

UNDERSTANDING THE ORIGIN AND MECHANISM OF HYDROGEN PRODUCTION IN THE BAYER PROCESS

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Abstract

Hydrogen production in Bayer process digestion is known to result from the reactions with sodium hydroxide of organic compounds from the bauxite and the liquor, even in the presence of added oxygen. A fundamental understanding of the degradation reactions of organic compounds that produce hydrogen is important in the development of improved wet oxidation processes in the Bayer industry and for refinery safety in general.

The hydrogen production potential of a bauxite ore was assessed over a range of temperatures (150–275 °C) and sodium hydroxide concentrations (0–6 M). Measurements on a range of lateritic bauxites showed that the hydrogen production potential is not simply related to the total organic carbon content of the parent bauxite, indicating that the types of organic compounds present are important. Therefore, the degradation of a range of organic compounds which represented various structural classes that could be present in Bayer process digestion was studied under similar conditions. The compounds investigated include aliphatic and aromatic carboxylates, aliphatic and aromatic hydroxycarboxylates, phenols and unsaturated carboxylates.

These results demonstrate a strong dependence of hydrogen production on the structure of the organic compounds involved, and provide further evidence in support of the ionic degradation mechanism involving base-catalysed oxidation by water which we have proposed previously.

Notation and units

Standard North American terminology is used: A is the alumina concentration as $\text{g Al}_2\text{O}_3 \text{ L}^{-1}$, C is the total caustic concentration as $\text{g Na}_2\text{CO}_3 \text{ L}^{-1}$ and S is the total soda concentration as $\text{g Na}_2\text{CO}_3 \text{ L}^{-1}$.

1. Introduction

Hydrogen is a component of the non-condensable gases generated during bauxite digestion (Graham et al., 2002) and the wet oxidation of Bayer process (Anderson et al., 2001; Arnsward et al., 1991; Baker et al., 2008; Brown, 1989). The production of hydrogen during wet oxidation processes is of particular concern due to its low-energy ignition, buoyancy and wide flammability limits in comparison to most other gases (Häussinger et al., 2007). Knowledge of the hydrogen production capacities of bauxite ores and the degradation reactions of specific classes of organic compounds in Bayer liquors is therefore important to the development of improved wet oxidation processes.

Two different degradation mechanisms have been proposed to explain the reactivity of Bayer organic compounds, such as sodium tartrate, in alkaline solutions. In the presence of oxygen, free radical intermediates are likely to be involved (Dong et al., 2010a; 2010b; Tardio et al., 2005), consistent with the observation that tartrate can facilitate the degradation of succinate, which was unreactive under the same conditions in the absence of tartrate. On this basis, a free-radical mechanism was proposed for the wet oxidation of tartrate and the co-oxidation of succinate (Tardio et al., 2005). In the absence of oxygen, an ionic degradation mechanism involving base-catalysed oxidation by water has been proposed (Loh et al., 2008a; 2010). The significance of this mechanism in the current context is that it not only explains the occurrence of oxidative reactions under anaerobic conditions (Armstrong and Healy, 2006; Loh et al., 2008b; Power and Tichbon, 1990; Yamada et al., 1981), but also shows how and why hydrogen gas can be produced even in the presence of oxygen.

To develop a better understanding of the degradation reactions of Bayer organic compounds, a purpose-built autoclave, gas sampling and measurement unit, collectively known as the CSIRO

Wet Oxidation Facility, has been established at the Australian Minerals Research Centre in Perth. The system can be operated up to 280 °C and 1125 psi, enabling investigations over the full range of Bayer unit operations. The purpose of this work is to (1) measure the hydrogen production capacities of bauxite ores sourced from the major bauxite provinces of the world, (2) define the reaction conditions that promote hydrogen production, (3) identify the specific structural features that result in hydrogen generation from different classes of organic compounds, (4) provide quantitative information on the products of reaction, and (5) interpret the results in terms of reaction mechanisms.

