significantly from the bulk pH. This elevated pH would promote the trimerisation of the aldehyde at the electrode surface. However, at this point the authors believe that the use of a flow system, constantly refreshing the surface

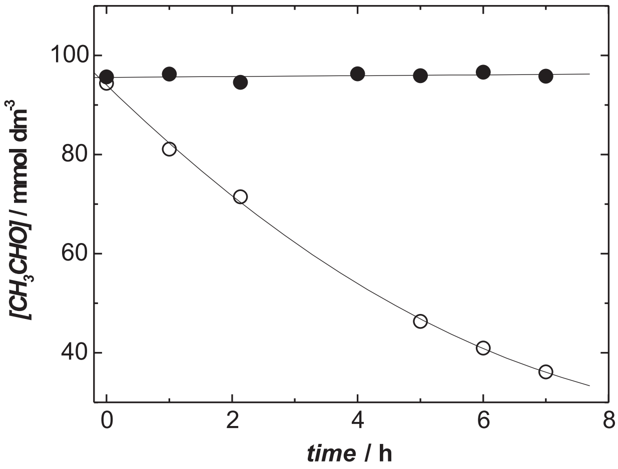

Figure 3. Variation of concentration of 0.10 mol dm^{-3} acetaldehyde in 0.5 mol dm^{-3} H_2SO_4; (○) under N_2 flux and (●) standing solution.

electrolyte, would reduce this effect, though not remove it completely. The quantity of trimer observed during the electrolysis did not vary greatly from those seen for the solutions in Figure 3.

The above observations would support the hypothesis that acetaldehyde is partially removed from solution by the oxygen gas evolved at the anode. The same effect is seen for propionaldehyde and *n*-butyraldehyde. This is supported by the fact that aldehyde solubility decreases with chain length and that less of the hydrated form is present. This is shown clearly during the oxidation of 0.01mol dm^{-3} aldehydes, where a decrease in the carbon balance as a function of chain length is seen, but similar calculated pH values are obtained. This would explain the behaviour seen in Figure 2.

Products

As stated the principal products of the oxidation of C1, C2, C3 and C4 aldehydes are the respective carboxylic acids and CO_2. Carboxylic acids are known to be resistant towards chemical or electrochemical oxidation. The carboxylic acids studied here displayed no activity towards oxidation at the $Ti/Ru_{0.3}Ti_{0.7}O_2$ anode with the exception of formic acid which was observed to oxidize to CO_3^{2-}.[10,14]

Because of the tendency of the aldehydes studied to evolve from solution, the rate of carboxylic acid formation can be considered a true indicator of the reaction of the aldehyde at the electrode surface. From Figure 4 it is possible to see that the observed conversion rates of the aldehydes to carboxylic acids are affected by the number of carbons in the aliphatic chain, *i.e.* the greater the chain length, the lower the carboxylic acid yield. Normalisation of the rate constants with respect to the real hydrate concentration results in a similar dependence on chain length to that seen for the unnormalised constants. The observed and normalized rates of formation of the respective carboxylic acids (mmol s^{-1}) are shown in Table 1.

It can be seen that the rate of carboxylic acid formation falls with chain length. This observation can be attributed to the fact that acetaldehyde is present in the gem-diol (hydrated) form at only 58%, whereas formaldehyde is present at ~100%. Given the fact that solutions of acetaldehyde, propionaldehyde and *n*-butyraldehyde have been shown to liberate aldehyde gas, it is probable that the species reacting to give the respective carboxylic acids is the gem-diol or some species of that type. This would be in agreement with Sibille *et al.*[5] and Fleury *et al.*[6] where the gem-o-late ($R-CH(O^-)OH$) anion is suggested as the electro-active species. In this way, the lower quantity of the gem-diol in solution would mean less electro-active species to

