Low Temperature Wet Oxidation and Catalytic Wet Oxidation of Specific Organic Compounds in Highly Alkaline Solution (Synthetic Bayer Liquor)

James Tardio
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Department of Applied Chemistry
Faculty of Applied Science
RMIT University
Melbourne, Victoria, Australia

Certificate of Authenticity

The work described herein was performed by the author in the Department of Applied Chemistry, RMIT University and Alcoa World Alumina, Kwinana, Western Australia from September 1997 – March 2001.

The work reported is (to the best of the author's knowledge) novel, and has not been submitted, in any form, for the purpose of obtaining any other degree or qualification. All work is that of the author alone, apart from that outlined below.

- The majority of organics analyses by GC was performed by Alcoa World Alumina's Research and Development laboratory, Kwinana, Western Australia.

James Tardio

James Tardio

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Publications

The following publications have resulted from the work undertaken as part of this research program.

1.Tardio, J., Bhargava, S., and Eyer, S. 2000. "Copper catalysed Wet Oxidation in alkaline media." *Proceedings of 2nd Asia-Pacific Congress on Catalysis,* Sydney, Australia, PA13.

2. Eyer, S., Bhargava, S., Sumich, M., Akolekar, D., Nyeboer, H., and Tardio, J. 2000. "Catalysed wet oxidation applied to highly alkaline, Bayer process solutions." *Proceedings of 2nd Asia-Pacific Congress on Catalysis,* Sydney, Australia, A12.

3. Eyer, S., Bhargava, S., Tardio, J., and Akolekar, D. 2002. "Selective Organic Removal from the Alumina Industrial Liquor: Wet Oxidation and Catalytic Wet Oxidation of Disodium Malonate." *Ind. Eng. Chem. Res.* 41(5), 1166.

4. Bhargava, S., Eyer, S., Sumich, M., Tardio, J., Akolekar, D., and Nyeboer, N. 2000. "Removal of Organics from Bayer Liquor." *Light Met.,* 45.

5. Tardio, J., Bhargava, S., Eyer, S., Latham, K. and Akolekar, D. 2002. "Low Temperature Wet Oxidation of Sodium salts of Mono- and Di- Carboxylic acids in Synthetic Bayer Liquor." In preparation.

The following publications have resulted from work related to this research program

1. Eyer, S., Bhargava, S., Nyeboer, H., Akolekar, D., and Tardio, J. 2000. "Evidence for non-hydroxide copper complexes during catalysed wet oxidation in highly alkaline solution." *Proceedings of 2nd Asia-Pacific Congress on Catalysis*, Sydney, Australia, PA4.

2. Eyer, S., Bhargava, Tardio, J. 2000. "Oxidation of disodium malonate to disodium oxalate and sodium carbonate during low temperature, copper-catalysed, wet oxidation." *Proceedings of 2nd Asia-Pacific Congress on Catalysis*, Sydney, Australia, PA5.

The following confidential technical reports have resulted from the work undertaken as part of this research program.

1. Tardio, J and Bhargava, S. 1999. "Wet Oxidation of Selected Organics in Synthetic Bayer Liquor." *Catalytic Wet Oxidation (CWO) Research and Data Conference*, Booragoon, WA.

2. Eyer, S., Bhargava, S., Sumich, M., Akolekar, D., Nyeboer, H., and Tardio, J. 1999. "The "0.6" Barrier." *Catalytic Wet Oxidation (CWO) Research and Data Conference*, Booragoon, WA.

3. Eyer, S., Bhargava, S., Sumich, M., Akolekar, D., Nyeboer, H., and Tardio, J. 1999. "Catalytic Wet Oxidation : The Long Term Impact on Bayer Organics." *Catalytic Wet Oxidation (CWO) Research and Data Conference*, Booragoon, WA.

Abstract

Low temperature (165°C) Wet Oxidation (WO) and Catalytic Wet Oxidation (CWO) of 12 organic compounds has been studied in highly alkaline, high ionic strength solution (simulating that encountered in the Bayer process used to refine alumina) for the first time. Most (11 out of 12) of the 12 organic compounds studied (formic, acetic, propionic, butyric, oxalic, malonic, succinic, glutaric, citric, lactic, malic and tartaric acids) have been identified in various worldwide Bayer liquors. The various aspects of WO and CWO studied for each of the above-mentioned compounds were as follows;

- Extent of complete oxidation to carbonate (i.e. extent of removal of organic compound)
- Extent of overall oxidation (i.e. extent of complete oxidation and partial oxidation to stable products)
- The product(s) formed from partial (incomplete) oxidation
- The reaction mechanism occurring
- Why certain compounds undergo low temperature WO and/or CWO in highly alkaline, high ionic strength solution
- The ability of various transition metal oxides to catalyse the WO of the selected organic compounds

Of the 12 organic compounds studied only six (formic, malonic, citric, lactic, malic and tartaric acids) underwent appreciable (>2% overall oxidation) WO in isolation under the reaction conditions used (4.4 – 7.0 M NaOH, 165°C, 500 kPa Po_2, 2 hours). Each of these six compounds underwent some complete oxidation and therefore can be partly removed

from highly alkaline, high ionic strength solution using low temperature WO. The order of extent of complete oxidation determined was as follows tartaric > citric > malonic > formic > lactic > malic. All of these compounds also underwent some partial oxidation under the reaction conditions used, excluding formic acid, which only underwent complete oxidation. Oxalic acid was a major product of partial oxidation of all of the above-mentioned compounds (excluding formic acid), while acetic acid was a major product of partial oxidation of citric, lactic, malic and tartaric acids.

The WO of formic, malonic, citric, lactic, malic and tartaric acids varied considerably with NaOH concentration over the NaOH concentration range studied (4.4 – 7.0 M). The extent of overall oxidation undergone by each of these compounds increased significantly with increasing NaOH concentration. All of the compounds that underwent appreciable WO under the reaction conditions studied contained hydrogen(s) significantly more acidic then the compounds that did not undergo appreciable WO, thus indicating that only organic compounds that contain acidic (albeit weakly acidic) hydrogens undergo low temperature (165 °C) WO in highly alkaline, high ionic strength solution.

Two different reaction mechanisms were identified to occur during low temperature WO in highly alkaline, high ionic strength solution. Malonic and formic acids underwent WO predominantly via a free radical based reaction mechanism, while citric, lactic, malic and tartaric acids underwent WO predominantly via an ionic based reaction mechanism.

The six organic compounds that did not undergo appreciable WO in isolation (acetic, propionic, butyric, oxalic, succinic and glutaric acids) all underwent appreciable WO when in the presence of malonic acid undergoing low temperature WO. Hence, low temperature WO of all of the above-mentioned compounds can be initiated by free radical intermediates produced by malonic acid undergoing WO in highly alkaline, high ionic strength solution.

The ability of several transition metal oxides to catalyse the WO of the chosen 12 organic compounds was investigated. Of the transition metal oxides studied CuO was clearly the most active. Five of the organic compounds studied (malonic, citric, lactic, malic and tartaric acids) were catalytically wet oxidised by CuO in highly alkaline, high ionic strength solution in isolation. The order of catalytic activity observed was malonic > tartaric > lactic > malic > citric.

Two different catalytic reaction mechanisms were identified for CuO catalysed WO in highly alkaline solution for the organic compounds studied. CuO catalysed the WO of malonic acid predominantly by catalysing the formation of free radical intermediates. CuO catalysed the WO of citric, lactic, malic and tartaric acids predominantly via a complexation-based reaction mechanism.

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List of Abbreviations

°C	degrees Celsius
Ag	silver
Al	aluminium
AR	analytical reagent
ATR	attenuated total reflection
AWA	Alcoa World Alumina
Bi	bismuth
C	carbon
Co	cobalt
Cu	copper
COD	chemical oxygen demand
C_n	number of carbon atoms
CE	capillary electrophoresis
CWO	catalytic wet oxidation
Exp	experimental
Fe	iron
FTIR	Fourier transform infrared
g/L	gram per litre
GC	gas chromatography
H	hydrogen
h	hour
k	rate constant

kg	kilogram
K	equilibrium constant
LR	laboratory reagent
M	mole per litre
Me	metal
min	minute
mg/L	milligram per litre
Mn	manganese
Mo	molybdenum
MS	mass spectrometry
na	not available
nd	not detected
Na	sodium
NA	not applicable
Ni	nickel
O	oxygen
OC	organic carbon
p	para
P	pressure
ppm	parts per million
Pd	palladium
S	sulphur
Sub	substrate

T	temperature
Theor	theoretical
TOC	total organic carbon
V	vanadium
WO	wet oxidation

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1. Introduction.

There are many industrial chemical processes used today which although being economically viable in the current economy, still contain significant room for improvement in terms of productivity. An example of such a process is the Bayer process that is used to produce alumina, the precursor to aluminium metal.

The Bayer process is affected by a number of factors that hinder productivity. Of these factors, it is widely accepted that unwanted organic compounds, introduced into the process with the aluminium ore (bauxite), clearly have the most significant effect on productivity. Due to the closed, cyclic nature of the Bayer process, only minimal removal of organic compounds occurs through waste run-off and alumina refineries therefore experience a net increase in unwanted organic compounds over time until a steady state level is reached. Methods for removal of these organic compounds have been, and still are, of great interest to the alumina industry.

This thesis investigates the chemistry involved in a potential organics removal process, Wet Oxidation (WO)/ Catalytic Wet Oxidation (CWO). This process removes organic compounds in the liquid phase by oxidising them, using an oxidising gas such as oxygen or air, to the relatively harmless products of carbon dioxide (which is converted into carbonate under the alkaline conditions used in the Bayer process) and water. WO/CWO has been the subject of considerable research over the last two-three decades, which is illustrated by the comprehensive review of Mishra *et al* [1995]. However, the majority of research into WO/CWO has concentrated on systems having neutral or acidic pH. Hence, there has been a lack of research conducted on WO/CWO for systems of basic pH, the pH encountered in the Bayer process. While some of the knowledge obtained on the WO/CWO process in pH neutral or acidic conditions can be readily transferred to basic conditions, such as the dependence of reaction rate on oxidising gas partial pressure, which controls the rate of physical transfer of oxygen at the gas/liquid interface, some significant differences have been identified [Imamura *et al* 1982a, Lin and Chuang 1994, Mishra *et al* 1993, Lin and Ho 1996, Baillod and Faith 1983, Keen and Baillod 1985]. These differences which are usually attributed to the differences in molecular structure that occurs for certain organic compounds at varied pH (eg. the conversion of carboxylic acids to conjugate base form with increasing pH), suggest the need for more research to be conducted on WO/CWO under alkaline conditions.

In the study described herein, model organic compounds (most of which have been identified in various worldwide Bayer liquors) have been used to investigate WO and CWO at moderately low temperature (165°C) under Bayer-like (highly alkaline) conditions. The various aspects of WO/CWO studied include: WO of specific organic compounds at moderately low temperature; the ability of various transition metal oxides to catalyse WO of specific organic compounds; the extent of complete oxidation of specific organic compounds (extent of conversion to carbonate and water i.e. extent of organic removal); the extent of partial oxidation and the products formed from partial oxidation of specific organic compounds; and the type(s) of reaction mechanism(s) occurring during uncatalysed and catalysed wet oxidation.

1.2 Literature review.

1.2.1 The Bayer process.

As mentioned previously, the Bayer process is used to produce alumina (Al_2O_3), which is in turn converted to aluminium using the Hall-Heroult process. The Bayer process, developed by Karl Josef Bayer in 1888, is still the only economically viable process for producing alumina from bauxite ore. The Bayer process can be broken down into four main stages: digestion, clarification, precipitation and calcination. These four main stages and other sub-stages involved in alumina production are shown in Figure 1.1.

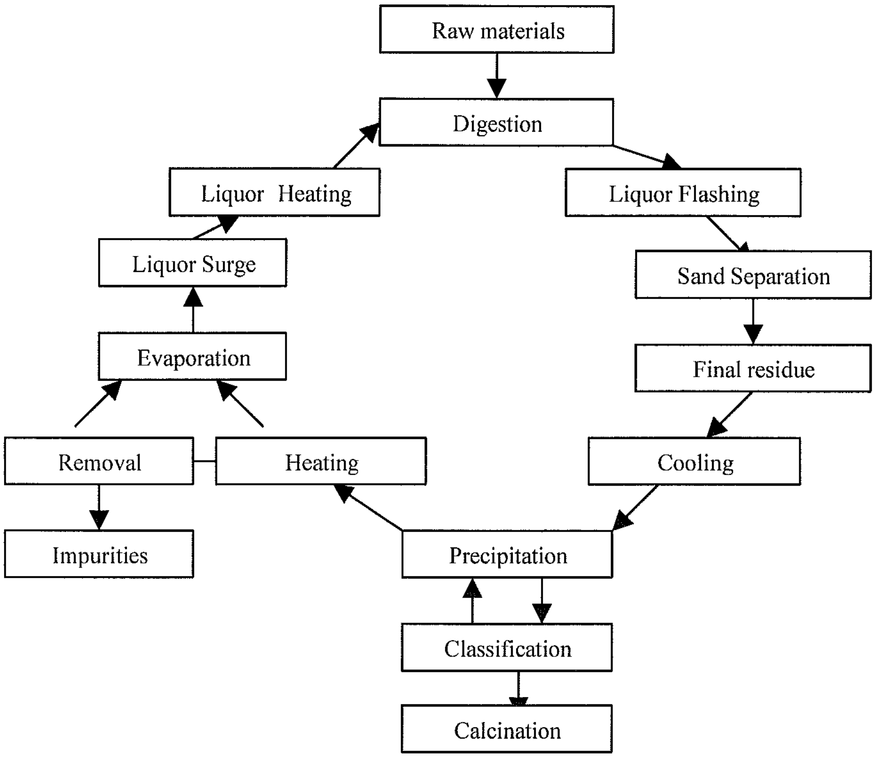

Figure 1.1 *Schematic representation of the Bayer process depicting its' cyclic nature.*

The first main stage in the Bayer process, *digestion*, involves dissolution of aluminium containing compounds present in the bauxite ore in a hot caustic solution (equations 2.1, 2.2). Three main types of aluminium compounds are found in bauxite: gibbsite ($Al(OH)_3$), boehmite ($AlO(OH)$) and diaspore ($AlO(OH)$). The type(s) of aluminium compound(s) present in bauxite strongly influence the digestion conditions required, with dissolution of gibbsite occurring more easily (145°C and 4-5M NaOH) compared to boehmite and diaspore (170-265°C and up to 7M NaOH).

$$Al(OH)_{3\,(s)} + NaOH_{(aq)} \xrightarrow{\text{heat}} Na^+Al(OH)_4^-{}_{(aq)} \qquad (2.1)$$

$$AlO(OH) + NaOH_{(aq)} + H_2O \xrightarrow{\text{heat}} Na^+Al(OH)_4^-{}_{(aq)} \qquad (2.2)$$

The next main stage in the Bayer process, *clarification*, involves removal of the insoluble portion of the bauxite remaining after digestion. This insoluble portion consists predominantly of silica, and iron and titanium oxides, and is commonly referred to as 'red-mud'. These solids are removed using a combination of settling and filtration processes.

The third main stage in the Bayer process, *precipitation*, is essentially the reverse of the digestion stage (equation 2.3). Gibbsite is precipitated from Bayer liquor by cooling and seeding with high surface area gibbsite. It is during this stage that dissolved organic impurities have their most significant adverse effects. These effects are discussed in detail in section 1.2.2.1.

$$Na^+Al(OH)_4^-{}_{(aq)} \longrightarrow Al(OH)_{3\,(s)} + NaOH_{(aq)} \qquad (2.3)$$

The final stage of the Bayer process, *calcination*, involves the conversion of gibbsite to alumina (equation 2.4). This is achieved by removing moisture and converting hydroxide ions to water at extremely high temperatures (900 - 1100°C). The conditions used in calcination can be varied to produce aluminas with different properties.

$$2Al(OH)_{3\,(s)} \longrightarrow Al_2O_{3(s)} + 3H_2O_{(l)} \qquad (2.4)$$

1.2.2 Organic compounds encountered in the Bayer process

As mentioned earlier, bauxite ore contains a number of non-aluminium containing compounds, which are introduced into the Bayer process with the ore. Of these many unwanted compounds, organic compounds, clearly have the most adverse effects on the Bayer process.

Bauxite ores usually contain only 0.05 - 0.5% organic material [Mc Intosh 1985]. However due to the closed cyclic nature of the Bayer process (refer to Figure 1.1) unwanted organic compounds which enter, and are not removed during clarification, build up over time before a steady state level is reached. The level of organic compounds present in Bayer liquor is usually expressed in terms of Total Organic Carbon (TOC). TOC levels in various worldwide Bayer liquors are given in Table 1.1.

Table 1.1 *TOC in various worldwide Bayer liquors.*

Country	TOC (g/l)	Reference
Australia - Kwinana	37.8	Zoldi *et al* 1988
Australia – Pinjarra	27.6	Zoldi *et al* 1988
Australia – Gladstone	23.0	Jayaweera *et al* 1981
Africa	5.5	Yamada *et al* 1973
Hungary – Ajka	4.1	Zoldi *et al* 1988
Hungary – Almasfuzito	6.1	Zoldi *et al* 1988
India	11.6	Zoldi *et al* 1988
Italy	22.5	Zoldi *et al* 1988
Jamaica – low temp digestion (135°C)	8.5	Lever 1978
Jamaica- High temp digestion (240°C)	15.0	Lever 1978
South East Asia	8.1	Yamada *et al* 1973
USA	15.2	Zoldi *et al* 1988
USSR	5.2	Zoldi *et al* 1988

The composition of the organic compounds that enter the Bayer process with the bauxite ore, and the composition of organic compounds at steady state in Bayer liquor differ considerably. This is due to partial degradation/oxidation of some of the organic compounds under the harsh conditions of the Bayer process. A detailed description of the organic compounds in bauxite ore is not within the scope of this project, as this project is based on the removal of organic compounds from Bayer liquor and not bauxite ore (a subject area in its own right), hence only the composition of organic compounds in Bayer liquor is discussed.

Several comprehensive studies, investigating the composition of organic compounds in Bayer liquors have been published. Lever [1978] classified the organic compounds found in Bayer liquors from two different alumina refineries into three groups:

(i) humic matter, consisting of high molecular weight organic compounds and their initial degradation products;

(ii) intermediate "building block" organic compounds; and

(iii) the major group, the lower molecular weight degradation products such as acetic, formic, oxalic and malonic acids

Guthrie *et al* [1984] identified a number of organic compounds in Bayer liquor using GC/MS. The organic compounds identified by Guthrie *et al* [1984] are shown in Table 1.2. Niemela [1993] also thoroughly investigated the composition of low and medium molecular weight organic compounds in a Western Australian refinery liquor, identifying and quantifying over 100 different organic compounds.

The available literature on the composition of organic compounds in Bayer liquors illustrates the vast and diverse range of organic compounds encountered in the Bayer process. This vast and diverse range of compounds undoubtedly continues to cause many difficulties to those studying the chemistry of these compounds in Bayer liquor.

Table 1.2 *Organic compounds identified in Bayer liquor by Guthrie et al [1984].*

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1.2.2.1 Problems caused by organic compounds.

A wide array of organic compounds have been shown to have adverse affects on various stages of the Bayer process [Ramana Rao and Chandwani 1997, Coyne 1989, Zoldi *et al* 1988, Brown 1991, Grocott and Rosenberg 1988, Sang 1988, Armstrong 1993, Alamdari 1993, Tran 1996, Coyne *et al* 1994, Atkins and Grocott 1988]. The adverse effects of organic compounds can generally be split into one of the following three major areas: effects on product yield (and hence productivity); effects on product quality; and effects on liquor handling/general process parameters. The adverse affects of organic compounds on product yield and product quality are clearly the most significant, as these problems affect the economic viability of an alumina refinery [Coyne 1989].

There has been a substantial amount of literature published on the effects of various types of organic compounds on gibbsite yield and quality [Ramana Rao and Chandwani 1997, Coyne 1989, Zoldi *et al* 1988, Brown 1991, Grocott and Rosenberg 1988, Watling 1999, Smith *et al* 1995]. For example, sodium tartrate, sodium gluconate, adonitol and mannitol were shown by Coyne [1989] to cause decreases in gibbsite precipitation yield. Glucoisaccharinate was also shown by The [1980] to decrease gibbsite precipitation yield. Sato and Kazama [1971] and Yamada *et al* [1973] also found organic compounds to hinder gibbsite precipitation yield though neither of these authors' identified the types of organic compounds used in their experiments. A number of organic compounds have been shown to cause adverse affects on gibbsite quality. Glucoisaccharinate [The 1980, Brown 1986] and acetic, lactic, formic and succinic acids [Brown 1986] have been shown to produce a higher proportion of precipitated gibbsite with smaller particle size (fining).

Fine gibbsite particles cause difficulties in handling/transportation. Other adverse affects on gibbsite quality, attributed to organic compounds include discolouration caused by coloured organic compounds (humic/fulvics) [Coyne 1989] and increased soda (Na_2O) content in gibbsite caused by compounds containing relatively acidic adjacent hydroxyl groups [Grocott and Rosenberg 1988].

Apart from their adverse affects on product yield and quality, organic compounds also affect other areas of the Bayer process. Organic compounds have been shown to cause: caustic losses due to formation of organic sodium salts; foaming of Bayer liquor, which leads to handling difficulties; increased liquor viscosity which leads to restricted flow; and reduction of the settling rates of insoluble oxides with a corresponding lowering of their removal rate.

1.2.2.2 Removal of organic compounds.

A number of organic compound removal processes have been investigated and implemented over the years, with each of these processes having to contend with the harsh conditions used in the Bayer process (sodium hydroxide concentration > 4.0 M, temperatures 80 – 270 °C). Some of the most well-known removal processes which have been investigated and/or implemented include: the removal of sodium oxalate, liquor burning and Wet Oxidation (WO)/Catalytic Wet Oxidation (CWO).

Sodium oxalate removal has received considerable attention, with a number of removal processes being reported in the literature [Gnyra and Lever 1979; Gnyra 1981; Atkins and Grocott 1993; Perotta and Williams 1995, The and Bush 1987, Hollanders and Boom 1994]. Alcoa World Alumina's Australian refineries currently remove sodium oxalate using a side stream process. This process involves evaporation of the liquor which causes a decrease in oxalate stability (oxalate has a relatively low solubility in Bayer liquor). The destabilised liquor is then seeded with high surface-area sodium oxalate to induce crystallisation. The solid sodium oxalate produced is then removed by filtration. Unfortunately this method is relatively inefficient, requiring a large amount of oxalate seed to achieve a small amount of crystallisation.

The removal of organic compounds via liquor burning has been aptly referred to as a "sledge hammer" approach [Nyeboer 1999]. This process removes all organic compounds by incinerating them at extremely high temperatures. The main advantage of this process is that all organic compounds are removed. The main disadvantages of liquor burning are its high start-up costs and low throughput (high costs allow for only relatively small kilns to be used). Although there are many disadvantages associated with liquor burning it still has been implemented at two of Alcoa World Alumina's Western Australian refineries.

The WO/CWO process removes organic compounds from Bayer liquor by oxidising them in the liquid phase, using an oxidising gas such as oxygen or air, to the relatively harmless products of carbon dioxide (which is converted to carbonate in alkaline solution) and water. The main advantages of this process are its cleanliness (no difficult to handle chemicals required), its potential to treat large volumes in a relatively short time, and its operating costs (if conducted at relatively low temperature). The main disadvantage at low temperature is that only a low percentage of organic compounds are completely oxidised to carbon dioxide [Eyer 2000]. However, the low percentage conversion that occurs at relatively low temperature can possibly be overcome using a catalyst.

Whilst there have been a number of organic compound removal processes implemented at alumina refineries over the last three decades, there still remains great interest in either new or improved removal processes. This is understandable, as the removal of organic compounds from Bayer liquor is an ongoing challenge as organic compounds are continually being added to the process with the bauxite ore.

Of the removal processes that have been investigated, the low temperature (<165°C) CWO process, which is the subject of this project, has potential as an improved organics' removal process. This potential does however rely heavily on the development of a suitable catalyst(s) for use under Bayer process conditions. The research conducted on WO and CWO in general, and more specifically under Bayer and Bayer-like conditions, is discussed in detail in the following sections.

1.2.3 Wet Oxidation.

Before discussing the chemistry of WO in the presence of a catalyst (i.e. CWO) it is appropriate to discuss the chemistry of the uncatalysed process (i.e. WO). According to Debellefontaine *et al* [1996] the oxidation of organic compounds by WO involves two steps. The first step, the transfer of oxygen from the gas phase to the liquid phase is a *physical* step. The second step, the chemical reaction between the organic compound and dissolved oxygen is a *chemical* step. The chemical reaction of organic compounds in WO is assumed to proceed via a free radical chain reaction. A simplified diagram of this reaction is shown in Figure 1.2.

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Figure 1.2 *Simplified diagram of a possible free-radical chain reaction occurring in WO [Debellefontaine et al 1996].*

The overall mechanism for WO is therefore dependent on both the rate of oxygen transfer from the gas phase to the liquid phase and the ability of the organic compound(s) present, and the intermediates formed, to undergo oxidation.

The only significant resistance to oxygen transfer is located at the gas-liquid interface (film model) with the three limiting cases being:

- Oxygen reacts within the film because of a rapid chemical reaction. In this way, the oxygen transfer rate is enhanced.
- Oxygen reacts within the bulk liquid where its concentration is close to zero. The overall rate is equal to the physical step of oxygen transfer.

●Oxygen concentration within the bulk liquid is equal to the interface (or equilibrium) concentration. The overall rate is the *chemical* step rate, and usually low.

The effect that the rate of oxygen transfer has on the overall rate can be eliminated through high mixing efficiency, which then enables unbiased kinetic rates to be determined (third case above).

The chemical reaction step depends strongly on the ability of an individual organic compound to undergo a free radical chain reaction. Free radical chain reactions consist of four main reaction steps: initiation, propagation, decomposition/degeneration and termination. Figure 1.3 shows the various radical chain reaction steps involved in the WO of organic compounds, proposed by a number of authors [Emanuel *et al* 1984, Mantzavinos *et al* 1996, Shende *et al* 1994, Tufano 1993]. The high number of possible reactions that can occur during WO inevitably causes the chemistry of WO to be quite complex. This complexity was demonstrated by the study of Day *et al* [1973] who proposed a sixteen step free radical mechanism for the oxidation of a simple, low molecular weight organic compound, propionic acid ($C_3H_6O_2$).

Initiation

$$RH + O_2 \rightarrow R\bullet + HOO\bullet \qquad (2.3.1)$$
$$2RH + O_2 \rightarrow 2R\bullet + H_2O_2 \qquad (2.3.2)$$
$$RH + \bullet OH \rightarrow R\bullet + H_2O \qquad (2.3.3)$$

Propagation

$$R\bullet + O_2 \rightarrow ROO\bullet \qquad (2.3.4)$$
$$ROO\bullet + RH \rightarrow ROOH + R\bullet \qquad (2.3.5)$$

Decomposition

$$ROOH \rightarrow RO\bullet + HO\bullet\text{, alcohols, ketones, acids} \qquad (2.3.6)$$
$$ROOH + RH \rightarrow R\bullet + RO\bullet + H_2O \qquad (2.3.7)$$

Termination

$$R\bullet + R\bullet \rightarrow R\text{-}R \qquad (2.3.8)$$
$$ROO\bullet + R\bullet \rightarrow ROOR \qquad (2.3.9)$$
$$ROO\bullet + ROO\bullet \rightarrow ROH + R_1COR_2 + O_2 \qquad (2.3.10)$$
$$2ROO\bullet \rightarrow ROOR + O_2 \qquad (2.3.11)$$

Figure 1.3 *Proposed free radical chain reactions involved in the WO of organic compounds.*

A number of studies on the WO of simple, low molecular weight organic compounds have been conducted [Randall and Knopp 1980, Randall 1981, Day *et al* 1973, Williams *et al* 1973, Shende and Levec 2000, Shende and Levec 1999a and 1999b]. This is due to these compounds usually being formed as "hard to oxidise" intermediates during WO (see simplified WO chemical reaction step Fig. 1.2). Figure 1.4 shows the reaction mechanisms proposed by Mantzavinos *et al* [1996] for the WO of the low molecular weight organic compounds acetic, formic and malonic acids. These compounds have all been identified in quite significant concentrations (in their sodium salt form) in Western Australian Bayer liquor [Niemela 1993].

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Figure 1.4 *Proposed reaction mechanisms for the oxidation of low molecular weight products formed in WO of organic compounds [Mantzavinos et al 1996].*

1.2.3.1 Wet oxidation and effect of solution pH.

The general chemistry involved in the chemical reaction step of WO discussed in section 1.2.3, is not necessarily applicable for WO in solution of any pH. It has been shown recently that the pH of the medium can have a significant effect [Imamura *et al* 1982a, Lin and Chuang 1994, Mishra *et al* 1993, Lin and Ho 1996]. The effect of pH variation on WO is however based upon relatively few experimental results. A significant amount of research on the WO process has been done using acidic or neutral pH conditions while in many cases authors have failed to even mention the pH of the medium used.

Merchant [1992] observed that the rate of wet oxidation increases with an increase in pH of the medium, while Foussard *et al* [1989] observed the opposite trend, in their studies of formate, oxalate and acetate wet oxidation. Mishra *et al* [1995] state that the wet oxidation of both formic and acetic acids is faster than that of their respective anions formate and acetate because of the higher resonance energy for the anions compared to their acid derivatives (less effective resonance due to separation of charges). Mishra *et al* [1993] also studied the effect of pH on the WO of p-cresol. They found that under alkaline conditions (pH 13.5) p-cresol is oxidised much faster than in acidic or neutral conditions, though the reduction in Chemical Oxygen Demand (COD) (a parameter used to measure bulk organic concentration) is notably slower. They explained this as being due to the carboxylic acids that are formed in the oxidation of p-cresol being in the form of their sodium salts which are very resistant to oxidation. Lin *et al* [1996] found that either increasing or decreasing the pH of the medium (using an initial neutral pH) led to an increase in COD removal in their WO studies using desizing wastewater. Lin *et al* [1996] stated they were not exactly sure why increased COD removal occurred at high and low pH and tentatively attributed this to wet oxidation being promoted by the H^+ or OH^- free radicals which could be produced in the higher and lower pH environments. Chang *et al* [1995] studied the effect of altering pH on the WO of phenol and p-chlorophenol. Chang *et al* [1995] observed that oxidation of both phenol and p-chlorophenol was favoured when alkaline conditions (pH 10.0) were employed. Chang *et al* [1995] however did not discuss possible reasons for their observations.

Foussard *et al* [1989] discussed the WO reaction mechanism of the sodium salt of a low molecular weight carboxylic acid, sodium acetate. These authors proposed a chain reaction mechanism for the wet oxidation of sodium acetate, where the initial oxidation product is a hydroperoxide (HO-O-CH_2-COONa) that decomposes into methanal and carbon dioxide. This reaction pathway is very similar to that proposed by Mantzavinos *et al* [1996] for the WO of acetic acid (Figure 1.4).

The lack of research on the affect of pH (and in particular WO in alkaline solution) has inevitably led to a scarce amount of available information on WO reaction mechanisms in alkaline solution. Apart from the work of the authors discussed above, little work has been done to establish the effect of pH on WO, while even less has been done to establish the reaction mechanisms of wet oxidation of the sodium salts of the low molecular weight carboxylic acids which are generally formed in WO under alkaline conditions.

1.2.4 Catalytic Wet Oxidation.

Catalytic Wet Oxidation has been studied extensively in the last three decades in an attempt to overcome the high temperatures usually required to achieve a high degree of WO [de Leitenberg *et al* 1996, Gallezot *et al* 1996, Levec and Pintar 1995, Baldi *et al* 1974 Sadana and Katzer 1974, Katzer *et al* 1976, Levec *et al* 1976, Levec and Smith 1976]. As this project involved the investigation of transition metal based catalysts only the literature concerning transition metal based catalysts is discussed.

1.2.4.1 Mechanisms of metal catalysed oxidations.

There have been a number of proposed mechanisms presented in the literature describing the role of various metal catalysts in CWO. In general, there are three main types of metal catalysed oxidation mechanisms [Sheldon 1995]: homolytic catalysis (free radical auto oxidation); coordination catalysis; and gas phase (Mars-Van Krevlen mechanism).

The first type of metal catalysed oxidation mechanism, homolytic catalysis, involves the promotion of free radical reactions by a metal-based catalyst. The promotion of free radical reactions involves the catalyst introducing a catalytic cycle through the reduction-oxidation homolytic reactions of hydroperoxides (equations 2.5 –2.7), which are formed in the chemical reaction step of WO (Figure 1.2).

$$\mathrm{ROOH} + \mathrm{Me}^{(n-1)+} \rightarrow \mathrm{RO}\bullet + \mathrm{Me}^{n+} + \mathrm{OH}^- \quad \text{reduction} \qquad (2.5)$$

$$\mathrm{ROOH} + \mathrm{Me}^{n+} \rightarrow \mathrm{ROO}\bullet + \mathrm{Me}^{(n-1)+} + \mathrm{H}+ \quad \text{oxidation} \qquad (2.6)$$

The alkyl peroxy radicals (ROO•) produced in equation 2.6 react with the starting organic compound(s) to produce more hydroperoxides (equation 2.7).

$$\mathrm{ROO}\bullet + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R}\bullet \qquad (2.7)$$

The second type of mechanism involves the oxidation of a coordinated substrate by a metal ion. The oxidised form of the metal is subsequently regenerated by reaction of the reduced form with dioxygen. An example of this type of mechanism is shown in equations 2.8 - 2.9.

$$H_2C{=}CH_2 + Pd^{II} + H_2O \longrightarrow CH_3CHO + Pd^{o} + 2H^{+} \qquad (2.8)$$

$$Pd^{o} + 0.5\,O_2 + 2H^{+} \xrightarrow{[Cu^{II}]} Pd^{II} + H_2O \qquad (2.9)$$

The third type of metal catalysed oxidation mechanism, gas phase (Mars-Van Krevlen mechanism), is mostly applicable to gas-phase oxidations. In this reaction mechanism, an oxometal species oxidises the substrate and the reduced form is subsequently re oxidised by dioxygen (equations 2.10 – 2.11).

$$Me^{n} = O + Sub \longrightarrow Me^{n-2} + SubO \qquad (2.10)$$

$$Me^{n-2} + O_2 \longrightarrow 2Me^{n} = O \qquad (2.11)$$

$Me^{n} = V^{v}, Mo^{vI}$, etc. (exception ; Ag)

1.2.4.2 Transition metal oxidation catalysts.

A number of studies using transition metal-based compounds as CWO catalysts have been presented in the literature [Imamura *et al* 1982a, Imamura 1982b, Shende and Mahajani 1997, Mantzavinos et al 1996, Wakabayshi and Okuwaki 1988, Ito *et al* 1989, Debellefontaine *et al* 1996, Lin and Ho 1996]. Most of these studies however have been conducted under pH neutral or acidic conditions and hence are not completely relevant to this project. There have however been some studies conducted under alkaline conditions, investigating the ability of various transition metal based compounds (Cu, Mn, Co, Fe and Ni) to catalyse the WO of various organic compounds [Wakabayshi and Okuwaki 1988, Mishra *et al* 1993, Debellefontaine *et al* 1996].

Brown [1989] studied $CuSO_4.H_2O$ CWO of Bayer liquor (which contained the typical organic compounds found in Bayer liquor, namely acetic, formic, propionic, oxalic and succinic acids). While Brown did not propose a reaction mechanism, it was stated that in the absence of organic carbon compounds the copper ions crystallise out as black copper(II)oxide (CuO). This was due to the tetra hydroxy cuprate ion, $[Cu(OH)_4]^{2-}$, (the form in which the majority of soluble copper is present under the reaction conditions) presumably being stabilised in solution by complex formation with for eg., benzene carboxylic acids. Hence, it is possible that copper catalysed the WO of various compounds in Bayer liquor via the coordination catalysis mechanism mentioned earlier in section 1.2.4.1.

Mishra *et al* [1993] investigated the ability of CuO to catalyse the WO of p-cresol in alkaline conditions (pH 13.5). They found that COD removal decreased significantly with increasing pH, where COD content was found to be 9378 mg/L after 30 minutes at pH 13.5, while at pH 9 it was 3100 mg/l. The reason given for this difference in COD removal was the same as that mentioned earlier in section 1.2.3.1, i.e. that the sodium salts of low molecular weight carboxylic acids, which are formed at high pH are very resistant to oxidation.