2. Experimental

2.1 The autoclave facility

Bauxite digestion and thermal degradation experiments were carried out in a 2 L Inconel® 600 autoclave (Parr Instruments Co., IL, U.S.A.). Experiments were also performed in a 2 L Parr zirconium (Zr 705) autoclave to enable detection of any possible effect on product yields of the materials of construction of the Inconel® autoclave. The production of hydrogen and low molecular weight (LMW) carboxylate products in both autoclaves were the same within experimental error. Duplicate experiments were within ± 0.05 mole % hydrogen. The oxygen and hydrogen concentrations in the headspace were measured using online electrochemical sensors. A detailed description of the autoclave facility is provided elsewhere (Costine et al., 2010a).

2.2 Bauxite digestion studies

Bauxite digestion experiments were conducted using a range of bauxite ores in 1 L of either pure caustic solution or sodium aluminate solution. Pure caustic solutions were prepared by dissolving the appropriate mass of NaOH pellets (>97%, 1%

Na₂CO₃, Rowe Scientific) in deionised water. Sodium aluminate solutions were prepared by dissolving high-purity gibbsite (OP25 hydrate) in hot sodium hydroxide solution at atmospheric pressure. Sodium carbonate (AR) was dissolved separately in hot water and then added to the sodium aluminate solutions. The solution was pressure filtered through a 0.45 mm Supor membrane before dilution to volume with deionised water. Bauxite (260 g) was then added to the solution.

2.3 Thermal degradation of organic compounds

All organic compounds were AR grade and used as received. Of the 49 compounds investigated (see Figure 4), 29 have been specifically identified in actual Bayer liquors (Power and Loh, 2010). The initial concentration was 40 mM for all the compounds except oxalate, terephthalate and trimesate, for which 5 mM was used because of their limited solubility. Solutions of each organic compound were made up by adding the required mass of organic compound to a pure caustic solution. The degradation of two structurally similar hydroxycarboxylates, DL-3-hydroxybutanoate and DL-malate, and their corresponding unsaturated carboxylates, trans-2-butenoate and maleate, were studied in particular detail. A solution volume of 1 L was used for each experiment. The autoclave was then sealed and inserted into the heating cavity.

2.4 System preparation

After confirmatory pressure testing, the autoclave and gas sampling system were purged with nitrogen. When the concentration of residual oxygen in the headspace was below 0.01 mole % the excess nitrogen pressure was released. The solutions were heated at a rate of approximately 5 °C min⁻¹, with stirring, to the designated temperature. The time at which the required temperature was reached was taken as the nominal starting point of the reaction.

2.5 Gas analysis

In order to measure the hydrogen content at the end of each autoclave run, the internal cooling coil circuit of the autoclave was activated to rapidly reduce the temperature. For example, this would cool the contents from 250 °C to 175 °C within 2 min and to 25 °C within 30 min. Once at 25 °C the autoclave was pressurised with a known amount of nitrogen to establish a controlled flow of the headspace gas to the hydrogen sensor. The internal pressure and temperature of the cooled autoclave were noted just before gas sampling. The measurements from the hydrogen analyser were obtained in mole % and were converted to moles of hydrogen using the general gas equation. The accuracy and precision of the gas analysis method were quantified by measurements of a range of hydrogen calibration gas mixtures and also by direct measurement of hydrogen production from the reaction of aluminium wire in sodium hydroxide solution as previously described (Costine et al., 2010b).

2.6 Solution analysis

Capillary electrophoresis and ion chromatography were used to measure the concentrations of the following LMW carboxylate products: formate, acetate, oxalate, malonate, succinate and lactate (Power et al., 2011). Molar yields were calculated as the number of moles of product formed per mole of organic compound used.

3. Results and discussion

3.1 Bauxite digestion studies

3.1.1 Screening study

Figure 1 shows the production of hydrogen after the digestion of seven lateritic bauxites in synthetic liquor at 150 °C and 250 °C. The bauxites were sourced from five of the major global bauxite provinces. The experiments were designed to target a

constant final free caustic concentration because the production of hydrogen from organic compounds in the bauxite was found to be base catalysed and [OH⁻] is a factor in the first order rate constant (see Section 3.1.3). Hydrogen production is greater at 250 °C than at 150 °C for all seven bauxites. The effect is greatest for bauxites 1 and 2, which produce moderate amounts of hydrogen at 150 °C and large amounts at 250 °C, and for bauxites 6 and 7, which produce little hydrogen at 150 °C but moderate amounts at 250 °C.

