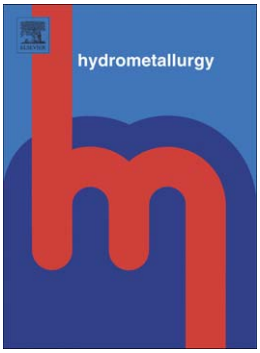


Decomposition of bayer process organics: Low-molecular-weight carboxylates

T. Machold, E. Macedi, D.W. Laird, P.M. May, G.T. Hefter

PII: S0304-386X(09)00173-X
DOI: doi: 10.1016/j.hydromet.2009.06.005
Reference: HYDROM 3030

To appear in: *Hydrometallurgy*

Received date: 19 December 2008
Revised date: 18 June 2009
Accepted date: 24 June 2009

Please cite this article as: Machold, T., Macedi, E., Laird, D.W., May, P.M., Hefter, G.T., Decomposition of bayer process organics: Low-molecular-weight carboxylates, *Hydrometallurgy* (2009), doi: 10.1016/j.hydromet.2009.06.005

Decomposition of Bayer Process Organics: Low-Molecular-Weight Carboxylates

T. Machold, E. Macedi [a], D.W. Laird, P.M. May, and G.T. Hefter *

School of Chemical and Mathematical Sciences, Murdoch University, Murdoch, WA 6150, Australia

[a] Current address: Institute of Chemical Sciences, University of Urbino, 61029 Urbino, Italy

* Corresponding author. Tel.: +61893602226, Fax.: +61893606452 E-mail:G.Hefter@murdoch.edu.au

ABSTRACT

The degradation of twenty-one low-molecular-weight organic carboxylates has been studied at 90 and 180 °C in a synthetic Bayer liquor consisting of 6 mol kg^{-1} aqueous NaOH solution for periods of up to 36 days. The reactions were monitored and the major degradation products identified by HPLC and NMR spectroscopy. The carboxylates chosen for study either could be intermediates, or occur as a result of decomposition of organic matter in the Bayer process. Aliphatic carboxylates without hydroxyl substituents were stable at 90 °C but decomposed at 180 °C, except for formate, acetate, oxalate and succinate. The corresponding aromatic carboxylates were stable even at 180 °C. Both aliphatic and aromatic carboxylates with hydroxyl substituents were unstable at 90 °C, except for lactate and 4-hydroxybenzoate. The most frequently detected decomposition products for both aliphatic and aromatic carboxylates were formate, acetate, oxalate, succinate and lactate. Phenolate was also observed for some aromatic carboxylates. These products are briefly discussed with reference to possible mechanisms for the degradation reactions.

Keywords: Bayer process; organic compounds; degradation, carboxylates, sodium hydroxide solution

1. Introduction

Organic matter enters the Bayer process during dissolution of bauxite ore in concentrated sodium hydroxide solution at elevated temperatures. This is significant as it is well known that the presence of some organic species, particularly oxalate, in process Bayer liquors has deleterious outcomes with respect to both product quality and quantity (Lever, 1978; Guthrie et al., 1984). Even the thermodynamically stable carbonate ion, which is a degradation product of many organic species in hot concentrated caustic solutions, has various negative effects on the Bayer process and must be controlled by costly 're-causticisation' procedures (Hudson, 1987). The impact of organic impurities in Bayer plants is potentially serious even though the amount of organic matter in feedstock ore is generally quite low: ca. 0.05 – 0.5 wt% of total organic carbon in Australian bauxites (Whelan et al., 2003a). This is because the caustic liquor is continuously recycled, which creates, under typical process conditions, a dynamic steady-state of the total organic carbon (TOC) load in which inputs and outputs are more or less balanced.

Organic matter in Bayer liquors is derived from two main sources: plant root systems that penetrate deep into the bauxite deposits from overlying vegetation (Ellis et al., 2002a, 2002b) and humic material that has accumulated over the history of the bauxite deposit through geochemical and bacterial transformation of plant and animal matter (Power and Tichbon, 1990; Swift, 1999). The high-molecular-weight organic biopolymers (lignin, cellulose, and humic substances) arising from these sources are quickly degraded during digestion of the bauxite ore to three main types of low-molecular-weight (LMW) organic anions: benzene-carboxylates, phenolates, and

aliphatic carboxylates (Lever, 1978; Whelan et al., 2003a). However, these species can react further in the hot concentrated NaOH (aq) to form simpler species. Thus, an understanding of the reactivity of these LMW organics in Bayer liquors is of considerable importance for predicting their effects on the production process and for developing appropriate mitigation procedures, such as selective degradation by wet oxidation.

Most information currently available in the public domain about the LMW organic compounds in Bayer liquors is related to their qualitative identification. Only a few studies have reported on their reactivity or the mechanism(s) by which they are transformed into the more stable species, such as oxalate, acetate and formate, that are routinely found in these liquors (Tardio et al., 2004; Loh et al., 2008a, 2008b). For example, Ellis et al. (2002a, 2002b) identified ca. 50 organic compounds, mainly the anions of organic acids, which could be generated from typical source biopolymers. However, these studies were carried out on a relatively short time scale (48 h, the approximate residence time of liquor in a single Bayer plant cycle) and the identification of so many compounds suggests that some are probably intermediates in the breakdown of biopolymers. As certain amounts of these organic intermediates, along with relatively stable species like acetate and oxalate will remain in the liquor during recycling, it is of interest to explore their longer term behaviour under typical Bayer processing conditions.