Imamura *et al* [1982a] investigated the effect of increasing pH on the activity of a Co/Bi complex oxide used for the WO of acetic acid. They reported that a significant decrease in the rate of oxidation (in terms of ppm TOC/min) occurred as the pH was increased. The decrease in rate was explained by the low affinity of the acetate ion toward Co/Bi, hence leading to the assumption that Co/Bi has basic sites that adsorb acetic acid in the first step of the reaction when the reaction conditions are acidic.

Wakabayashi and Okuwaki [1988] found that increasing pH resulted in an increase in acetate ion oxidation using an iron powder catalyst in a nickel reactor. The nickel reactor was found to corrode under the experimental conditions employed, and hence nickel oxide also acted as a co catalyst for the oxidation reaction. Wakabayashi and Okuwaki [1988] proposed a base catalysed oxidation mechanism for the oxidation of acetate in the presence of iron powder and nickel oxide (Figure 1.5), where the rate of formation of nickel oxide appears to be one of the rate-determining steps. The main product of the oxidation reaction is oxalate ion. This reaction pathway is therefore significantly different to that proposed by Mantzavinos *et al* [1996] for the uncatalysed WO of acetic acid (Figure 1.4) where formic acid and formaldehyde are thought to be the main products and intermediates formed.

[Copyrighted material omitted. Please consult the original thesis.]

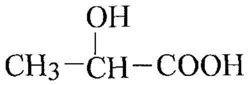
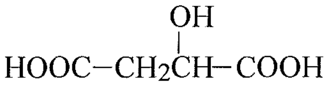
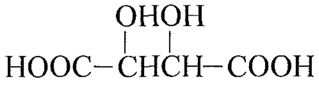
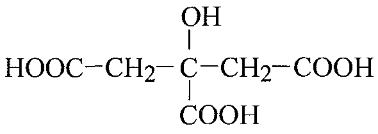
Figure 1.5 *Base catalysed oxidation mechanism proposed by Wakabayashi and Okuwaki [1988] for the CWO of acetate.*

The literature reviewed demonstrates that solution alkalinity can have quite varying effects on CWO for a variety of catalyst/organic systems. The reasons for these varying effects remain unclear mainly due to the lack of research conducted on CWO under alkaline conditions. This research short-fall has also led to a lack of understanding of the types of metal-catalysed oxidation mechanisms that may occur under alkaline conditions. A better understanding of the mechanisms occurring is of great interest to the alumina industry (and other industries where alkaline conditions prevail eg. pulp-paper and petroleum) due to the potential of CWO as a viable organics removal process.

1.2.5 Research Objectives.

The main research objectives of this PhD are outlined in the proceeding paragraphs. These objectives were chosen in an attempt to fill the void that existed in the literature regarding the chemistry (type of reaction mechanisms) occurring during low temperature WO and CWO in alkaline media in general. The organic compounds used in this study (Table 1.3) were chosen based on their prevalence in Bayer liquors worldwide, and their varying molecular structures.

Table 1.3 *Organic compounds studied.*

Organic compound	Molecular structure
Formic	$H-COOH$
Acetic	CH_3-COOH
Propionic	CH_3CH_2-COOH
Butyric	$CH_3CH_2CH_2-COOH$
Oxalic	$HOOC-COOH$
Malonic	$HOOC-CH_2-COOH$
Succinic	$HOOC-CH_2CH_2-COOH$
Glutaric	$HOOC-CH_2CH_2CH_2-COOH$
Lactic	 $CH_3-\overset{\overset{OH}{\vert}}{C}H-COOH$
Malic	 $HOOC-CH_2\overset{\overset{OH}{\vert}}{C}H-COOH$
Tartaric	 $HOOC-\overset{\overset{OH}{\vert}}{C}H\overset{\overset{OH}{\vert}}{C}H-COOH$
Citric	 $HOOC-CH_2-\underset{\underset{COOH}{\vert}}{\overset{\overset{OH}{\vert}}{C}}-CH_2-COOH$

Objective One - Wet Oxidation

To investigate the uncatalysed WO of various organic compounds encountered in the Bayer process under Bayer-like conditions at relatively low temperature (165°C).The main areas investigated for the various compounds studied included:

-Extent of complete oxidation

-Extent of partial oxidation

-Products formed from partial oxidation

-Effect of solution alkalinity on complete and partial oxidation

-Type of reaction mechanism occurring

Objective Two – Transition Metal Oxide catalysed WO.

To investigate the ability of various transition metal oxides to catalyse the WO of various organic compounds encountered in the Bayer process under Bayer like conditions at relatively low temperature (165°C).The various areas investigated included:

-Effect of catalyst(s) on the extent of complete oxidation

-Effect of catalyst(s) on the extent of partial oxidation

-Effect of catalyst(s) on the products formed from partial oxidation

-Type(s) of metal catalysed oxidation mechanism(s) occurring

Objective Three – Fate of specific organic compounds in highly alkaline WO and CWO.

To investigate why certain compounds do/do not undergo uncatalysed and catalysed WO at low temperature under Bayer like conditions.

IMPORTANT NOTE – Organic compounds structures in highly alkaline solution.

Throughout the text of this thesis, all organic compounds are referred to in their acid form although they exist in their sodium salt/anion form in Bayer-like (highly alkaline) solution. This has been done in order to remain consistent with the majority of literature published on organics related Bayer research [Guthrie *et al* 1984, Yamada *et al* 1981, Matyasi *et al* 1986, Zoldi *et al* 1988, Baker *et al* 1995, The *et al* 1985, Watling 2000 and Ramana Rao and Chandwani 1997]. The reaction mechanisms presented in this thesis have however been drawn using the anionic form of the compounds studied as the type(s) of reactions proposed are for the anion form of these compounds.

CHAPTER 2

EXPERIMENTAL

2.1 Materials.

2.1.1 Synthetic Bayer liquor.

All Wet Oxidation (WO) and Catalytic Wet Oxidation (CWO) experiments, unless stated otherwise, were conducted in a highly alkaline solution (4.4M NaOH) simulating that encountered in alumina refining. This solution is hereafter referred to as synthetic Bayer liquor. The composition and method for preparing synthetic Bayer liquor are given in section 2.2.1.1. The following chemicals were used without further purification: Aluminium hydroxide, $Al(OH)_3$, (C31- Alcoa World Alumina); sodium hydroxide, NaOH, (97.5%, BDH Chemicals); sodium carbonate, Na_2CO_3, (99.9%, BDH Chemicals); sodium sulfate, Na_2SO_4, (99.0-100.5%, BDH Chemicals); sodium chloride, NaCl, (99.5%, BDH Chemicals); sodium phosphate, Na_3PO_4, (98-102%, Ajax); and silicic acid (Sigma). Milli-Q water was used to prepare all synthetic Bayer liquors.

2.1.2 Gas.

Oxygen (Linde) with a minimum purity of 99.5% was used in all WO and CWO experiments.

2.1.3 Organic compounds.

The following organic compounds were used without further purification; formic acid, $CHCOOH$, (BDH Chemicals); acetic acid, CH_3COOH, (BDH Chemicals); propionic acid, CH_3CH_2COOH, (98.0%, BDH Chemicals); butyric acid, $CH_3(CH_2)_2COOH$, (BDH Chemicals); oxalic acid, $HOOCCOOH$, (99.5%, May and Baker); malonic acid, $HOOCCH_2COOH$, (98.0+%, BDH Chemicals); succinic acid, $HOOC(CH_2)_2COOH$, (99.0+%, BDH Chemicals); glutaric acid, $HOOC(CH_2)_3COOH$, (99.0%, Merck); lactic acid, $CH_3CHOHCOOH$, (BDH Chemicals); DL-malic acid, $HOOCCHOHCH_2COOH$, (99.0%, BDH Chemicals); (+/-) tartaric acid, $HOOCCHOHCHOHCOOH$, (99.5%, May and Baker); and citric acid, $HOOCCOH(CH_2COOH)_2$, (AR, Sigma).

2.1.4 Transition metal oxides.

The following transition metal oxides were used without further purification in CWO experiments; copper(II)oxide, CuO, (99.0+%, Aldrich); iron(III)oxide, Fe_2O_3, (95%, BDH Chemicals); cobalt(II/III)oxide, Co_3O_4, (pro analysi, Merck); manganese(IV)oxide, MnO_2, (LR, Ajax); and nickel(III)oxide, Ni_2O_3, (extra pure, Merck).

2.2 Methods.

2.2.1 Preparation of synthetic Bayer liquor.

2.2.1.1 Preparation of 'standard' synthetic Bayer liquor.

2.4 L batches of synthetic Bayer liquor were prepared as follows; NaOH (422.40 g) was dissolved in ~1L milli-Q water in a 2L plastic beaker. Once dissolution of the NaOH was complete, $Al(OH)_3$ (366.95 g), was added slowly whilst heating (~100°C) and stirring. In a separate beaker, Na_2CO_3 (101.76 g), was dissolved in ~ 500 mL hot milli-Q water and then added to the sodium aluminate solution (heating and stirring continuously). NaCl (48.00 g), Na_2SO_4 (60.00 g), Na_3PO_4 (0.88 g) and silicic acid (2.56 g) were then dissolved as much as possible in ~ 500 mL hot milli-Q water in a separate beaker before being added to the sodium aluminate solution containing Na_2CO_3. The resulting synthetic liquor was then allowed to heat and stir continuously for ~ 1 hour to ensure complete dissolution of all components. The synthetic Bayer liquor was then filtered (vacuum) while hot (~80°C) through a Whatman No.1 filter paper. Any solids remaining (inorganic salts) on the filter paper after filtration were dissolved using hot milli-Q water. The filtered synthetic Bayer liquor was then made up to 2.4 L with hot milli-Q water and separated immediately into four equal portions.

The resulting composition of the prepared synthetic Bayer liquor was confirmed using a variety of analytical methods outlined in section 2.2.4.1. The composition of standard synthetic Bayer liquor used in this study is given in Table 2.1.

Table 2.1 *Composition of standard synthetic Bayer liquor.*

Compound	Concentration (g/L)
Al	100.0 (expressed as Al_2O_3) (1.96 M)
NaOH	176.0 (4.40 M)
Na_2CO_3	42.4 (0.40 M)
Na_2SO_4	25.0 (0.18 M)
NaCl	20.0 (0.34 M)
Na_3PO_4	0.37 (0.002 M)
Si	0.82 (expressed as SiO_2) (0.014 M)

Although the amount of sodium hydroxide used to prepare synthetic Bayer liquors was the amount required to give a concentration of 4.4 M, the actual 'free' hydroxide ion concentration in the synthetic Bayer liquors used was significantly lower due to the reaction between sodium hydroxide and aluminium hydroxide (equation 3.1). The actual 'free' hydroxide ion concentration in the synthetic Bayer liquors used is 2.44 M.

$$Al(OH)_{3\,(s)} + NaOH_{(aq)} \xrightarrow{heat} Na^{+}Al(OH)_4^{-}{}_{(aq)} \qquad (3.1)$$

2.2.1.2 Preparation of high alkalinity (5.7 and 7.0 M NaOH) synthetic Bayer liquors.

High alkalinity synthetic Bayer liquors were prepared using a similar method to that outlined in section 2.2.1. The only difference between the two methods was the volume of water used to prepare the highly alkaline liquors. Batches of the highly alkaline liquors were made up to 2.0 L in total (cf. 2.4 L for standard batches) and split into 4 x 500 mL portions. The final alkalinity required was then achieved by addition of 100 mL of an extremely alkaline solution (7.85 or 15.70 M NaOH solution depending on alkalinity required) directly to the autoclave vessel already containing the slightly concentrated 500 mL portion of synthetic Bayer liquor, just prior to conducting the WO/CWO experiment. Highly alkaline synthetic Bayer liquors were prepared partly *in situ* to avoid precipitation of some of the inorganic species present in synthetic Bayer liquor, at room temperature, prior to the solution being transferred to the autoclave. The 'free' hydroxide ion concentration in 5.7 M and 7.0 M synthetic Bayer liquors was 3.74 M and 5.04 M respectively.

2.2.2 Standard Wet Oxidation and Catalytic Wet Oxidation test procedure

2.2.2.1 Apparatus.

All reactions, unless stated otherwise, were conducted in a 1.2 L inconel autoclave (Parr Instruments Co. USA). The autoclave was equipped with a magnetically driven stirrer (consisting of two six blade impellers), and fittings for gas addition and sample removal. The autoclave set-up also included a Parr 4843 controller to allow temperature and stirrer speed to be maintained at predetermined values. Pressure readings were also obtained using the controller via a pressure transducer directly attached to the autoclave assembly.

A schematic of the autoclave set up used is shown in Figure 2.1.

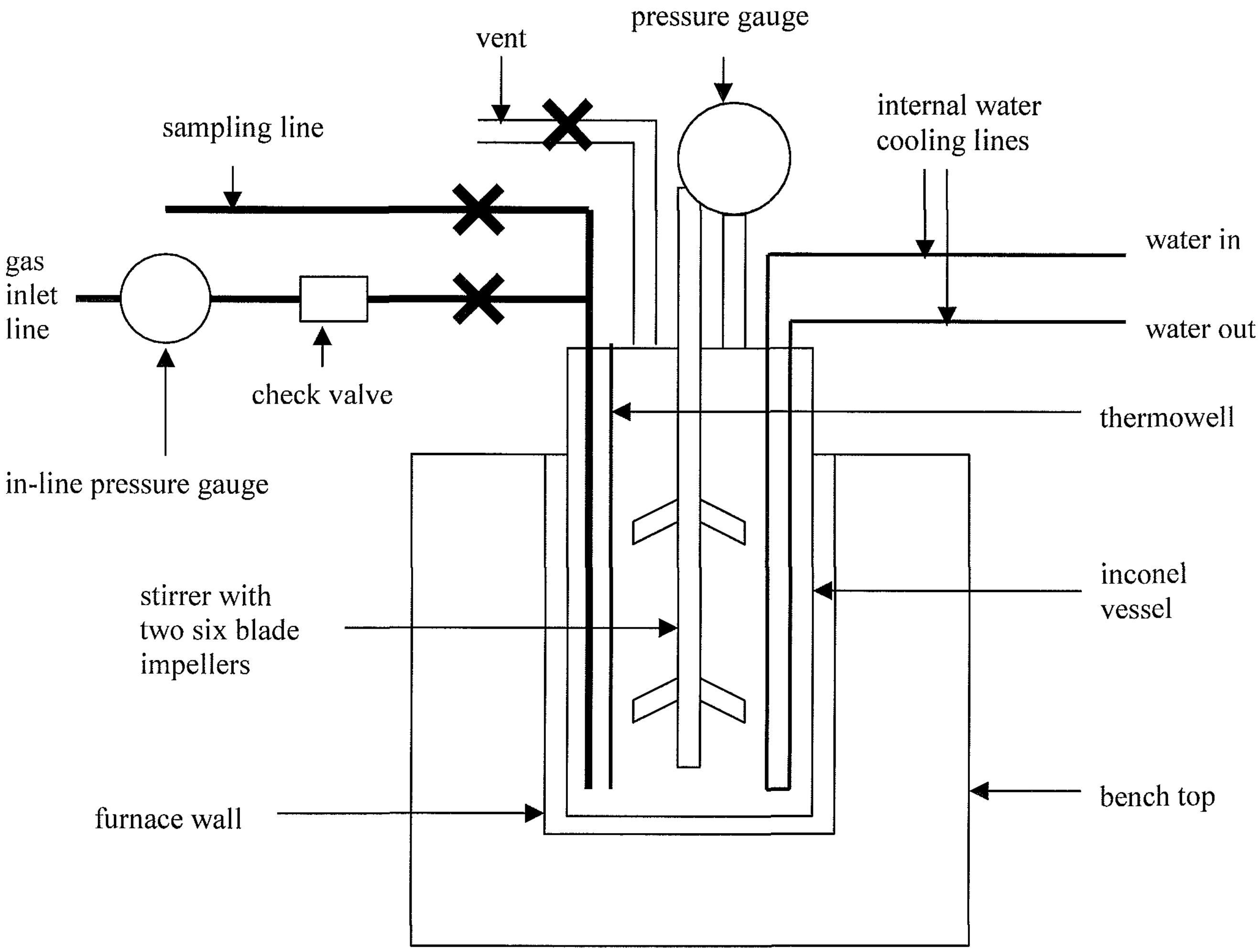


Figure 2.1 *Schematic diagram of autoclave set-up.*

2.2.2.2 WO/CWO test procedure.

All autoclave reactions, unless stated otherwise, were conducted as follows; 600 mL of synthetic Bayer liquor was added to the reaction vessel, followed by the organic compound(s) to be studied and catalyst (if needed). All organic compounds used were added in their acid form (as purchased), though it can be readily assumed that all acids investigated were quickly converted to their sodium salt form in synthetic Bayer liquor (based on pKa values of the organics studied and the pH of synthetic Bayer liquor (pH>=14)). The reaction vessel was then sealed and evacuated (water vacuum) to –67 kPa to remove oxygen in the headspace area, to minimise the possibility of oxygen induced oxidation before reaching the set point temperature. The reaction solution was then stirred and heated until reaching the desired set point temperature. The time at reaching the set point temperature was designated time zero. Once the desired temperature was reached oxygen was added at the partial pressure required. The partial pressure of the added gas was then maintained (manually) at the required amount throughout the course of the reaction. Samples were removed at pre-determined times throughout the course of the reaction.

2.2.2.3 Sample removal and treatment procedures.

All samples were removed from the autoclave at high temperature and pressure via the sample removal line (Figure 2.1). Prior to the removal of samples the incoming gas line was closed (except for time zero samples which were taken just prior to gas addition) and 15-20 mL of the reaction solution was allowed to rinse through the sampling line to remove any solution remaining in the line from prior samples. 20-30 mL of the reaction solution was then removed and diluted (1:4, milli-Q water) immediately. Samples were then cooled to room temperature (cold water bath) and filtered through a Whatman no. 42 filter paper. The filtrates were then collected and stored in non-transparent plastic bottles for analysis.

2.2.3 Standard Wet Oxidation and Catalytic Wet Oxidation reaction conditions.

The reaction conditions outlined below were used for all WO/CWO experiments, unless stated otherwise, and are hereafter referred to as standard reaction conditions. The standard reaction conditions chosen for this project were based on a combination of factors. These included the main aim of the project (to investigate the chemistry of low temperature WO/CWO of various organic compounds), relevant literature, instrumental and analytical limitations, safety considerations and initial testing results.

- Temperature- 165°C
- Impeller speed – 1000 rpm
- Oxygen (WO and CWO) partial pressure – 500 kPa
- Total pressure – 980 kPa
- Organic concentration – 1.875 g/L as C
- Volume – 600mL standard synthetic Bayer liquor (see Table 3.1)
- Catalyst concentration – 5.0 g/L
- Two hour reaction time, upon reaching set point temperature

2.2.4 Analytical methods.

2.2.4.1 Analysis of synthetic Bayer liquor composition.

The ALIAN Automated Titration system, developed by Alcoa World Alumina for the automated analysis of Bayer process liquors, was used to determine NaOH, Na_2CO_3 and Aluminium concentrations in synthetic Bayer liquors. The titration system is based upon the work of Watts and Utley [Watts and Utley 1956]. The titration procedure can be explained as follows:

1. $Na^{+-}OH$ in the form $Na^+Al(OH)_4^-$ is liberated by the addition of excess gluconate complexing agent:

$$Na^+Al(OH)_4^- + (Gluc)^- \longrightarrow Na^{+-}OH + Al(OH)_3(Gluc)^-$$

2. The free $Na^{+-}OH$ plus the $Na^{+-}OH$ liberated from $Na^+Al(OH)_4^-$ and CO_3^{2-} is then titrated with acid to pH~10:

$$OH^- + CO_3^{2-} + 2H^+ \longrightarrow H_2O + HCO_3^-$$

3. Excess acid is then added to convert the HCO_3^- to CO_2, which is driven off by a stream of nitrogen:

$$x\,HCO_3^- + XS\,H^+ \longrightarrow CO_{2(g)} + (XS-x)H^+$$

4. The equivalent amount of OH^- (to the excess acid) is added, and the acid titrated to pH~8.1. The titre is thus equivalent to the number of moles of HCO_3^- that reacted with the excess acid.

5. Excess KF is added to liberate the OH^- combined with the aluminium:

$$XS\,KF + Al(OH)_3(Gluc)^- \longrightarrow K_2NaAlF_{6(s)} + 3OH^-$$

6. The liberated OH^- is titrated with acid to give the equivalent aluminate concentration.

Capillary electrophoresis (CE) was used to determine chloride (Cl^-) and sulphate (SO_4^{2-}) concentration [Mullet and Houghton 1999]. Electrophoresis is a technique where charged ions or molecules in an electrolyte are separated by differential migration under an applied electric field.

Phosphorous (P) and silicon (Si) concentration were determined using a Perkin-Elmer, Optima 3000 inductively coupled plasma atomic emission spectrometer (ICP-AES). All samples were diluted (milli-Q water) and acidified (concentrated hydrochloric acid) prior to analysis. A detailed description of the method used is given elsewhere [Eyer and Leavy 1997].

2.2.4.2 Analysis of organic compounds.

The concentration of the following organic compounds were determined using gas chromatography: formic, acetic, butyric, oxalic, malonic, succinic, glutaric, lactic, malic and fumaric acids. The concentration of three of the organic compounds studied could not be determined directly due to various difficulties; propanoic acid (eluted under extraction solvent): citric and tartaric acids (high polarity of these compounds meant they could not be determined using the same column as the other acids studied). The WO and CWO and of these three compounds was therefore determined based on their conversion into inorganic carbon (CO_3^{2-}) and other reaction products identified. This method proved to be successful as the major products resulting from WO and CWO of these compounds could be determined quantitatively.

The method used to detect and quantify organics was as follows; a sample (after 1:5 dilution) is acidified (conc. nitric acid) and reacted with a derivatising agent (methanol/chloroform) at 60°C for ~60 minutes, converting the organic compounds present in the sample into their corresponding methyl esters. These methyl esters are then extracted into chloroform, and a portion of the extracted sample analysed by the GC. The esters of the organic compounds are then separated by the GC column and the amount originally present determined by comparison with known standards and an internal standard (chloroacetic acid) which had been added to the derivatising agent. The GC parameters used were as follows:

Column -	Supelcowax 10 (12 m, i.d. 0.2 mm)
Carrier gas -	Hydrogen
Injector temperature -	220°C
Detector temperature -	230°C (FID)
Temperature programme -	70°C for 1 minute 70°C – 120°C for 2.5 minutes 120°C –170°C for 0.5 minutes held at 170°C for 0.2 minutes
Injection type –	split

2.2.4.3 Organic carbon concentration.

Organic carbon concentration (and conversion of organic carbon into inorganic carbon, CO_3^{2-}) was determined quantitatively using a 1010 Total Organic Carbon Analyser (O-I Analytical). Samples were diluted (milli-Q water) to 10 –100 ppm (organic carbon concentration) and acidified (10 ml conc. orthophosphoric acid per 100 mL diluted solution (conc. orthophosphoric acid, AR, BDH Chemicals)) prior to analysis. The organic carbon concentration is then determined as follows:

1. The instrument is calibrated using a series of organic carbon standards prepared from potassium hydrogen pthalate (Aldrich) and milli-Q water.
2. Samples are then automatically injected into the instrument reaction chamber where they are reacted with further acid (5% w/v ortho phosphoric acid) to convert any remaining inorganic carbon (CO_3^{2-}) to carbon dioxide, which is then removed by a stream of nitrogen (instrument grade).
3. The remaining organic carbon is then oxidised to CO_2 using sodium persulphate (200g/L) and UV light.
4. The CO_2 liberated is then detected using an IR detector, and used to evaluate the amount of organic carbon in the origin sample.

2.2.4.4 Analysis of metal ion concentration.

Dissolved Copper (Cu) concentration in CWO experiments was determined using a Perkin-Elmer, Optima 3000 inductively coupled plasma atomic emission spectrometer (ICP-AES). All samples were diluted (milli-Q water) and acidified with hydrochloric acid prior to analysis. A detailed description of the method used is given elsewhere [Eyer and Leavy 1997].

CHAPTER 3

WET OXIDATION AND CATALYTIC WET OXIDATION OF STRAIGHT CHAIN, C_2-C_5, DICARBOXYLIC ACIDS

3.1 Introduction.

Low molecular weight dicarboxylic acids (such as oxalic, malonic and succinic acids) make up a significant proportion of the Total Organic Carbon (TOC) in various worldwide Bayer liquors. This is due to a number of these compounds being relatively stable products formed from degradation of higher molecular weight compounds such as humic acids that are introduced into the Bayer process with the bauxite ore. Low molecular weight dicarboxylic acids adversely affect alumina refining in a number of ways (refer to section 1.2.2.1) hence removal of these compounds is of particular interest to the alumina refining industry.

In this chapter low temperature (165°C) Wet Oxidation (WO) and Catalytic Wet Oxidation (CWO) of four straight chain dicarboxylic acids has been investigated under Bayer-like (highly alkaline) conditions. The dicarboxylic acids investigated in this chapter: oxalic; malonic; succinic and glutaric, have been identified in various worldwide Bayer liquors (Table 3.1). A few of the dicarboxylic acids studied in this chapter have also been identified in various other industrial waste streams. Ingale *et al* [1996] identified succinic and glutaric acids in the waste stream from a cyclohexane oxidation unit while Chang *et al* [1993] reported the presence of glutaric acid in spent caustic wastewater from a petrochemicals-manufacturing process.

Table 3.1 *Low molecular weight dicarboxylic acids studied in this chapter that have been identified in various worldwide Bayer liquors.*

Country/Region	Dicarboxylic acids identified that are studied in this chapter	Reference
Australia - WA	oxalic, malonic, succinic, glutaric	Niemela [1993]
India	oxalic, succinic, glutaric	Ramano Rao and Chandwani [1997]
Hungary	oxalic, succinic, glutaric	Zoldi *et al* [1988]
West Indies	malonic, succinic, glutaric	Baker *et al* [1995]
na	oxalic, malonic, succinic, glutaric	Guthrie *et al* [1984]
Japan	oxalic, succinic, glutaric	Yamada *et al* [1981]
Germany	oxalic, succinic	Brown [1989]
Hungary	oxalic, succinic, glutaric	Matyasi *et al* [1986]

na = not available

Low molecular weight dicarboxylic acids have also been identified as reaction intermediates and 'hard-to-oxidise' (refractory) compounds produced from partial WO and CWO of larger molecules. Mantzavinos *et al* [1996] identified oxalic acid as a major product in CWO of p-coumaric acid in alkaline (pH=12) solution. Lee and Kim [2000] also identified oxalic acid as a reaction intermediate in CWO of maleic acid.

3.2 Background.

Low molecular weight dicarboxylic acids are most likely present as reactants or reaction intermediates in the WO/CWO of a number of industrial waste streams and process liquors. However due to the majority of studies presented in the literature relying solely on bulk organics measurement techniques such as TOC and Chemical Oxygen Demand (COD) [De Angelo and Wilhemi 1983, Zhang and Chuang 1998, Lin and Ho 1996] there is scarce literature on the composition's of organic compounds in pre and post oxidised industrial waste streams and process liquors.

There is a significant amount of literature available however on the WO and CWO of low molecular weight dicarboxylic acids in simple aqueous solutions, as it is readily acknowledged that these compounds are present in industrial waste streams and liquors. A summary of WO and CWO (limited to research conducted using transition metal based catalysts) studies presented in the literature on the low molecular weight dicarboxylic acids studied in this chapter is given in Table 3.2.

While there has been a significant amount of research conducted on WO and CWO of several low molecular weight dicarboxylic acids over the last three decades, most of this work has however been conducted under similar reaction conditions (acidic solution at high temperature (>200°C)). Hence, there is a lack of literature on WO and CWO of low molecular weight dicarboxylic acids in alkaline solution at low temperature. The only study found in the literature investigating the WO/CWO of a low molecular weight dicarboxylic acid in a simple alkaline solution is the research of Debellefontaine *et al* [1996] on the WO/CWO of potassium oxalate. This study was however conducted at high temperature (230°C), and solution pH was not reported. The results of this study are presented in Table 4.3. Debellefontaine *et al* [1996] do not discuss the reaction mechanism of potassium oxalate WO/CWO in detail.

Table 3.2 *Summary of WO and CWO studies of low molecular weight dicarboxylic acids.*

Dicarboxylic acid	Catalyst	Temperature (°C)	Oxygen pressure	pH	Acid reduction	TOC reduction	Reference
Oxalic	none	225-245	0.69-1.03 MPa	acidic	na	30%, 245°C 5 h	Shende and Mahajani [1994]
Oxalic	$CuSO_4$	120-150	0.69-1.38 MPa	acidic	na	na	Shende and Mahajani [1994]
Oxalic	none	220	15 bar	acidic	na	72%, 2 h	Shende and Levec [1999]
Oxalic	none	112	1.0 MPa	1.4	na	0 %, 20 min	Imamura *et al* [1982b]
Oxalic	none	140	1.0 MPa	1.4	na	27.0 %, 20 min	Imamura et al [1982b]
Oxalic	none	160	1.0 MPa	2.5	na	90.0 %, 20 min	Imamura *et al* [1982]
Oxalic	none	200	0.110 mol O_2 added	acidic	dec	na	Ito *et al* [1989]
Malonic	none	200	0.110 mol O_2 added	acidic	dec	na	Ito *et al* [1989]
Succinic	Co_2O_3	200	0.110 mol O_2 added	acidic	52 %, 2.67 h	27 %, 2.67 h	Ito *et al* [1989]
Succinic	none	248	1.0 MPa	3.2	na	58.6 %, 20 min	Imamura *et al* [1982b]
Succinic	none	240-260	na	na	20-35%	32-64%	Merchant [1992]
Glutaric	none	248	1.0 MPa	8.1	na	72.5 %, 20 min	Imamura *et al* [1982]
Glutaric	none	240-260	na	na	32-54%	24-32%	Merchant [1992]

dec = decomposition occurred in absence of Co_2O_3 at 200°C
na = not available

Table 3.3 *WO/CWO of potassium oxalate [Debellefontaine et al 1996].*

[Copyrighted material omitted. Please consult the original thesis.]

While there is a significant lack of literature on WO/CWO of low molecular weight dicarboxylic acids in simple alkaline solution, there have been a few studies conducted on this class of compounds in complex alkaline solution (Bayer liquor). Yamada *et al* [1981] investigated Cu^{2+} catalysed WO of oxalic, succinic and glutaric acids in Bayer liquor. Matyasi *et al* [1986] also investigated the WO of oxalic, succinic and glutaric acids in Bayer liquor. Both of these investigations were however conducted at high temperature (≥ 235°C, Yamada *et al* [1981] and ≥ 200°C, Matyasi *et al* [1986]). The results of these studies are summarised in Table 3.4. Neither of the above mentioned author's discussed/proposed reaction mechanism(s).

Table 3.4 *Summary of WO and CWO studies conducted for low molecular weight dicarboxylic acids in Bayer liquor.*

Dicarboxylic	Catalyst	Temp (°C)	Oxygen pressure	Acid reduction	Reference
Oxalic	none	260	na	55.56%	Yamada *et al* [1981]
Oxalic	Cu^{2+}	235	na	42.22%	Yamada *et al* [1981]
Oxalic	Cu^{2+}	260	na	22.22%	Yamada *et al* [1981]
Succinic	none	260	na	61.18%	Yamada *et al* [1981]
Succinic	Cu^{2+}	235	na	54.12%	Yamada *et al* [1981]
Succinic	Cu^{2+}	260	na	94.12%	Yamada *et al* [1981]
Glutaric	none	260	na	100%	Yamada *et al* [1981]
Oxalic	none	200	40 bar $(\text{total})^+$	2.9-3.2%*	Matyasi *et al* [1986]
Oxalic	none	242	50 bar $(\text{total})^+$	6.64-2.3%*	Matyasi *et al* [1986]
Succinic	none	200	40 bar $(\text{total})^+$	17.72-15.2%*	Matyasi *et al* [1986]
Succinic	none	242	50 bar $(\text{total})^+$	11.16-19.0%*	Matyasi *et al* [1986]
Glutaric	none	200	40 bar $(\text{total})^+$	1.06-0.9%*	Matyasi *et al* [1986]
Glutaric	none	242	50 bar $(\text{total})^+$	0.30-.54%*	Matyasi *et al* [1986]

na = not available
* change in % composition of total organics in liquor.
$^+$ total system pressure

Although there have been a few studies investigating WO/CWO of low molecular weight dicarboxylic acids in alkaline solution there is no available literature on low temperature (165°C) WO/CWO of low molecular weight dicarboxylic acids in simple, alkaline solution. Hence, there is also no literature available on the chemistry occurring during the WO/CWO of low molecular weight dicarboxylic acids in alkaline solution. In this chapter, the chemistry of low temperature WO/CWO of low molecular weight dicarboxylic acids in simple highly alkaline solution is to the author's best knowledge, investigated for the first time.

3.3 Experimental.

Refer to chapter 2 for all materials, methods, procedures and methods of analyses used for the experimental work conducted in this chapter.

3.4 Results and Discussion.

3.4.1 Wet Oxidation.

3.4.1.1 Extent of WO, TOC reduction and reaction products.

Low temperature (165°C) WO of oxalic, malonic, succinic and glutaric acids in synthetic Bayer liquor (highly alkaline solution) was investigated. The extent of WO, TOC reduction and products formed from partial oxidation, under standard test conditions (refer to section 2.2.3), for the dicarboxylic acids studied are presented in Tables 3.5 and 3.6 respectively. Malonic acid was the only compound that underwent appreciable WO (>2% conversion to carbonate and other low molecular weight compounds). Thermal degradation (i.e. degradation in the absence of oxygen) of malonic acid did not occur. Although malonic acid underwent appreciable WO (18.5 %) under the reaction conditions used, only 7.6 % of the initial amount (1.87 g OC/L) was completely removed (oxidised to carbonate), with the remaining oxidised carbon being converted to lower molecular weight compounds (oxalic and formic acids). The products formed from malonic acid WO in order of increasing amount (in terms of carbon) were oxalic acid >

carbonate > and formic acid. These three products accounted for >98% of the malonic acid oxidised.

Table 3.5 *Extent of WO and TOC reduction under standard test conditions (refer to section 2.2.3).*

Dicarboxylic acid	Extent of WO (%) 2h	TOC reduction (%) 2h
Oxalic	<2	<2
Malonic	18.5	7.6
Succinic	<2	<2
Glutaric	<2	<2

Table 3.6 *Reaction products under standard test conditions (refer to section 2.2.3).*

	Reaction products (g Organic Carbon / L), 2h		
Dicarboxylic acid	Oxalic	Carbonate	Formic
Oxalic	NA	NA	NA
Malonic	0.19 (55.1)	0.14 (41.0)	0.02 (4.8)
Succinic	NA	NA	NA
Glutaric	NA	NA	NA

% proportion (in terms of carbon) of total oxidation products in parentheses
NA = Not Applicable

The ability of malonic acid to undergo WO under the standard test conditions (and the lack of WO observed for the other compounds tested) was assumed to be due to the comparatively more acidic alpha hydrogens present in malonic acid. Malonic acid contains two adjacent electron-withdrawing groups either side of the central carbon (refer to Table 1.3 for molecular structure of malonic acid), which could possibly react with the hydroxide present in synthetic Bayer liquor (4.4 M NaOH). This assumption was based on the base catalysed WO reaction mechanism proposed by Wakabayashi and Okuwaki [1988] (refer to Figure 1.10) and Furuya *et al* [1985]. Based on the assumption mentioned above it was decided to investigate the effect of [OH$^-$] on the WO of malonic acid (and the other dicarboxylic acids).

3.4.1.2 Effect of [OH$^-$] on WO, TOC reduction and reaction products.

The effect of [OH$^-$] on the extent of WO, TOC reduction and reaction products formed, for the dicarboxylic acids studied is given in Table 3.7 and Figure 3.1 respectively. The WO of malonic acid is clearly affected by [OH$^-$], with a significant increase in the extent of WO occurring with increasing [OH$^-$], confirming that the WO of malonic acid in highly alkaline solution may occur via removal of a slightly acidic alpha hydrogen.

The type of reaction products formed from the WO of malonic acid was unaffected by [OH$^-$], with the same reaction products (oxalic, carbonate and formic) observed over the [OH$^-$] range studied. The reaction products identified accounted for >98% of the oxidised malonic acid in all tests. The distribution of reaction products did however change slightly with increasing [OH$^-$]. The proportion of oxalic acid formed increased between 4.4 M and 7.0 M NaOH, while the reverse trend occurred for carbonate. The proportional yield of formic acid decreased slightly with increasing [OH$^-$] over the concentration range studied. The order of the amount of products formed did however remain the same over the range of [OH$^-$] studied (oxalic acid > carbonate > formic acid).