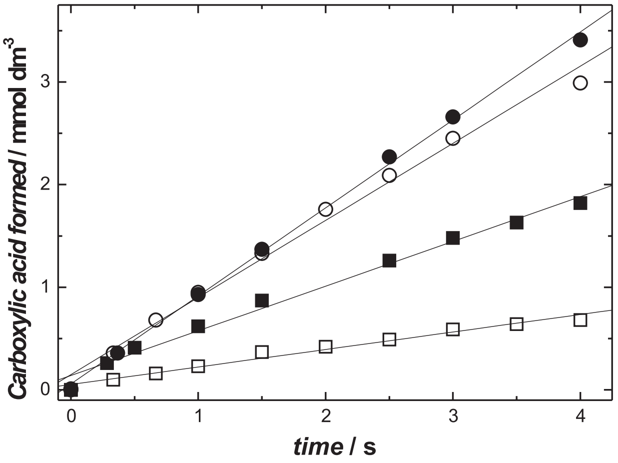

Figure 4. Dependence of formation of carboxylic acids with electrolysis time for the oxidation of 0.01 mol dm^{-3} aldehydes in 0.5 mol dm^{-3} H_2SO_4 at 40 mA cm^{-2}; (●) formic acid, (○) acetic acid, (■) propionic acid and (□) butyric acid.

Table 1. Values for the rate of formation of R-COOH, production of CO_2, carbon balance and initial EOI[b] determined for the electrolysis at a $Ti/Ru_{0.3}Tiu_{0.7}O_2$ electrode of C1, C2, C3 and C4 aldehydes

	Rate of carboxylic acid formation (mmol dm^{-3} s^{-1})		CO_2 produced (mmol dm^{-3} s^{-1})		CO_2 produced (%)		Carbon Balance (%)		Initial EOI[b]	
	0.01 mol dm^{-3}	0.10 mol dm^{-3}	0.01 mol dm^{-3}	0.10 mol dm^{-3}	0.01 mol dm^{-3}	0.10 mol dm^{-3}	0.01 mol dm^{-3}	0.10 mol dm^{-3}	0.01 mol dm^{-3}	0.10 mol dm^{-3}
Formaldehyde	-	-	1.25	3.95	9.50	2.70	99	92	0.06	0.72
Acetaldehyde	$(2.25 \times 10^{-4})^a$	$(8.10 \times 10^{-4})^{a,b}$	1.00	1.19	5.36 $(7.30)^b$	0.64 $(0.87)^b$	95	64	0.14	0.75
	$(3.06 \times 10^{-4})^b$	(11.00×10^{-4})								
Propionaldehyde	$(1.34 \times 10^{-4})^a$	$(4.90 \times 10^{-4})^a$	0.04	0.13	0.14	0.05	72	31	0.11	0.74
	$(2.13 \times 10^{-4})^b$	$(7.64 \times 10^{-4})^b$			$(0.22)^b$	$(0.08)^b$				
n-Butyraldehyde	$(0.55 \times 10^{-4})^a$	-	0.05	-	0.18	-	50	-	0.28	-
	$(1.18 \times 10^{-4})^b$				$(0.39)^b$					

[a] observed rate constant;

[b] normalised with respect to the real concentration and hydrate percentage.

react at the electrode surface. It is also apparent that stereochemical factors influence the reaction, *i.e.* the rate of carboxylic acid formation is much slower for *n*-butyraldehyde than for propionaldehyde in spite of the fact that both have similar quantities of the gem-diol in solution.

The same tendency can be seen in the production of CO_2, (Table 1). In Figure 5 the different quantities of CO_2 produced for the various aldehydes are presented. It is apparent that the quantity of CO_2 produced falls markedly with increase in the number of carbons in the aliphatic chain; this is represented in terms of the overall percentage (carbon balance) of CO_2 in Table 1. In Figure 5 the apparent existence of a plateaux is due to the method of determination (on-line pH analysis – please see experimental section). For high concentrations the result is a smooth curve.[10] However, the sensitivity of the process is dependent on the pH of the $Ba(OH)_2$ trap and the quantity of CO_2 produced. At the lower concentrations involved here the quantity of CO_2 produced tends to "leap" from one point to the next, when the quantity of $BaCO_3$ formed is sufficient to result in a change in the pH.