Previous studies of the degradation of organic compounds in highly alkaline aqueous solutions used gas chromatography (GC) as the analytical method (Guthrie et al., 1984; Ellis et al., 2002a, 2002b). While GC is an excellent tool for qualitative and quantitative determinations of organic species in Bayer liquors, extensive sample preparation, including an esterification step, is required. High performance liquid

chromatography (HPLC) has also been used successfully to analyse LMW organic compounds in Bayer liquors (Susic and Armstrong, 1990; Whelan et al., 2003b; Xiao et al., 2006). This method has the advantage of avoiding a derivatisation step, thus reducing overall analysis time; it also alleviates concerns about possible thermal degradation of labile intermediates at the much higher temperatures required by GC. The approach taken in the present study was to employ HPLC with a column specifically manufactured for organic acid detection. While HPLC provides qualitative and quantitative analyses, it is still an *indirect* method because some manipulation of the sample is required prior to injection. To ensure that compounds identified by HPLC were not artefacts of the sample workup, *direct* analysis of the caustic solutions by ^{13}C nuclear magnetic resonance (NMR) spectroscopy was also employed.

To provide insights into the long term degradation of LMW organic carboxylates in Bayer liquors the compounds chosen were allowed to react in a synthetic Bayer liquor consisting of 6 mol kg^{-1} (*m*) NaOH aqueous solution at elevated temperatures for periods of up to 36 days (d). The compounds selected for these experiments have either been reported to be present in actual Bayer liquors or are potential intermediates in the degradation of source biopolymers. The reaction products obtained were examined for possible patterns of decomposition.

2. Experimental

Experiments were conducted at 90 and 180°C. The former temperature was chosen to facilitate detection of short lived intermediates that could help in understanding underlying reaction mechanisms. The latter was a convenient upper

limit that corresponds approximately to typical operating temperatures of 'low-temperature' Bayer-process digestion reactors. The duration of the experiments was varied in order to examine how compounds might react, if present in a Bayer liquor, through a number of cycles in a plant.

2.1 Apparatus and procedure

Reactions in aqueous concentrated caustic solutions at 90ºC were carried out in 50 mL screw-capped polypropylene tubes (Kartell, Italy) for periods of up to 36 d. in a covered thermostated water bath controlled to ± 2ºC

At 180ºC, up to 12 stainless steel reaction vessels each containing 5 mL of solution were placed in a converted isopiestic chamber, partially evacuated, and then heated in a silicone oil bath (Hefter et al., 1997) for up to 12 d. The temperature was controlled to ± 0.5ºC. To minimize the possible effects of oxygen on the present reactions, all solutions were prepared from thoroughly degassed water and care was taken to restrict contact of the solutions with air.

The reactions of all compounds were performed in duplicate; no significant differences in the degradation products were detected.

2.2 Selection of carboxylates

The sodium salts of twenty-one organic carboxylates were chosen initially for investigation. All compounds were analytical grade, purchased from Sigma-Aldrich (USA), Fluka (Germany), or BDH Chemicals (UK). A preliminary study of the sodium salts of caprate (decanoate) and myristate (tetradecanoate) showed that they

were essentially insoluble in 6 *m* NaOH and did not decompose in the hot caustic solution. This lowered the number of compounds investigated in detail to nineteen (Table 2). Initial concentrations of the sodium carboxylates were 0.1 *m* except for oxalate which had a concentration of ~0.006 *m* due to its low solubility in caustic solutions (Tromans, 2003). All solutions were vacuum-filtered through a PTFE membrane (47 mm diameter, 0.45 μm pore width, Pall, USA).

2.3 HPLC analysis

Chemicals and standards: All solvents were of HPLC grade (Lab-Scan, Thailand) and were filtered (nylon membrane, 47 mm diameter, 0.2 μm pore width, Alltech, Australia) prior to use. Buffers were prepared from analytical grade compounds (Univar, Australia) unless otherwise noted. Standard solutions of the organic salts were prepared by dissolution in high purity water (Ibis Technology Ultra Pure System, Australia). The standard solutions were also used to check the purity of the organic salts. In some cases minor contamination of the standards was inevitable due to the reactive nature of the material (e.g., according to the manufacturer, sodium malate contains up to 1 % by weight of fumarate).

Sample preparation: 2.0 mL of the sampled solution was diluted and acidified to pH 2.0 using 0.5 *M* HCl and the volume adjusted to 25 mL with high purity water. A 2.0 mL portion of this stock solution was filtered (PTFE syringe filter, 0.45 μm, Pall, USA) directly into a 1.5 mL glass auto sampler vial (Shimadzu).

Chromatographic conditions: data from the HPLC system (Prominence, Shimadzu, Japan), equipped with an auto sampler (SIL-20A) and photodiode array detector (PDA, SPD-M20A), were processed using Shimadzu LC Real Time Analysis

software. Samples (20 µL) were separated isocratically on a thermostated (25 °C) 5 µm Prevail Organic Acid column (150 mm x 4.6 mm, Grace Discovery Sciences, USA) at a flow-rate of 1.0 mL/min. Aliphatic acids were determined using a mobile phase of 25 mM KH_2PO_4 buffered to pH 2.10 with H_3PO_4, with detection at 215 nm. A mobile phase consisting of 2:3(v/v) acetonitrile: 25 m*M* KH_2PO_4(aq) solution buffered at pH 2.10 with H_3PO_4 was used for the analysis of aromatic acids, with detection at 254 nm.

2.4 NMR analysis

The ^{1}H- and ^{13}C-NMR spectra for all compounds were obtained in D_2O (Sigma-Aldrich) and NaOH prior to heating (Table 1). Spectra were then recorded for all samples after 12 d at 90 or 180°C. A Bruker Avance DPX 300 spectrometer was used to record ^{1}H- and ^{13}C-NMR spectra at frequencies of 300 MHz and 75 MHz, respectively, using standard Bruker pulses. The number of scans collected was variable but was typically 32 for ^{1}H spectra and 20,000 for ^{13}C spectra. Spectra were processed using the XWin-NMR software package.