Increasing [OH$^-$] did not have an effect on the WO of the other dicarboxylic acids studied, as these compounds did not undergo appreciable WO even at extremely high alkalinity (7.0 M NaOH). This result was expected for oxalic acid as this compound does not have any hydrogen atoms that can be removed. It was assumed however that succinic and glutaric acids, which do contain slightly acidic alpha hydrogens (which are however comparatively less acidic than those on malonic acid) could possibly have undergone appreciable WO (>2%) in extremely alkaline solution. As no WO was observed over the [OH^-] range studied this would suggest that either sodium hydroxide is not a strong enough base to remove the weakly acidic alpha hydrogens on succinic and glutaric acids, or that the activation energy required for this reaction to take place at a measurable rate is not available under the experimental conditions used (refer to section 3.2.3). As the main aim of this project was to study low temperature (165°C) WO, the possibility of an energy barrier was not investigated further.

Table 3.7 *Extent of WO with increasing [NaOH]. Standard reaction conditions (refer to section 2.2.3), except for synthetic Bayer liquor [NaOH] (refer to section 2.2.1.2).*

Dicarboxylic acid	Extent of WO (%) after 2h at various alkalinity		
	4.4M NaOH	5.7 M NaOH	7.0 M NaOH
Oxalic	<2	<2	<2
Malonic	18.5 (7.6)	29.6 (12.7)	39.5 (15.0)
Succinic	<2	<2	<2
Glutaric	<2	<2	<2

TOC reduction in parentheses.

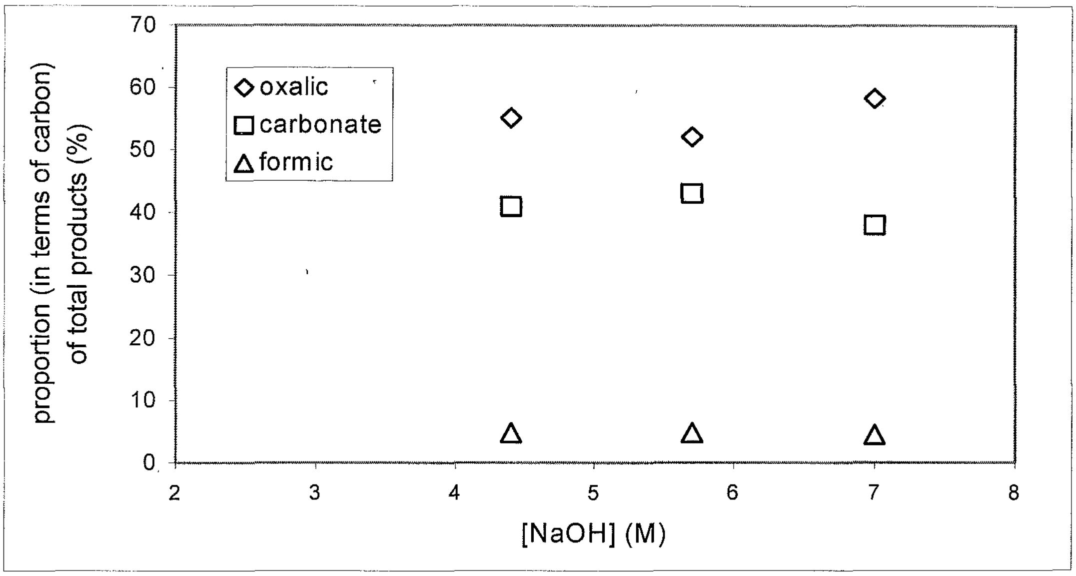


Figure 3.1 *Effect of [OH⁻] on malonic acid WO product distribution. Standard reaction conditions (refer to section 2.2.3) except for synthetic Bayer liquor [NaOH] (refer to section 2.2.1.2).*

3.4.1.3 WO reaction mechanism studies.

3.4.1.3.1 Type of reaction mechanism occurring during malonic acid WO.

The general type of reaction mechanism (ionic and/or free radical chain) occurring during the WO of malonic acid was studied by an indirect method, as the reaction conditions used in WO tests (4.4 M NaOH, 165°C, 980 kPa total pressure) did not readily allow *in situ* probing of the reaction. To test the possibility that the WO of malonic acid was occurring via a free radical chain reaction it was decided to investigate the effect that the presence of the other dicarboxylic acids studied had on the WO of malonic acid and vice versa. These tests were based on the assumption that if malonic acid was being wet oxidised via a free radical chain reaction then any free radicals produced could possibly interact with other organic compounds present. The composition of reactants used for these tests is given in Table 3.8.

Table 3.8 *Composition of organic mixtures used in co oxidation tests.*

Organics	Malonic concentration g/L (mol/L)	Oxalic, succinic or glutaric concentration g/L (mol/L)	Mol ratio (malonic : added dicarboxylic)
Malonic blank	19.80 (0.190)	NA	NA
Malonic – oxalic*	19.77 (0.190)	2.28 (0.027)	7.04 : 1
Malonic - succinic	19.10 (0.184)	4.33 (0.037)	4.97 : 1
Malonic - glutaric	19.71 (0.189)	5.02 (0.038)	4.97 : 1

NA = Not Applicable
*Due to the limited solubility of oxalic acid in highly alkaline solution a different ratio was used

Figure 3.2 shows the effect of malonic acid undergoing WO on added succinic and glutaric acids. Succinic and glutaric acids, shown earlier to undergo no appreciable (>2%) WO in isolation (Table 3.5), were oxidised significantly when present in the same solution as malonic acid undergoing WO. Hence, malonic acid WO in highly alkaline solution occurs via a free radical chain reaction mechanism.

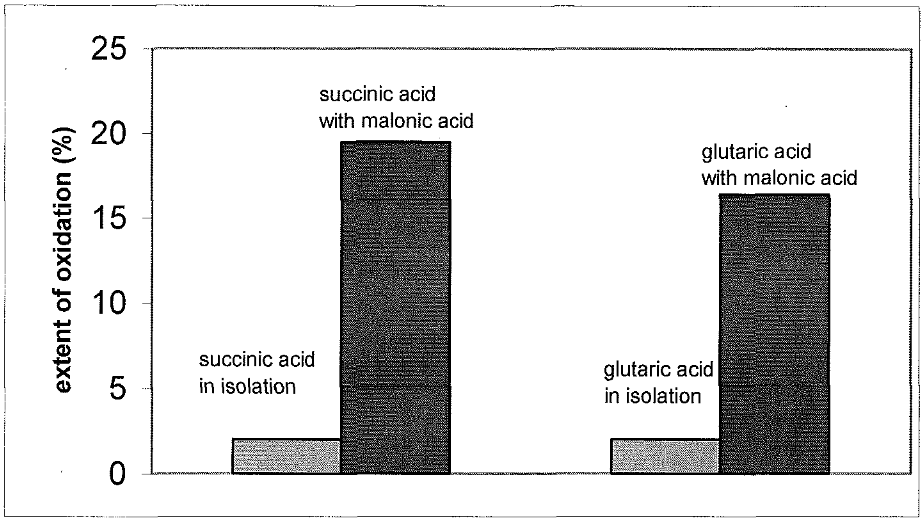


Figure 3.2 *Effect of malonic acid wet oxidation on succinic and glutaric acids. Standard reaction conditions (refer to section 2.2.3), except 5:1 mol ratio of malonic: succinic and malonic: glutaric (refer to Table 3.8).*

The ability of the free radicals produced in malonic acid WO to co oxidise oxalic acid was also studied. As oxalic acid is a significant product of malonic acid WO its co oxidation could not be studied quantitatively. The amount of oxalic acid co oxidised by malonic acid was determined semi-quantitatively. This was done by subtracting the amount of oxalic acid formed during malonic acid WO in isolation from the amount formed during the co oxidation test, therefore giving the amount of oxalic acid remaining from that which had been added at the beginning of the test. Based on this semi-quantitative method it was established that oxalic acid is also co oxidised by free radicals produced during malonic acid wet oxidation.

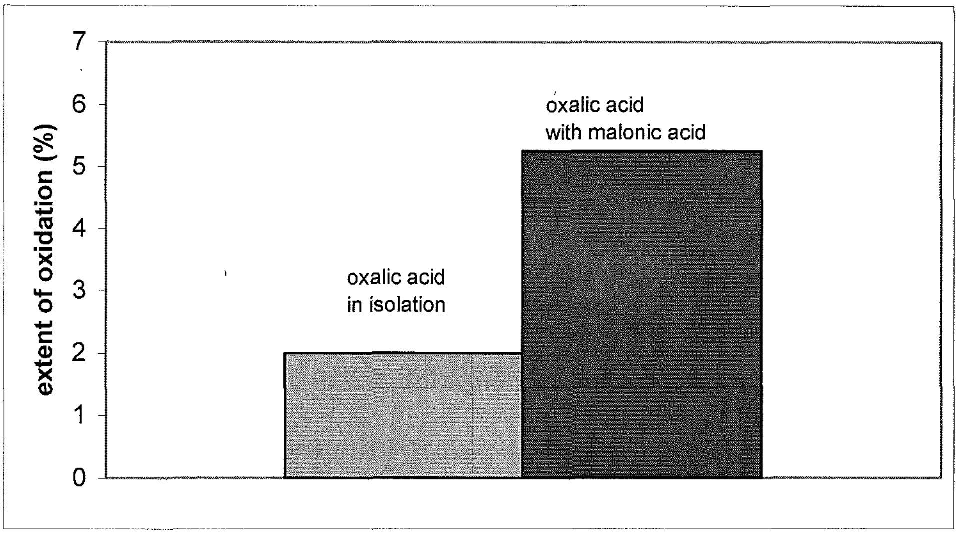


Figure 3.3 *Effect of malonic acid wet oxidation on oxalic acid. Standard reaction conditions (refer to section 2.2.3), except 7:1 mol ratio of malonic: oxalic (refer to Table 3.8).*

The extent to which oxalic acid was co oxidised by malonic acid (5.25 %) was much less than the extent of co oxidation undergone by succinic (19.50 %) and glutaric (16.40 %) acids. This is most likely due to oxalic acid containing no hydrogen atoms (which are usually readily abstracted by free radical intermediates), and also the slightly lower ratio of oxalic acid to malonic acid used. The slight difference in the extent of co oxidation undergone by succinic and glutaric acids is most likely due to a number of factors such as differences in molecule size, number of active sites (sites from which hydrogen can be abstracted), relative mobility and number of oxidised intermediates formed and their ability to propagate/initiate further free radical reactions.

The effect that added oxalic, succinic and glutaric acid had on the extent of malonic acid WO is shown in Table 3.9. Added succinic and oxalic acid had very little effect on the extent of malonic acid WO. Added glutaric acid however hindered the WO of malonic acid appreciably. The low extent of malonic acid oxidation that occurred in the presence of glutaric acid could be due to a number of factors. One possible explanation could involve the size and structure of glutaric acid making this compound susceptible to multiple attack by free radical intermediates which otherwise would initiate the oxidation of unreacted malonic acid. Another possible explanation could involve the size and nature of the intermediates formed from glutaric acid WO.

Table 3.9 *Effect of added dicarboxylic acids on malonic acid WO. Standard reaction conditions (refer to section 2.2.3) except for organics concentrations (Table 3.8).*

Added dicarboxylic acid	Extent of malonic acid WO (%), 2h
None	16.6
Oxalic	14.2
Succinic	19.2
Glutaric	10.1

3.4.1.3.2 Reaction products for co oxidation tests.

The reaction products identified in the co oxidation tests are given in Table 3.10. The three main reaction products identified for malonic acid WO tests in isolation were as expected identified in each of the co oxidation tests.

The succinic acid co oxidation test gave three other reaction products, acetic acid, fumaric acid and malic acid. The distribution of the other three reaction products (oxalic acid, carbonate and formic acid) also differed significantly to the distribution observed in the malonic acid WO test in isolation (Table 3.10). A decrease in the proportion of carbonate and oxalic acid and an increase in the proportion of formic acid occurred. Hence, formic acid, acetic acid, fumaric acid and malic acid are products of succinic acid co oxidation.

The glutaric acid co oxidation test gave four other reaction products, acetic acid, fumaric acid, succinic acid and malic acid. The distribution of the other three reaction products (oxalic, carbonate and formic) also differed significantly to the distribution observed in the malonic acid WO test in isolation (Table 3.10). A higher proportion of carbonate and formic acid and a lower proportion of oxalic acid were observed. Hence, the products of glutaric acid co oxidation are carbonate, formic acid, acetic acid, fumaric acid, succinic acid and malic acid.

The oxalic acid co oxidation test gave the same reaction products as the malonic acid WO test in isolation, oxalic acid, carbonate and formic acid. The distribution of reaction products was however slightly different. A slightly higher proportion of carbonate and slightly lower proportion of oxalic acid was observed. This implies that carbonate is the main product of oxalic acid oxidation.

Table 3.10 *Reaction products identified in co oxidation tests.*

Dicarboxylic acid co oxidised	Reaction products (Organic Carbon g/L), 2 h Oxalic	Carbonate	Formic	Acetic	Fumaric	Succinic	Malic	Mass balance (%)
None	0.59 (52.0)	0.49 (43.0)	0.06 (5.5)	nd	nd	nd	nd	100.5
Oxalic	0.50 (49.8)	0.47 (46.8)	0.06 (5.5)	nd	nd	nd	nd	102.1
Succinic	0.71 (44.1)	0.58 (36.0)	0.14 (8.7)	0.05 (3.1)	0.07 (4.3)	NA	0.07 (4.3)	100.6
Glutaric	0.34 (31.8)	0.55 (51.4)	0.10 (9.3)	0.03 (2.5)	0.02 (1.9)	0.02 (1.5)	0.02 (1.9)	98.8

Proportions of reaction products given in parentheses.
nd = not detected
NA = Not Applicable

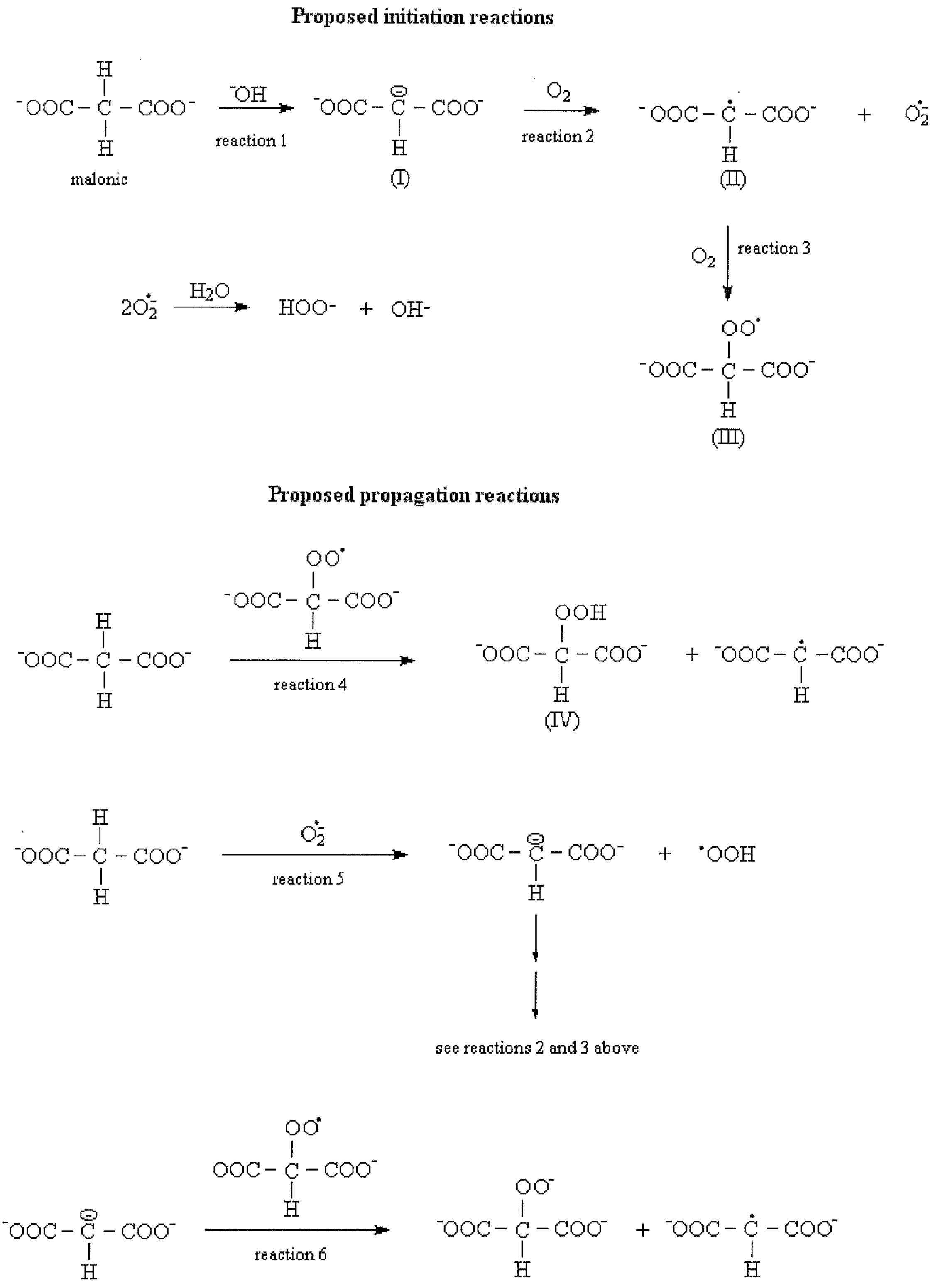
3.4.1.4 Proposed WO reaction mechanisms.

3.4.1.4.1 Proposed reaction mechanism for malonic acid WO.

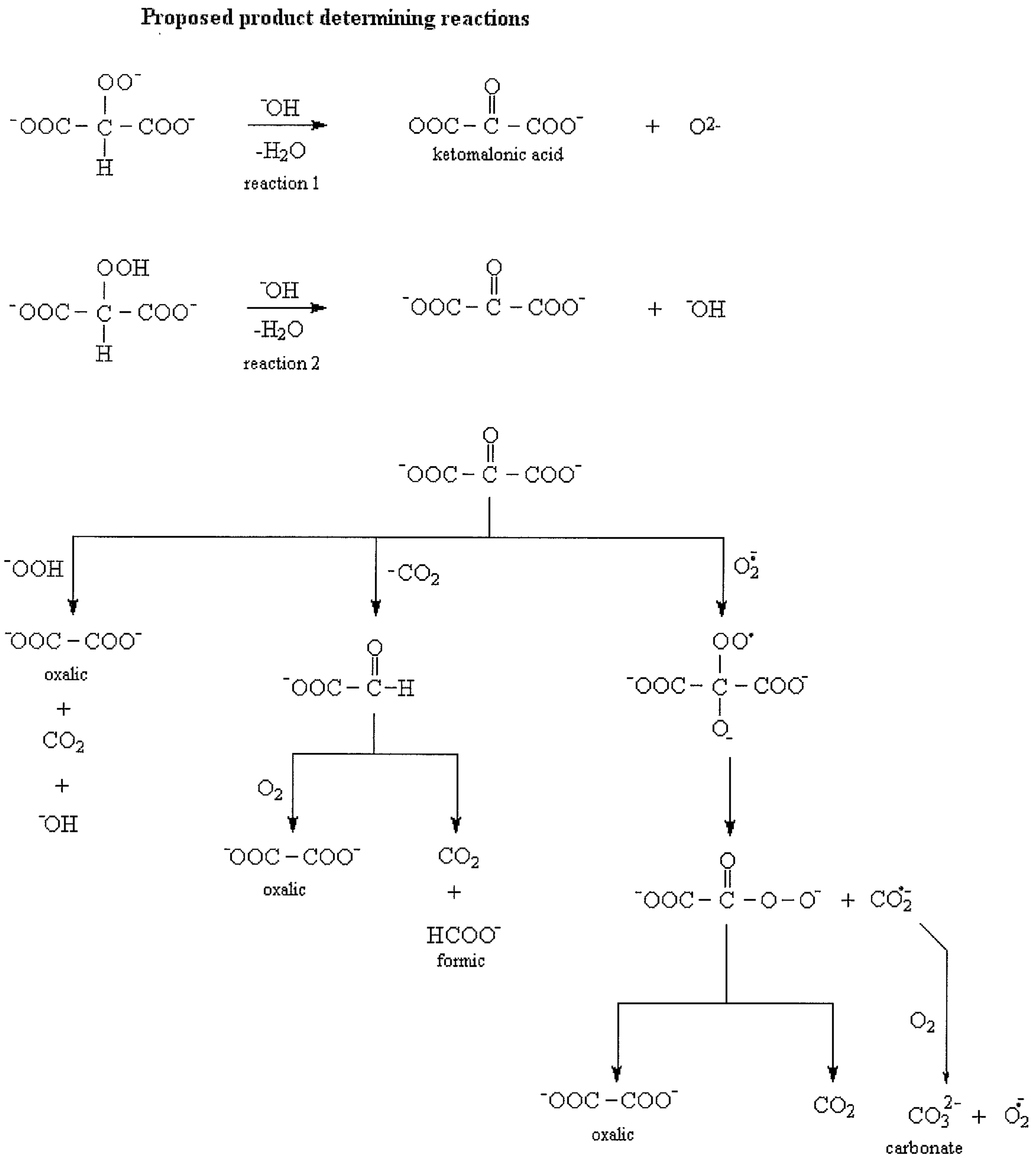
A reaction mechanism for malonic acid WO in highly alkaline solution was proposed using the experimental results discussed in sections 3.4.1.1 – 3.4.1.3 (Reaction schemes 3.1a and 3.1b). The initiation reaction in the proposed reaction mechanism is the removal of a slightly acidic α-Hydrogen from the central carbon of malonic acid by hydroxide (reaction 1, Reaction scheme 1a), analogous to the first step in the reaction mechanism proposed by Wakabayashi et al [1988] for WO of acetic acid in highly alkaline solution. The resulting malonic carbanion (I) formed then reacts with oxygen (reaction 2, Reaction scheme 3.1a) to form an intermediate free radical species (II) and highly reactive superoxide ($O_2^{\cdot-}$). Further reaction of II with oxygen (reaction 3, Reaction scheme 3.1a) would readily follow leading to the formation of a highly reactive peroxy radical intermediate (III).

Three possible propagation reactions are proposed for malonic acid WO (reactions 4 – 6, Reaction scheme 3.1a). The first of these proposed reactions (reaction 4, Reaction scheme 3.1a) leads to the formation of a hydroperoxide intermediate (IV), and a new malonic radical. Another possible propagating reaction can occur from reaction between O_2 and malonic acid (reaction 5, Reaction scheme 3.1a), leading to formation of a malonic radical intermediate. The final propagating step proposed involves reaction between malonic carbanion and species III (reaction 6, Reaction scheme 3.1a) leading to the formation of a peroxy anion intermediate and a new malonic radical.

Proposed product determining reactions for malonic acid WO are presented in Reaction scheme 3.1b. The peroxy anion and hydroperoxide intermediates produced from the initiation and propagation reactions would readily react with hydroxide ion under the highly alkaline conditions, leading to the formation of ketomalonic acid, a compound that has been identified during malonic acid WO [Eyer *et al* 2002] in highly alkaline solution. It is proposed that ketomalonic acid can undergo a number of possible reactions under the reaction conditions used. Those reactions that account for the products identified are presented in Reaction scheme 3.1b. Based on the product distribution data obtained for the WO of malonic acid (Table 3.6), the reaction pathways leading to only oxalic acid and carbonate formation are most likely favoured as only a small proportion of formic acid is produced during malonic WO. However due to the possibility of side reactions of both oxalic (a small extent of *in situ* co oxidation would occur based on the findings discussed in section 3.4.1.3) and formic acids the major product determining pathway(s) cannot be predicted with a high degree of confidence.



Reaction scheme 3.1a *Proposed initiating and propagating reactions for malonic acid WO in highly alkaline solution.*



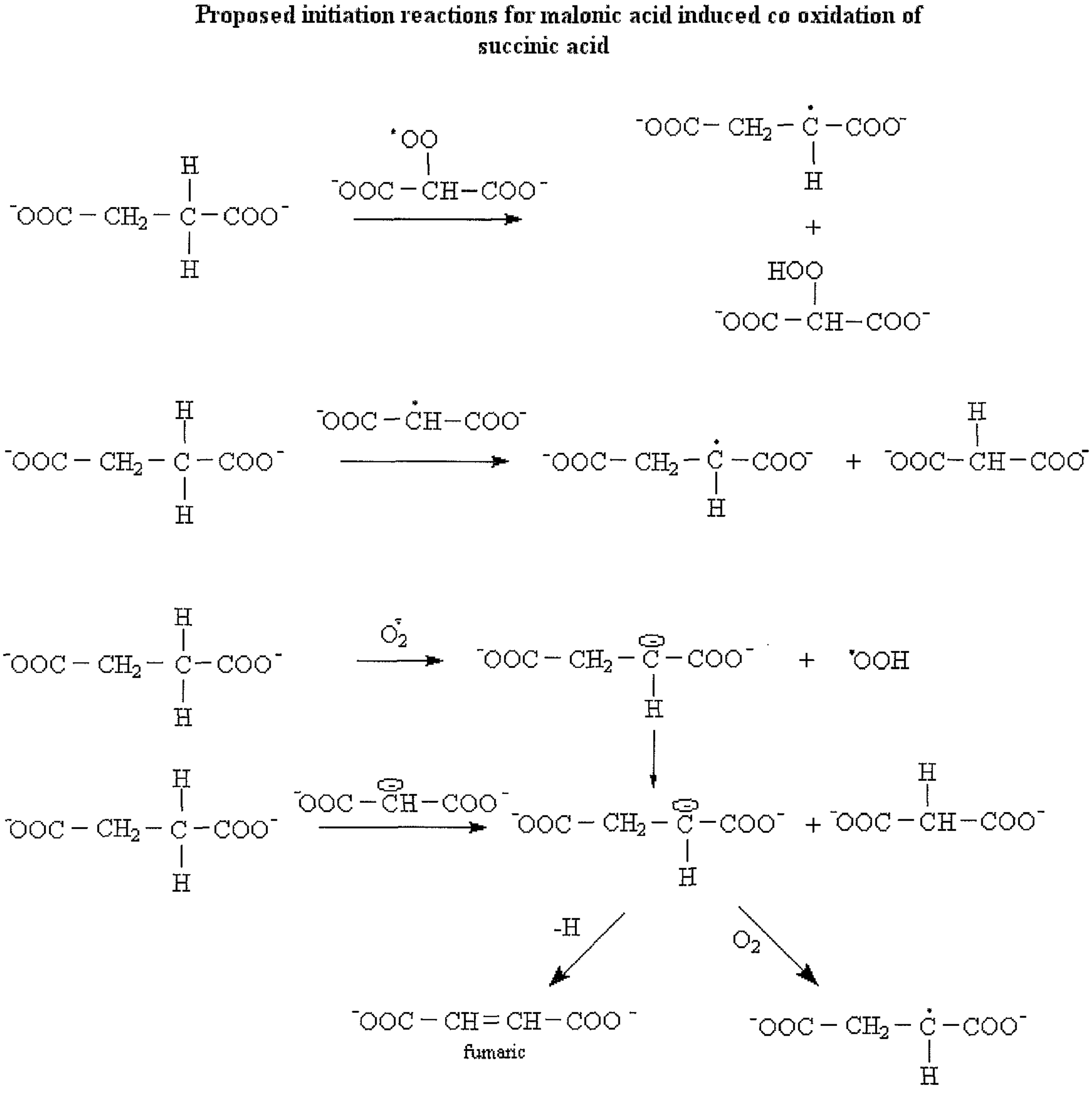
Reaction scheme 3.1b *Proposed product determining reactions for malonic acid WO under highly alkaline conditions.*

3.4.1.4.2 Proposed reaction mechanisms for malonic acid induced co oxidation of succinic and glutaric acids.

Proposed reaction mechanisms for the co oxidation of succinic (Reaction schemes 3.2a and 3.2b), and glutaric (Reaction schemes 3.3a and 3.3b) acids were determined based on the experimental results discussed in section 3.4.1.3. Similar mechanisms are proposed for the co oxidation of succinic and glutaric acids by free radicals produced during malonic acid WO.

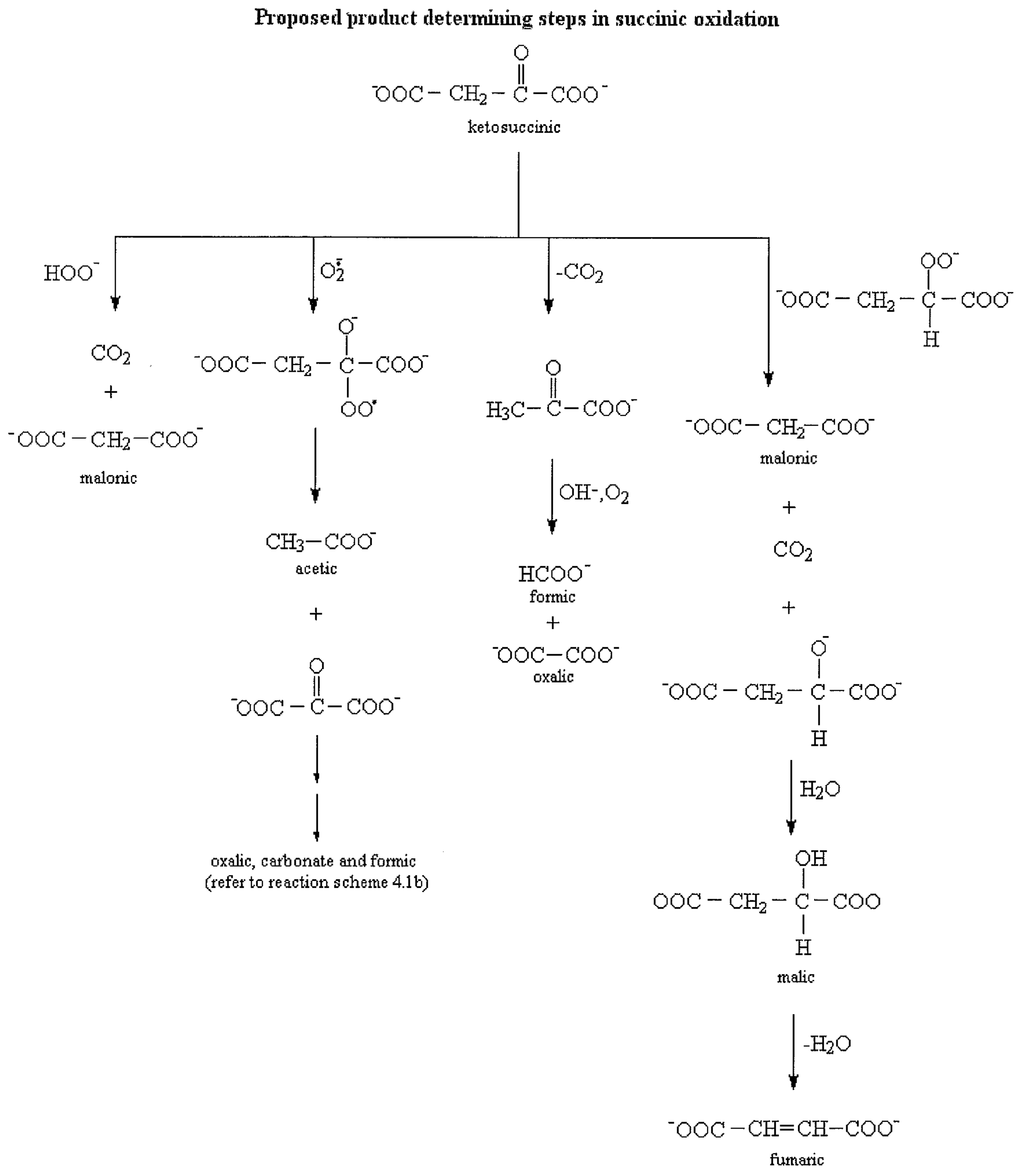
A number of possible initiating steps are proposed in the co oxidation of succinic and glutaric acids (Reaction schemes 3.2a and 3.3a). The presence of trace amounts of fumaric acid at time zero in the succinic acid co oxidation tests (and the lack of trace amounts of fumaric acid in succinic acid WO tests in isolation) provided supportive evidence for possible initiation of succinic acid WO via hydrogen abstraction by malonic carbanion. No experimental evidence could be obtained to support the other initiating steps proposed. Propagation of succinic acid co oxidation most likely occurs via reactions similar to those proposed for malonic acid WO (via peroxy and alkyl radical intermediates).

The subsequent reaction steps in the co oxidation of succinic and glutaric acids leading to product formation are presented in Reaction schemes 3.2b and 3.3b respectively. The type of reactions undergone by each of these compounds once initiated are assumed to be similar to those outlined in the proposed reaction mechanism for malonic acid WO (section 3.4.1.4.1). The reactions included in the proposed reaction schemes for both compounds account for all of the products identified, various other possible reactions that also lead to the reaction products identified are included in appendix 1. Due to the high possibility of side reactions (co oxidation) of the reaction products in each case it is not possible to predict with a high degree of confidence the major product determining pathways.