The concentration of total organic carbon (TOC) extracted from the different bauxites after digestion is also shown in Figure 1. The results show that hydrogen production potential is not simply related to the concentration of TOC extracted during digestion, indicating that it is the nature and distribution of organic compounds present that are most important.

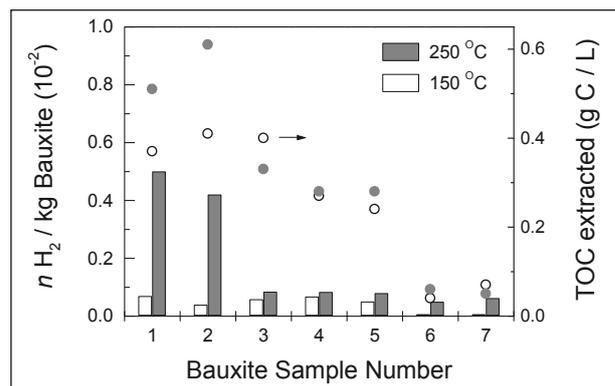


Figure 1. The number of moles of H₂ produced per kilogram of bauxite and the TOC extracted after digestion of seven different lateritic bauxites. *Conditions:* temperature = 250 °C, time at temperature = 20 min, final A, C and S = 167–179 g L⁻¹, 232–262 g L⁻¹ and 264–307 g L⁻¹, respectively.

3.1.2 Effect of temperature

The production of hydrogen from bauxite no. 1 over the range of temperatures typically encountered in Bayer digestion is shown in Figure 2. In this case, the specific hydrogen production ranged from 0.06 moles H₂/t bauxite at 150 °C to 9.6 moles H₂/t bauxite at 275 °C.

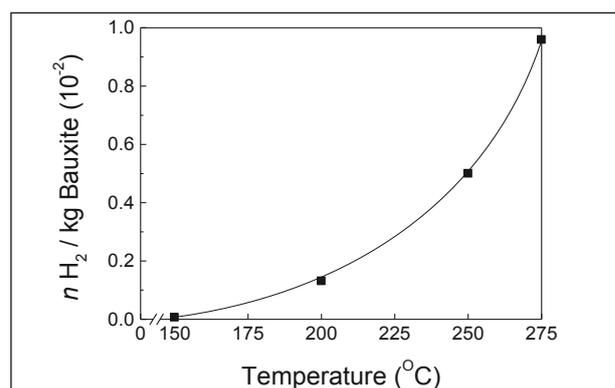


Figure 2. The number of moles of H₂ produced per kilogram of bauxite no. 1. *Conditions:* temperature = 150–275 °C, time at temperature = 20 min, initial A, C and S = 90 g L⁻¹, 255 g L⁻¹ and 300 g L⁻¹, respectively.

3.1.3 Effect of NaOH concentration

Figure 3 shows the effect of the final free caustic concentration on the production of hydrogen from bauxite no. 1 after digestion in both pure caustic and synthetic liquor consisting of aluminate and carbonate. The points show the experimental data and the line represents the number of moles of hydrogen produced according to a pseudo-first order law in which [OH⁻] appears as a factor in the rate constant. The results suggest a rapid dissolution of the reactive organic compounds and pre-equilibrium with OH⁻, followed by first order degradation. The presence of aluminate

and carbonate in the synthetic liquors was found to have little effect on the production of hydrogen, consistent with a dominant base-catalysed degradation mechanism. This is consistent with the behaviour of individual compounds that degrade with the formation of hydrogen (see Section 3.2.3).

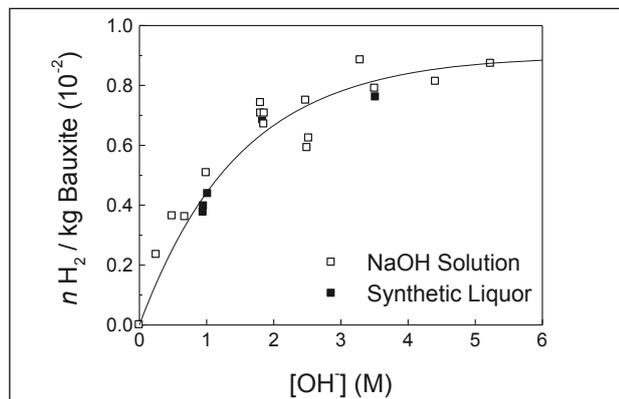


Figure 3. The number of moles of H₂ produced per kilogram of bauxite no. 1. The points show the experimental data and the line shows the first order degradation model. *Conditions:* temperature = 250 °C, time at temperature = 20 min, final C = 0–277 g L⁻¹.