Sample preparation: ~1 mL of the reaction solution was mixed with 0.2 mL of D_2O (99.75% isotopic purity) and placed in a Teflon tube inside a 5 mm o.d. glass NMR tube. A small amount of d_4-MeOH (δ_H = 2.9883 ppm; δ_C = 48.77 ppm) was added to calibrate each spectrum.

3. Results and discussion

3.1 Qualitative validation of analytical approach

The data obtained from the two analytical techniques (HPLC and NMR) were complementary and provided insights into the behaviour of the selected LMW organic species in highly alkaline solutions. Compounds were considered stable if there was no detectable change to their NMR spectra **and** no significant additional peaks appeared in the chromatograms from commencement of heating until sampling. The identity of degradation products was ascertained by comparing retention times with those of standard solutions (Table 3) and by NMR analysis (Table 1).

The complementary nature of the HPLC and NMR data is demonstrated by detailed examination of the reaction of malate. The chromatograms of malate after several days of reaction in caustic solution under various conditions are shown in Figure 1. The HPLC retention times for malate (t_r = 2.5 min) and other species were established by analysis of appropriate standard solutions. Literature data indicate that fumarate can be formed from malate in caustic solution at elevated temperatures (Tardio et al., 2004). However, as can be seen in Fig. 1 curve a, some fumarate (t_r = 8.1 min) was detected even before the solution was heated. The presence of a small amount of fumarate in the initial solution was expected as the standard malate solution contains up to 1% fumarate. Nevertheless, the observed peak area for fumarate before heating is consistent with the partial decomposition of malate in the caustic solution at room temperature. After 12 d at 90°C (Fig. 1, curve b) the malate peak decreased, the fumarate peak increased, and oxalate (t_r = 1.7 min) was formed. This pattern was repeated at 24 d (Fig. 1, curve c). However, after 36 d at 90°C (Fig. 1, curve d), while much of the malate had degraded, none of the intermediate fumarate remained; instead, acetate (t_r = 3.8 min) was detected along with oxalate and a very small amount of an unidentified product at t_r ~ 4.4 min.

It is notable that the amount of fumarate formed is not as great as appears from visual inspection of the chromatograms (Fig. 1). This is because the UV absorptivity (ε_{max}) of its alkene chromophore is approximately 250 times greater than that of the carboxylic group (Silverstein et al., 1991). The persistence of fumarate for up to 12 and 24 d, followed by its complete disappearance after 36 d reaction time, implies a shifting equilibrium between malate degradation and fumarate formation/degradation.

At 180°C, degradation of malate occurred much more rapidly than at 90°C. Thus after 12 d of reaction (Fig. 1, curve e) only traces of malate and fumarate were detected but now oxalate, acetate, formate (t_r = 1.9 min), lactate (t_r = 3.1 min), and succinate (t_r = 5.7 min) were observed. The reaction products identified by HPLC after 12 d at 90 and 180°C were qualitatively confirmed by NMR spectroscopy, except for sodium oxalate which was too sparingly soluble to produce a reasonable signal. Although both ^{1}H- and ^{13}C-NMR spectra were recorded for identification of the organic species, the latter were more useful because the chemical shifts provided positive identification without the overlapping that occurred in the ^{1}H-NMR spectra.

A quantitative analysis (mass balance) of the present results was not possible for three reasons. First, gaseous and/or highly volatile products (H_2, CH_4, formaldehyde, acetaldehyde) may be formed but will not be detected by the methods used. Second, the formation of carbonate, a likely end product from decarboxylation reactions, was not monitored by HPLC because it is lost during the acidification step. Carbonate is also an inevitable contaminate of caustic solutions from atmospheric CO_2. Third, some precursors (terephthalate, coumarate), or possible products that precipitate during the acidification step, cannot be quantitatively determined by the present HPLC procedure. In spite of these difficulties semi-quantitative analysis based

upon relative peak areas was performed whenever possible and the results are included in Table 2.

3.2 Effect of trace oxygen

It is well known that oxygen can have a significant effect on the rates and mechanisms of degradation of organics in concentrated alkaline solutions (Loh et al., 2008a, 2008b). While care was taken to minimize the presence of oxygen throughout the experiments (Section 2.1), two further tests were conducted at 90ºC using the readily decomposed malate to check if small amounts of oxygen in the headspace of the polypropylene tubes, oxygen diffusion through the tube walls, and/or opening of the tubes during sampling affected the results over the length of reaction times.

First, the degradation of malate was studied in an autoclave filled with N_2 and using rigorously de-oxygenated solutions. The second experiment involved the decomposition of malate in two sealed polypropylene tubes, one of which was kept closed throughout while the other was opened regularly to simulate removal of material for analysis and to allow ingress of air. In both cases the reaction products were identical to those obtained using the experimental protocol described in Section 2. Since malate is one of the most reactive of the carboxylates studied, these results indicate that the presence of small amounts of atmospheric or dissolved oxygen are unlikely to have significant effects on the reactions.