Proposed initiation reactions for malonic acid induced co oxidation of succinic acid

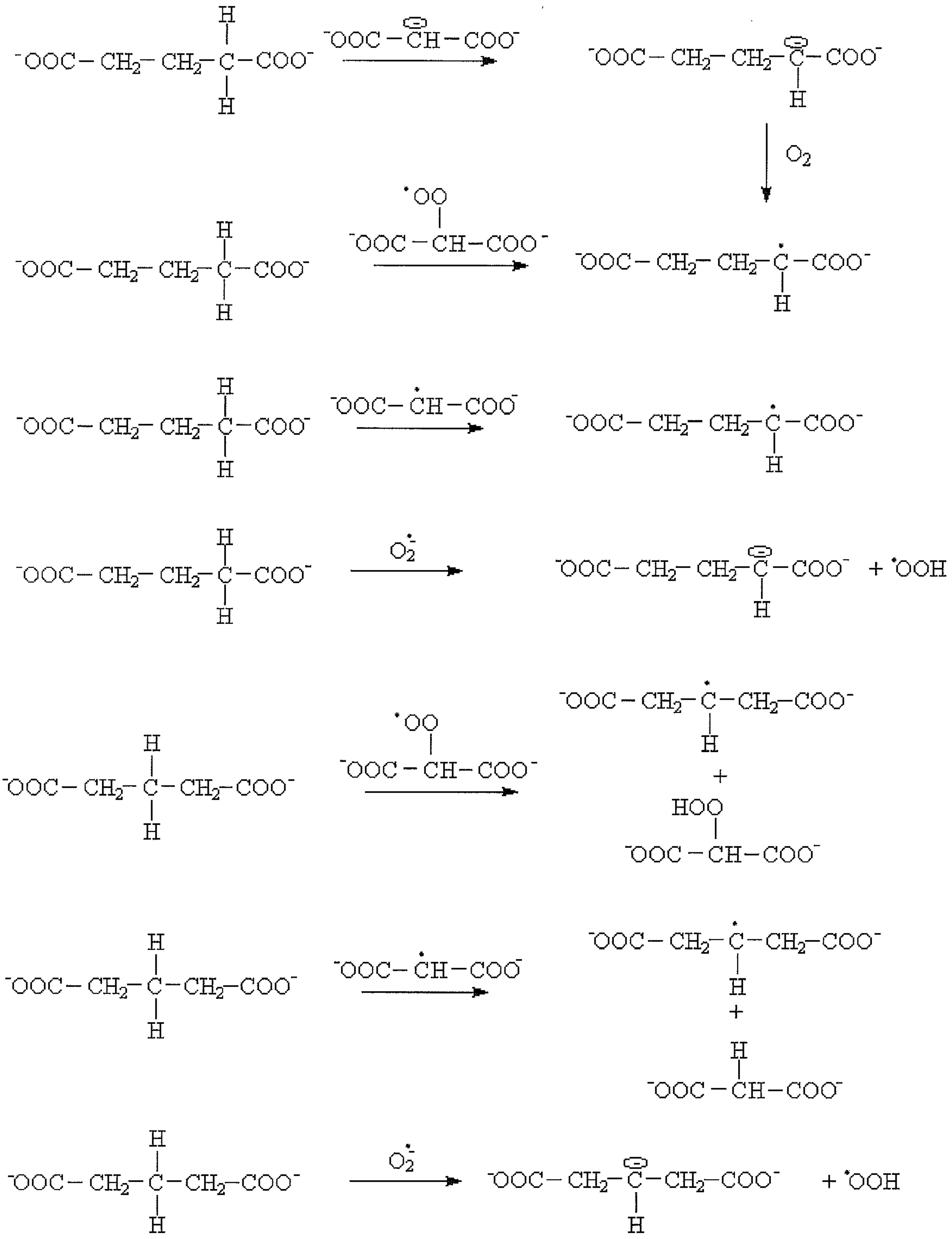
Reaction Scheme 3.2a *Proposed initiating reactions for malonic acid induced co oxidation of succinic acid.*



Proposed product determining steps in succinic oxidation

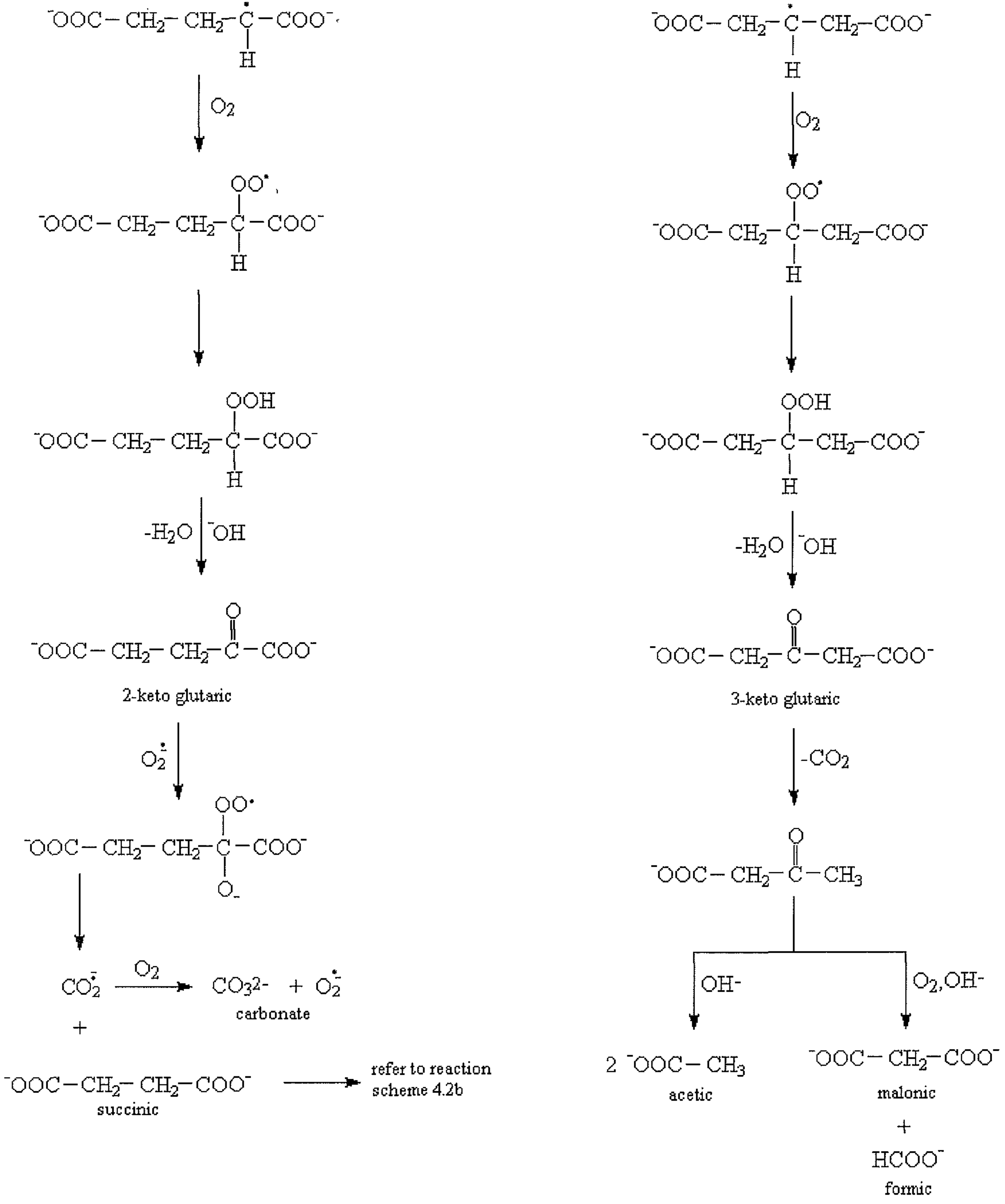
Reaction scheme 3.2b *Proposed product determining reactions for malonic acid induced co oxidation of succinic acid.*

Proposed initiating reactions for malonic acid induced co oxidation of glutaric acid



Reaction scheme 3.3a *Proposed initiating reactions for malonic acid induced co oxidation of glutaric acid.*

Proposed product determining reactions for malonic acid induced co oxdiation of glutaric acid



Reaction scheme 3.3b *Proposed product determining reactions for malonic acid induced co oxidation of glutaric acid.*

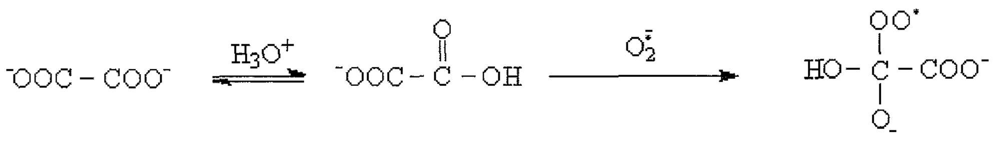
3.4.1.4.3 Proposed reaction mechanism for malonic acid induced co oxidation of oxalic acid.

A proposed reaction mechanism for malonic acid induced co oxidation of oxalic acid was determined using the experimental results discussed in section 3.4.1.3 (Reaction scheme 3.4). It must be emphasised however that due to oxalic acid being a major product of malonic acid WO it was required to assume that the amount of oxalic acid produced from malonic acid in the presence of added oxalic acid was similar to that produced in isolation. Hence, the amount of added oxalic acid co oxidised could only be determined semi-quantitatively, and therefore the mechanism proposed does involve some speculation.

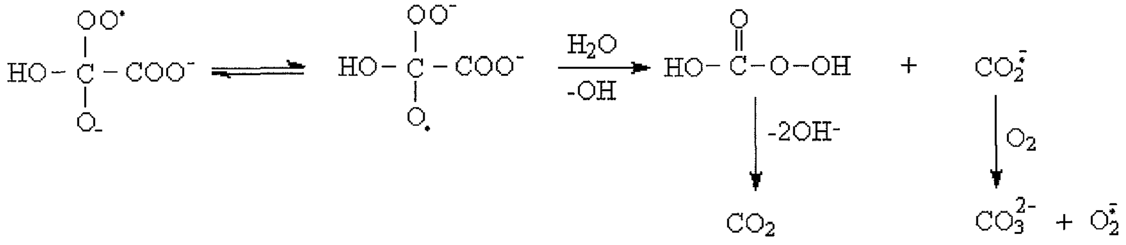
Because oxalic acid does not contain hydrogen atoms that can be abstracted by free radical species to initiate oxidation, initiation must occur via reaction with either of the carbonyl carbons present in oxalic acid. As the aforementioned reaction requires oxalic acid to be present in its mono acidic form, and only a small percentage of oxalic acid would exist in its mono acidic form under the highly alkaline conditions used, the aforementioned reactions would not be expected to occur to a great extent. This is supported by the low extent of co oxidation calculated semi-quantitatively (5.25 %).

It is proposed that the initiation reaction for oxalic acid co oxidation is reaction between superoxide and oxalic acid, which leads to formation of a highly unstable peroxy radical intermediate. It is proposed that this intermediate undergoes subsequent rearrangement and cleavage reactions similar to the reactions proposed by Schuchmann *et al* [1995] for oxidation of ketomalonic acid in alkaline solution by superoxide generated by pulseradiolysis. Subsequent reactions of the intermediates formed leads to the formation of the only product identified for oxalic acid co oxidation, carbonate.

Proposed initiating steps for malonic acid induced co oxidation of oxalic acid



Proposed product determining reactions for malonic acid induced co oxidation of oxalic acid



Reaction scheme 3.4 *Proposed initiating and product determining reactions for malonic acid induced co oxidation of oxalic acid.*

3.4.2 Catalytic Wet Oxidation.

3.4.2.1 Catalyst screening.

The ability of several transition metal oxides to catalyse the WO of the four dicarboxylic acids, all present in the same synthetic Bayer liquor (for composition of organics refer to Table 3.11), was studied. The results of these tests are presented in Table 3.12. CuO was clearly the most active of the transition metal oxides tested, achieving more than 70 per cent more overall oxidation and TOC removal than the next best catalyst. Yamada *et al* [1981] found $CuSO_4$ to be a far superior catalyst than $Fe_2(SO_4)_3$, $NiSO_4$, $CoSO_4$ and $MnSO_4$ for catalysing high temperature (>230 °C) WO of low molecular weight dicarboxylic acids in Bayer liquor (refer to Table 3.4)

Table 3.11 *Composition of dicarboxylic acids used in catalyst screening tests.*

Dicarboxylic acid	Acid conc. (g/L)	Organic carbon conc. (g/L)
Oxalic	9.843	1.875
Malonic	5.405	1.875
Succinic	4.600	1.875
Glutaric	4.115	1.875
TOTAL	**23.963**	**7.500**

Table 3.12 *Screening of transition metal oxides. Standard reaction conditions (refer to section 2.2.3) except for organics' concentrations (refer to Table 3.11). Data for individual compounds is presented in Appendix 2.*

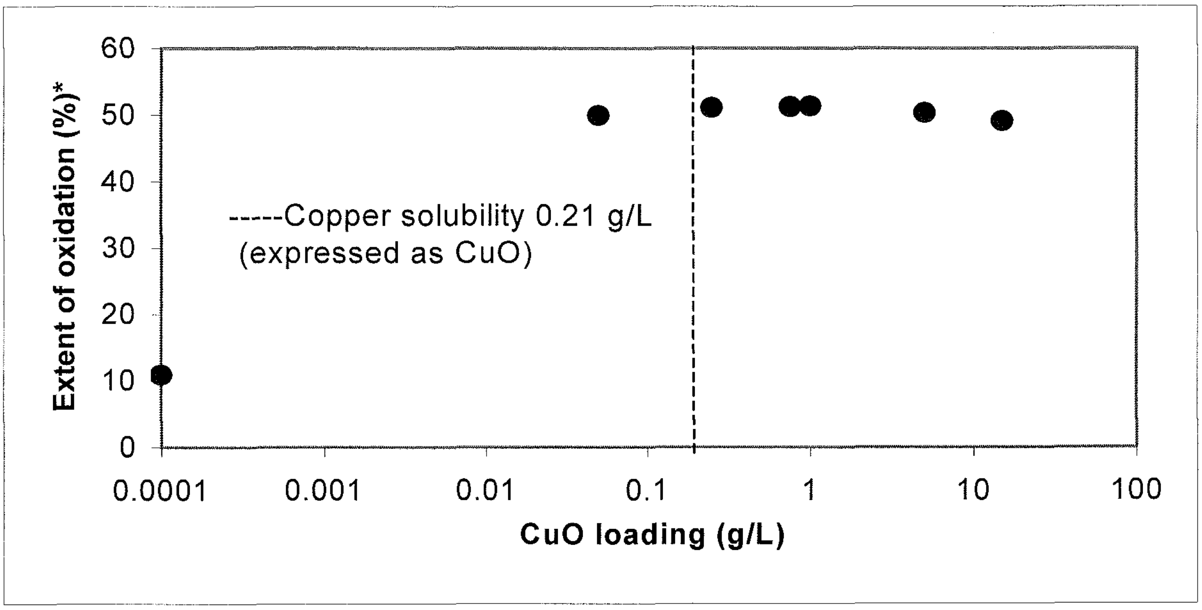
Catalyst	Extent of wet oxidation (%)*	TOC removed (%)
none	10.9	1.9
CuO	50.3	22.5
Ni_2O_3	33.7	13.0
Co_2O_3	21.4	13.1
MnO_2	16.7	6.4
Fe_2O_3	9.6	3.0

*(% oxidation malonic + % oxidation succinic + % oxidation glutaric)/3.
Oxalic acid concentration increased during all tests, hence the extent of wet oxidation undergone by the oxalic acid added at the beginning of the test could not be measured.

As CuO was a superior catalyst compared to the other catalysts investigated, it was decided to concentrate solely on the catalytic mechanism exhibited by this compound during low temperature CWO in highly alkaline solution.

3.4.2.2 CuO catalysed WO of dicarboxylics – heterogenous or homogenous mechanism?

The first aspect of the CuO CWO reaction mechanism investigated was the phase of CuO predominantly responsible for the catalytic activity observed. Due to CuO being slightly soluble in alkaline solution [Mc Dowell and Johnston 1936] it was decided to investigate the effect that CuO had on the extent of WO above and below its solubility limit. It was anticipated that if the catalytic mechanism was predominantly homogenous then the amount of catalytic activity observed would not increase above the solubility limit of the catalyst and vice versa if it was predominantly heterogenous no catalytic activity would be observed below the solubility limit of the catalyst. This was done by investigating the effect that CuO loading had on the extent of WO. The solubility limit of CuO was determined using the average of the two highest values of soluble copper measured during the CuO loading tests (0.16 g/L @ 60 min for the 5.0 g/L test and 0.17 g/L @ 0 min for the 15.0 g/L test). The results of the CuO loading tests are shown in Figure 3.4. CuO clearly exhibits significant activity below its solubility limit (0.165 g/L as Cu, 0.21 g/L, expressed as CuO), whilst showing no significant increase in activity above its solubility limit. Hence, CuO catalyses the WO of the dicarboxylic acids studied predominantly via a homogenous mechanism.



*(% oxidation malonic + % oxidation succinic + % oxidation glutaric)/3.

Figure 3.4 *Effect of CuO loading on WO of dicarboxylic acids. Standard reaction conditions (refer to section 2.2.3) except for varied CuO concentration and organics' concentration (refer to Table 3.11). Data for individual compounds and TOC removal are presented in Appendix 2.*

3.4.2.3 CuO catalysed WO of dicarboxylic acids in isolation.

Before conducting any further investigation into the catalytic mechanism exhibited by CuO it was decided to investigate the ability of CuO to catalyse the WO of each of the dicarboxylic acids in isolation. The results of these tests (extent of WO, TOC reduction and reaction products) are presented in Tables 3.13 and 3.14 respectively. The tests in isolation revealed that CuO only catalysed the WO of malonic acid in isolation. Hence, the oxidation of succinic and glutaric acids observed in the CuO catalysed WO bulk tests (refer to Tables 9.1 and 9.3 Appendix 2) was due to co oxidation by malonic acid and not due to direct CuO catalysis.

Based on the results obtained it was assumed that the most likely reason CuO catalysed the WO of malonic acid, and not the other dicarboxylic acids, was due to uncatalysed WO of malonic acid occurring via a free radical chain reaction (refer to section 3.4.1.3). It was assumed that CuO most likely propagated (catalysed) the free radical chain reaction occurring during malonic acid WO. As the other dicarboxylic acids studied did not undergo uncatalysed WO there is no free radical chain reaction to propagate. From the experimental results obtained CuO is unable to initiate appreciable wet oxidation of oxalic, succinic and glutaric acids under the reaction conditions used.

The reaction products identified for CuO catalysed WO of malonic acid were the same as identified in the uncatalysed tests (carbonate, oxalic acid and formic acid), hence a similar reaction pathway occurs in both cases. The distribution of products was however different for the uncatalysed and CuO catalysed tests. A slightly higher proportion of oxalic acid (and lower proportion of carbonate) and a significantly lower proportion of formic acid were produced in the CuO catalysed test.

Table 3.13 *CuO catalysed WO of dicarboxylic acids in isolation. Standard reaction conditions (refer to section 2.2.3).*

Dicarboxylic acid	Uncatalysed oxidation (%)	Uncatalysed TOC reduction (%)	CuO catalysed oxidation (%)	CuO catalysed TOC reduction (%)
Oxalic	<2	<2	<2	<2
Malonic	18.5	7.6	98.3	38.8
Succinic	<2	<2	<2	<2
Glutaric	<2	<2	<2	<2

Table 3.14 *Reaction products for CuO catalysed WO in isolation. Standard reaction conditions (refer to section 2.2.3).*

	Reaction products (g Organic Carbon/L), 2 h		
Dicarboxylic acid	Oxalic	Carbonate	Formic
Oxalic	NA	NA	NA
Malonic	1.09 (59.6)	.72 (39.4)	.02 (0.9)
Succinic	NA	NA	NA
glutaric	NA	NA	NA

% proportion of total oxidation products in parentheses
NA = Not Applicable

3.4.2.4 CuO catalysed WO of malonic acid – mechanism studies.

The reaction mechanism occurring during CuO catalysed WO of malonic acid was investigated by the same method used for the uncatalysed mechanism (co oxidation method). It was anticipated that if the predominant role of CuO in CWO of malonic acid was to propagate a free radical chain reaction, and hence increase the number of free radical intermediates, then the increased number of free radicals produced would lead to increased co oxidation of an added compound. The initial concentrations of malonic acid and added dicarboxylic acid used for the CuO catalysed co oxidation tests were identical to the amounts used in the analogous uncatalysed tests (Table 3.8).

The results of the CuO catalysed co oxidation tests are presented in Figures 3.5 – 3.7. The increased extent of malonic acid WO due to CuO catalysis did lead to an increase in extent of co oxidation for the dicarboxylics studied. Hence, the assumption that CuO catalysed WO of malonic acid occurred via the generation of increased free radicals was supported by the co oxidation tests.

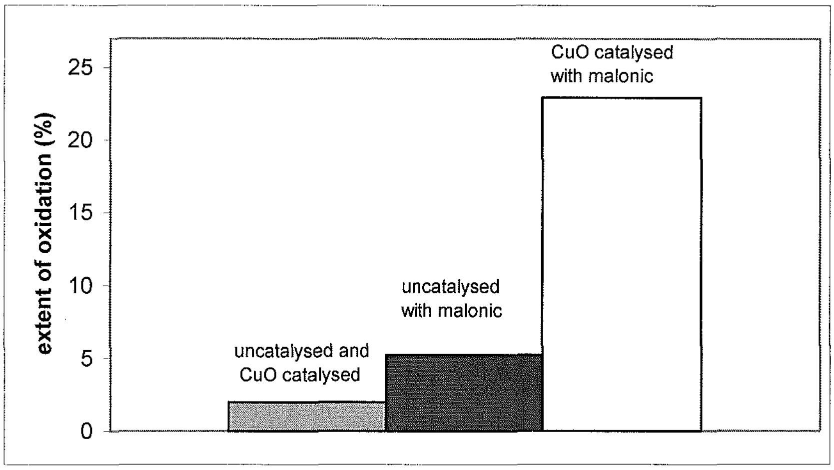


Figure 3.5 *Effect of uncatalysed and CuO catalysed WO of malonic acid on oxalic acid WO.*

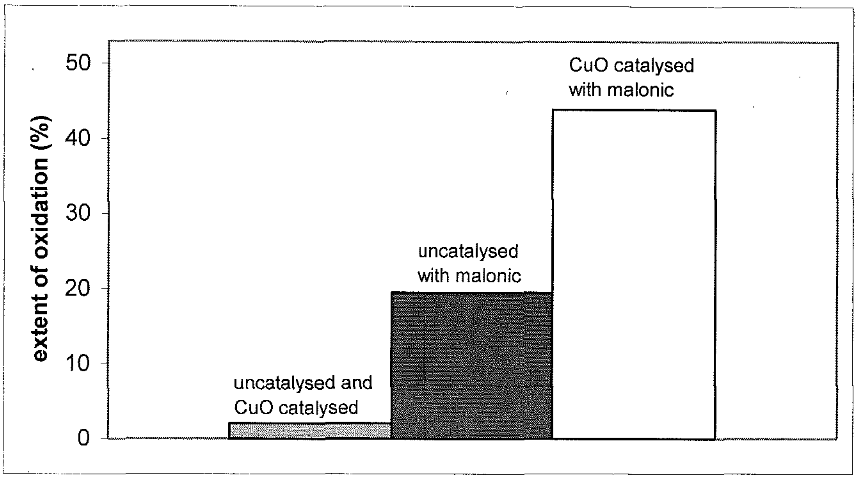


Figure 3.6 *Effect of uncatalysed and CuO catalysed WO of malonic acid on succinic acid WO.*

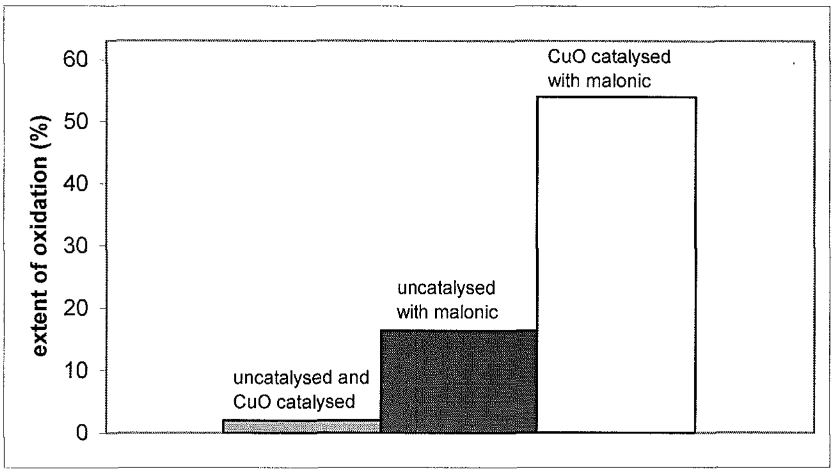


Figure 3.7 *Effect of uncatalysed and CuO catalysed WO of malonic acid on glutaric acid WO.*

The extent to which oxalic, succinic and glutaric acids underwent CuO catalysed malonic acid induced co oxidation (glutaric > succinic > oxalic) did not follow the same trend as observed for uncatalysed co oxidation (succinic > glutaric > oxalic). Oxalic acid underwent the least amount of co oxidation in each case, however glutaric acid was observed to undergo co oxidation to a greater extent than succinic acid in the catalysed reaction compared to the uncatalysed reaction. A possible reason for this reversal could involve the formation of malonic acid as an intermediate in glutaric oxidation which would lead to an increased amount of malonic acid overall, hence altering (increasing) the initial ratio of malonic acid to glutaric acid. This could possibly lead to an increase in the number of co oxidising species, which in turn could lead to an increase in the amount of glutaric acid co oxidised. The effect of increasing the ratio of malonic acid to added dicarboxylic acid is discussed in section 3.4.2.6.

The effect that added oxalic, succinic and glutaric acids had on CuO catalysed malonic acid WO is shown in Table 3.15. The dicarboxylic acids added for the co oxidation tests had very little effect on malonic acid oxidation. This was different to the analogous uncatalysed tests where the extent of malonic acid oxidation was considerably less when glutaric acid was present. This difference could possibly be due to the abundant amount of free radicals expected to be present in the CuO catalysed reaction lessening the competitive effect of glutaric acid.

Table 3.15 *Effect of added organic compounds on CuO catalysed WO of malonic acid.*

Organic compound added	Extent of malonic acid WO after 120 min (%)
None	93.0
Oxalic	93.1
Succinic	90.9
Glutaric	90.0

3.4.2.5 Reaction products for CuO catalysed co oxidation tests.

The reaction products identified for the CuO catalysed co oxidation tests are given in Table 3.16. The products formed in each of the CuO catalysed co oxidation tests were the same as those identified in the analogous uncatalysed tests, indicating that both systems share a similar reaction mechanism.

A comparison of the product distributions for the uncatalysed and CuO catalysed co oxidation tests is presented graphically in Figures 3.8 – 3.10. In each case a significant increase in carbonate production and decrease in oxalic production was observed. This same trend was observed for CuO catalysed WO of a high concentration of malonic acid in isolation (Table 3.16). Hence the increased carbonate formation (and decreased oxalic formation) observed in the co oxidation tests was most likely due to a change in product distribution occurring for CuO catalysed WO of malonic acid at the concentration used in co oxidation tests.

The proportion of all other reaction products (formic, acetic, fumaric, malic and succinic) was significantly lower in the CuO catalysed tests. This is most likely due to the increase in the proportional contribution of the products of malonic acid WO, which effectively lowers the proportional amount of products formed from co oxidation of the added dicarboxylic acids.

Table 3.16 *Reaction products for CuO catalysed co oxidation tests.*

	Reaction products (Organic Carbon g/L), 2 h							
Dicarboxylic acid co oxidised	Oxalic	Carbonate	Formic	Acetic	Fumaric	Succinic	Malic	Mass balance (%)
None	2.33	3.76	0.06	nd	nd	nd	nd	100.7
	(38.0)	(61.5)	(1.0)					
Oxalic	2.08	3.88	0.06	nd	nd	nd	nd	97.3
	(33.6)	(62.7)	(1.0)					
Succinic	2.56	3.60	0.095	0.04	0.18	NA	0.18	100.3
	(38.5)	(54.2)	(1.4)	(0.6)	(2.8)		(2.8)	
Glutaric	2.46	4.02	0.14	0.12	0.03	0.01	0.03	95.7
	(34.6)	(56.5)	(2.0)	(1.7)	(0.4)	(0.2)	(0.4)	

% proportion (in terms of carbon) of total products in parentheses

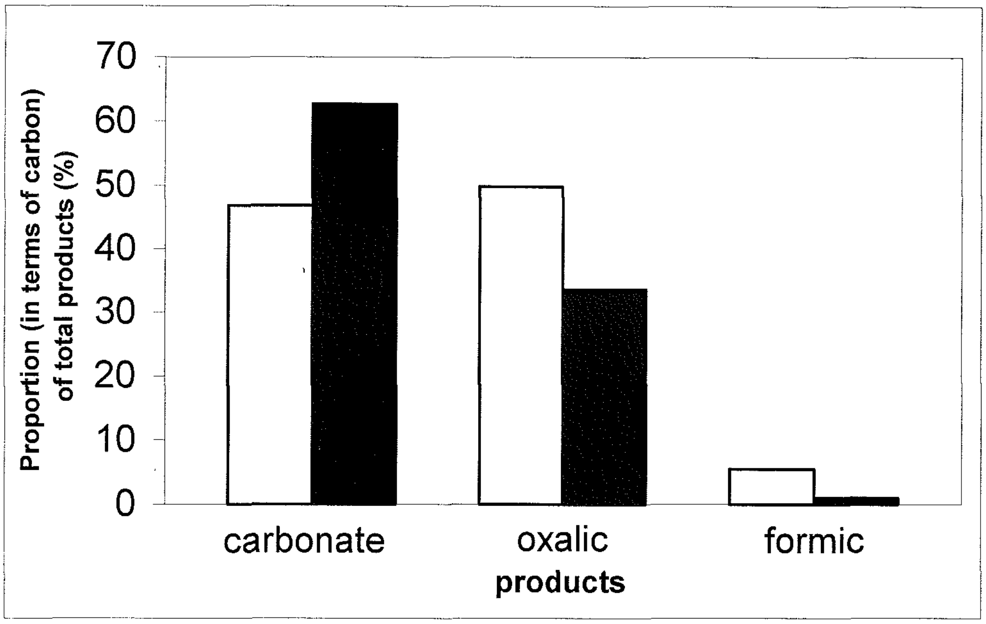


Figure 3.8 *Comparison of product distributions for uncatalysed and CuO catalysed malonic acid co oxidation of oxalic acid. Open bars – uncatalysed, filled bars- CuO catalysed.*

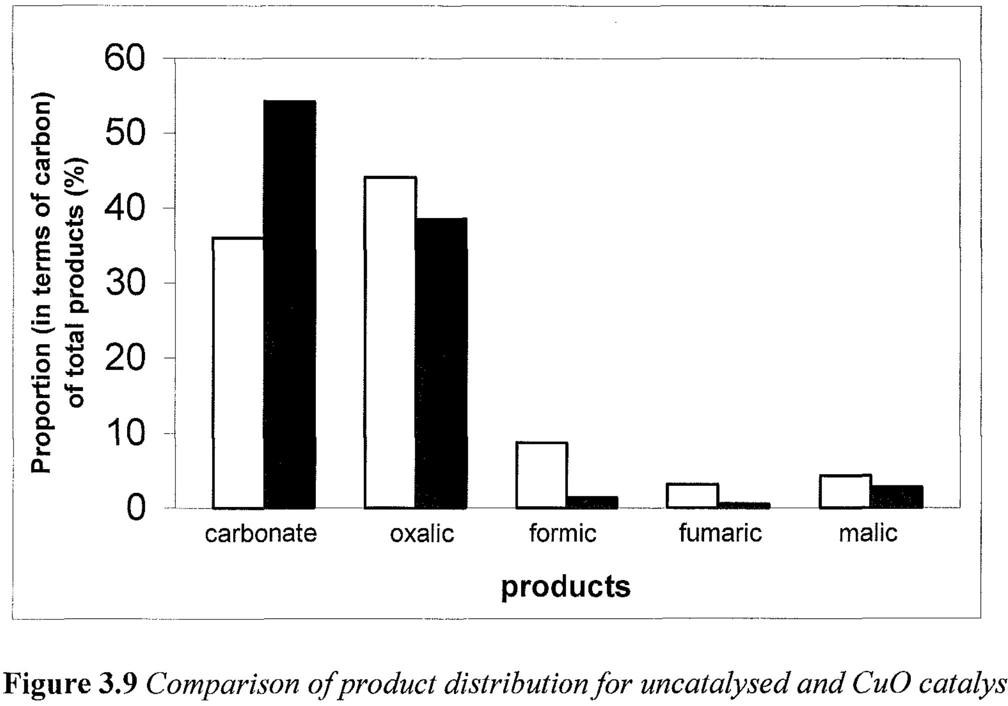


Figure 3.9 *Comparison of product distribution for uncatalysed and CuO catalysed malonic acid co oxidation of succinic acid. Open bars – uncatalysed, filled bars- CuO catalysed.*

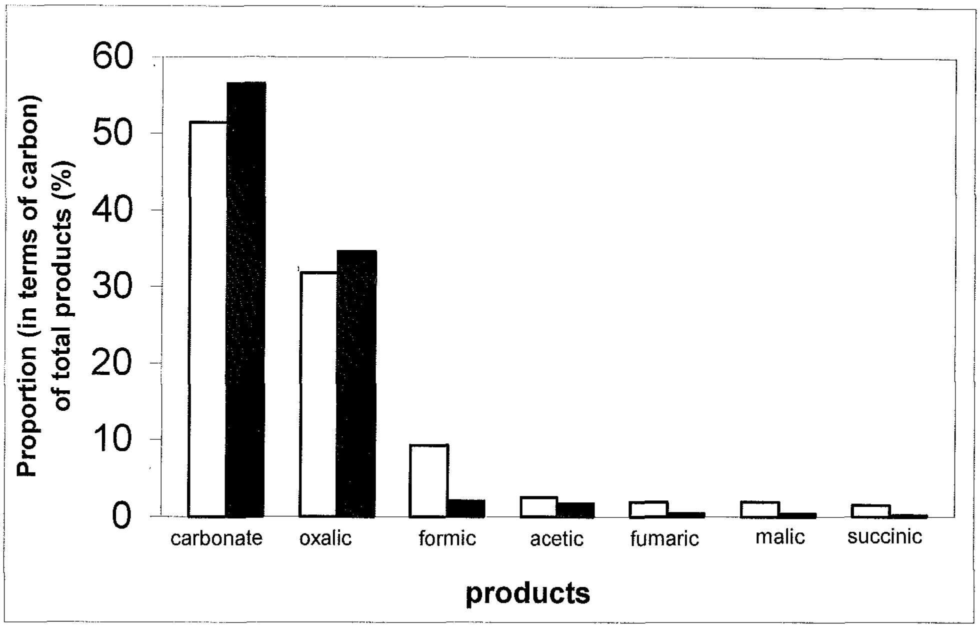


Figure 3.10 *Comparison of product distribution for uncatalysed and CuO catalysed malonic acid co oxidation of glutaric acid. Open bars – uncatalysed, filled bars- CuO catalysed.*

3.4.2.6 Effect of initial malonic acid : dicarboxylic acid.

The effect of initial malonic acid concentration (the ratio of malonic acid to added dicarboxylic) on the extent of co oxidation was investigated to confirm the hypothesis in section 3.4.3.4 that the higher than expected CuO catalysed co oxidation of glutaric acid was due to an increase in malonic acid to glutaric acid ratio. Succinic acid was used as the added compound rather than glutaric acid to allow for a more accurate measurement of the ratio of malonic acid to added compound (based on the assumption that a significant amount of malonic acid is not produced during succinic acid co oxidation).

It was anticipated that if free radicals generated during CuO catalysed malonic acid WO did not react with unreacted malonic acid then the extent to which a compound is co oxidised by malonic acid would increase with increasing malonic acid concentration up to an infinite concentration. If however the reverse were true it was expected that an excessive amount of malonic acid would hinder the co oxidation of another compound as the excessive unreacted malonic acid would compete with the co oxidising compound for free radicals to react with.

Figure 3.11 shows the effect of increasing the malonic acid to succinic acid ratio on the extent of succinic oxidation using a fixed concentration of succinic acid. The extent to which succinic acid is co oxidised by malonic acid does increase up to a molar ratio of six, however at a molar ratio of 12 the extent of co oxidation clearly decreases. This data supports a CuO catalysed mechanism for malonic acid which involves free radicals produced during the reaction initiating the oxidation of unreacted malonic, hence an auto-oxidation mechanism is supported by the experimental data. This however only became apparent when an excessive amount of unreacted malonic acid was present in solution, an amount sufficient to significantly compete with the co oxidisable compound, succinic acid.

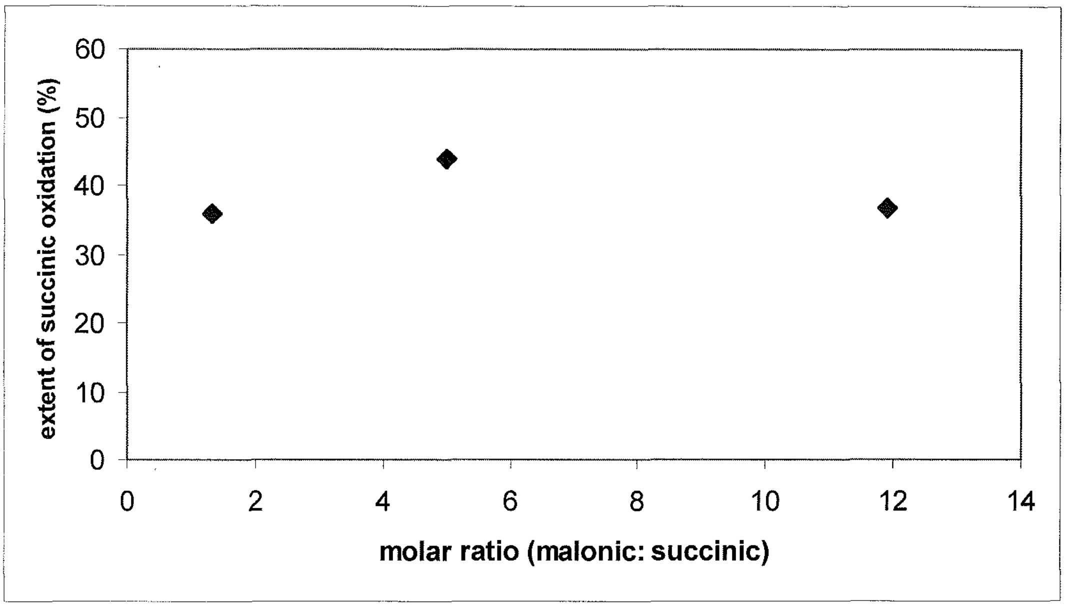


Figure 3.11 *Effect of malonic acid to succinic acid ratio on extent of succinic acid oxidation. (Fixed concentration of succinic acid used, 1.87gOC/L).Standard reaction conditions except for agitation speed, 870 rpm (experiments conducted in autoclave with maximum agitation speed of 870 rpm).*

3.4.2.7 Effect of [OH$^-$] on CuO catalysed co oxidation.

The effect of [OH$^-$] on CuO catalysed co oxidation was also studied in an attempt to determine the role of hydroxide ion in CuO catalysed malonic acid WO and co oxidation in general. Before investigating the effect of [OH$^-$] on co oxidation it was decided to investigate the effect of [OH$^-$] on CuO catalysed WO of malonic acid in isolation. As the extent of CuO catalysed WO for malonic acid at 4.4M NaOH was already considerably high (>90%), no significant effect was expected. This was supported by the experimental results (Figure 3.12), with only a slight increase in extent of oxidation occurring with increasing [OH$^-$].