3.2 Thermal degradation of organic compounds

3.2.1 Screening study

The assessment of the hydrogen production potential of a range of bauxite ores indicated that the types of organic compounds present are important (Section 3.1.1). Little work has been reported to date on the production of hydrogen from specific classes of organic compounds in sodium hydroxide solutions. Therefore, a study of the alkaline degradation of various organic compounds that could be present in Bayer liquors was undertaken.

Figure 4 shows the production of hydrogen and LMW carboxylates during the anaerobic degradation of 49 organic compounds at 250 °C. The results are grouped according to the structural classes of the compounds. The C₁–C₇ aliphatic compounds without hydroxy groups are relatively stable under these conditions. They produce little or no hydrogen gas, and the observed LMW carboxylate products account for <3% of the carbon in the parent compounds.

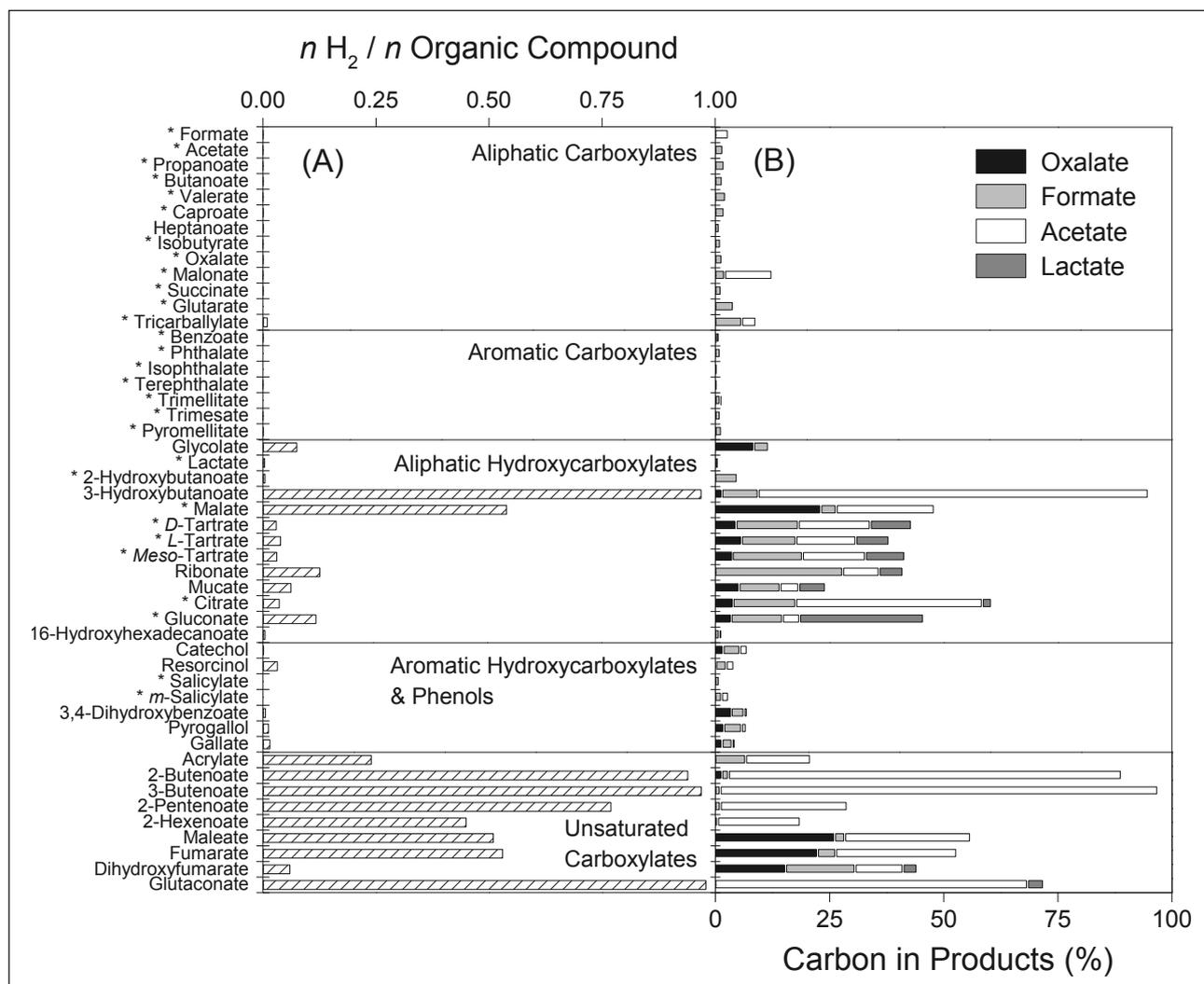


Figure 4. (A) The number of moles of H₂ produced per mole of the organic compound and (B) the distribution of LMW products. * indicates compounds that have been identified in Bayer liquor (Power and Loh, 2010). *Conditions:* temperature = 250 °C, time at temperature = 15 min, [NaOH] = 3.77 M.

The anaerobic degradation of the non-hydroxylated aromatic carboxylates generated only trace quantities of hydrogen and LMW carboxylate products, indicating that benzene ring opening is negligible under these conditions, consistent with the results of Picard et al. (2002). A similar observation was noted for the group of aromatic hydroxycarboxylates and phenols, in which the LMW carboxylates detected accounted for only 1–8% of the carbon balance. In contrast, it is known that the