3.3 Stability of LMW carboxylates

Of the 19 compounds investigated in detail, only six (acetate, oxalate, succinate, benzoate, phthalate, and terephthalate) were found to be stable at both 90°C and 180°C (Table 2). The stability of formate at 180 °C was tested only for 3 d due to operational constraints but it is almost certainly stable over longer periods since it was found as a degradation product for a number of the carboxylates investigated (Fig. 1, curve e; Table 4) and has been reported in industrial Bayer liquors (Lever, 1978). Malonate, glutarate, adipate, pimelate, lactate, phthalate, terephthalate, and 4-hydroxybenzoate were stable at 90°C over 36 d but underwent significant degradation when held at 180°C for 12 d. Gluconate, salicylate, and coumarate started decomposing within 12 d at 90°C. Malate, gallate, and tartrate were the least stable, with the first two compounds beginning to decompose upon addition to the 6 *m* NaOH even at room temperature. These results suggest that the present carboxylates can be grouped into three main classes. In order of increasing reactivity they were: (a) those that show no sign of decomposition up to 180°C; (b) those that are stable at 90°C but decompose at 180°C, and (c) those that decompose at 90°C or lower.

3.4 Degradation products

By monitoring the target compounds over periods of up to 36 d using both HPLC and NMR, it was possible to determine the main degradation products and, to some extent, the intermediates that were formed. Not surprisingly, the organic species most frequently produced (Table 4) by the decomposition of the parent ions were found to be formate, acetate, and oxalate, all of which are stable in caustic solutions at elevated temperatures (Table 2) and are well-known constituents of plant Bayer liquors.

A number of general trends are apparent regarding the decomposition products. All decomposing carboxylates, except 4-hydroxy-benzoate, produced oxalate and formate. Acetate was formed from all carboxylates containing hydroxyl groups, except for 4-hydroxy-benzoate (no acetate detected) and malonate (no hydroxyl group but acetate formed). Lactate and phenolate are intermediates in some of the degradation reactions. Lactate was observed as a degradation product of aliphatic hydroxy-carboxylates but itself degrades to oxalate, acetate and formate (Table 4). Phenolate was produced from 4-hydroxy-benzoate at 180°C and salicylate at 90°C and 180°C but was not detected as a reaction product from any of the other aromatic carboxylates possibly because of their more rapid degradation and/or different degradation pathways available due to the different number and kind of substituents on the benzene ring.

Under such circumstances intermediate phenolate may degrade to aliphatic carboxylates or react with itself or the starting material to produce condensed aromatic compounds. This is particularly likely for gallate which is known to oxidise easily (Tulyathan, 1989; Slawinska and Slawinski, 1975) and which decomposes almost instantly when dissolved in caustic solution even at room temperature. Decomposition of coumarate also occurs fairly quickly as the aliphatic products of ring opening are detected within 12 d at 90°C. These data suggest that direct decarboxylation (March, 1992) may be an important degradation pathway for aromatic carboxylates. Such reactions appear to occur more readily if there is hydroxyl subsitution on the aromatic ring *ortho* to the carboxylate moiety (compare salicylate with 4-hydroxy-benzoate, Table 2) although further investigations are required to establish the generality of this observation.

The formation of thermally stable C_2, C_3, and C_4 simple aliphatic carboxylates is consistent with the known persistence of these compounds in industrial Bayer liquors. Recent studies of the wet oxidation of LMW gibbsite-yield inhibitors (such as tartrate, gluconate, gallate, and various alcohols) in alkaline aluminate solutions indicated that the final degradation products of these compounds were also acetate, formate, and oxalate (Tardio et al., 2004; Loh et al., 2008a, 2008b). The current study supports these findings and also indicates that these three species are derived from hydroxylated aliphatic carboxylates at 90°C. Additionally, the final degradation products of LMW aromatic carboxylates are the same as for their aliphatic counterparts although it appears that phenolate may be a key intermediate in the degradation of the former.

3.5 General degradation pathways

The results presented above show that the LMW carboxylates formed in plant Bayer liquors from the degradation of biopolymers present in bauxite ores, will decompose further in hot caustic solutions to acetate, oxalate, and formate. However, there does not appear to be a single degradation pathway.

Two mechanisms have been proposed to explain the degradation of C_4 and C_5 carboxylates in caustic solutions. Wet oxidation studies (Tardio et al., 2004) suggested a free radical mechanism involving molecular oxygen, although no direct evidence of radical formation was presented. More recently, Loh et al. (2008b) have shown that the major oxidation products of organics in Bayer liquors (oxalate, acetate, and formate) are also formed under anaerobic conditions. This led them to propose an ionic mechanism involving base-catalysed oxidation by water, similar to that of the

Cannizzaro reaction (March, 1992). The advantage of this mechanism is that it predicts formation of H_2, which is consistent with its appearance in the non-condensable gas stream of alumina production facilities (Brown, 1989).

Results from the present study indicate that aliphatic and aromatic mono- and di-carboxylate ions without secondary hydroxyl groups are stable in 6 *m* NaOH at 90°C. Significant degradation of LMW carboxylates at this temperature appears to be related to the presence of hydroxyl substituents, presumably because they allow a nucleophilic attack on a neighbouring C atom (Loh et al., 2008b). At 180°C it seems that direct decarboxylation may play a significant part in the degradation of the investigated carboxylates. The results presented in this paper also support the thesis (Loh et al., 2008b) that oxidative degradation of LMW carboxylates does not require the presence of oxygen.

3.6 Degradation of malate

The decomposition of malate in the absence of oxygen provides further insights into the mechanisms of the degradation of LMW aliphatic carboxylates in concentrated NaOH(aq). At 90°C, as discussed above, malate decomposes initially mostly to fumarate but ultimately to acetate and oxalate (Section 3.1, Fig. 1). The formation of fumarate is consistent with the observations of Tardio et al. (2004) and corresponds to the dehydration of malate (shown as the first step in Scheme 1). Acetate and oxalate probably form by oxidative cleavage by water (Scheme 2), as proposed for tartrate by Loh et al. (2008b). This pathway may also operate in parallel with that of Tardio et al. (2004), which would account for the formation of oxalate early in the reaction although not for the absence of acetate (Fig. 1, curve b).