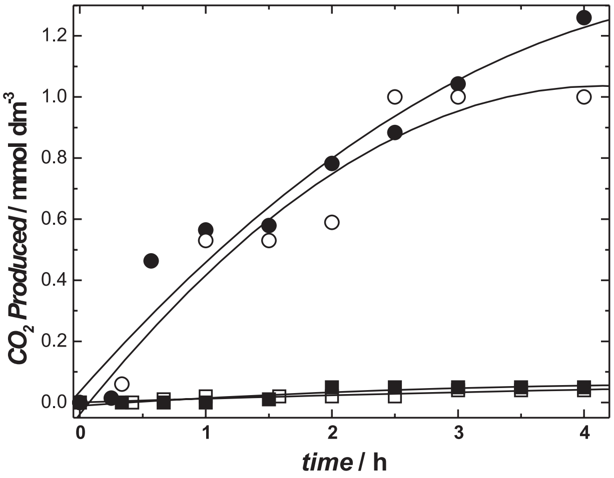

Figure 5. Production of CO_2 during the electrolysis of 0.01 mol dm^{-3} aldehydes in 0.5 mol dm^{-3} H_2SO_4 at 40 mA cm^{-2}; (●) formaldehyde, (○) acetaldehyde, (■) propionaldehyde and (□) *n*-butyraldehyde.

The effect of lower aldehyde concentrations is shown by the production of larger percentages of CO_2. In Table 1 it is possible to see that at 0.01 mol dm^{-3} aldehyde the amount of CO_2 produced, as a percentage of the total organic content, is greatly increased. All the aldehydes studied (with exception of *n*-butyraldehyde) demonstrate the same tendency. For electrolysis of 0.01 mol dm^{-3} acetaldehyde the quantity of CO_2 produced is 5.36% compared to 0.64% at 0.10 mol dm^{-3}. Burke and Murphy suggested that the oxidation of methanol on RuO_2 occurs via the formation of OH_{ads} on the electrode surface, equations 1 to 2:[15]

$$H_2O \rightarrow OH_{ads} + H^+ + e^- \quad (1)$$
$$CH_3COH + OH_{ads} \rightarrow HCHO + H_3O^+ + e^- \quad (2)$$

The HCHO produced and its oxidation products can then be oxidised in the same way, equations 3 to 4:

$$HCHO + OH_{ads} \rightarrow HCOOH + H^+ + e^- \quad (3)$$
$$HCOOH + OH_{ads} \rightarrow CO_2 + H_3O^+ + e^- \quad (4)$$

Burke and Murphy observed that the CO_2 yield decreased with increasing CH_3OH concentration and suggested that this was due to the presence of CH_3OH displacing the reaction products in equations in 3 and 4. Similar observations were made during the oxidation of formaldehyde *i.e.* the greater the quantity of formaldehyde, the lesser the quantity of CO_2 produced.[10]

Instantaneous current efficiency (ICE)

The current efficiency of the oxidation of the aldehydes used in this study can be estimated using the "instantaneous current efficiency" (ICE).[13] In this study the instantaneous current efficiency (ICE) was determined by the oxygen flow rate method, where the oxygen flow rate in the absence of the organic to be oxidized and in its presence are measured and compared, according to equation 5:[13]

$$ICE = \frac{V_0 - V_t}{V_0} \quad (5)$$

where V_o is the flow-rate of O_2 (cm^3 min^{-1}) measured in the absence of the organic and V_t (cm^3 min^{-1}) in the presence of the organic. The average current efficiency over the electrolysis can be described as the "electrochemical oxidation index" (EOI):

$$EOI = \frac{\int_0^\tau (ICE)dt}{\tau} \quad (6)$$

where t is the electrolysis time when the ICE is almost zero (*i.e.* $V_0 \approx V_t$). During the early stages of the electrolysis the value of the ICE can be described as the "initial EOI" (*i.e.* ICE ~ EOI).[10,16]