wet oxidation of aqueous solutions of aromatic compounds using molecular oxygen can result in significant ring breakage probably preceded by hydroxylation (Singla et al., 2004). This produces a variety of intermediates that undergo further oxidation to more stable LMW carboxylic acids (Mishra et al., 1995).

This screening study has shown that the production of hydrogen from the aliphatic hydroxycarboxylates is significantly influenced by the number of hydroxy groups (e.g. malate produces more hydrogen than tartrate) and also by their relative placement (e.g. 3-hydroxybutanoate produces more hydrogen than 2-hydroxybutanoate). It was found that the C₄ carboxylates with

a single β -hydroxy substituent, $-\text{CHOH.CH}_2\text{CO}-2^-$, such as malate and 3-hydroxybutanoate, are particularly reactive under these conditions and produce a high proportion of hydrogen gas. In alkaline solutions, β -hydroxycarboxylates exist in equilibrium with their corresponding α,β -unsaturated carboxylates (Miltenberger, 2005) and this class of compounds was also found to readily degrade to produce hydrogen gas. The wet oxidation of monoaromatic compounds yields α,β -unsaturated carboxylic acids as intermediate products through decarboxylation and benzene ring-opening reactions (Mishra et al., 1995). Given that Bayer liquors generally contain a significant aromatic content (Power and Loh, 2010), it is likely that the use of wet oxidation to remove organic compounds from liquor could result in the formation of unsaturated carboxylates as intermediate products.

3.2.2 Effect of temperature

The effect of temperature on the product yields from 2-butenate and maleate and their corresponding β -hydroxycarboxylates, 3-hydroxybutanoate and malate, is shown in Figure 5.