When reacted with 6 *m* NaOH at 180°C, malate decomposes to lactate, oxalate, acetate, and formate (Fig. 1, curve e). Lactate may result from direct decarboxylation of malate (Scheme 3), analogous to the reaction of organic acids with NaOH (March, 1963), while oxalate, acetate and formate may be produced from both malate and lactate via the base-catalysed oxidation by water (Schemes 1 and 2). Possible support for direct decarboxylation is provided by the formation of phenolate from salicylate and 4-hydroxy-benzoate. Decarboxylation of acetate and formate would produce CH_4 and H_2, respectively, both of which are known to form under industrial conditions (Brown, 1989; Loh et al., 2008a, 2008b). Oakwood and Miller (1950) obtained methane in high yield (98.9%) when acetate was heated with NaOH, albeit at much higher temperatures (ca. 370°C) than employed here.

4. Conclusions

Of the 19 compounds studied in detail only acetate, oxalate, succinate, benzoate, phthalate, and terephthalate were stable at temperatures up to 180°C. This is significant because all stable aliphatic species are known to be decomposition products of higher molecular weight carboxylates (Table 4) and are known constituents of Bayer process solutions. All of the $\geq C_4$-carboxylates with hydroxyl substituents, such as malate and tartrate, appear to be more reactive than those without, such as succinate. The major decomposition products of most of the decomposing carboxylates were oxalate, acetate, and formate. The studied aliphatic carboxylates without hydroxyl groups produced only oxalate, acetate, and formate whereas those with hydroxyl groups, except for lactate, additionally produced lactate and succinate. Products from decomposing aromatic compounds were phenolate,

succinate, oxalate, acetate, and formate. Long chain aliphatic carboxylates ($\geq C_{10}$) have a low solubility in caustic solution but appear to be reasonably stable at 90°C as no reaction products could be detected. The results from this study suggest that base-catalysed oxidation by water may be a viable mechanism for the decomposition of LMW aliphatic and aromatic mono- and di-carboxylates in hot concentrated caustic solutions. However, direct decarboxylation may be an important process, especially for aromatics.

Acknowledgements

This work was funded by Australian and international alumina companies (Alcoa World Alumina, BHP Billiton / Worsley Alumina, Hydro Aluminium Metal Products, Rio Tinto Alcan, and UC Rusal) through the AMIRA International collaborative research project P507C entitled "Thermodynamic Characterisation of Organics in Bayer Liquor", and by the Australian Government through the Australian Research Council (Linkage Grant No. LP0776541). The authors thank Dr Kate Rowen for advice regarding the mechanisms.

References

Brown, N., 1989. Kinetics of copper-catalysed oxidation of Bayer liquor organics. Light Metals, 23-27

Ellis, A.V., Wilson, M.A., Forster, P., 2002a. Bayer poisons: degradation of Klason lignin in sodium hydroxide at 145 °C. Ind. Eng. Chem. Res., 41, 6493-6502

Ellis, A.V., Wilson, M.A., Kannangara, K., 2002b. Bayer poisons: degradation of angiosperm and gymnosperm water-soluble extracts in sodium hydroxide at 145 °C. Ind. Eng. Chem. Res., 41, 2842-2852

Guthrie, J.D., The, P.J., Imbrogno, W.D., 1984. Characterization of organics in Bayer liquors. Light Metals, 127-146

Hefter, G., May, P.M., Marshall, S.L., Cornish, J., Kron, I., 1997. Improved apparatus and procedures for isopiestic studies at elevated temperatures. Rev. Sci. Instrum., 68, 2558-567

Hudson, L.K., 1987. Alumina production. In: Burkin, A.R. (Ed.), Critical Reports on Applied Chemistry Vol. 20, Wiley, pp 11-44

Lever, G., 1978. Identification of organics in Bayer liquor. Light Metals, 71-83

Loh, J., Brodie, G., Power, G., Vernon, C., 2008a. The effects of wet oxidation on hydrate yield inhibitors in alkaline aluminate solutions. Light Metals, 181-186

Loh, J., Brodie, G., Power, G., Vernon, C., 2008b. Mechanisms of degradation of hydrate yield inhibitors by wet oxidation. In: Proceedings of 8th International Alumina Quality Workshop (7-12 September, Darwin, Australia) pp 199-205

March, J., 1963. The decarboxylation of organic acids. J. Chem. Educ., 40, 212-213

March, J., 1992. Advanced Organic Chemistry: Reactions, Mechansims, and Structure, 4th ed., Wiley, New York

Oakwood, T.S., Miller, M.R., 1950. The decarboxylation of simple fatty acids. J. Am. Chem. Soc., 72, 1849

Power, G.P., Tichbon, W., 1990. Sodium oxalate in the Bayer process: Its origin and effects. In: Proceedings of the Second International Alumina Quality Workshop, Perth Australia, pp 99-115

Silverstein, R.M., Bassler, G.C., Morrill, T.C., 1991. Spectrometric Identification of Organic Compounds, 5th ed., Wiley, New York (Chapter 7)

Slawinska, D., Slawinski, J., 1975. Chemiluminescent flow method for determination of formaldehyde. Anal. Chem., 47, 2101-2109

Susic, M., Armstrong, L.G., 1990. High-performance liquid chromatographic determination of humic acid in sodium aluminate solution. J. Chromatogr., 502, 443-446