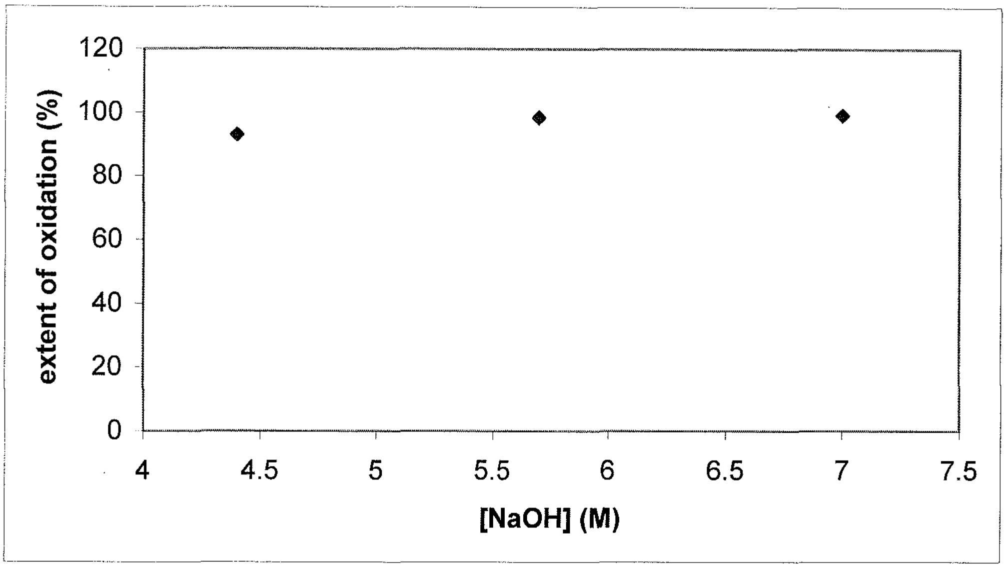


Figure 3.12 *Effect of [OH⁻] on CuO catalysed WO of malonic acid.*

Of more interest was the effect of [OH⁻] on product distribution. Figure 3.13 shows the effect of increasing [OH⁻] on the product distribution for CuO catalysed WO of malonic acid. The proportion of oxalic acid produced increases and the proportion of carbonate decreases with increasing [OH⁻]. This same trend was also observed for uncatalysed WO of malonic acid however it only occurred when the [OH⁻] was increased from 5.7 M to 7.0 M. This would suggest that in both cases hydroxide ion reacts with the same product determining intermediate, causing increased formation of oxalic acid (and a corresponding decrease in carbonate formation).

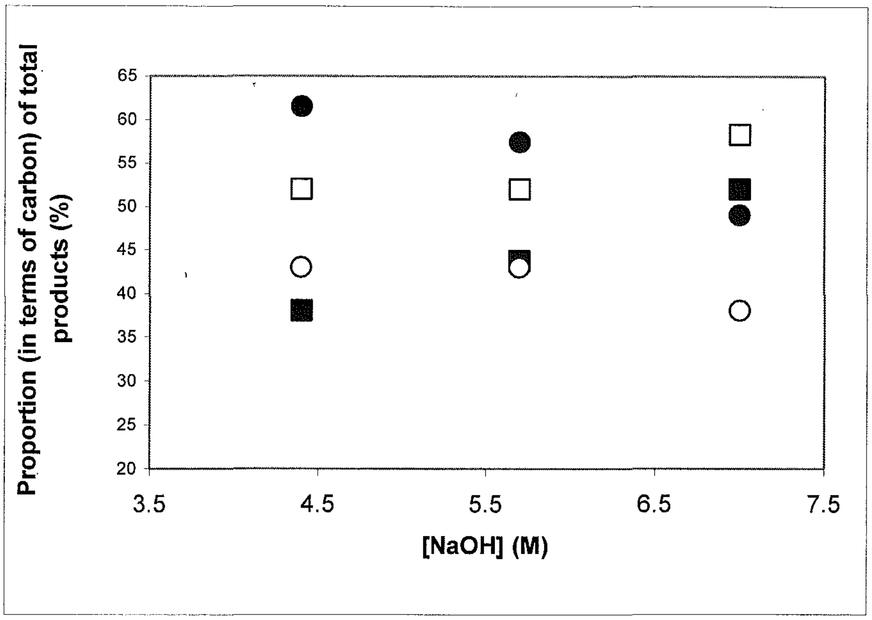


Figure 3.13 *Effect of [OH⁻] on product distribution in CuO catalysed WO of malonic. Oxalic (□), carbonate (O),closed symbols CuO CWO, open symbols WO.*

The affect of [OH⁻] on CuO catalysed malonic acid induced co oxidation of succinic acid is presented in Figure 3.14. The extent of succinic acid oxidation increases significantly with increasing [OH⁻]. This is most likely due to an increase in the number of malonic acid molecules which produce free radicals via reaction with hydroxide ion and oxygen, hence lowering the number of malonic acid molecules available for reaction with malonic free radical intermediates, whilst also producing more free radical intermediates capable of reacting with succinic acid. Another possibility could involve base catalysed WO of an intermediate(s) formed during succinic acid oxidation that also produces free radical intermediates capable of co oxidation. The increase in soluble copper, which occurs with increasing [OH⁻] [Mc Dowell and Johnston 1936], may also have contributed to the increased extent of co oxidation of succinic acid. Increased soluble copper could increase the number of free radical intermediates produced via increased decomposition of hydroperoxide intermediates.

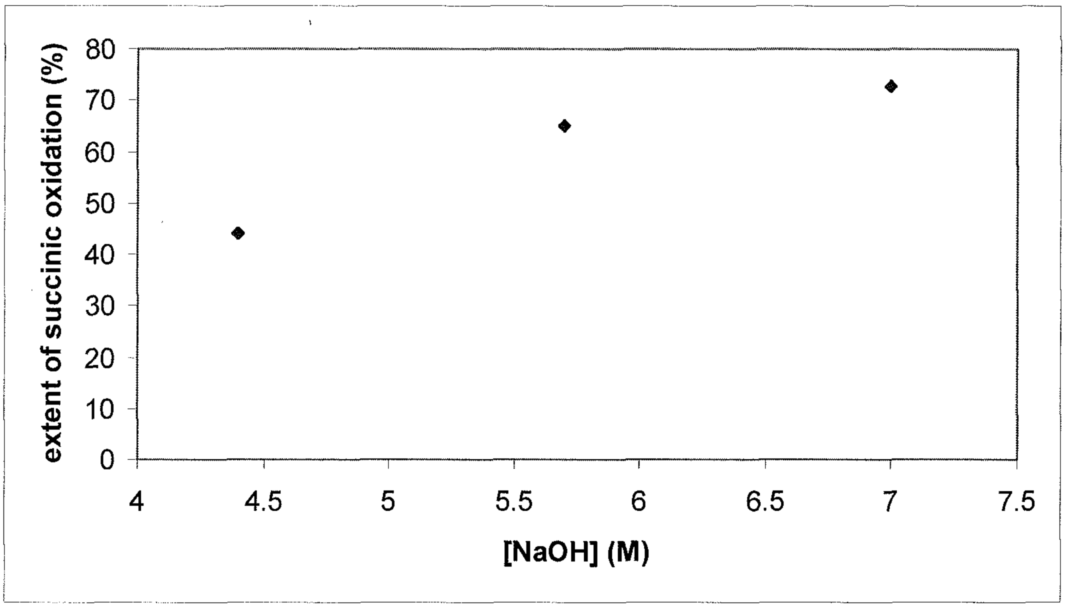


Figure 3.14 *Effect of $[OH^-]$ on extent of CuO catalysed malonic acid induced co oxidation of succinic acid.*

3.4.2.8 Proposed role(s) of CuO catalyst in CuO catalysed WO of malonic acid.

3.4.2.8.1 Effect of CuO on extent of overall oxidation.

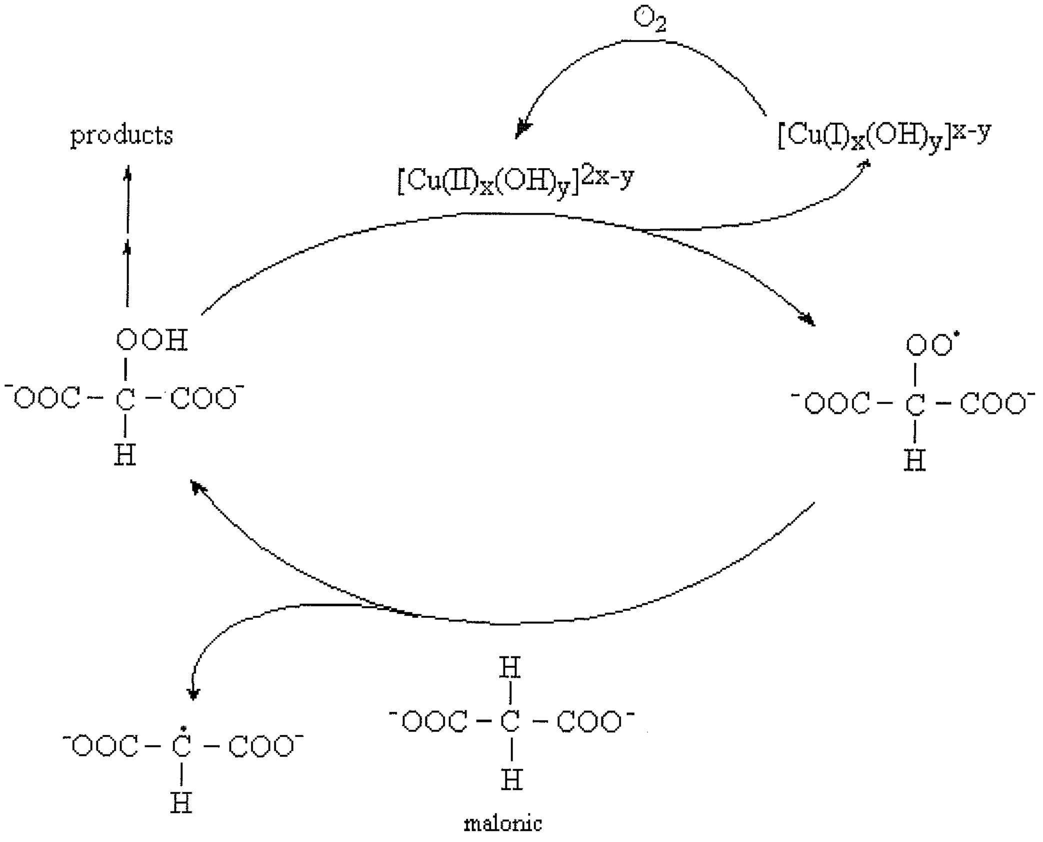
Based on the experimental results discussed in the preceding sections of this chapter it is clear that the soluble portion of CuO (section 3.4.3.2), significantly catalyses the WO of malonic acid in highly alkaline solution (~80% increase in extent of oxidation). It is also clear from the experimental results discussed that the soluble portion of CuO catalyses the WO of malonic acid by producing an increased number of free radical intermediates. It is proposed that the soluble copper hydroxy complexes, generated via dissolution of

CuO under the highly alkaline conditions used, can generate increased free radical intermediates by various different reactions (Reaction scheme 3.5). One possible mode of catalysis that would lead to an increased number of free radical intermediates and an increase in the extent of overall oxidation are the well-documented reactions that involve the generation of chain-initiating radicals via metal-catalysed decomposition of alkyl hydroperoxides [Sheldon 1995] (Reaction scheme 3.5). Another mode of catalysis that could also occur during CuO catalysed WO of malonic acid involves direct initiation via a copper superoxo species (Reaction scheme 3.5). This mode of catalysis would also lead to increased production of free radical intermediates, and hence an increase in extent of overall oxidation.

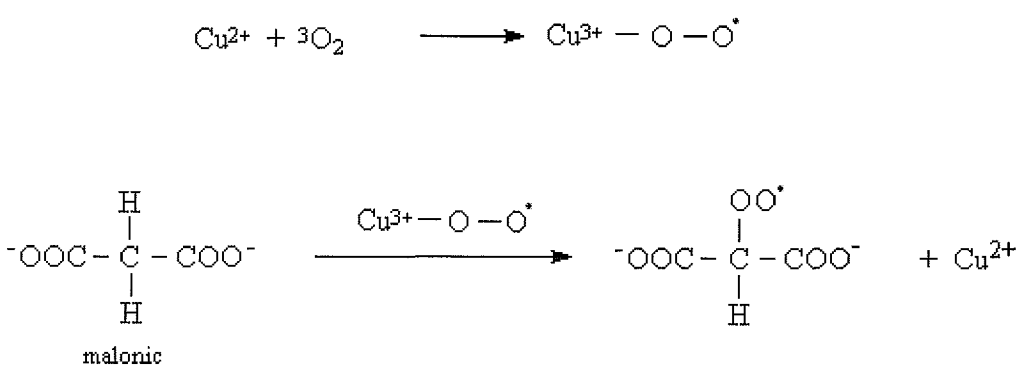
3.4.2.8.2 Effect of CuO on distribution of products from malonic acid WO.

The products identified for both CuO catalysed WO and uncatalysed WO of malonic acid were identical, hence CuO catalysis does not effect the type of products formed. The distribution of products for CuO catalysed and uncatalysed WO of malonic acid did however differ. The extent of this difference was also effected significantly by the initial concentration of malonic acid (Table 3.17). At low initial malonic acid concentration (1.87 g OC/L) a significantly higher proportion of oxalic acid and lower proportion of carbonate was produced in the CuO catalysed test, whereas the reverse trend was observed when a high initial concentration was used (7.01 g OC/L). The higher proportion of oxalic acid produced in the low initial malonic acid concentration CuO catalysed reaction could be due to the undissolved portion of CuO (~ 4.0 g/L) scavenging

Generation of chain initiating radicals



Initiation via copper superoxo species



Reaction scheme 3.5 *Possible catalytic roles of dissolved CuO species in CuO catalysed WO of malonic acid.*

free radicals which could otherwise co oxidise the oxalic acid produced *in situ* to carbonate. This 'quenching' effect of excess catalyst was also observed to occur (in terms of extent of overall oxidation) for the tests conducted using all four dicarboxylic acids in the same solution at high CuO loading (Figure 3.4). The 'quenching' effect of an inert metal oxide on WO has also been described elsewhere [Lee 2000]. The 'quenching' effect would not have as significant an effect on the high initial concentration test due to the ratio of oxalic acid produced to undissolved CuO being significantly lower. Another possible reason for the low proportion of oxalic acid produced in the high initial concentration test could involve an equilibrium effect, as a significant amount of oxalic acid was produced (2.33 g OC/L).

Table 3.17 *Effect of initial concentration on extent of oxidation and product distribution for CuO catalysed and uncatalysed WO of malonic acid.*

Initial malonic acid concentration (g OC/L)	Uncatalysed/Catalysed	Extent of oxidation (%), 2h	Product distribution (%) Oxalic	 Carbonate	 Formic
1.87	uncatalysed	18.5	55.1	41.0	4.8
1.87	CuO catalysed	98.3	59.6	39.4	0.9
7.01	uncatalysed	16.6	52.0	43.0	5.5
7.01	CuO catalysed	93.0	38.0	61.5	1.0

3.4.2.9 Proposed mechanisms for CuO catalysed malonic acid induced co oxidation of succinic, glutaric and oxalic acid.

3.4.2.9.1 Effect of CuO on extent of oxidation for CuO catalysed induced co oxidation of succinic, glutaric and oxalic acid.

CuO clearly catalyses the co oxidation of succinic, glutaric and oxalic acids (refer to section 3.4.3.4). It is proposed that CuO indirectly catalyses the WO of succinic, glutaric and oxalic acids via similar reactions proposed for malonic acid WO, by increasing the number of free radical intermediates capable of initiating WO. As CuO catalysed WO of succinic, glutaric and oxalic acids in isolation did not occur, one of the roles of CuO proposed to possibly occur in malonic acid WO, initiation via a copper superoxo species (Reaction scheme 3.5), does not occur for succinic, glutaric and oxalic acids. Hence, the increased extent of oxidation which occurred for succinic, glutaric and oxalic acids in the CuO catalysed systems is most likely due to copper hydroxy species catalysing the generation of chain initiating radicals (Reaction scheme 3.5).

3.4.2.9.2 Effect of CuO on products for CuO catalysed malonic acid induced co oxidation of succinic, glutaric and oxalic acids.

The type of products identified for CuO catalysed malonic acid induced co oxidation of succinic, glutaric and oxalic acids, were identical to those identified in the analogous uncatalysed systems. This indicates that a similar reaction mechanism occurs in both cases. The distribution of products observed for the three malonic-dicarboxylic acid mixtures CuO catalysed tests did differ to the analogous uncatalysed tests. The main variation occurred in the proportion of carbonate and oxalic acid produced, with significantly more carbonate and less oxalic acid being produced in the catalysed reactions. This same trend was observed for CuO catalysed WO of malonic acid in isolation (Table 3.16), and as the products of malonic acid oxidation would comprise the majority of the total products produced during the co oxidation tests (>80%), the observed trend in carbonate and oxalic acid production is most likely due to malonic acid WO.

3.5 Conclusions and Recommendations.

The chemistry of low temperature (165°C) WO and CuO catalysed WO of oxalic, malonic, succinic and glutaric acids in highly alkaline solution has been studied in detail to the author's best knowledge for the first time. The following conclusions were made based on the above-mentioned study:

Malonic acid is partially removed (7.6 %) by WO (completely wet oxidised to carbonate) in highly alkaline solution under the standard reaction conditions used (4.4 M NaOH, 165°C, 500 kPa PO_2). Malonic acid also undergoes partial oxidation under these reaction conditions. Oxalic and formic acids are formed from the partial oxidation of malonic acid in highly alkaline solution.

Malonic acid undergoes low temperature WO in highly alkaline solution via a free radical chain reaction mechanism. The extent to which malonic acid undergoes WO is significantly affected by $[OH^-]$. The extent to which malonic acid undergoes WO increases significantly with increasing $[OH^-]$ over the $[OH^-]$ range used in this study. It is proposed that the initial reaction in malonic acid WO is removal of a slightly acidic hydrogen by hydroxide ion.

Oxalic, succinic and glutaric acids are not wet oxidised significantly (completely or partially) when in isolation, under the reaction conditions used in this study (4.4 – 7.0 M NaOH, 165°C, 500 kPa PO_2). Hence, these compounds cannot be removed from highly alkaline solution by low temperature WO when in solution in isolation.

Oxalic, succinic and glutaric acids are however co oxidised by free radical intermediates produced during malonic acid WO. Hence, these compounds can be removed from highly alkaline solution via low temperature co oxidation.

Low temperature WO of malonic acid in highly alkaline solution is catalysed by dissolved CuO species (copper hydroxy complexes of the general form, $[Cu(II)_x(OH)_y]^{2x-y}$). The mechanism proposed involves the generation of chain-initiating radicals via metal-catalysed decomposition of alkyl hydroperoxides.

Dissolved CuO species can indirectly catalyse the WO of oxalic, succinic and glutaric acids in the presence of malonic acid by increasing the number of free radical intermediates, that are capable of co oxidation, generated during malonic acid WO.

Co oxidation of oxalic acid requires further investigation, as removal of this compound is of great interest to the alumina industry. It would be of interest to determine the species (or species') produced during malonic acid WO and CuO catalysed WO that is capable of co oxidising oxalic acid. If this can be achieved then methods for producing such species (or species') would be of particular interest.

Further investigation into catalysts that can catalyse low temperature WO of oxalic, succinic and glutaric acids is needed. One possible type of catalyst which may be successful in catalysing the WO of succinic and glutaric acids at low temperature is one that contains highly basic sites that could possibly initiate the WO of these compounds via extraction of an α-hydrogen. The side reaction of such a catalyst with water may however make development of such a catalyst difficult.

CHAPTER 4

WET OXIDATION AND CATALYTIC WET OXIDATION OF C_1-C_4 STRAIGHT CHAIN MONOCARBOXYLIC ACIDS

4.1 Introduction.

WO/CWO of low molecular weight monocarboxylic acids (in particularly acetic acid) has been the subject of considerable research over the last three decades. This is due to a number of compounds from this class being extremely hard to oxidise. This can lead to compounds from this class actually increasing in concentration during WO/CWO as they are usually formed from the partial oxidation of higher molecular weight compounds.

WO/CWO of low molecular weight monocarboxylic acids is also of particular interest to the alumina industry as compounds from this class (such as formic and acetic acids) contribute to a significant portion of the TOC in various worldwide Bayer liquors. Bayer processing problems attributed to this class of organics are discussed in section 1.2.2.1. Low molecular weight monocarboxylic acids have also been identified in various other waste streams/process liquors. Chang *et al* [1993] identified formic and acetic acids in spent caustic wastewater from a petrochemicals manufacturing process, while Ingale *et al* [1996] identified acetic and propionic acids in the waste stream from a cyclohexane oxidation unit.

Low molecular weight monocarboxylic acids have also been identified as reaction intermediates and "hard-to-oxidise" (refractory) compounds produced from the WO/CWO of a number of larger molecules present in various industrial waste streams/process liquors. Mishra *et al* [1993] identified acetic acid as a major product in CuO catalysed WO of p-cresol in neutral solution, however in alkaline solution (pH 13.5) no acetic acid was produced. Mantzavinos *et al* [1996] identified formic acid in WO and CuO.ZnO-Al_2O_3 catalysed WO of p-coumaric acid. Mantzavinos *et al* [1996] also reported that at high alkalinity (pH 12) considerably more formic acid was produced compared to the test conducted in acidic solution (pH 3.5). Furuya *et al* [1985] found acetic acid to be a major product in the WO of a number of organic compounds (adipic acid, phenol, 4-hydroxycinnamic acid, 4-methoxycinnamic acid and 3-cyclohexylpropionic acid) in their study conducted in extremely alkaline solution (25 mol NaOH / kg H_2O).

In this chapter the WO/CWO of four straight chain mono carboxylic acids (formic, acetic, propionic and butyric), all of which have been identified in various worldwide Bayer liquors (Table 4.1), has been investigated.

Table 4.1 *Monocarboxylic acids studied in this chapter that have been identified in various worldwide Bayer liquors.*

Country/region	Monocarboxylic acids identified	Reference
Australia	formic, acetic, propionic, butyric	Niemela [1993]
India	formic, acetic, propionic, butyric	Romano Rao and Chandwani [1997]
Hungary	formic, acetic, propionic, butyric	Matyasi *et al* [1986]
Hungary	formic, acetic, propionic, butyric	Zoldi *et al* [1988]
West Indies	formic, acetic, propionic, butyric	Baker *et al* [1995]
na	formic, acetic, propionic, butyric	Guthrie *et al* [1984]
Germany	formic, acetic, propionic	Brown [1989]
Japan	formic, acetic	Yamada *et al* [1981]

na = not available

4.2 Background.

WO/CWO of low molecular weight monocarboxylic acids (particularly acetic acid) has been studied extensively over the last three decades. This is due to these compounds being "hard-to-oxidise" (refractory) products from the WO/CWO of larger molecules present in a number of industrial waste streams/process liquors. The majority of studies conducted have used single compounds in simple aqueous solutions. A summary of some of the many studies conducted on WO/CWO (limited to studies using transition metal based catalysts) of the monocarboxylic acids investigated in this chapter is given in Table 4.2.

Table 4.2 *Summary of various WO/CWO studies of monocarboxylic acids that are studied in this chapter.*

Monocarboxylic acid	Catalyst	Temp (°C)	Oxygen pressure	pH	Acid reduction	TOC reduction	Reference
Formic	none	240-270	8 bar	acidic	24% at 240°C 90% at 270°C, 2h	24% at 240°C 90% at 270°C, 2h	Shende and Levec [1999]
Formic	Co_2O_3	200	.110 mol of O_2	acidic	84%	84%	Ito *et al* [1989]
Formic	Cu(II) $(NO_3)_2$	250	1.0 MPa	1.9	na	64.7%, 1h	Imamura *et al* [1988]
Formic	none	112	1.0 MPa	2.8	na	17.3%, 20 min	Imamura *et al* [1982b]
Acetic	none	300-320	25-60 bar	acidic	9% at 300°C 20% at 320°C, 3h	9% at 300°C 20% at 320°C, 3h	Shende and Levec [1999]
Acetic	none	250	5.0 MPa	>14	98.6%, 2h	22.2%, 2h	Furuya *et al* [1985]
Acetic	none*	230	5.0 MPa	>14	80%, 6h	na	Wakabayashi and Okuwaki [1988]
Acetic	none	235	2.9 MPa	2.5-3.4	na	10%, 2h	Imamura *et al* [1982a]
Acetic	Cu(II) $(NO_3)_2$	235	2.9 MPa	2.5-3.4	na	43%, 2h	Imamura *et al* [1982a]
Propionic	none	500 F	500 psi	acidic	na	55%, 1.67h	Day *et al* [1973]
Propionic	none	250	5.0 MPa	>14	na	41.7%, 2h	Furuya *et al* [1985]
Propionic	Co_2O_3	200	.110 mol of O_2	acidic	55%	41%	Ito *et al* [1989]
Propionic	none	290-310	30 bar	acidic	44% at 290°C 88% at 310°C, 2h	na	Shende and Levec [1999]
Propionic	none	248	1.0 MPa	4.5	na	6.9%, 20 min	Imamura *et al* [1982b]
Butyric	none	250	5.0 MPa	>14	na	29.9%, 2h	Furuya et al [1985]
Butyric	none	257	5.17 MPa	acidic	69%, 3 h	na	Williams *et al* [1974]
Butyric	Co_2O_3	200	.110 mol of O_2	acidic	51%	40%	Ito *et al* [1989]
Butyric	none	248	1.0 MPa	3.5	na	17.5%, 20 min	Imamura *et al* [1982b]

* Authors indicate that Ni leached from reactor vessel catalyses reaction
na = not available

From the literature summarised in Table 4.2 it is clear that the majority of WO/CWO studies on low molecular weight monocarboxylic acids have been conducted in acidic/neutral solution. There have however been two comprehensive studies conducted on the WO/CWO of acetic [Wakaybayashi and Okuwaki 1988, Furuya *et al* 1985], propionic and butyric acids [Furuya *et al* 1985] in alkaline solution.

Wakaybayashi and Okuwaki [1988] investigated high temperature (230-250°C) WO/CWO (Cu, Ni, Co, Mn, Fe and Cr) of acetic acid in highly alkaline solution (5 mol NaOH/ kg H_2O). Wakaybayashi and Okuawaki [1988] found that acetic acid WO was strongly dependant on NaOH concentration (Table 4.3). These authors proposed a base and metal oxide catalysed oxidation mechanism for CWO of acetic acid in highly alkaline solution (refer to section 1.2.4.2).

Table 4.3 *Effect of NaOH concentration on acetic acid WO in Ni reactor* [Wakabayshi and Okuwaki 1988].*

[Copyrighted material omitted. Please consult the original thesis.]

The other major study conducted on WO of monocarboxylic acids in highly alkaline solution is the high temperature (250°C) study conducted by Furuya *et al* [1985]. Furuya *et al* [1985] studied the WO of acetic, propionic and butyric acids in extremely alkaline solution (25 mol NaOH/ kg H_2O). The results of the study conducted by Furuya *et al* [1985] are presented in Table 4.2. Furuya *et al* [1985] reported that appreciable WO of acetic (98.6% acid reduction), propionic (41.7% TOC reduction) and butyric (29.9% TOC reduction) occurred under the reaction conditions used. The WO of acetic acid was also found to be strongly dependent on [NaOH], with an increase in extent of WO occurring with increasing [NaOH] over the concentration range studied (5.0 – 25.0 mol NaOH/ kg H_20). Furuya *et al* [1985] proposed a base catalysed oxidation mechanism for acetic acid, similar to that proposed by Wakabayshi and Okuwaki [1988].

[Copyrighted material omitted. Please consult the original thesis.]

Figure 4.1 *Base catalysed mechanism proposed for acetic acid WO [Furuya et al 1985].*

WO/CWO of monocarboxylic acids in complex alkaline solution (Bayer liquor) has also been studied. Yamada *et al* [1981] and Matyasi *et al* [1986] investigated the WO/CWO of formic, acetic, propionic and butyric acids in industrial Bayer liquor. The results of these studies are summarised in Table 4.4. Reaction mechanisms were not discussed in both of these studies.

Table 4.4 *WO/CWO of monocarboxylic acids in industrial Bayer liquor.*

Monocarboxylic	Catalyst	Temp (°C)	Oxygen pressure	Acid reduction	Reference
Formic	none	260	na	85.7%, 1h	Yamada *et al* [1981]
Formic	Cu^{2+}	235	na	79.6%, 1h	Yamada *et al* [1981]
Formic	Cu^{2+}	260	na	89.8%, 1h	Yamada *et al* [1981]
Acetic	none	260	na	7.9%, 1h	Yamada *et al* [1981]
Acetic	Cu^{2+}	235	na	22.7%, 1h	Yamada *et al* [1981]
Acetic	Cu^{2+}	260	na	84.6%, 1h	Yamada *et al* [1981]
Formic	none	200	40 bar (total)$^+$	3.26-3.31%*	Matyasi *et al* [1986]
Formic	none	242	50 bar (total)$^+$	2.02-0.0%*	Matyasi *et al* [1986]
Acetic	none	200	40 bar (total)$^+$	35.9-28.0%*	Matyasi *et al* [1986]
Acetic	none	242	50 bar (total)$^+$	25.88-21.88%*	Matyasi *et al* [1986]
Propionic	none	200	40 bar (total)$^+$	3.2-2.45%*	Matyasi *et al* [1986]
Propionic	none	242	50 bar (total)$^+$	1.51-1.93%*	Matyasi *et al* [1986]
Butyric	none	200	40 bar (total)$^+$	0.6-0.35%*	Matyasi *et al* [1986]
Butyric	none	242	50 bar (total)$^+$	0.50-0.38%*	Matyasi *et al* [1986]

*change in % composition of total organics in liquor

$^+$ total system pressure

WO/CWO of low molecular weight monocarboxylic acids has been the subject of considerable research over the last three decades. A small percentage of this research has been conducted on WO/CWO of monocarboxylic acids at high temperature (>200°C) in alkaline solution, while the majority of studies have been conducted at high temperature

(>200°C) in acidic solution. Apart from the high temperature (>230°C) research of Wakaybayshi and Okuwaki [1988] on the WO/CWO of acetic acid in alkaline solution (2.0 - 5.0 mol NaOH/ kg H_2O) there has been no other research presented in the literature investigating the chemistry occurring during WO/CWO in Bayer-like solution (4.4 M NaOH). In this chapter, the chemistry occurring in low temperature WO/CWO of low molecular weight monocarboxylic acids in Bayer-like solution is investigated, to the best of the author's knowledge, for the first time.

4.3 Experimental.

Refer to chapter 2 for all materials, methods, procedures and methods of analyses used for the experimental work conducted in this chapter.

4.4 Results and Discussion.

4.4.1 Wet Oxidation.

4.4.1.1 Extent of WO, TOC reduction and reaction products under standard test conditions.

The WO of formic, acetic, propionic and butyric acids was studied under standard test conditions (refer to section 2.2.3). The results of these tests (extent of WO and TOC reduction) are presented in Table 4.5. Of the four monocarboxylics studied only formic acid underwent appreciable wet oxidation under the reaction conditions used. Formic acid did not undergo thermal degradation (i.e. degradation in the absence of oxygen). The only product identified from formic acid WO was carbonate, which accounted for >98% of the oxidised formic acid. Hence formic acid can be removed by WO in highly alkaline solution, the degree of removal achieved under the reaction conditions used was however very low (5.5 %).

Table 4.5 *Extent of WO for monocarboxylic acids under standard test conditions (refer to section 2.2.3).*

Organic	Extent of Wet Oxidation (%), 2 h	TOC reduction (%), 2h
Formic	5.5	5.5
Acetic	<2	<2
Propionic	<2	<2
Butyric	<2	<2

A possible reason for formic acid being the only compound oxidised under the standard conditions was thought to be the difference in acidity of the hydrogen atom in this compound compared to the hydrogen atoms of the other monocarboxylics studied. Hence, it was decided to investigate the effect that [OH$^-$] had on the WO of formic acid and the other monocarboxylic acids.

4.4.1.2 Effect of [OH$^-$] on WO.

The effect that [OH$^-$] had on the WO of the monocarboxylics studied is presented in Table 4.6. [OH$^-$] clearly affected the WO of formic acid, with a significant increase in extent of oxidation occurring with increasing [OH$^-$]. [OH$^-$] however did not influence the reaction products of formic acid WO with carbonate being the only product identified, accounting for >98% of the formic acid oxidised.

[OH$^-$] did not affect the WO of the other monocarboxylic acids studied with neither of these compounds undergoing appreciable WO even at extremely high alkalinity (7.0 M

NaOH). The lack of WO of these compounds is most likely due to either sodium hydroxide not being a strong enough base to abstract the hydrogens on these compounds and/or there being insufficient energy for this reaction to take place. Based on the WO studies of acetic acid in highly alkaline solution conducted by Wakabayshi and Okuwaki [1988] (refer to Table 4.3) the temperature used in this study (165°C) was not high enough for WO to occur. As this project involved the investigation of low temperature WO, the possibility of an energy barrier was not investigated.

Table 4.6 *Effect of alkalinity on WO of monocarboxylics under standard test condtions (refer to section 2.2.3), except for synthetic Bayer liquor [NaOH] (refer to section 2.2.3.1).*

	Extent of WO (%) after 2h at varying [NaOH]		
Organic	4.4 M	5.7 M	7.0 M
Formic	5.5 (5.5)	8.5 (8.5)	14.2 (14.2)
Acetic	<2	<2	<2
Propionic	<2	<2	<2
Butyric	<2	<2	<2

TOC reduction in parentheses

4.4.1.3 WO reaction mechanism studies.

Based on the results obtained on the WO of formic acid it was decided to investigate the type of reaction mechanism (free radical or ionic) taking place during formic acid WO. The indirect co oxidation method used to investigate the WO of malonic acid was also used to investigate the WO of formic acid. However, as formic acid only underwent a relatively low extent of WO under standard conditions (5.5%) it was decided to investigate the WO of formic at high alkalinity (7.0 M NaOH) to increase the ease of detecting any co oxidation that may occur. Succinic acid was chosen as the compound to be co oxidised.

No significant co oxidation of succinic acid was detected in the formic acid – succinic acid co oxidation test and the extent of WO observed for formic acid was not significantly different to that observed for formic acid in isolation. Hence based on the results obtained from the co oxidation test formic acid is not capable of co oxidising succinic acid. Therefore, either no free radicals are produced during formic acid WO or the free radicals that are produced do not react with succinic acid. As any free radical produced during formic acid WO would be a methyl-type free radical, which are extremely unstable compared to primary, secondary and tertiary free radicals [Sheldon 1995], the possibility of free radicals being produced during formic acid WO and degrading before having the opportunity to react with succinic acid could not be completely ruled out. Hence, it was decided to investigate the mechanism of formic acid WO by an alternative method.

4.4.1.3.1 Effect of formic acid on malonic acid WO.

It was decided to investigate the WO reaction mechanism of formic acid by studying the effect that it had on malonic acid WO. It was assumed that if free radicals produced by formic acid were extremely short lived and hence unlikely to react with any other compounds then formic acid should be capable of hindering the WO of malonic acid, by scavenging free radicals that otherwise could react with unreacted malonic acid, and therefore hinder the auto oxidation of malonic acid.

The results of the formic acid – malonic acid co oxidation test are given in Table 4.7. Formic acid clearly hinders malonic acid oxidation significantly, with nearly 50 per cent less malonic acid undergoing oxidation in the presence of added formic acid, hence supporting the assumption that free radicals formed from formic acid oxidation are extremely short lived. This is also supported by the total amount of oxidation (oxidation of malonic acid plus formic acid) being significantly lower than that observed for the dicarboxylic acid co oxidation tests, indicating that free radicals formed from formic acid are unlikely to propagate the oxidation of other compounds in solution.

Table 4.7 *Effect of added compounds on malonic acid WO.*

Co oxidised organic	Initial mol ratio malonic: co oxidised compound	Extent of WO (%), 2h	
		Co oxidised compound	Malonic acid
None	NA	NA	16.6
Formic	5.04 : 1	9.6 (4.1)*	**8.3**
Oxalic	7.04 : 1	5.25	14.21
Succinic	4.97 : 1	19.5	19.2
Glutaric	4.97 : 1	16.4	10.1

* Extent of co oxidation in parentheses.

While the experimental data obtained for formic acid WO does not provide evidence to support the presence of free radical intermediates in formic acid WO it does provide evidence that if free radicals are present they are incapable of co oxidising other species (succinic and malonic acids) in solution. Therefore it is unlikely if free radicals are produced that they could react with unreacted formic acid, hence auto oxidation would most likely not occur. Therefore, formic acid WO most likely does not occur via a free radical *chain* mechanism.