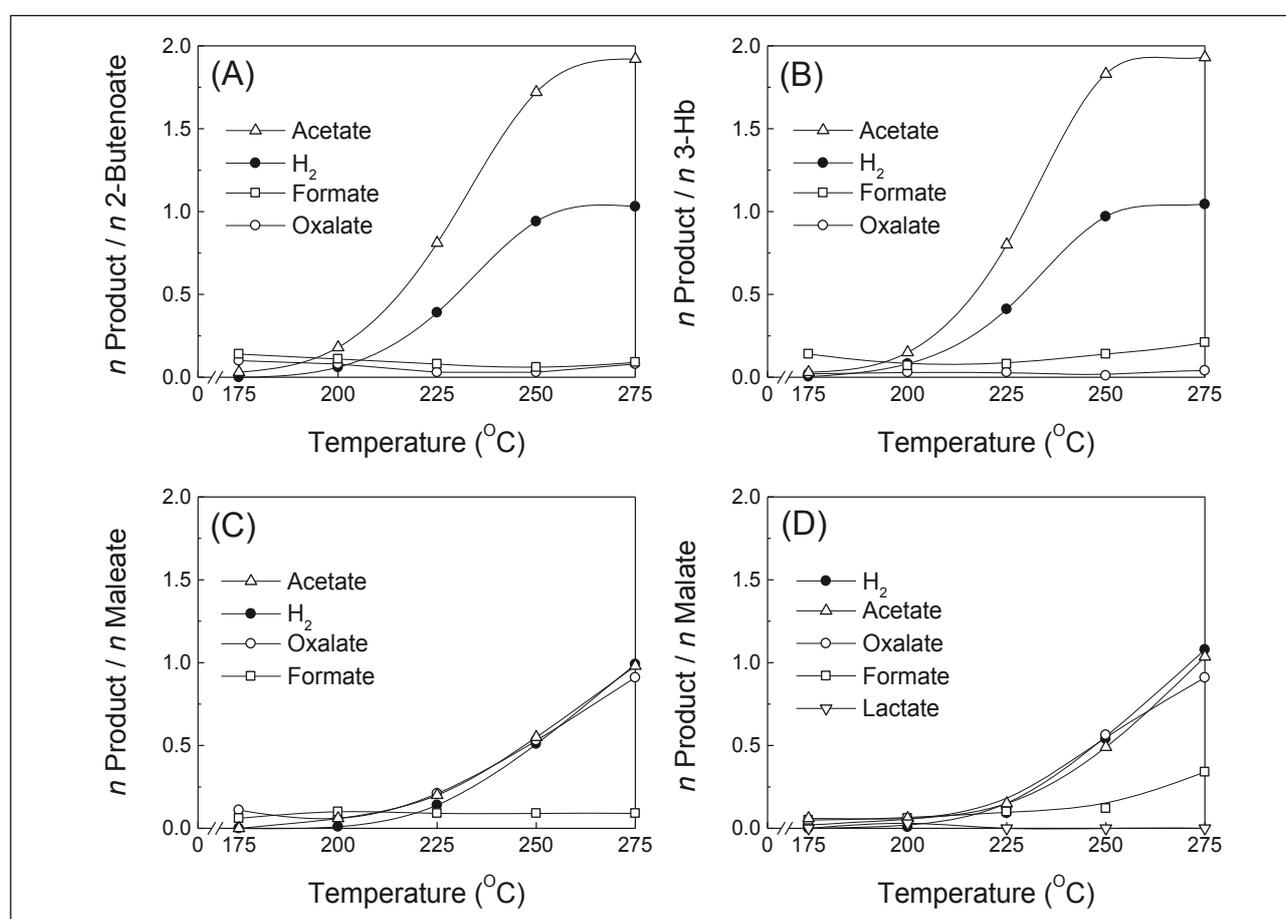


Figure 5. The number of moles of H₂ and LMW carboxylate products produced per mole of (A) 2-butenate, (B) 3-hydroxybutanoate (3-Hb), (C) maleate and (D) malate. *Conditions:* temperature = 175–275 °C, time at temperature = 15 min, [NaOH] = 3.77 M.

For 2-butenate and 3-hydroxybutanoate (Figure 5A and B), little reaction occurs below 200 °C. The only major product other than hydrogen is acetate, accompanied by small amounts of formate and oxalate over the full temperature range. The molar sum of organic products to the hydrogen produced is slightly above 2:1. Acetate accounts for about 92% of the organic products, with about 4% formate and 4% oxalate. These organic products account for 100% of the initial carbon after 15 min at 275 °C.

Similarly, for maleate and malate (Figure 5C and D), little reaction occurs below 200 °C. Hydrogen, acetate and oxalate are the main products with the ratio of the molar yields of these products being about 1:1:1 over the full temperature range. The amount

of formate produced was small and constant up to 275 °C. At this temperature the observed LMW products accounted for almost all of the initial carbon after 15 min. The appearance of lactate from malate degradation at 200 °C is consistent with previous work at similar temperatures (Machold et al., 2009), although the formation of this product in only trace quantities implies that the direct decarboxylation of malate is minor under the current conditions.

The product distributions are independent of temperature which indicates that only the rates, but not the mechanisms change with temperature.