Swift, R.S., 1999. Macromolecular properties of soil humic substances: Fact, fiction and opinion. Soil Sci., 164, 790-802

Tardio, J., Bhargava, S., Eyer, S., Sumich, M., Akolekar, D.B., 2004. Interactions

between specific organic compounds during catalytic wet oxidation of Bayer liquor. Ind. Eng. Chem. Res., 43, 847-851

Tromans, A.J., 2003. Solution Chemistry of Some Dicarboxylate Salts of Relevance to the Bayer Process. Ph.D. Thesis, Murdoch University, Perth, Australia

Tulyathan, V., Boulton, R.B., Singleton, V.L., 1989. Oxygen uptake by gallic acid as a model for similar reactions in wines. J. Agric. Food Chem., 37, 844-849

Watling, H., Loh, J., Gatter, H., 2000. Gibbsite crystallization inhibition: 1. Effects of sodium gluconate on nucleation, agglomeration and growth. Hydrometallurgy, 55, 275-288

Whelan, T.J., Ellis, A.V., Kannangara, G.S.K., Marshall, C.P., Smeulders, D.E., Wilson, M.A., 2003a. Macromolecules in the Bayer process. Rev. Chem. Eng., 19, 431-471

Whelan, T.J., Kannangara, G.S.K., Wilson, M.A., 2003b. Increased resolution in high-perfomance liquid chromatograph spectra of high-molecular-weight organic components of Bayer liquors. Ind. Eng. Chem. Res., 42, 6673-6681

Xiao, J.B., Chen, X.Q., Jiang, X.Y., Sheng, D.W., 2006. Rapid separation and analysis of 6 organic acids in Bayer liquors by RP-HPLC after solid-phase extraction. Anal. Chim., 96, 347-354

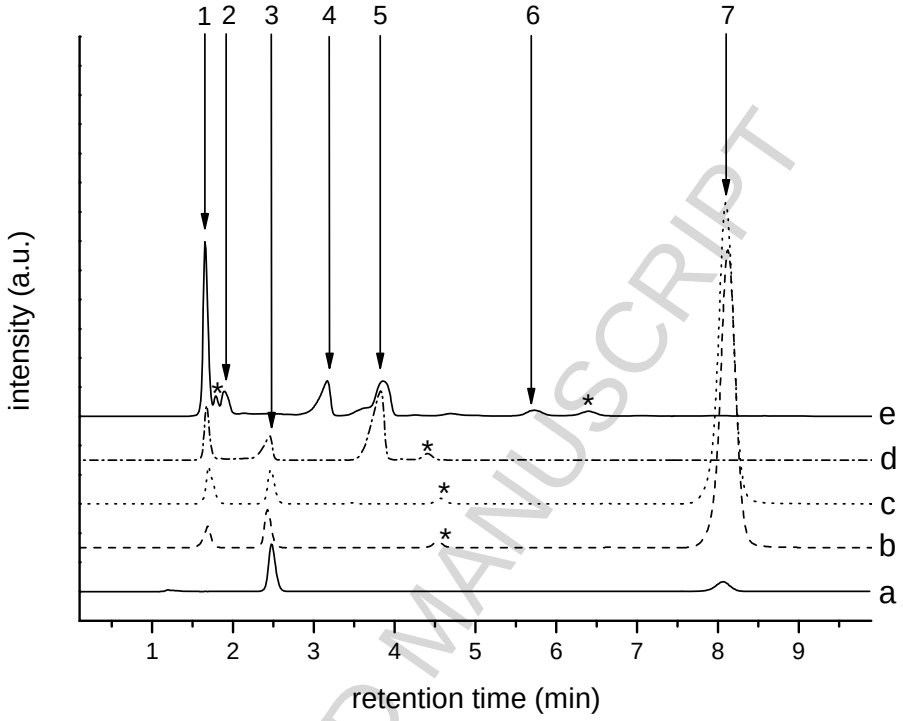
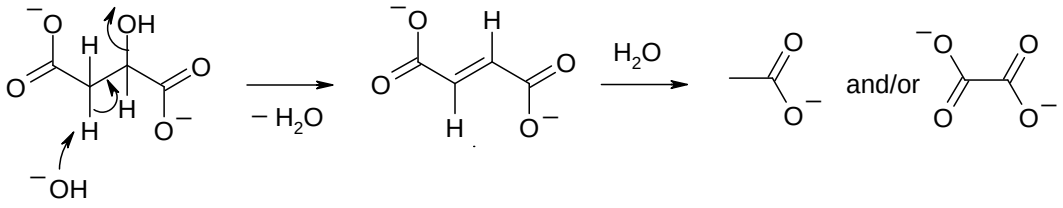
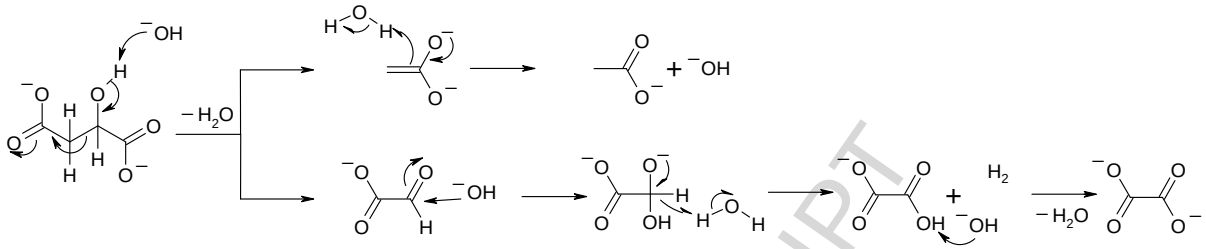