4.4.1.3.2 Malonic acid induced co oxidation of acetic, propionic and butyric acids – can these refractory compounds be co oxidised at low temperature?

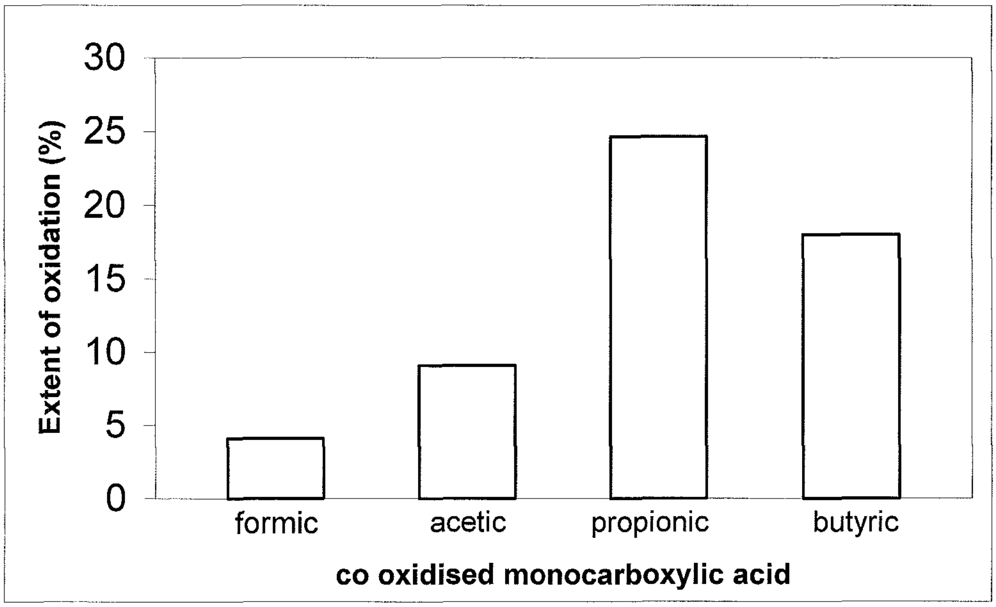
As neither of the three other monocarboxylics studied (acetic, propionic and butyric) underwent appreciable WO in isolation under the standard test conditions it was decided to investigate if these compounds could be co oxidised by the free radicals produced during malonic acid WO. The concentrations of malonic acid and added monocarboxylic acid used in these tests are given in Table 4.8.

Table 4.8 *Composition of organic mixtures used in co oxidation tests.*

Organics	Malonic acid concentration g/L (mol/L)	Acetic, propionic or butyric acid concentration g/L (mol/L)	Mol ratio (malonic : added monocarboxylic)
Malonic blank	19.80 (0.190)	NA	NA
Malonic - acetic	20.27 (0.195)	2.27 (0.038)	5.13 : 1
Malonic -propionic	20.24 (0.195)	3.05 (0.041)	4.76 : 1
Malonic - butyric	20.27 (0.195)	3.43 (0.039)	5.00 : 1

NA = Not Applicable

The results of the malonic acid - monocarboxylics co oxidation tests are presented in Figure 4.2. The free radicals produced during malonic acid WO clearly co oxidise each of the monocarboxylic acids studied. The extent of co oxidation observed for each of the monocarboxylic acids was as follows, propionic > butyric > acetic > formic. This order can be attributed to type of free radical intermediates (primary, secondary) that would form during co oxidation of the respective compounds. Similar secondary radicals would form in the case of butyric and propionic acids, whereas less stable primary radicals (that would hence be less likely to propagate the formation of free radical intermediates) would form during acetic acid oxidation. The difference in the extent of co oxidation undergone by propionic and butyric acids is most likely due to a number of factors such as differences in molecule size, number of active sites (sites from which hydrogen can be abstracted), relative mobility and number/reactivity/structure of oxidised intermediates formed and their ability to propagate/initiate further free radical reactions.



*Extent of propionic acid oxidation determined using product quantities (not direct chromatographic measurement – refer to section 2.4.)

Figure 4.2 *Extent of malonic acid induced co oxidation of acetic, propionic and butyric acids. Standard test condtions (refer to section 2.2.3), except for organics' concentrations (refer to Table 4.8).*

The effect that each of the added monocarboxylic acids had on the extent of malonic acid WO is presented in Table 4.9. Added acetic acid had very little effect. Added propanoic and butyric acids significantly hindered the WO of malonic acid. This is most likely due to a combination of the higher amount of formic acid produced in each of these systems

(Table 4.10) and the high number of sites on each of these compounds containing hydrogen atoms that can react with free radical intermediates, hence allowing these compounds to compete with unreacted malonic acid for free radical intermediates. The latter proposal is supported by the high extent of co oxidation undergone by propionic and butyric acids.

Table 4.9 *Effect of added monocarboxylic acids on extent of malonic acid WO.*

Co oxidised organic	Mol ratio malonic: co oxidised compound	Extent of WO (%)	
		Co oxidised compound	Malonic acid
None	NA	NA	16.6
Formic	5.04: 1	9.6 (4.1)*	8.3
Acetic	5.13 : 1	9.1	15.9
Propionic	4.76 : 1	24.6	12.6
Butyric	5.00 : 1	18.0	10.2

* Extent of co oxidation

4.4.1.3.3 Products of malonic acid induced co oxidation of acetic, propionic and butyric acids.

The products identified for malonic acid induced co oxidation of acetic, propionic and butyric acids are presented in Table 4.10. The major products of malonic acid WO in isolation (oxalic, carbonate and formic) were, as expected, formed in each of the co oxidation tests. The only other product identified was acetic acid. This was produced in small quantities in malonic acid induced co oxidation of propionic and butyric acid.

The distribution of products in the co oxidation tests are given in Table 4.10. A slight increase in oxalic acid and formic acid (and decrease in carbonate) production in the acetic acid co oxidation test implies that oxalic and formic acids are the major products of acetic acid oxidation. The product distributions for both the propionic and butyric acids co oxidation tests were very similar. A significant increase in carbonate and formic acid and decrease in oxalic acid production occurred, indicating that carbonate and formic acid are major products formed from the co oxidation of these compounds. A small quantity of acetic acid was also produced from the co oxidation of propionic and butyric acid.

Table 4.10 *Reaction products identified in malonic acid induced co oxidation of monocarboxylic acids.*

	Reaction products (Organic Carbon g/L), 2 h				
Monocarboxylic acid co oxidised	Oxalic	Carbonate	Formic	Acetic	Mass balance (%)
None	0.59 (52.0)	0.49 (43.0)	0.06 (5.5)	nd	100.5
Formic	0.30 (48.9)	0.34 (54.8)	NA	nd	103.7
Acetic	0.64 (53.0)	0.48 (39.4)	0.08 (6.6)	NA	98.9
Propionic	0.42 (34.3)	0.68 (55.4)	0.10 (7.9)	0.03 (2.4)	~100.0
Butyric	0.33 (31.6)	0.63 (61.3)	0.10 (9.3)	0.02 (1.6)	103.9

4.4.1.4 Proposed Wet Oxidation Mechanisms.

4.4.1.4.1 Proposed mechanism for formic acid WO.

Based on the experimental results discussed in sections 4.4.1.1- 4.4.1.3 a reaction mechanism was determined for formic acid WO (Reaction scheme 4.1). Based on the strong influence of [OH$^-$] on the extent of formic acid WO it is assumed that hydroxide ion most likely has a significant role in the initiation of formic acid WO. Two possible initiation steps, both dependent on hydroxide ion, are proposed for formic acid WO in highly alkaline solution. One possible initiation reaction involves simultaneous reaction of hydroxide ion and oxygen to generate a formic radical intermediate. The other possible initiation reaction involves in situ production of superoxide[1] ($O_2^{\cdot -}$) and subsequent reaction of this species with formic acid which also leads to the formation of a formic radical intermediate. Reaction of the formic radical intermediate with oxygen would lead to the formation of a peroxy radical. Due to the observed lack of ability of formic acid to propagate the formation of free radical intermediates (section 4.4.1.4) it is proposed that the free radical intermediates formed react rapidly via reactions 1,2 and 3 (Reaction scheme 4.1). This is in accordance with the chemistry of methyl radical intermediates which are extremely unstable compared to primary, secondary and tertiary radical intermediates [Sheldon 1995]. The only product formed during formic acid WO, carbonate, is proposed to form via the aforementioned reactions.

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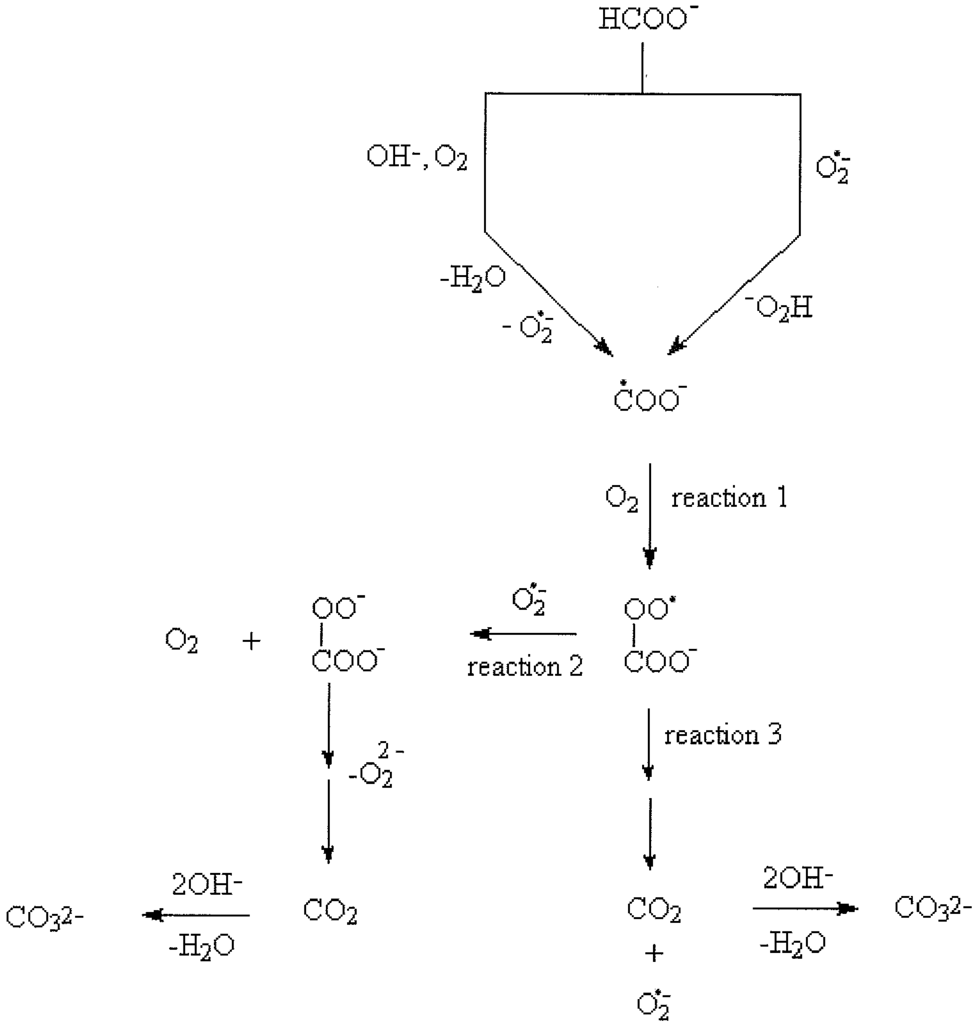
[1] it has been proposed by Eyer [2000] that superoxide formation is possible under similar conditions to those used in this study

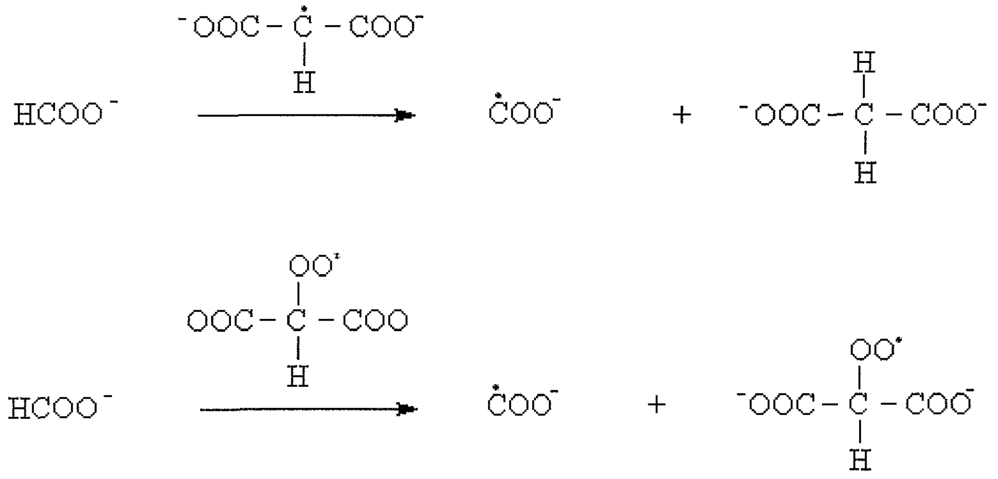


Reaction scheme 4.1 *Proposed mechanism for formic acid WO.*

4.4.1.4.2 Proposed mechanisms for malonic acid induced co oxidation of formic, acetic, propionic and butyric acids.

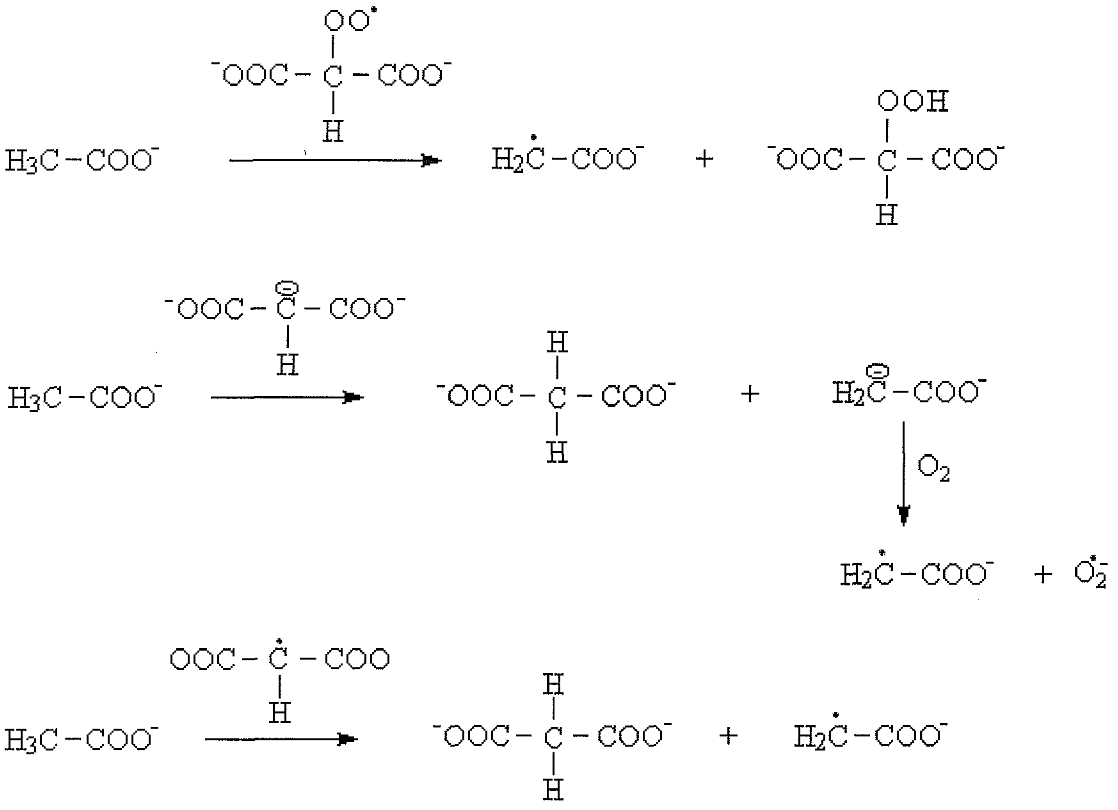
Reaction mechanisms were determined for malonic acid induced co oxidation of formic, acetic, propionic and butyric acids (Reaction schemes 4.2 - 4.5) based on the experimental results discussed in sections 4.4.1.4 – 4.4.1.6. The initiation and propagation steps proposed for malonic acid induced co oxidation of the monocarboxylic acids studied are similar to the initiation reactions proposed for malonic acid induced co oxidation of succinic and glutaric acids (Reaction schemes 3.2 and 3.3). It is proposed that co oxidation is initiated via free radical intermediates produced during malonic acid WO. Proposed product determining reaction steps are given for each of the co oxidation reactions (Reaction schemes 4.2 - 4.5) accounting for the various products identified. Due to the possibility of reaction products also undergoing co oxidation it is not possible to determine with a high degree of confidence the major product determining reaction steps.

Proposed initiation reactions for malonic acid induced co oxdiation of formic acid



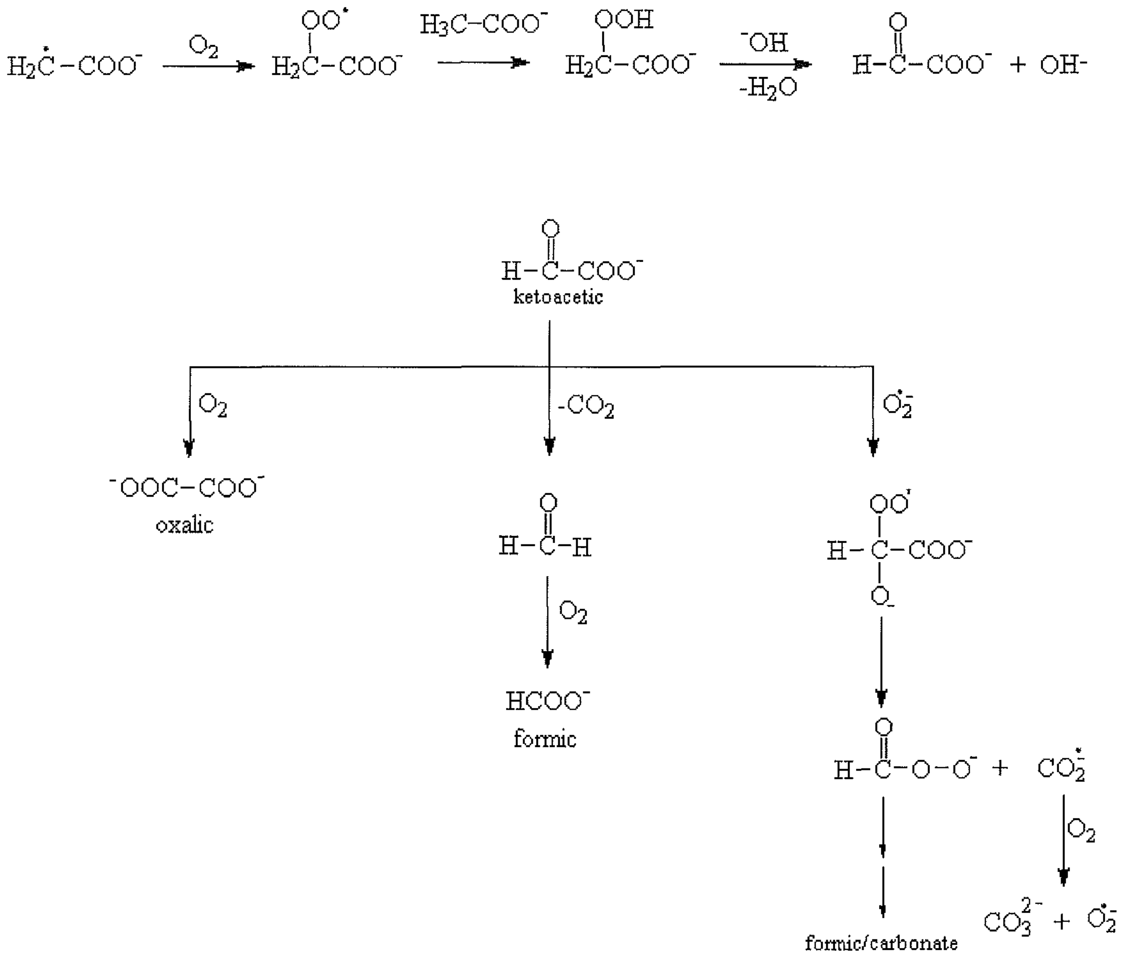
Reaction scheme 4.2 *Proposed initiation reactions for malonic acid induced co oxidation of formic acid. (refer to Reaction scheme 4.1 for proposed product determining reactions).*

Proposed initiation reactions for malonic acid induced co oxidation of acetic acid



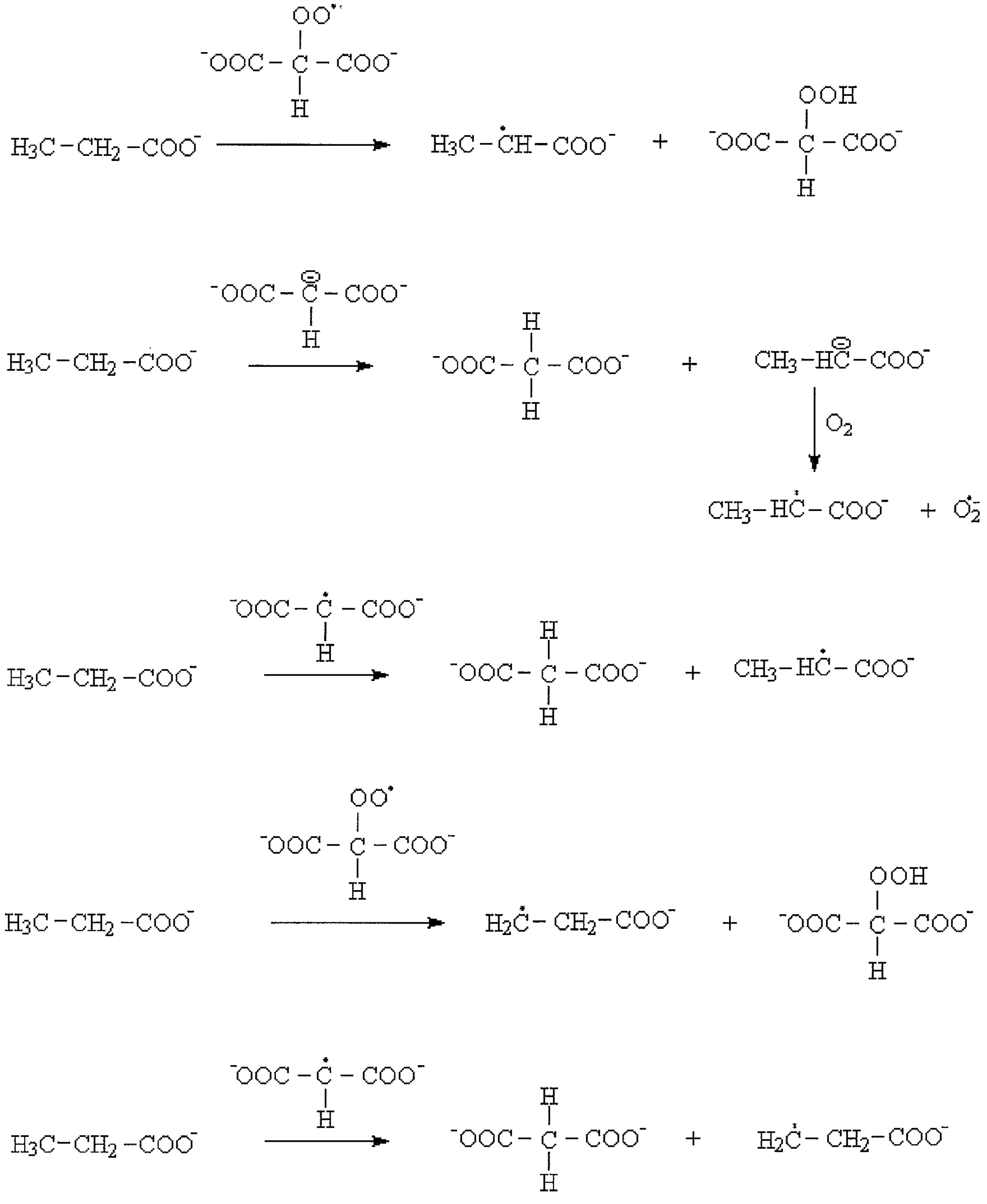
Reaction scheme 4.3a *Proposed initiation reactions for malonic acid induced co oxdiation of acetic acid.*

Proposed product determining reactions for malonic acid induced co oxidation of acetic acid



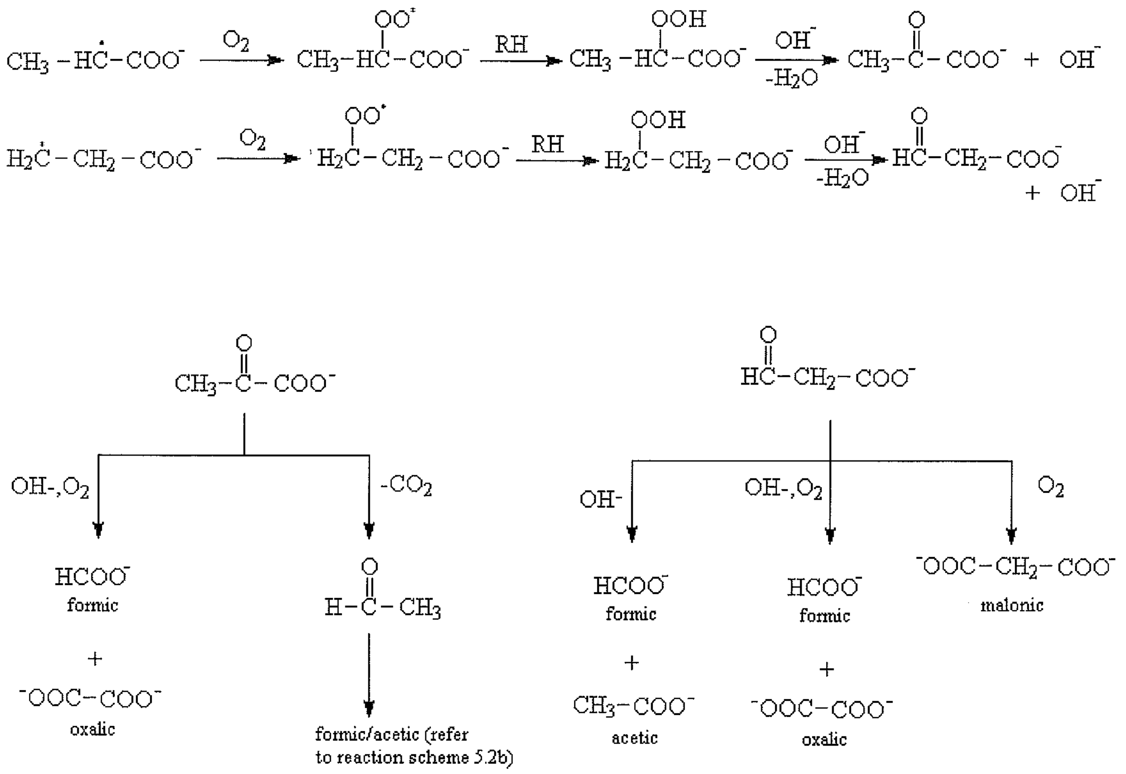
Reaction scheme 4.3b *Proposed product determining reactions for malonic acid induced co oxidation of acetic acid.*

Proposed initiation reactions for malonic acid induced WO of propionic acid



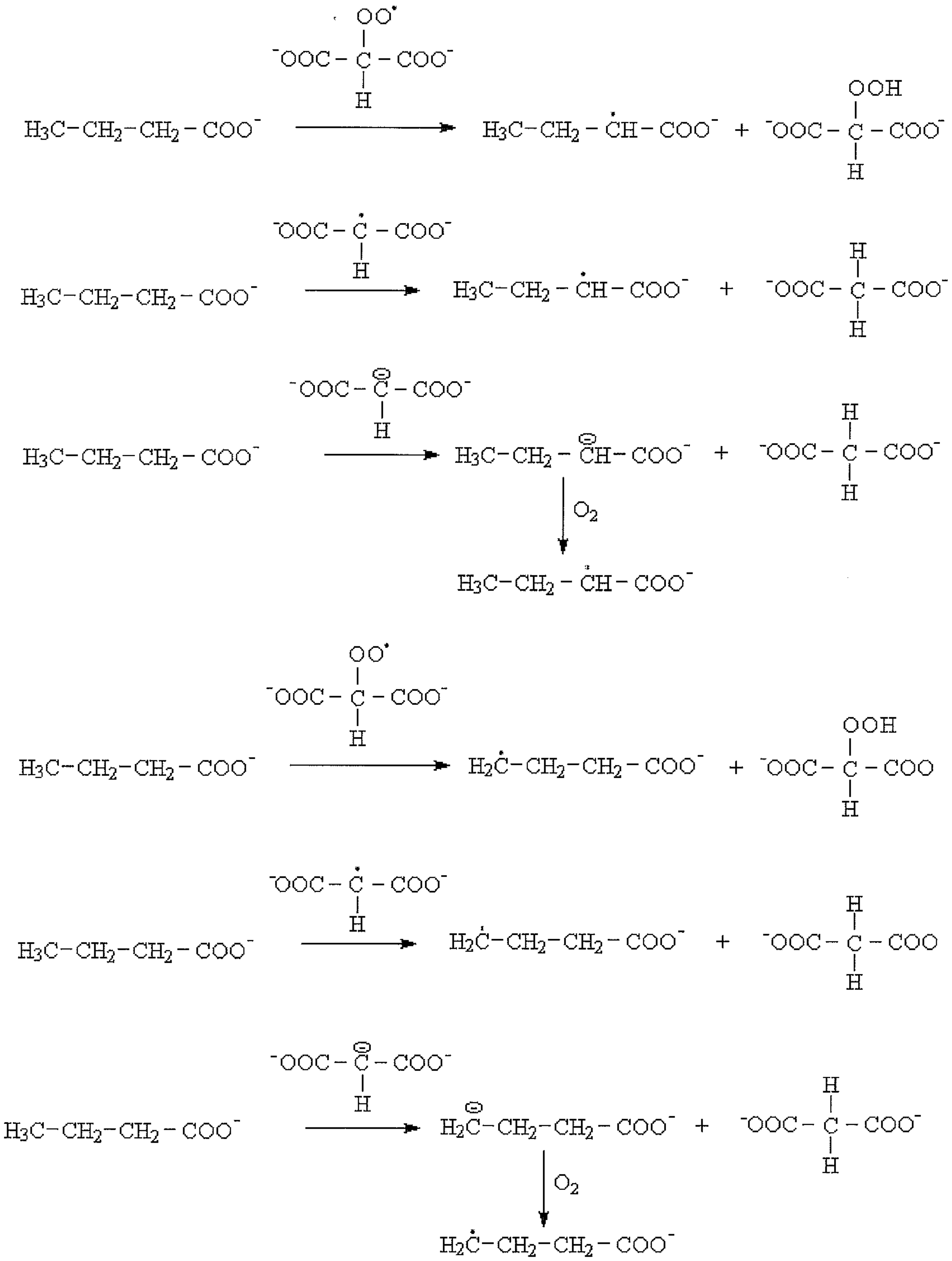
Reaction scheme 4.4a *Proposed initiation reactions for malonic acid induced co oxidation of propionic acid.*

Proposed product determining reactions for malonic acid induced co oxidation propionic acid

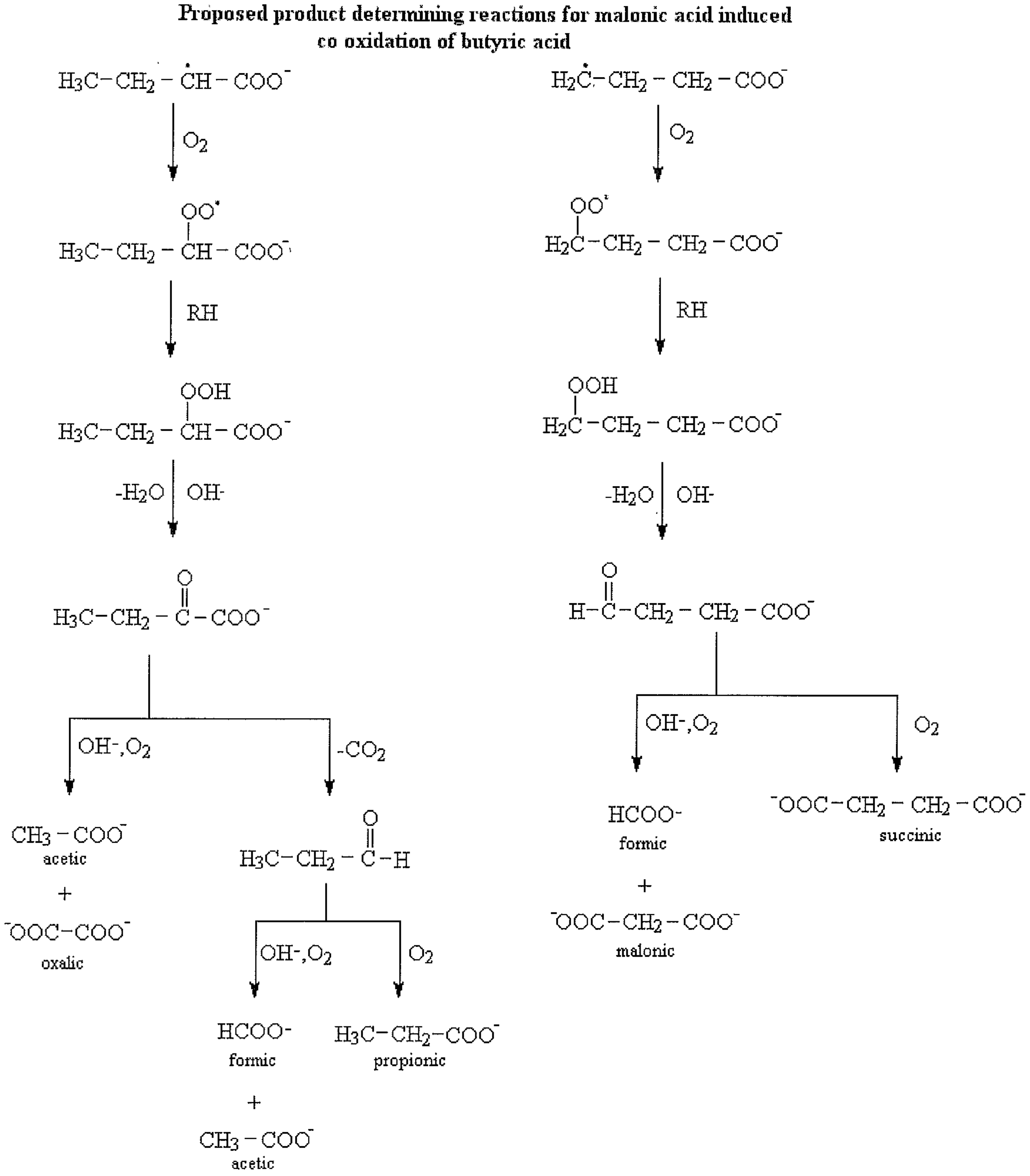


Reaction scheme 4.4b *Proposed product determining reactions for malonic acid induced co oxidation of propionic acid.*

Proposed initiation reactions for malonic acid induced co oxidation of butyric acid



Reaction scheme 4.5a *Proposed initiation reactions for malonic acid induced co oxidation of butyric acid.*



Proposed product determining reactions for malonic acid induced co oxidation of butyric acid

Reaction scheme 4.5b *Proposed product determining reactions for malonic acid induced co oxidation of butyric acid.*

4.4.2 Catalytic Wet Oxidation.

4.4.2.1 Catalyst screening.

The ability of several transition metal oxides to catalyse the WO of the monocarboxylic acids, all present in the same solution, was investigated. None of the catalysts tested (CuO, Ni_2O_3, MnO_2, Co_2O_3 and Fe_2O_3) displayed significant activity (>2% increase in overall oxidation compared to uncatalysed test). The lack of catalytic activity observed suggested that if any free radicals were produced from formic acid WO then these free radicals are so short lived that they are not propagated by any of the transition metal oxides studied. The lack of catalytic activity of the transition metal oxides tested indicates that these compounds are unable to initiate the WO of the mono carboxylic acids tested under the reaction conditions used.