3.2.3 Effect of NaOH concentration

NaOH concentration was found to have a significant influence on the production of hydrogen from 3-hydroxybutanoate and malate as shown in Figure 6, suggesting that the degradation reactions are base-catalysed. This first order dependence on $[\text{OH}^-]$ is consistent with a single dominant degradation mechanism over the range of NaOH concentrations studied.

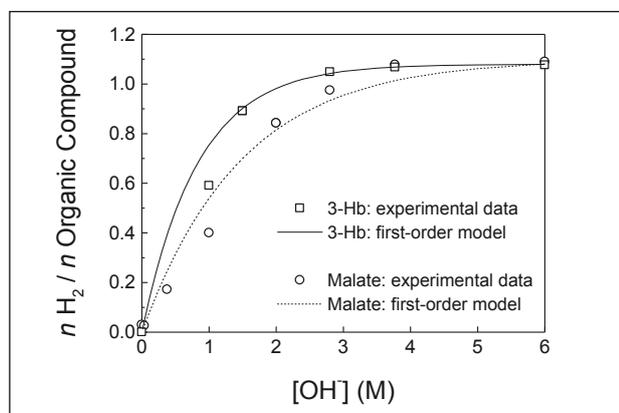
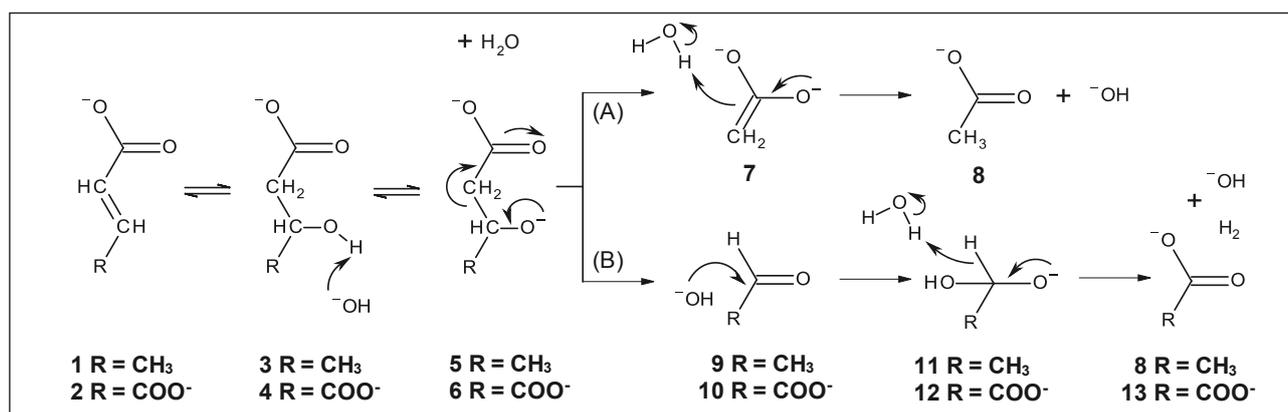


Figure 6. The number of moles of H_2 produced per mole of 3-hydroxybutanoate (3-Hb) and malate. The points show the experimental data and the lines show the first order degradation models. Conditions: temperature = 275 °C, time at temperature = 15 min, $[\text{NaOH}] = 0\text{--}6\text{ M}$.



Scheme 1. The proposed degradation mechanism for 2-butenate (1), maleate (2), 3-hydroxybutanoate (3) and malate (4) (Machold et al., 2009) in the explanation of the results presented in Figure 5.

Based on the mechanism proposed for the degradation of 2-butenate (1) and 3-hydroxybutanoate (3), the expected molar ratio of acetate to hydrogen is 2:1 and the formation of oxalate as a major product is not expected. Based on the reaction mechanism proposed for maleate (2) and malate (4), the expected molar ratio of the products – acetate, hydrogen and oxalate – is 1:1:1. For all of these compounds, one mole of hydrogen is produced per mole of the parent compound consumed. These mechanistic interpretations are consistent with the nature and amounts of the products observed as shown in Figure 5.

The observed stoichiometry of the formation of hydrogen from the β -hydroxycarboxylates studied (Figure 5) suggests that the hydration of their unsaturated counterparts, 2-butenate and fumarate, respectively, is favourable under these conditions. Consistent with this, the base-catalysed hydration of fumarate produces malate between 90–175 °C (Erickson and Alberty, 1958; Machold et al., 2009) and there is a patent which describes the near-quantitative conversion of maleate to malate by heating in alkaline solution between 140–190 °C (Connor and Kretschmar, 1994). The nature and amounts of products observed are the same when either the β -hydroxycarboxylates or their corresponding unsaturated carboxylates are used as the starting materials.