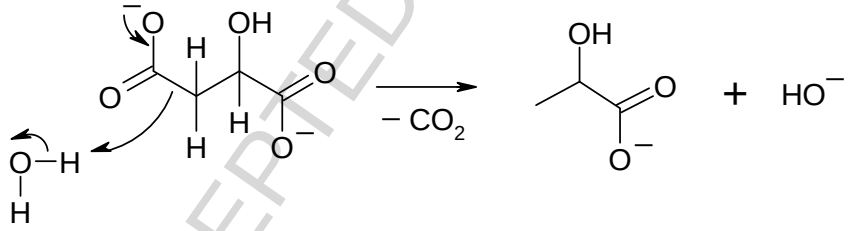
Figure 1. Chromatograms of malate in 6 *m* NaOH (aq) at elevated temperatures over time: (a) prior to heating; (b) after 12 d at 90 °C; (c) after 24 d at 90 °C; (d) after 36 d at 90 °C; (e) after 12 d at 180 °C. Peaks: (1) oxalate; (2) formate; (3) malate; (4) lactate; (5) acetate; (6) succinate; (7) fumarate; * unidentified.



Scheme 1. Hydroxide promoted dehydration of malate to fumarate (cf. Tardio et al., 2004), followed by oxidative cleavage with water to produce acetate and/or oxalate.

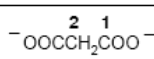
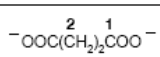
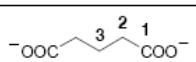
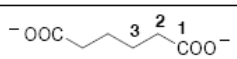
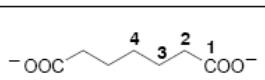
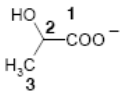
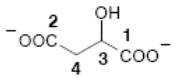
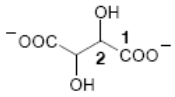
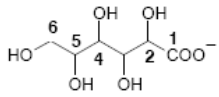
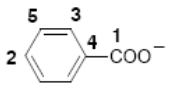


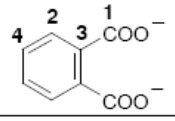
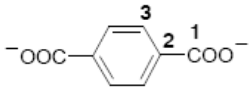
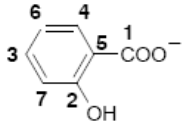
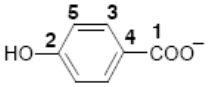
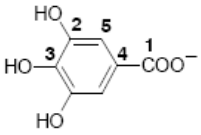
Scheme 2. Ionic mechanism: direct conversion of malate to oxalate and acetate analogous to the proposed mechanism for the decomposition of tartrate (Loh et al., 2008b)



Scheme 3. Proposed direct decarboxylation mechanism for the formation of lacate from malate.

Table 1. ^{13}C-NMR chemical shifts for the investigated carboxylates in D_2O and 6 *m* NaOH (aq) [a]

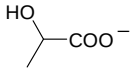
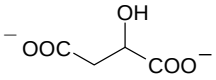
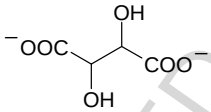
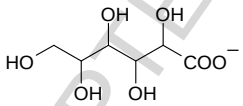
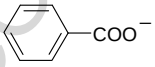
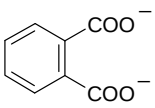
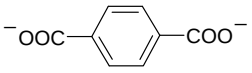
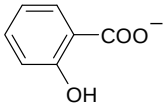
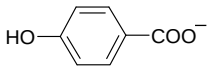
Carboxylate	Structure	Solvent	^{13}C-NMR Chemical Shifts δ_C (carbon number)
Aliphatic			
formate		D_2O NaOH	171.0 (1) 171.2 (1)
acetate		D_2O NaOH	181.3 (1); 23.4 (2) 181.2 (1); 23.8 (2)
malonate		D_2O NaOH	177.4 (1); 47.6 (2) 177.7 (1); 47.8 (2)
succinate		D_2O NaOH	176.9 (1); 28.6 (2) 182.3 (1); 33.9 (2)
glutarate		D_2O NaOH	177.7 (1); 33.6 (2); 19.5 (3) 182.9 (1); 36.9 (2); 22.6 (3)
adipate		D_2O NaOH	178.6 (1); 33.3 (2); 23.6 (3) 183.6 (1); 37.3 (2); 25.7 (3)
pimelate		D_2O NaOH	178.9 (1); 33.5 (2); 27.5 (3); 23.8 (4) 183.8 (1); 37.4 (2); 28.5 (3); 25.5 (4)
lactate		D_2O NaOH	182.4 (1); 68.3 (2); 20.0 (3) 183.2 (1); 68.2 (2); 20.8 (3)
malate		D_2O NaOH	176.1 (1); 174.1 (2); 66.6 (3); 38.1 (4) 181.1 (1); 179.7 (2); 70.0 (3), 42.4 (4)
tartrate		D_2O NaOH	178.5 (1); 73.6 (2) 180.3 (1); 74.6 (2)
gluconate		D_2O NaOH	178.6 (1); 73.8 (2); 72.2 (3); 70.9 (4); 70.7 (5); 62.3 (6) 180.8 (1); 75.7 (2); 75.1 (3); 72.7 (4); 71.2 (5); 63.5 (6)
Aromatic			
benzoate		D_2O NaOH	175.5 (1); 136.0 (2); 131.1 (3); 128.7 (4); 128.1 (5) 175.3 (1); 135.8 (2); 131.2 (3); 128.7 (4); 128.2 (5)