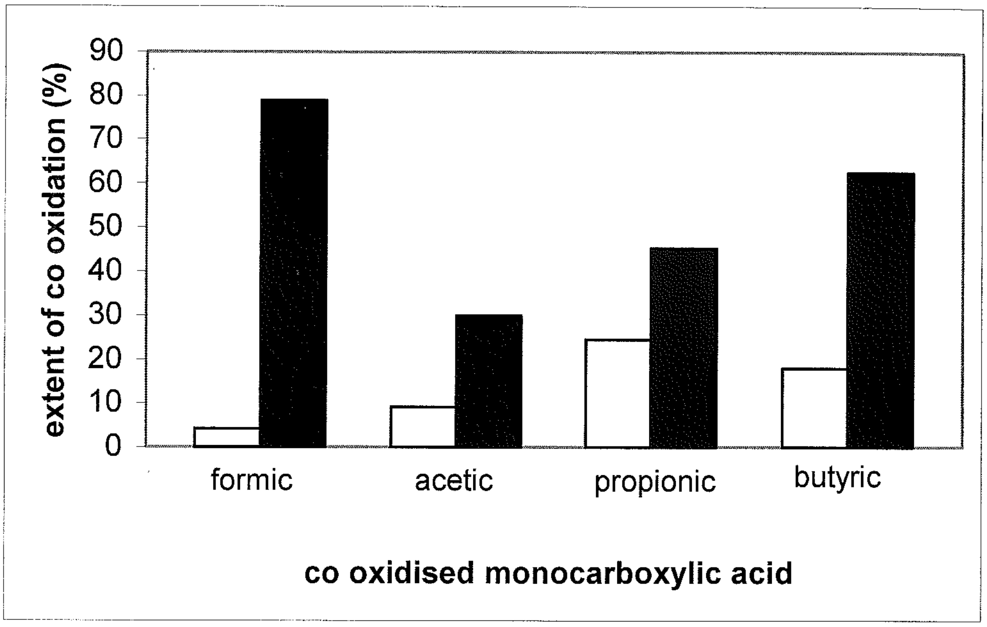
As no significant catalytic activity was observed for the transition metal oxides studied it was decided to investigate if the monocarboxylic acids could be indirectly catalysed by CuO via malonic acid.

4.4.2.2.1 Indirect CuO catalysed WO of monocarboxylic acids.

The ability of CuO to indirectly catalyse the WO of the mono carboxylics studied via free radical intermediates produced during malonic acid oxidation was investigated. The quantities of malonic acid and added monocarboxylic acid used are given in Table 4.11. Figure 4.3 shows that CuO significantly indirectly catalyses the WO of all of the mono carboxylic acids studied. The order of the extent of indirect CuO catalysed WO observed (formic > butyric > propionic > acetic) is significantly different to that observed for the analogous uncatalysed tests (propionic > butyric > acetic > formic). The most significant difference occurred for formic acid, which underwent the least amount of co oxidation in the uncatalysed tests and the greatest amount of co oxidation in the CuO catalysed test. The most likely explanation for this significant difference could be due to there being an abundant amount of co oxidising species' available in the CuO catalysed test, and that only one co oxidising species would be required per molecule of formic acid for complete oxidation to occur.

Table 4.11 *Composition of reaction mixtures used in CuO catalysed malonic acid induced co oxidation of formic, acetic, propionic and butyric acids.*

Organics	malonic concentration g/L (mol/L)	monocarboxylic concentration g/L (mol/L)	Mol ratio (malonic : added monocarboxylic)
Malonic blank	19.80 (0.190)	NA	NA
Malonic - formic	20.27 (0.195)	1.87 (0.041)	4.76 : 1
Malonic - acetic	20.27 (0.195)	2.27 (0.038)	5.13 : 1
Malonic -propionic	20.24 (0.195)	3.05 (0.041)	4.76 : 1
Malonic - butyric	20.27 (0.195)	3.43 (0.039)	5.00 : 1



*Extent of propionic acid oxidation determined using product quantities (not direct chromatographic measurement).

Figure 4.3 *Uncatalysed (open bars) and CuO catalysed (closed bars) malonic acid induced co oxidation of monocarboxylic acids.*

4.4.2.2.2 Products of indirect CuO catalysed WO of monocarboxylic acids.

The distributions of reaction products observed for CuO catalysed malonic acid induced co oxidation of the monocarboxylic acids studied are presented in Table 4.12. The reaction products identified were the same as for the analogous uncatalysed tests (Table 4.12) hence indicating that a similar reaction mechanism occurs in both the uncatalysed and CuO catalysed reactions. The distribution of products did differ for the uncatalysed and CuO catalysed tests (Figures 4.4 – 4.7). For each system a higher proportion of carbonate and lower proportion of oxalic acid was produced. These changes in product distribution are most likely predominantly due to the changes in product distribution that occur for malonic acid WO (refer to Table 3.17).

Table 4.12 *Product distributions for CuO catalysed malonic acid induced co oxidation of formic, acetic, propionic and butyric acids.*

	Reaction products (Organic Carbon g/L), 2 h				
Mono carboxylic acid co oxidised	Oxalic	Carbonate	Formic	Acetic	Mass balance (%)
None	2.33 (38.0)	3.76 (61.5)	0.06 (1.0)	nd	100.7
Formic	2.40 (36.7)	4.18 (63.9)	NA	nd	100.6
Acetic	2.51 (38.3)	4.00 (61.0)	0.08 (1.2)	NA	100.5
Propionic	2.43 (35.2)	4.28 (62.0)	0.12 (1.8)	0.07 (1.0)	~100
Butyric	2.41 (34.3)	4.13 (58.8)	0.18 (2.5)	.17 (2.5)	98.1

% distribution of products in parentheses

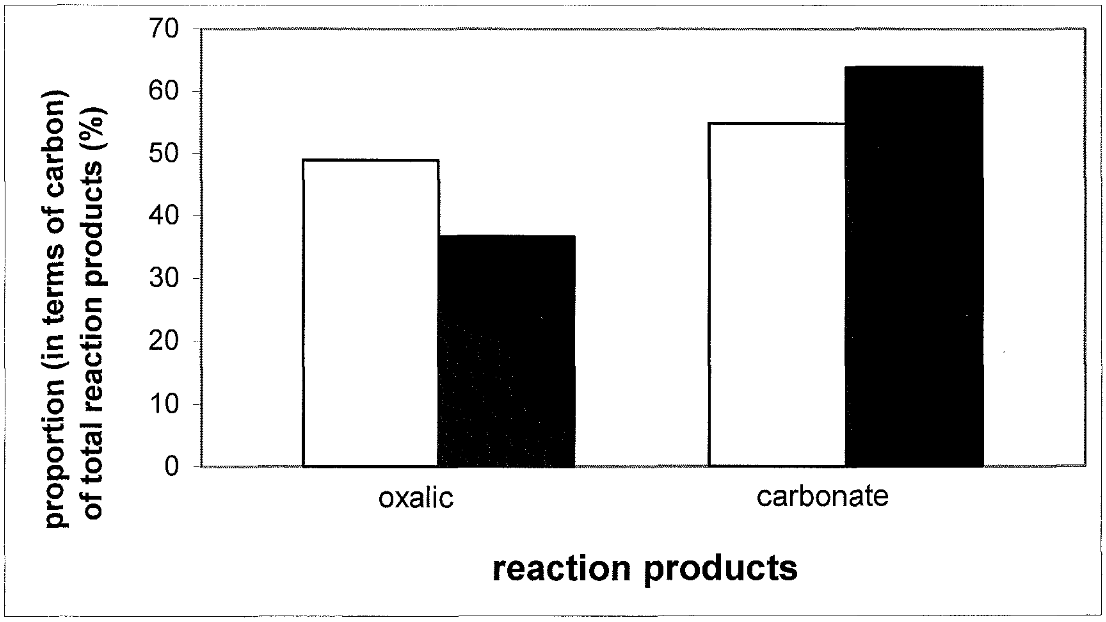


Figure 4.4 *Distribution of reaction products for uncatalysed (open bars) and CuO catalysed (closed bars) malonic acid induced co oxidation of formic acid.*

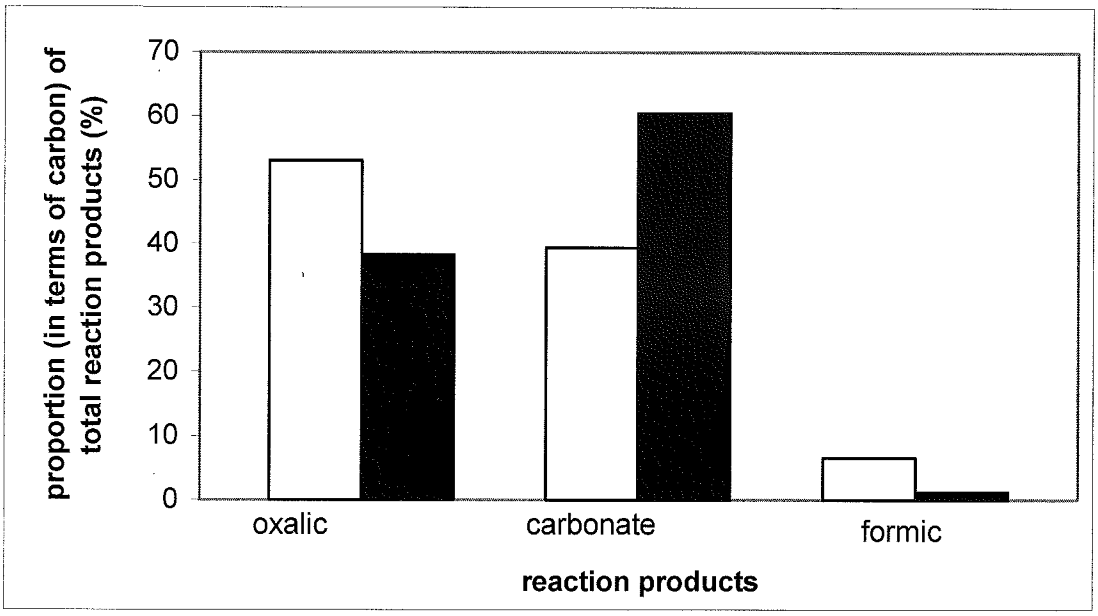


Figure 4.5 *Distribution of reaction products for uncatalysed (open bars) and CuO catalysed (closed bars) malonic acid induced co oxidation of acetic acid.*

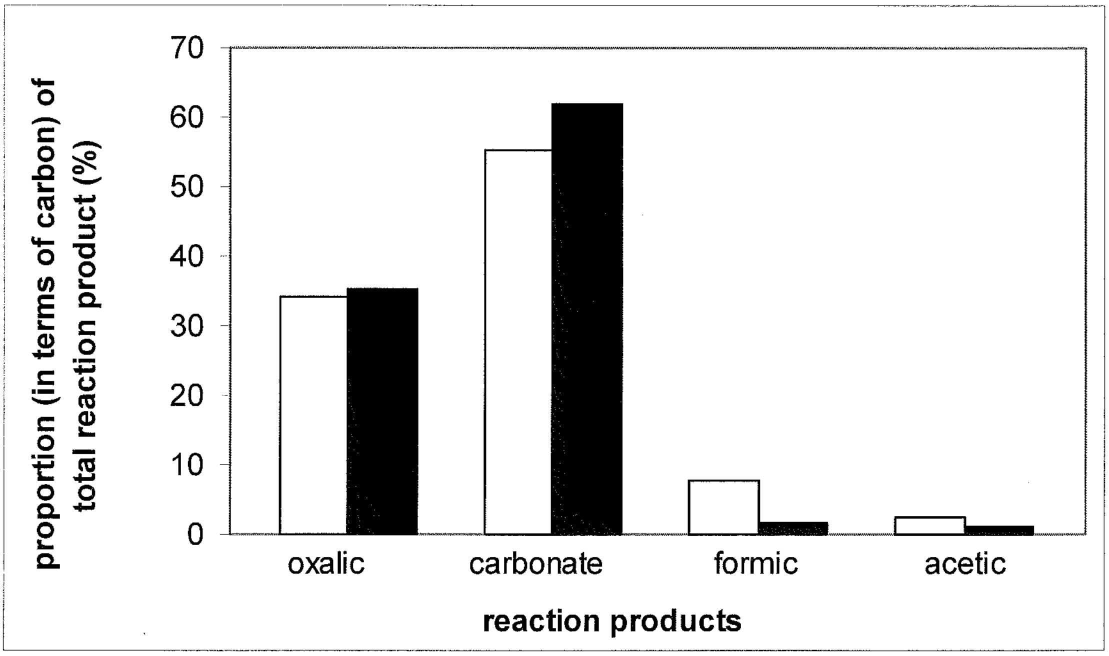


Figure 4.6 *Distribution of reaction products for uncatalysed (open bars) and CuO catalysed (closed bars) malonic acid induced co oxidation of propionic acid.*

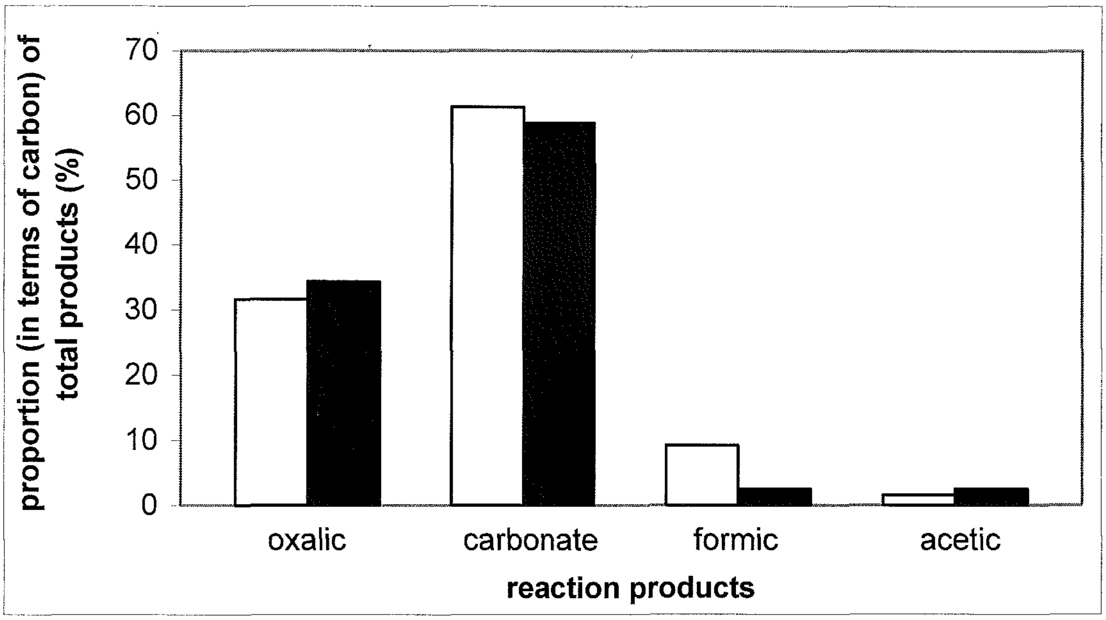


Figure 4.7 *Distribution of reaction products for uncatalysed (open bars) and CuO catalysed (closed bars) malonic acid induced co oxidation of butyric acid.*

4.4.2.3 Proposed mechanism for indirect CuO catalysed WO of formic, acetic, propionic and butyric acids.

It is proposed that indirect CuO catalysed WO of formic, acetic, propionic and butyric acids occurs via the same mechanism as that outlined in section 3.4.5 for indirect CuO catalysed WO of oxalic, succinic and glutaric acids (the main role of dissolved CuO species is to propagate the formation of free radical intermediates (Reaction scheme 3.5)). As CuO was unable to catalyse the WO of formic, acetic, propionic and butyric acids in the absence of free radical intermediates produced from malonic acid WO the proposed role of CuO involving formation of an intermediate copper-superoxo species (Reaction scheme 3.5) capable of initiating oxidation does not occur.

4.5 Conclusions and Recommendations.

The chemistry of low temperature (165°C) WO of formic, acetic, propionic and butyric acids in Bayer-like (highly alkaline) solution has been studied in detail to the author's best knowledge for the first time. The following conclusions were made based on the above-mentioned study:

Formic acid can be removed from highly alkaline solution by WO under the standard reaction conditions used (165°C, 4.4-7.0 M NaOH, 500 kPa PO_2, 2 hours). The extent of removal however is quite low (5.5 % after two hours). The only product of formic acid WO in highly alkaline solution is carbonate.

Formic acid WO is significantly affected by [OH^-]. The extent of WO undergone by formic acid increases with increasing [OH^-] (for the [OH^-] range studied). As the only product of formic acid WO is carbonate any increase in extent of WO undergone by formic acid also translates to an equal increase in extent of removal.

WO of formic acid most likely occurs via a free radical reaction mechanism. Based on the strong dependency of formic acid WO on [OH^-], hydroxide ion clearly plays a role in the reaction mechanism occurring. It is proposed that this role is most likely hydrogen atom removal. The experimental data obtained did not support a free radical *chain* mechanism occurring for formic acid WO. However, data was obtained which indicated that formic acid radicals are extremely short lived and unlikely to propagate the oxidation of other organic compounds under the reaction conditions used. Formic acid was shown to hinder the free radical chain mechanism that occurs for malonic acid WO.

Acetic, propionic and butyric acids can be co oxidised by free radical intermediates produced from malonic acid WO under the experimental conditions used.

Various transition metal oxides were unable to catalyse the WO of the monocarboxylics studied under the reaction conditions used.

CuO can indirectly catalyse the WO of formic, acetic, propionic and butyric acids by increasing the number of free radical intermediates (which are capable of co oxidising the above mentioned compounds) formed during malonic acid WO.

CHAPTER 5

WET OXIDATION AND CATALYTIC WET OXIDATION OF LOW MOLECULAR WEIGHT, C_3-C_6, HYDROXY CARBOXYLIC ACIDS

5.1 Introduction.

The adverse effects of hydroxy carboxylic acids (such as lactic, malic and tartaric acids) on the Bayer process have been the subject of considerable research over the last three decades [Ramana Rao and Chandwani 1997, Coyne 1989, Zoldi *et al* 1988, Brown 1991, Grocott and Rosenberg 1988, Sang 1988, Armstrong 1993, Alamdari 1993, Tran 1996, Coyne *et al* 1994, Atkins and Grocott 1988]. This is due to various compounds from this class of organics causing significant decreases in aluminium hydroxide yields, which in terms of an alumina refinery translates to a reduction in profits. Various compounds from this class of organics (such as lactic acid) have also been shown to cause 'fining' of alumina, which leads to handling and transportation problems. Other adverse effects of hydroxy carboxylic acids on the Bayer process are discussed in section 1.2.2.1.

Very few hydroxy carboxylic acids have been identified in other industrial waste-streams and process liquors, based on the WO/CWO literature reviewed. Two hydroxy carboxylic acids that have been mentioned in the WO/CWO literature include 3-hydroxy propionic acid and hydroxylcapronic acid. 3-hydroxy propionic acid has been proposed as an easy-to-oxidise intermediate formed during WO of phenol containing wastewaters [Devlin and Harris 1984]. Hydroxylcapronic acid has been identified in spent caustic wastewater from a petrochemicals-manufacturing process [Chang and Lin 1993].

In this chapter the WO and CWO of four hydroxy carboxylic acids: citric, lactic, malic and tartaric acids has been investigated. All of these compounds, except for tartaric acid, have been identified in various worldwide Bayer liquors (Table 5.1).

Table 5.1 *Hydroxy carboxylic acids studied in this chapter that have been identified in various worldwide Bayer liquors.*

Country/region	Hydroxy carboxylic acids identified	Reference
Australia-WA	lactic, malic,citric	Niemela 1993
Jamaica	lactic, malic	Baker 1995
na	lactic, malic	Guthrie 1984

na=not available

5.2 Background.

Due to the lack of available literature on the WO/CWO of hydroxy acids very little is known about the WO/CWO chemistry of this class of compounds. There is a substantial amount of literature available on the general oxidation/degradative oxidation reactions of this class of compounds using various chemical oxidants. The nature of reactions taking place using chemical oxidants is however a separate area of study and therefore will not be discussed here.

As no relevant literature is available on the WO/CWO of hydroxy carboxylic acids in highly alkaline solution, it is necessary to discuss the general chemistry of hydroxy carboxylic acids in alkaline solution. Two possible reactions of hydroxy carboxylic acids in alkaline solution which are particularly relevant to the reaction conditions that were used in this study are; base catalysed retro aldol reaction of β-hydroxy carboxylics [Roberts 1979, Ivanov and Mondeshka 1973] and decarboxylation of α-hydroxy carboxylic acids [March 1985]. No literature however was found involving the above-mentioned reactions and the hydroxy carboxylic acids and reaction conditions used in this study.

Due to the significant lack of literature on the WO/CWO of hydroxy carboxylic acids in highly alkaline solution, there is very little known about the types of reactions that take place during WO/CWO of this class of compounds. In this chapter, the WO/CWO of four hydroxy carboxylic acids in highly alkaline solution has been studied to the author's best knowledge for the first time, in an attempt to fill the void in the literature.

5.3 Experimental.

The materials, methods and analytical procedures used in the majority of WO and CWO experiments conducted in this chapter are given in chapter 2. Other materials, methods and analytical methods specific to this chapter are outlined in sections 5.3.1.1- 5.3.1.2.

5.3.1 Copper complexes of citric, lactic, malic and tartaric acids.

5.3.1.1 Materials.

Cupric citrate [$Cu_2(C_6H_4O_7)2.5\ H_2O$] (Hopkin and Williams) was used without further purification. Cupric lactate, malate and tartrate were prepared using their respective acids (refer to section 2.1.2) and cupric carbonate [$Cu(CO_3)$] (Hopkin and Williams) (cupric lactate and malate) and cupric acetate (BDH Chemicals) (cupric tartrate). Milli-Q water was used to prepare all solutions.

5.3.1.2 Preparation methods.

Cupric tartrate was prepared using the method of Massey [1973]. Cupric lactate and malate were prepared using the method of Asai *et al* [1959].

5.3.1.3 Characterisation methods and results.

The copper complexes were characterised using the following techniques; Total carbon (O-I-Analytical 1010 Total Organic Carbon Analyser, refer to section 2.2.4.3), water content (Thermogravimetric Analysis, Perkin Elmer Thermogravimetric Analyser TGA7) and copper (Atomic Absorption Spectrophotometry, Perkin Elmer Atomic Absorption Spectrophotometer 3110). The characterisation data is presented in Table 5.2.

Table 5.2 *Characterisation results for prepared copper salts of lactic, malic and tartaric acids.*

	% weight					
Copper complex	Cu		C		H_2O	
	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.
Cupric lactate ($Cu(C_3H_5O_3)_2.2H_2O$)	22.5	22.9	26.4	25.9	12.3	13.0
Cupric malate ($Cu(C_4H_4O_5).2H_2O$)	26.9	27.4	18.4	20.7	14.3	15.5
Cupric tartrate ($Cu(C_4H_4O_6).2.5\text{-}3.0\ H_2O$)	23.5	23.9	18.3	18.5	18.0	16.9-20.3

5.4 Results and Discussion.

5.4.1 Wet Oxidation.

5.4.1.1 Extent of WO, TOC reduction and reaction products under standard test conditions.

The WO of the hydroxy carboxylic acids chosen was studied under standard test conditions (refer to section 2.2.3). The results of these tests are presented in Table 5.3. All of the hydroxy acids studied underwent wet oxidation under the reaction conditions used, the extent of oxidation and TOC reduction observed in decreasing order being; tartaric > citric > lactic > malic. A significant amount of fumaric acid was detected at time zero for the malic acid WO test due to dehydration of malic acid. Hence, the actual decrease in malic acid concentration over the two hour test period was significantly higher than the value given in Table 5.3. However, as conversion of malic acid to fumaric acid (via dehydration) does not constitute an oxidation reaction this was not taken into account. The extent of oxidation given for malic acid was evaluated based on the quantities of oxidation products detected, the method also used to determine the extent of oxidation of citric and tartaric acids.

A small amount of non-oxidative degradation of citric and tartaric acids did occur during the heating up period before the addition of oxygen. However, as this was significantly low (<2%) the initial concentrations of these compounds at time zero were not significantly effected. As the main aim of this project was to investigate the extent of complete and partial oxidation in the presence of oxygen the above mentioned finding was not investigated further.

Table 5.3 *Extent of wet oxidation and TOC reduction of hydroxy carboxylic acids under standard test conditions.*

Organic	Extent of wet oxidation (%)	TOC reduction (%)
Citric	50.3*	12.0
Lactic	8.6	4.3
Malic	5.6*	2.2
Tartaric	51.0*	12.8

*Based on quantity of oxidation products identified

The reaction products identified for each of the compounds studied are given in Table 5.4. Three compounds, acetic and oxalic acids and carbonate accounted for >90% of the reaction products for all of the hydroxy carboxylic acids studied. These three compounds were the only products identified for lactic and malic acid WO. Trace amounts of formic and malonic acids were detected for tartaric and citric acid WO.

Table 5.4 *Products identified for WO of hydroxy carboxylic acids under standard test conditions (refer to section 2.2.3).*

	Reaction products (g Organic Carbon/L)					
Organic	Oxalic	Carbonate	Acetic	Formic	Malonic	Mass balance (%)
Citric	0.22 (22.5)	0.23 (23.9)	0.47 (49.0)	0.04 (3.6)	0.01 (0.6)	100*
Lactic	0.04 (22.3)	0.09 (50.3)	0.05 (28.4)	nd	nd	101.1
Malic^{+}	0.03 (30.5)	0.04 (39.0)	0.03 (30.5)	nd	nd	100*
Tartaric	0.37 (40.1)	0.23 (25.2)	0.23 (25.2)	0.08 (8.5)	0.01 (0.7)	100*

*Based on products formed

$^{+}$Significant amount of fumaric acid detected at time zero

% proportion (in terms of carbon) of total products in parentheses

5.4.1.2 Wet Oxidation mechanism studies.

The extent of WO observed for the hydroxy carboxylic acids studied was investigated further in an attempt to determine the type(s) of reactions occurring during WO. Based on the results of the previous two chapters it was decided to investigate the role of hydroxide ion in the WO of the hydroxy carboxylic acids studied.

5.4.1.2.1 Effect of [OH$^-$] on extent of WO.

The effect of [OH$^-$] on the extent of WO is given in Table 5.5. [OH$^-$] clearly has an effect on the extent of WO for each of the compounds studied. A significant increase in extent of WO occurs with increasing [OH$^-$] for all of the hydroxy carboxylic acids studied. The effect of [OH⁻] on the WO of citric, lactic, malic and tartaric acids is discussed in more detail in the proposed WO mechanisms section of this chapter (section 5.4.1.3).

Table 5.5 *Effect of [OH⁻] on extent of WO and TOC reduction of citric, lactic, malic and tartaric acids. Standard reaction conditions (refer to section 2.2.3) except for [NaOH] of various synthetic Bayer liquors.*

Organic	Extent of oxidation (%) at varying [OH⁻]		
	4.4 M NaOH	5.7 M NaOH	7.0 M NaOH
Citric	50.3 (12.0)	76.4 (14.6)	91.8 (15.0)
Lactic	8.6 (4.3)	29.0 (4.5)	60.0 (11.0)
Malic	5.6 (2.2)	19.5 (5.2)	33.7 (2.6)
Tartaric	51.0 (12.8)	87.3 (20.1)	90.0 (21.3)

Extent of TOC reduction (%) in parentheses

5.4.1.2.2 Effect of [OH⁻] on products.

The effect of [OH⁻] on products formed from partial WO of the hydroxy acids studied is presented in Figures 5.1 - 5.4. [OH⁻] did not have a significant effect on the type of products produced. The same major products were identified for all compounds, while some compounds which were only identified in trace amounts, such as malonic acid (citric and tartaric acid WO) and formic acid (lactic and malic WO) were not detected in all higher alkalinity tests. The absence of formic acid as a product for lactic and malic WO in the 4.4M NaOH test is most likely due to the amount formed being below detection limits. The absence of malonic acid as a product in citric and tartaric acid WO at high alkalinity is most likely due to malonic acid undergoing WO as soon as it is formed.

Although the types of products formed from WO of the hydroxy carboxylics studied did not vary with increasing [OH^-] significant differences did occur in the distribution of products (Figures 5.1 - 5.4). In all cases, the proportion of oxalic acid and acetic acid (excluding tartaric acid WO) produced increased with increasing [OH^-], while a corresponding decrease in the proportion of carbonate produced also occurred. The proportion of formic acid produced decreased in all cases with increasing [OH^-]. This is most likely due to formic acid WO also being base catalysed and that its rate of oxidation was most likely higher than it's rate of formation in the higher alkalinity tests.

Therefore, while increasing [OH^-] does increase the extent of oxidation of the hydroxy carboxylic acids studied it also adversely affects the product determining reaction pathways. Increasing [OH^-] leads to an increase in the proportional formation of two major products that are resistant to oxidation, oxalic and acetic acids, and a corresponding decrease in the proportional formation of carbonate. Hence, the increase in extent of oxidation achieved by increasing [OH^-] does not lead to a proportional increase in the extent of complete oxidation (compound removal).

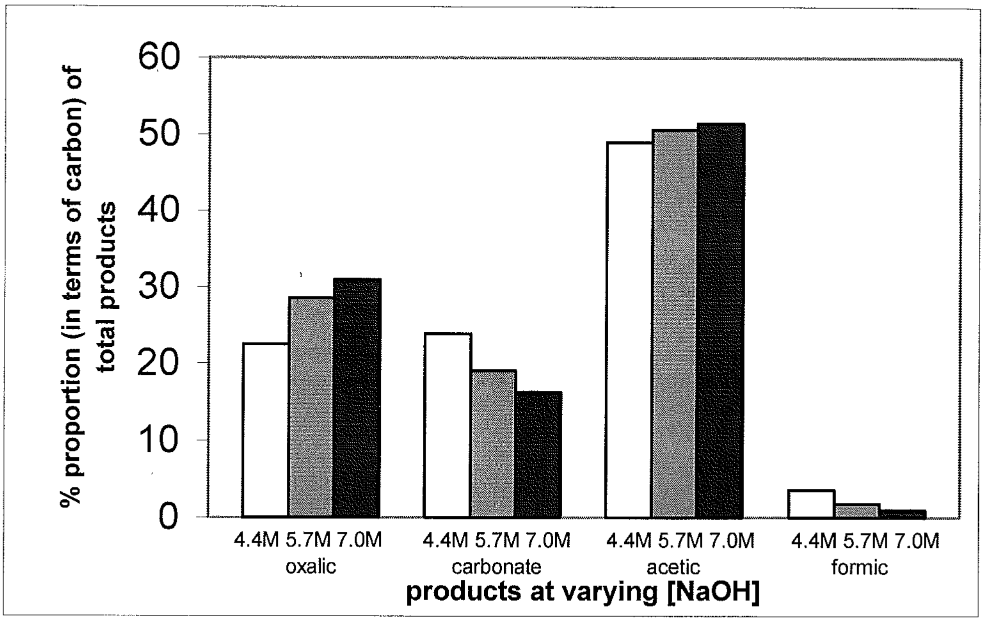


Figure 5.1 *Effect of [OH⁻] on product distribution for citric acid WO.*

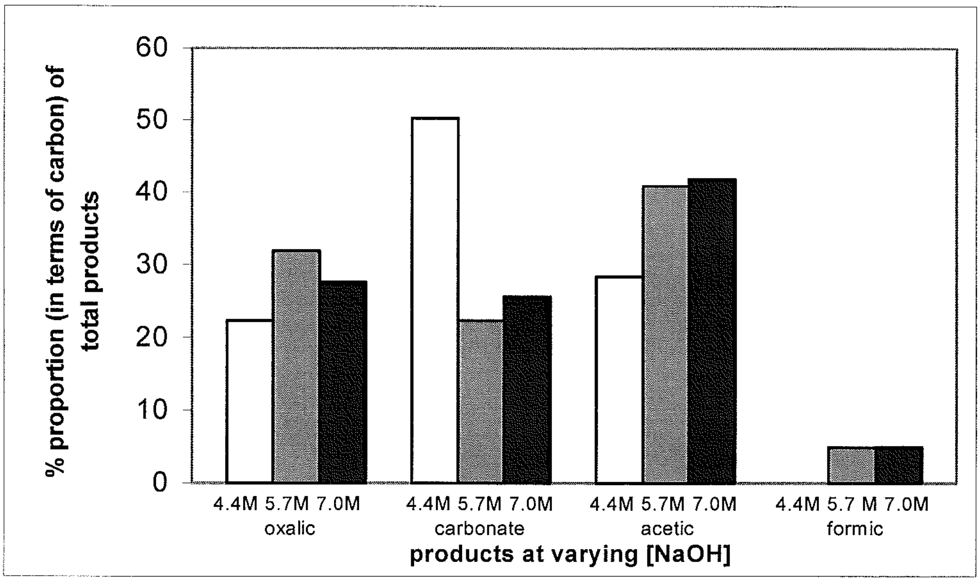


Figure 5.2 *Effect of [OH⁻] on product distribution for lactic acid WO.*

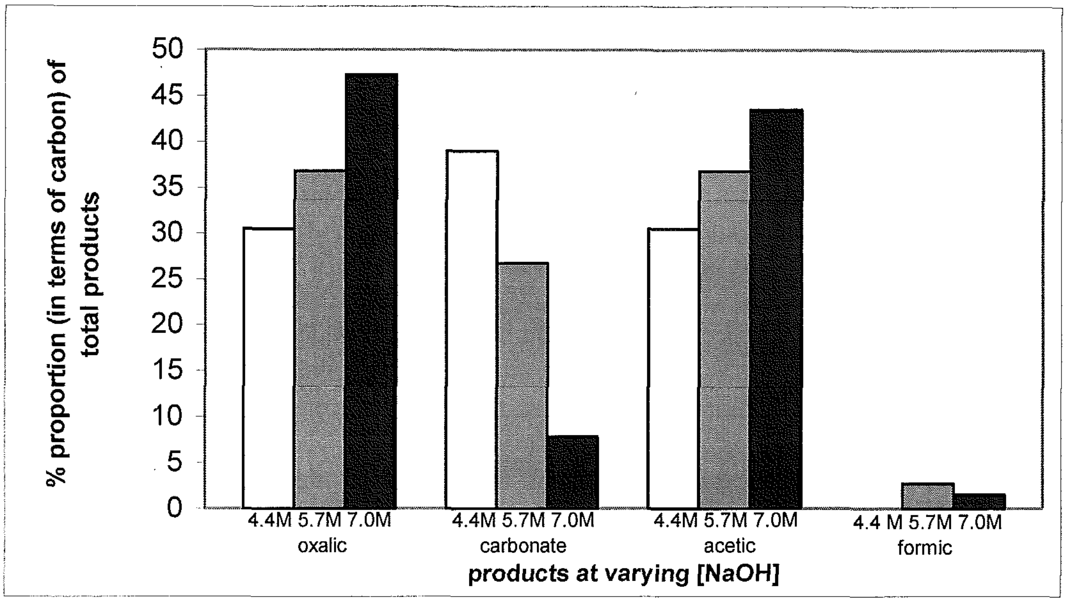


Figure 5.3 *Effect of [OH⁻] on product distribution for malic acid WO.*

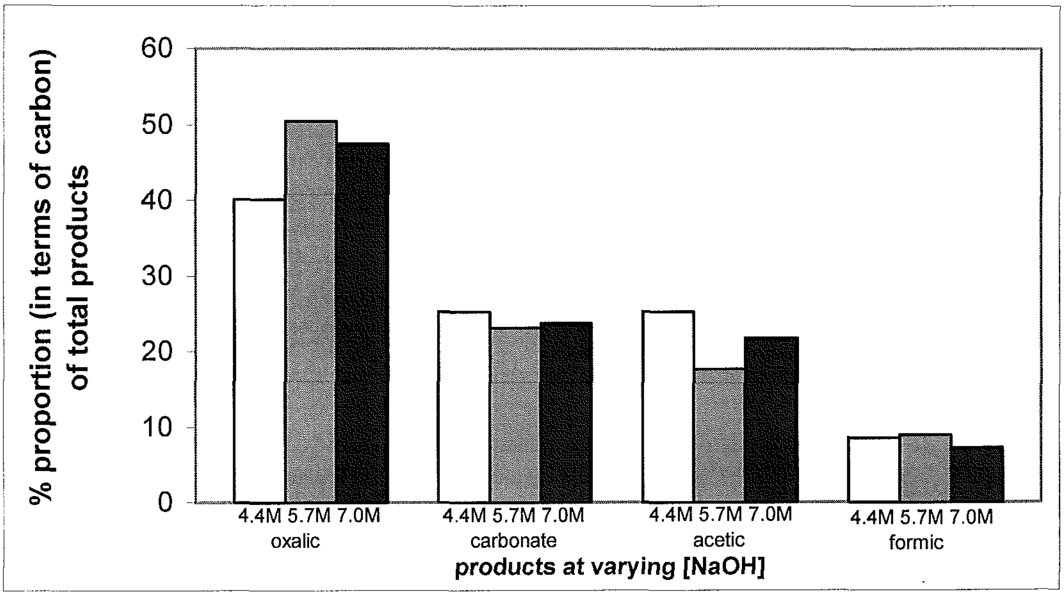


Figure 5.4 *Effect of [OH⁻] on product distribution for tartaric acid WO.*

5.4.1.2.3 Investigation of type of reaction mechanism occurring during WO of citric, lactic, malic and tartaric acids.

The next aspect of WO studied for each of the hydroxy carboxylics was the type of reaction mechanism (free radical or ionic) occurring during WO. The co oxidation method was again used to determine if free radical intermediates were being produced during the WO of the different hydroxy carboxylic acids, and hence if WO was occurring via auto oxidation. Succinic acid was chosen as the compound to be co oxidised as it was not identified as a product in the WO of any of the compounds studied. Due to the low extent of oxidation undergone by both lactic and malic acids at 4.4 M NaOH, it was decided to investigate the ability of these compounds to co oxidise at higher alkalinity (7.0 M NaOH) to maximise the number of free radical intermediates which could possibly be produced.