In Table 1 the values of the initial EOI for the respective aldehydes are shown. The values have been normalised with respect to the real hydrate concentration. In Figure 6 is presented the effect of normalizing the initial EOI for 0.10 mol dm^{-3} aldehyde. It is apparent that the normalised value is constant whereas the observed value is seen to fall linearly with chain length. For the lower concentration an increase in the normalized initial EOI is observed with chain length. The readings presented for 0.10 mol dm^{-3} aldehyde suggest that the extent of the inhibition of the production of O_2 is proportional to the hydrate content at higher concentrations, whereas at lower concentrations an effect of the “bulk” organic content is seen.

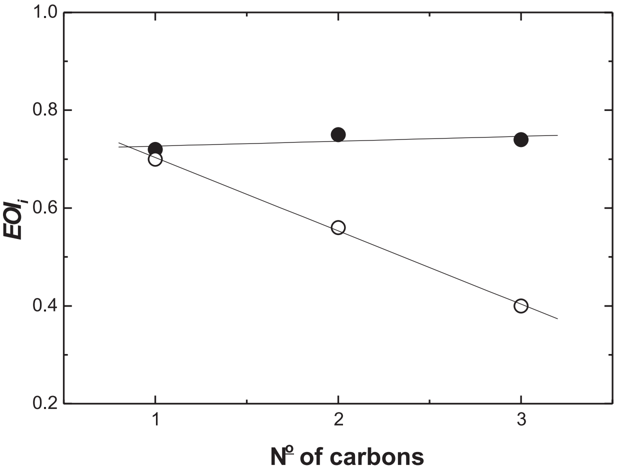

Figure 6. Dependence of the initial EOI with the length of the aliphatic chain during the electrolysis of 0.10 aldehydes in 0.5 mol dm^{-3} H_2SO_4 at 40 mA cm^{-2}; (●) normalised and (○) observed.

Conclusions

The electrochemical oxidation of formaldehyde, acetaldehyde, propionaldehyde and *n*-butyraldehyde at $Ti/Ru_{0.3}Ti_{0.7}O_2$ anodes using a filter-press cell has been presented. The results obtained indicate the following: *i*) The oxidation of straight chain, aliphatic aldehydes occurs via the hydrated species, the gem-diol. The rates of conversion to the respective carboxylic acids and the quantity of CO_2 produced are both directly affected by the quantity of gem-diol present in solution. In this way, formaldehyde presents the highest carboxylic yield and *n*-butyraldehyde the lowest. The quantity of CO_2 formed is also seen to be dependent on the quantity of gem-diol present. Stereo-chemical factors also influence the rate of formation of the products; *ii*) A decrease in the carbon balance is observed for acetaldehyde, propionaldehyde and *n*-butyraldehyde. This can be attributed to the liberation of the non-hydrated aldehyde, present in the form of a gas; *iii*) The efficiency of aldehyde oxidation at $Ti/Ru_{0.3}Ti_{0.7}O_2$ anodes decreases with the number of carbons in the aliphatic chain. This results in lower carboxylic acid yields. This fact, when compared with chemical methods, would appear to make the use of $i/Ru_{0.3}Ti_{0.7}O_2$ anodes unattractive for industrial synthesis purposes; *iv*) The carboxylic acids studied (with exception of HCOOH) are observed to be inactive on $Ti/Ru_{0.3}Ti_{0.7}O_2$ anodes. This suggests that caution should be taken when considering waste treatment of molecules that contain carbonyl and carboxylic functional groups using this anode.

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