3.3 Proposed degradation mechanisms

An ionic degradation mechanism, consistent with the formation and distribution of the main reaction products of 2-butenate (1) and maleate (2) and their corresponding β -hydroxycarboxylates, 3-hydroxybutanoate (3) and malate (4), is shown in Scheme 1. These reactions are analogous to the degradation mechanisms proposed for other hydroxycarboxylates, such as tartrate and threonate, in alkaline solution (Loh et al., 2008a; 2010). The reversible hydration of the unsaturated carboxylates yields their corresponding β -hydroxycarboxylates. Abstraction of the hydrogen of the β -hydroxy group can then result in cleavage of the carbon backbone of the parent compounds. In pathway A, which is common to all of the compounds, an alkene species (7) reacts with water to produce acetate (8) and regenerates a hydroxyl ion. The initial cleavage reaction also produces acetaldehyde (9) and glyoxylate (10) from 2-butenate and maleate, respectively (Pathway B). Subsequent nucleophilic attack by a hydroxyl ion on the carbonyl carbon results in an intermediate species (11, 12). These intermediate species undergo base-catalysed oxidation by water, involving a hydride transfer to a water molecule, to produce acetate (8) or oxalate (13), hydrogen gas and hydroxyl ion.

A base-catalysed mechanism has previously been shown to apply in the case of malonate (Dong et al., 2010a). In that case, $[\text{OH}^-]$ appears as a factor in the first-order rate constant as follows:

$$k = k_0 \times [\text{OH}^-]$$

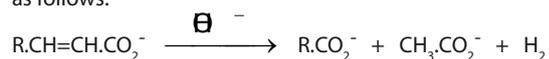
These current results also suggest a common rate-determining step involving a unimolecular reaction with OH^- . By analogy with the case of malonate, this may involve the abstraction of a hydrogen atom (in this case from a C–OH moiety, not C–H as in the case with malonates) and the formation of a pre-equilibrium with the deprotonated species (5, 6). This then reacts to produce hydrogen and LMW carboxylates, the nature of which depends on the starting compound (Scheme 1). The production of hydrogen during bauxite digestion also follows a pseudo first order law in which $[\text{OH}^-]$ appears as a factor in the rate constant and is indicative of a similar degradation mechanism.

4. Conclusions

The CSIRO Wet Oxidation Facility has been used to measure the hydrogen production capacities of a range of bauxite ores and of specific classes of organic compounds likely to be present in bauxite or Bayer liquor. This will provide a basis for strategies

to prevent or limit the formation of potentially explosive gas mixtures during Bayer digestion and industrial wet oxidation processes. The key findings from this study are that:

- The assessment of a range of lateritic bauxites showed that the hydrogen production potential is not simply related to the total organic carbon content of the parent bauxite, indicating that the types of organic compounds present are important. Hydrogen production during bauxite digestion follows pseudo-first-order reaction kinetics in which the rate constant contains $[\text{OH}^-]$.
- β -hydroxycarboxylates and the corresponding α,β -unsaturated carboxylates, which have been identified as intermediate products in wet oxidation studies, were found to be key hydrogen producers. These compounds decompose to produce one mole of H_2 per mole of the parent compound as follows:



where R is a hydrogen atom, an alkyl group or a carboxylate group.

- LMW aliphatic and aromatic carboxylates without hydroxy groups which are found in Bayer liquors produce little or no hydrogen gas under the oxygen-deficient conditions encountered in alumina refineries during digestion. Similarly, the aromatic hydroxycarboxylates and phenols studied were found to produce only small quantities of hydrogen.
- Quantitative analysis of the products of reaction of the unsaturated carboxylates studied indicates that the hydration of the $\text{C}=\text{C}$ double bond yields the corresponding β -hydroxycarboxylates, which then degrade via an ionic mechanism involving base-catalysed oxidation by water. This mechanism accounts for the observed stoichiometry of formation of hydrogen gas and the main LMW carboxylate products.

5. Acknowledgements

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