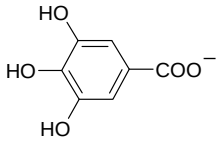
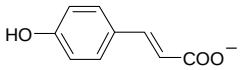
phthalate		D_2O	171.9 (1); 131.8 (2); 131.3 (3); 128.7 (4)
		NaOH	177.5 (1); 137.5 (2); 128.8 (3); 127.1 (4)
terephthalate		D_2O	not soluble
		NaOH	175.4 (1); 138.8 (2); 129.0 (3)
salicylate		D_2O	175.4 (1); 159.3 (2); 133.6 (3); 130.1 (4); 119.0 (5); 117.7 (6); 115.9 (7)
		NaOH	178.9 (1); 164.8 (2); 130.8 (3); 129.3 (4); 128.4 (5); 120.7 (6); 112.8 (7)
4-hydroxy-benzoate		D_2O	170.4 (1); 160.6 (2); 132.1 (3); 121.3 (4); 115.2 (5)
		NaOH	176.2 (1); 170.3 (2); 131.7 (3); 121.1 (4); 118.2 (5)
gallate		D_2O	170.1 (1); 144.4 (2); 138.0 (3); 120.8 (4); 110.0 (5)
		NaOH	177.0 (1); 152.7 (2); 142.6 (3); 125.2 (4); 107.6 (5)

[a] No NMR data were obtained for oxalate and coumarate due to their low solubilities

Table 2. Stability of LMW organic carboxylates in 6 *m* NaOH at 90 and 180 °C: S = stable, D = decomposing

Carboxylate	**Structure**	**Stability** [a]			
		90 °C			180 °C
		12 d	24 d	36 d	12 d
Aliphatic					
formate	$HCOO^-$	S	S	S	S [b]
acetate	CH_3COO^-	S	S	S	S

oxalate	$[(COO)_2]^{2-}$	S	S	S	S
malonate	$[CH_2(COO)_2]^{2-}$	S	S	S	D
succinate	$[(CH_2)_2(COO)_2]^{2-}$	S	S	S	S
glutarate	$[(CH_2)_3(COO)_2]^{2-}$	S	S	S	D
adipate	$[(CH_2)_4(COO)_2]^{2-}$	S	S	S	D
pimelate	$[(CH_2)_5(COO)_2]^{2-}$	S	S	S	D
lactate		S	S	S	D
malate [c]		D(20)	D(25)	D(90)	D
tartrate		D(50)	D(55)	D(>95)	D
gluconate [c]		D	D	D	D
Aromatic					
benzoate		S	S	S	S
phthalate		S	S	S	S [e]
terephthalate [f]		S	S	S	S [e]
salicylate		D(10)	D(20)	D(25)	D
4-hydroxy-benzoate		S	S	S	D

gallate [c,d]		D	D	D	D
coumarate [d,f]		D	D	D	D

[a] Numbers in parentheses are approximate decomposition percentages determined from HPLC peak areas; quantification at 180 °C was not possible due to solvent evaporation in the reaction vessels

[b] Over 3 d only

[c] Some decomposition occurred prior to heating

[d] No quantification possible due to unresolved HPLC peaks

[e] Traces of unidentified decomposition products observed

[f] Precipitated when acidified

Table 3. HPLC retention times (t_r) and wavelength(s) of maximum absorbance λ_{max} (as measured using the HPLC detector) for the investigated carboxylates and their main products.

Compound	**t_r / min)** [a]	**λ_{max} / nm** [a]
Aliphatic		

formic acid	1.9	190
acetic acid	3.8	190
oxalic acid	1.7	200
malonic acid	2.5	190
succinic acid	5.7	190
glutaric acid [b]	1.8	207
adipic acid [b]	1.9	207
pimelic acid [b]	2.1	196, 240
lactic acid	3.1	190
malic acid	2.5	207
tartaric acid	2.3	190
gluconic acid	1.8	190
fumaric acid	8.1	203
Aromatic		
benzoic acid	4.0	203, 222, 272
phthalic acid	2.0	203, 222, 241, 272
terephthalic acid	2.1	196, 240
salicylic acid	3.2	202, 222, 299
4-hydroxybenzoic acid	2.4	203, 221, 244
gallic acid [c]	–	–
coumaric acid	2.8	195, 322
phenol	4.1	203, 271

[a] Determined with 0.1 *m* solutions of the organic compound in H_2O acidified to pH 2.0

[b] HPLC analysis with detection at 215 nm using a mobile phase consisting of 2:3 (v/v) acetonitrile:25 mM KH_2PO_4 (aq) solution buffered at pH 2.10 with H_3PO_4

[c] λ_{max} could not be determined due to rapid decomposition

Table 4. Main products detected from decomposing organic carboxylates in 6 *m* NaOH solution at 90 °C and 180 °C.

Initial species	Main products
malonate [a]	oxalate, acetate, formate
glutarate [a]	oxalate, formate
adipate [a]	oxalate, formate
pimelate [a]	oxalate, formate
lactate [a]	oxalate, acetate, formate
malate	fumarate [b], succinate, lactate [c], oxalate, acetate, formate
tartrate	lactate [c], oxalate, acetate, formate [c]
gluconate	succinate, lactate, oxalate, acetate, formate
4-hydroxybenzoate	phenolate [c]
phthalate [a]	– [d]
terephthalate [a,e]	– [d]
gallate	succinate, oxalate, acetate, formate
coumarate [e]	succinate, oxalate, acetate, formate
salicylate	phenolate, succinate, oxalate, acetate, formate

[a] Stable at 90 °C (Table 2)

[b] Detected only at 90 °C

[c] Detected only at 180 °C

[d] Traces of unidentified products observed at 180 °C

[e] Precipitated when acidified