The results of the co oxidation tests conducted using each of the hydroxy acids and succinic acid are presented in Table 5.6. Citric acid was the only compound capable of co oxidising succinic acid, effectively co oxidising 9.05% of the added succinic acid.

Table 5.6 *Effect of WO of citric, lactic, malic and tartaric acids on succinic acid oxidation. Fixed initial succinic concentration, 1.87 g OC/L.*

Organic	Initial hydroxy carboxylic concentration (g OC/L)	Molar ratio, hydroxy carboxylic:succinic acid	Extent of hydroxy acid oxidation (%)	Extent of succinic oxidation (co oxidation) (%)
Citric	13.98	5:1	32.0	9.05
Lactic*	6.90	5:1	53.5	<2
Malic*	9.32	5:1	41.7	<2
Tartaric	9.34	5:1	41.0	<2

*tests conducted using 7.0 M NaOH synthetic Bayer liquors.

Hence based on the co oxidation tests, free radical intermediates capable of co oxidising succinic acid are produced during citric acid WO and not during the WO of lactic, malic and tartaric acids. The extent of co oxidation of succinic acid observed using citric acid (9.05 %) compared with malonic acid (19.2%) does however differ quite significantly when taking into account the respective amounts of both compounds oxidised (32.0% citric acid and 16.6% malonic acid). Due to the significant difference in the extent of oxidation occurring for citric and malonic acids and the respective extent of co oxidation observed using each of these compounds it was decided to investigate citric acid induced co oxidation more closely.

Examination of the reaction products in the citric-succinic co oxidation test revealed that a significant amount of malonic acid was produced during this test (0.04g OC /L of malonic acid detected at 2 h). Hence due to malonic acid being relatively easy to oxidise it could be assumed that the presence of malonic acid under the reaction conditions studied indicates that a significant amount of malonic acid must be produced for it to be present at a detectable quantity. The amount of malonic acid detected in the citric acid co oxidation test was also significantly higher than that detected in the other hydroxy carboxylic acids co oxidation tests. Based on the above findings it was concluded that the co oxidation exhibited by citric acid was most likely due to a significant amount of malonic acid being produced as an intermediate in citric acid WO and that the malonic acid produced during citric acid WO was most likely responsible for the co oxidation detected using citric acid. To confirm that the reaction mechanism occurring during citric acid WO was not predominantly free radical based the WO of citric acid was also studied in the presence of added formic acid, a compound shown in chapter 4 to hinder the free radical mechanism occurring during malonic acid WO. The results of this test showed that formic acid did not have a significant effect on citric acid WO. Hence, the predominant reaction mechanism occurring during citric acid WO, based on the experimental results obtained, is ionic in nature.

5.4.1.3 Proposed Wet Oxidation reaction mechanisms.

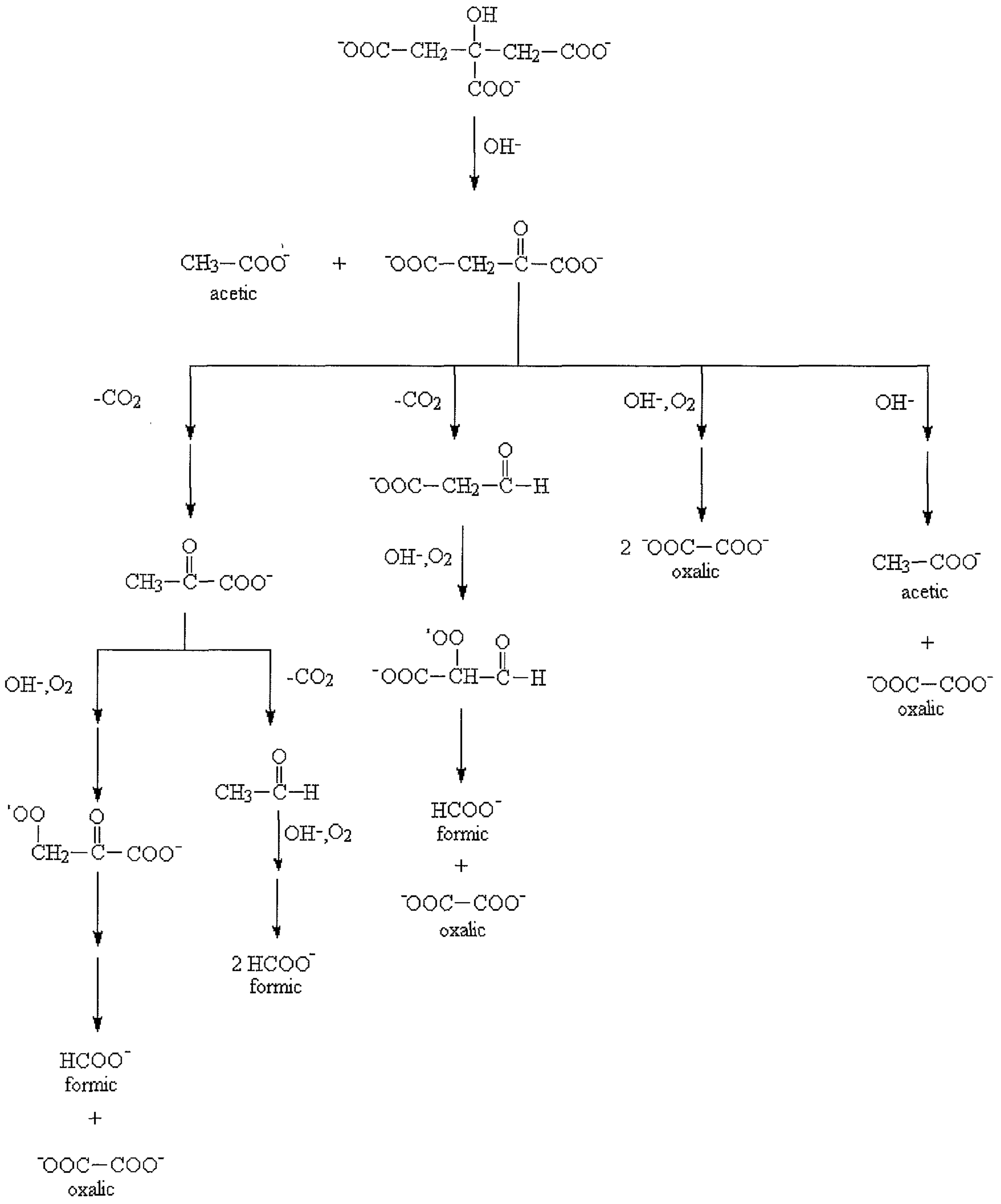
Proposed WO reaction mechanisms were determined for the WO of citric, lactic, malic and tartaric acids based on the experimental data discussed in sections 5.4.1.1- 5.4.1.2 and relevant literature. The proposed reaction mechanisms are presented in Reaction schemes 5.1 – 5.4.

The reaction mechanism for citric acid WO in highly alkaline solution was found to consist predominantly of ionic reactions, with some minor free radical reactions occurring. Hence the proposed reaction mechanism determined for citric acid WO incorporates both ionic and free radical reactions. Based on the dependency of the extent of citric acid WO on [OH$^-$] it is most likely that the first step in citric acid WO involves reaction with hydroxide ion. Based on the dependency on [OH$^-$] and the reaction products detected it is proposed that this first step is a base catalysed retro aldol reaction, a reaction known to occur for β-hydroxy acids [Roberts 1979]. This reaction leads to the formation of acetic acid and a β-keto dicarboxylic acid. The β-keto dicarboxylic acid formed can undergo a number of possible reactions under the reaction conditions used in this study (such as decarboxylation, oxidative cleavage, and hydroxide ion reaction with the carbonyl group and subsequent chain cleavage). Those reactions that account for the reaction products observed have been included in the proposed reaction mechanism presented in Reaction scheme 5.1. The effect of $[OH^-]$ on the distribution of reaction products is also accounted for in the proposed reactions given in Reaction scheme 5.1. It is proposed that the β-keto dicarboxylic acid formed in the initial reaction of citric acid, and various other intermediates formed from its degradation, do undergo some free radical based reactions, as this is the only feasible explanation for the high amount of oxalic acid formed during citric acid WO. Although the co oxidation of succinic acid by citric acid was initially proposed to be predominantly due to the malonic acid produced during citric acid WO, it is also likely that other free radical intermediates present also contributed to the co oxidation of succinic. Hence, it is also likely that some auto oxidation does occur during citric acid WO.

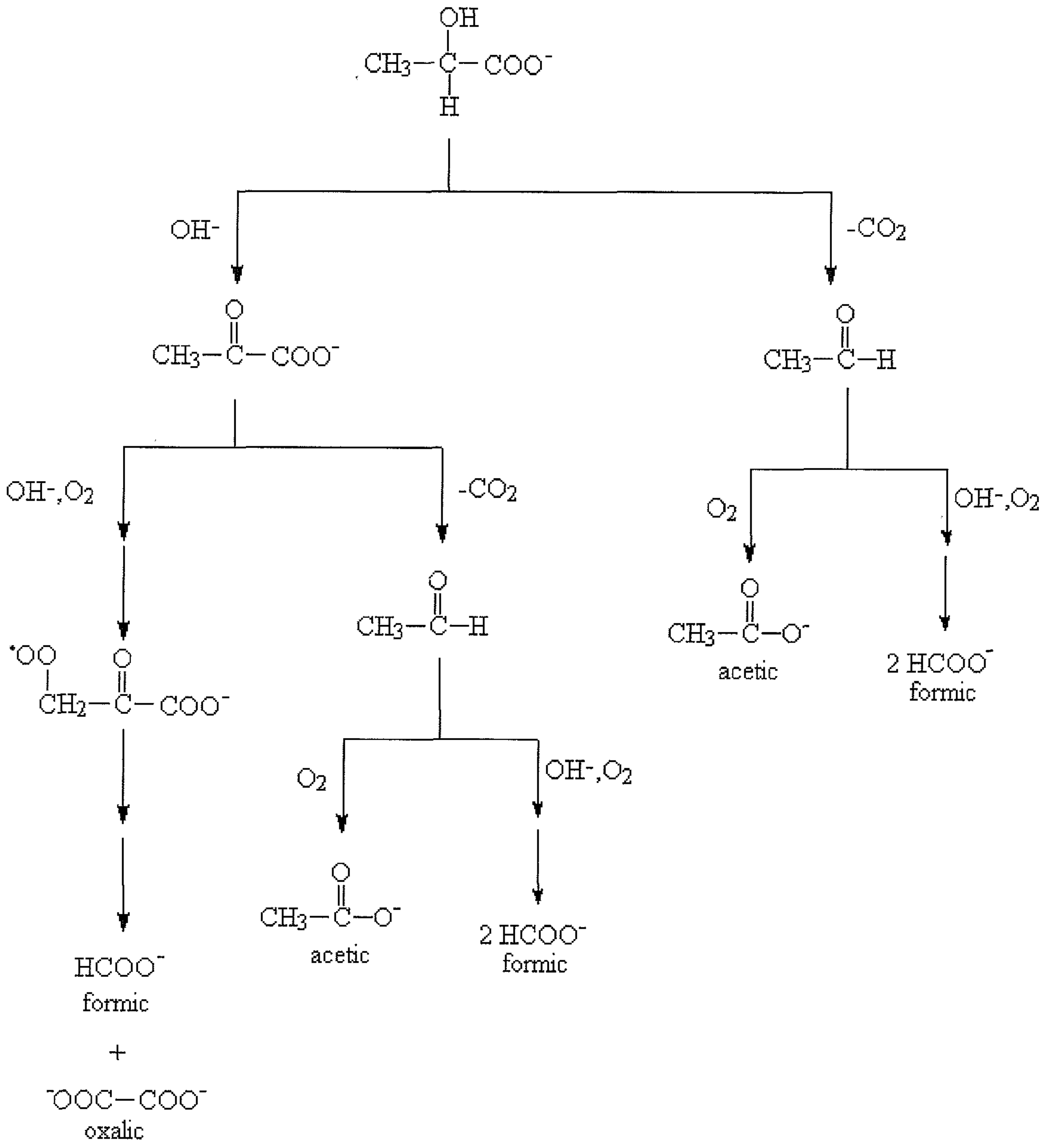
The reaction mechanism for lactic acid WO in highly alkaline solution was found to occur predominantly via ionic reactions as no experimental evidence was obtained to indicate that a free radical chain reaction was occurring. Based on the strong dependency of lactic acid WO on $[OH^-]$ it is proposed that the initial reaction in lactic acid WO is reaction between lactic acid and hydroxide ion. Two possible initiation reactions are proposed for lactic acid WO. The first possible reaction is proposed to be base catalysed oxidative decarboxylation leading to the formation of acetaldehyde. This reaction is known to occur for α-hydroxy acids (such as lactic acid) and can be achieved using alkaline hydrogen peroxide [March 1985]. The acetaldehyde formed in the initial reaction can undergo a number of reactions under the reaction conditions used. The reactions that account for the reaction products observed have been included in the proposed reaction mechanism presented in Reaction scheme 5.2. The other possible reaction of lactic acid involves removal of the hydroxyl group proton by reaction with hydroxide ion and subsequent hydride ion elimination leading to the formation of a keto acid intermediate (pyruvic acid). Subsequent reactions of this intermediate leading to the products formed are presented in Reaction scheme 5.2. The only feasible explanation for the formation of oxalic acid as a major reaction product involves free radical reactions occurring. However, no experimental evidence was obtained to support the presence of free radical intermediates. This could be due to only unstable primary free radicals could possibly form during lactic acid WO and also that the number of free radicals formed is restricted due to the intermediates from which they are possibly formed can also undergo ionic reactions.

The reaction mechanism for malic acid WO in highly alkaline solution was found to occur predominantly via ionic reactions as no experimental evidence was obtained to indicate the presence of free radical intermediates. Two possible initiation reactions are proposed to occur for malic acid WO. The first possible initial reaction for malic acid (a β-hydroxy carboxylic) WO is proposed to be the same as that undergone by citric acid (a base catalysed retro aldol reaction) based on the dependency of malic acid WO on [OH^-]. This reaction results in the formation of acetic and glyoxalic acids. Glyoxalic acid may undergo a number of possible reactions under the reaction conditions used. The subsequent reactions of the proposed intermediates leading to the products identified are presented in Reaction scheme 5.3. The high proportion of oxalic acid formed during malic acid WO is most likely due to the reaction intermediates formed undergoing free radical based reactions. The inability of these intermediates to co oxidise succinic acid is most likely due to the same reasons discussed for lactic acid WO, and hence any free radical chain reaction occurring during malic acid WO is extremely short. The other possible initiation reaction that is proposed for malic acid WO is decarboxylation. The extent to which this reaction occurs is most likely independent of [OH^-] based on the effect of [OH^-] on the distribution of products observed for malic acid WO.

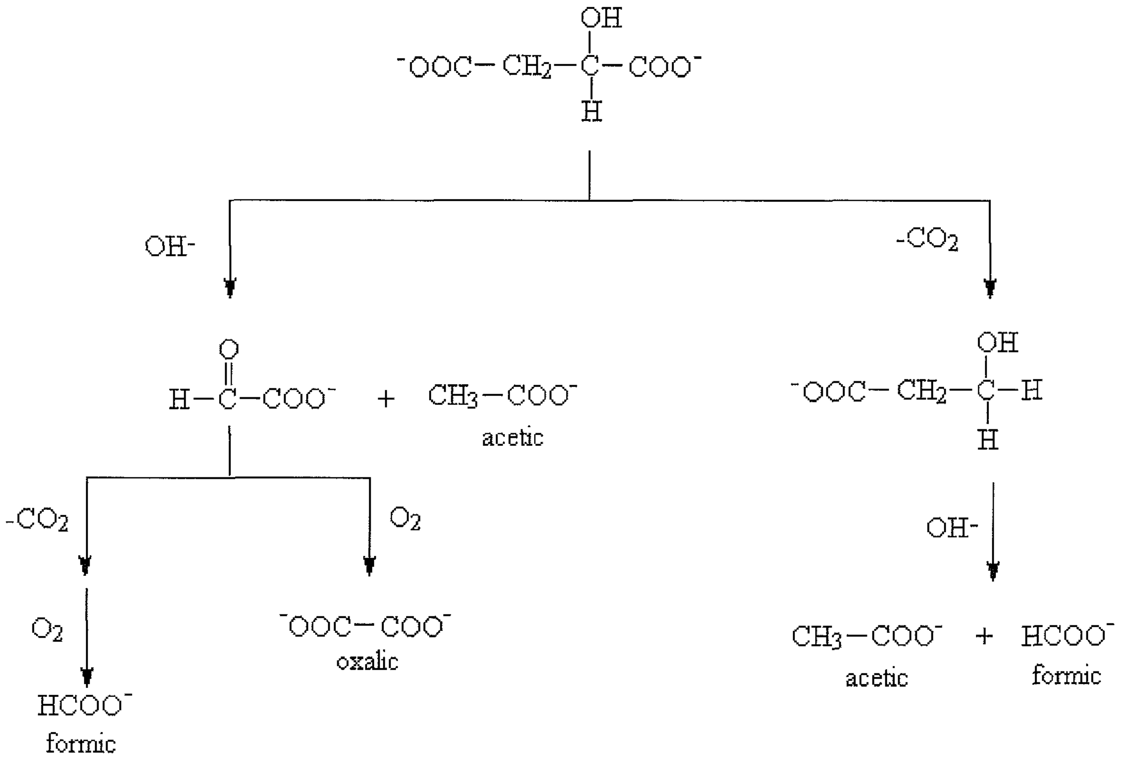
The reaction mechanism for tartaric acid WO in highly alkaline solution was found to occur predominantly via ionic reactions as no experimental evidence was obtained to indicate the presence of free radical intermediates. Two possible initial reaction steps are proposed to occur for tartaric acid WO in highly alkaline solution. The first possible initiation reaction, based on the significant effect of [OH^-] on the extent of tartaric acid WO, is a base catalysed retro aldol reaction. This reaction leads to the formation of glyoxalic and glycolic acids. Subsequent reactions of these compounds leading to the reaction products identified are presented in Reaction scheme 5.4. The other possible initiation reaction proposed is dehydration leading to the formation of keto succinic acid or malic acid. Subsequent reactions of these compounds are presented in Reaction schemes 5.1 and 5.3. The significantly high proportion of oxalic acid produced during the WO of tartaric is most likely due to free radical based reactions. The inability of the free radical intermediates produced to co oxidise succinic acid is most likely due to the same factors discussed for lactic acid WO.



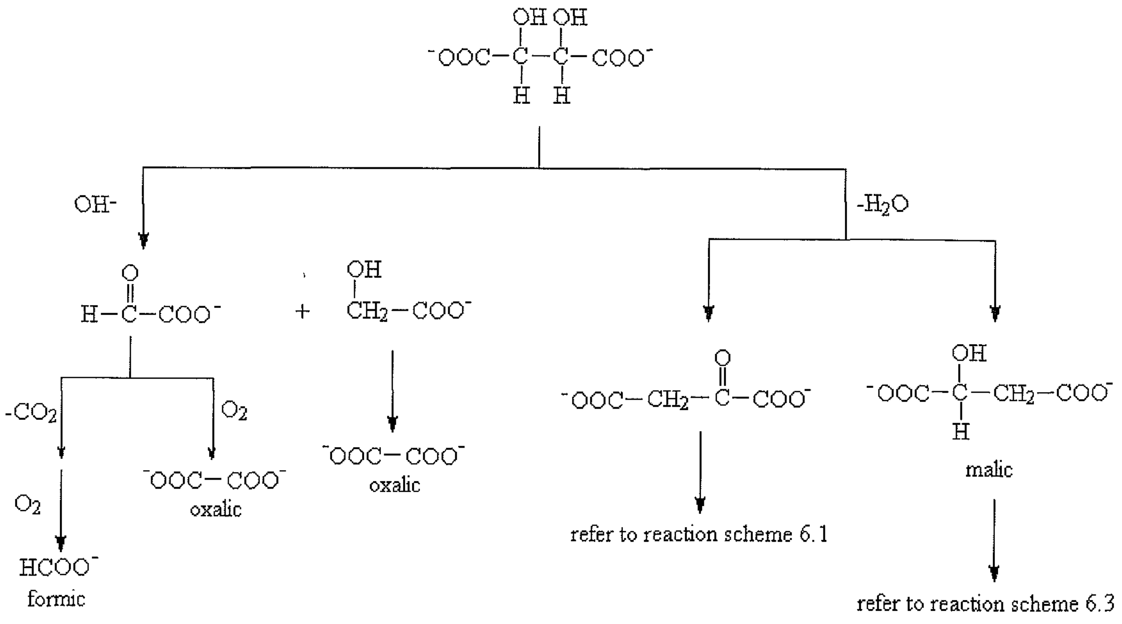
Reaction scheme 5.1 *Proposed reaction mechanism for citric acid WO.*



Reaction scheme 5.2 *Proposed reaction mechanism for lactic acid WO.*



Reaction scheme 5.3 *Proposed reaction mechanism for malic acid WO.*



Reaction scheme 5.4 *Proposed reaction mechanism for tartaric acid WO.*

5.4.2 Catalytic Wet Oxidation.

5.4.2.1 Catalyst screening.

The ability of several transition metal oxides to catalyse the WO of the chosen hydroxy carboxylic acids, all present in the same solution (all four hydroxy carboxylics at a concentration of 1.87 g OC/L for total concentration of 7.50 g OC/L), was studied. The results of the catalyst screening tests are given in Table 5.7. CuO clearly catalysed the WO of the hydroxy acids studied far greater than all the other transition metal oxides tested. As CuO was a superior catalyst to the other transition metal oxides tested it was decided to investigate in detail the catalytic reaction mechanism occurring during CuO catalysed WO of the hydroxy carboxylic acids chosen.

Table 5.7 *Bulk extent of WO and CWO for combined mixture of hydroxy carboxylic acids in the presence of various metal oxides. Standard reaction conditions (refer to section 2.2.3) except for organics' concentration (see above). Product data presented in Appendix 3.*

Metal oxide catalyst	Bulk extent of oxidation (%)*	TOC reduction (%)
None	33.6	14.9
CuO	61.0	21.0
Co_3O_4	34.8	13.2
Fe_2O_3	30.9	12.1
MnO_2	43.2	20.6
Ni_2O_3	32.5	11.9

* % oxidation (citric + lactic + malic + tartaric)/4

5.4.2.2 CuO catalysed WO – mechanism studies.

5.4.2.2.1 Heterogenous or homogenous catalysis.

As CuO is slightly soluble in alkaline solution (1.11 x 10^{-5} g Cu per litre in 2.212 M NaOH at 25°C [Mc Dowell and Johnston 1936]) and the concentration of CuO used in the screening test (5.0 g/L) was above the solubility limit of CuO it was decided to investigate which phase of the CuO was predominantly responsible for the catalysis observed. This was done by investigating the activity of CuO above and below its solubility limit, based on the assumption that if the soluble portion of CuO was predominantly responsible for the observed activity than no significant increase in activity would be observed above the solubility limit of the catalyst. The solubility limit of copper was determined using the average of the two highest amounts of soluble copper measured under the experimental conditions used (0.96 g/L Cu at time zero in 15.0 g/L CuO test and 0.91 g/L Cu at time zero in 5.0 g/L CuO test).

The results of the tests investigating the phase of CuO predominantly responsible for the observed catalytic activity are presented in Figure 5.5. From Figure 5.5 it can be seen that the extent of oxidation increases with increasing CuO concentration up until the solubility limit, it then plateaus close to the solubility limit before decreasing significantly at very high CuO concentration (15.0 g/L). The significant drop in activity at high CuO loading (15.0 g/L) is proposed to be due to a combination of the excess insoluble CuO acting as an inhibitive seeding surface that reduces the level of soluble copper available for catalysis (Figure 5.6) and possibly as a free radical scavenger. Significantly, the lowest level of soluble copper occurred in the 15.0 g/L test (0.069 g/L). Based on results obtained for the CuO loading tests the dissolved portion of the CuO catalyst, copper hydroxy species' of the general form $[Cu(II)_x(OH)_y]^{2x-y}$, are predominantly responsible for the observed catalytic activity, and therefore the catalysis occurring is homogenous in nature.

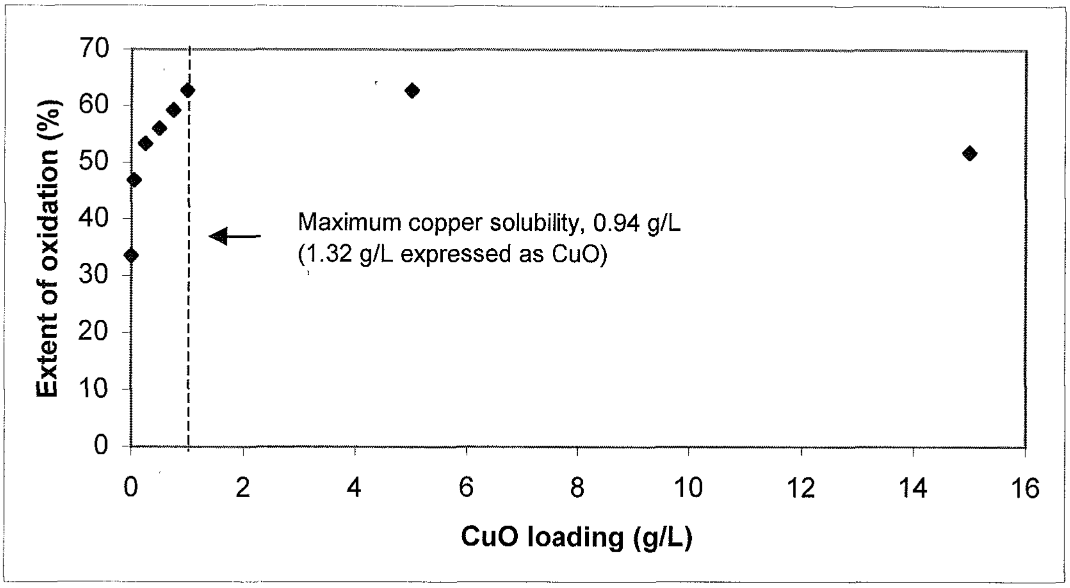


Figure 5.5 *Effect of CuO loading on extent of oxidation for mixture of hydroxy carboxylic acids. Standard reaction conditions (refer to section 2.2.3) except for organics' concentration (refer to section 5.4.2.1) and varied CuO concentration. Product data presented in Appendix 3.*

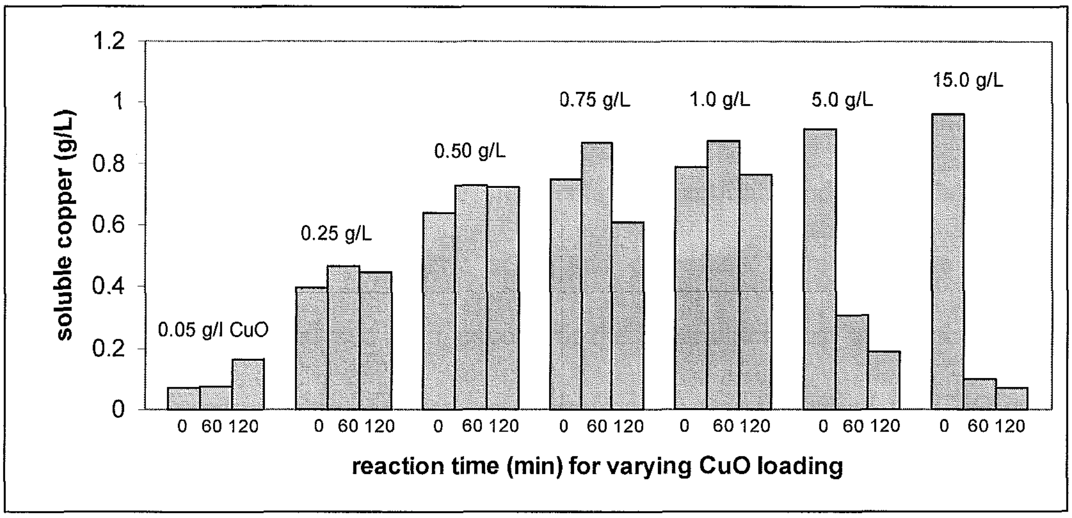


Figure 5.6 *Effect of CuO loading on soluble copper levels.*

5.4.2.2.2 Individual tests.

Before further investigation of the CuO catalysed reaction mechanism could be conducted it was necessary to investigate the ability of CuO to catalyse the WO of each of the hydroxy carboxylic acids individually. The results of the individual CuO catalysed WO tests are given in Table 5.8. CuO catalysed the WO of each of the hydroxy acids, the order of activity observed being, tartaric > lactic > malic > citric.

Table 5.8 *CuO catalysis of individual hydroxy carboxylics. Standard test conditions (refer to section 2.2.3).*

Organic	Extent of oxidation (%) WO	 CuO catalysed WO	 Activity (CuO – WO)
Citric	50.3 (12.0)	59.8 (14.4)	9.5
Lactic	8.6 (4.3)	43.0 (10.2)	34.4
Malic	5.6 (2.2)	32.2 (12.8)	26.6
Tartaric	51.0 (12.8)	90.1 (17.6)	39.1

TOC reduction in parentheses

The reaction products identified in CuO catalysed WO of citric, lactic, malic and tartaric acids are given in Table 5.9. The three major reaction products identified in the uncatalysed tests, oxalic and acetic acids and carbonate were also the three major products in the CuO catalysed tests, except for the tartaric acid test where acetic acid was only a minor product. One new product (formic acid) was identified for CuO catalysed WO of lactic and malic acids. This product was most likely not detected in the uncatalysed tests due to the low extent of wet oxidation undergone by each of these compounds which would have led to the amount formed being below detection limits. Malonic acid which was detected in uncatalysed WO of citric and tartaric acids was not detected in the corresponding CuO catalysed tests. This is most likely due to malonic acid undergoing rapid oxidation in the presence of CuO.

Table 5.9 *Reaction products for CuO catalysed WO of citric, lactic, malic and tartaric acids.*

	Reaction products (g Organic Carbon/L)			
Organic	Oxalic	Carbonate	Acetic	Formic
Citric	0.35	0.27	0.42	0.03
	(32.6)	(25.4)	(39.4)	(2.4)
Lactic	0.37	0.19	0.10	0.06
	(50.8)	(25.9)	(13.8)	(8.3)
Malic	0.23	0.24	0.10	0.02
	(38.4)	(40.8)	(17.4)	(3.0)
Tartaric	1.08	0.33	0.02	0.05
	(72.9)	(22.4)	(1.0)	(3.6)

Proportion (%) of total products in parentheses

A comparison of the product distributions for uncatalysed and CuO catalysed WO of citric, lactic, malic and tartaric acids are depicted graphically in Figures 5.7- 5.10. In all cases, there were significant differences in the distribution of products between the uncatalysed and CuO catalysed tests. The most significant differences occurring in all tests were a large increase in the proportion of oxalic acid produced and a large decrease in the proportion of acetic acid produced.

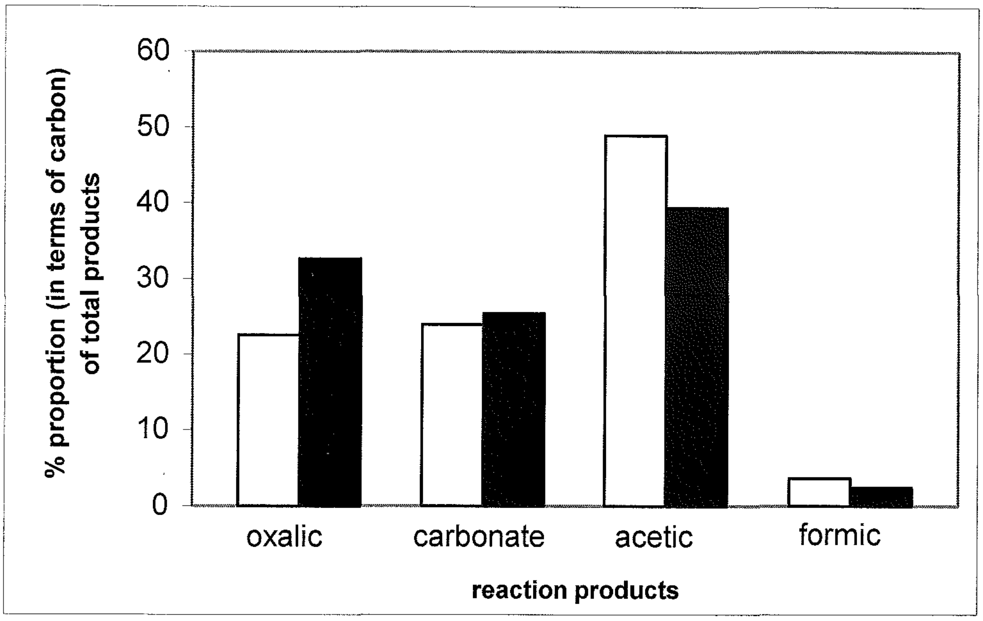


Figure 5.7 *Distribution of reaction products for uncatalysed (open bars) and CuO catalysed WO (closed bars) of citric acid.*

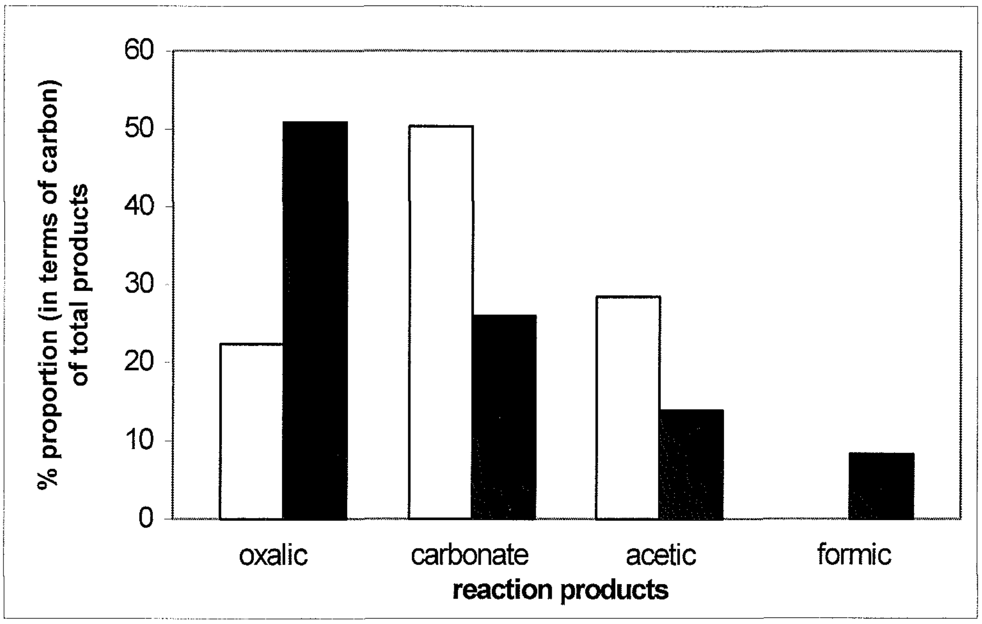


Figure 5.8. *Distribution of reaction products for uncatalysed (open bars) and CuO catalysed WO (closed bars) of lactic acid.*

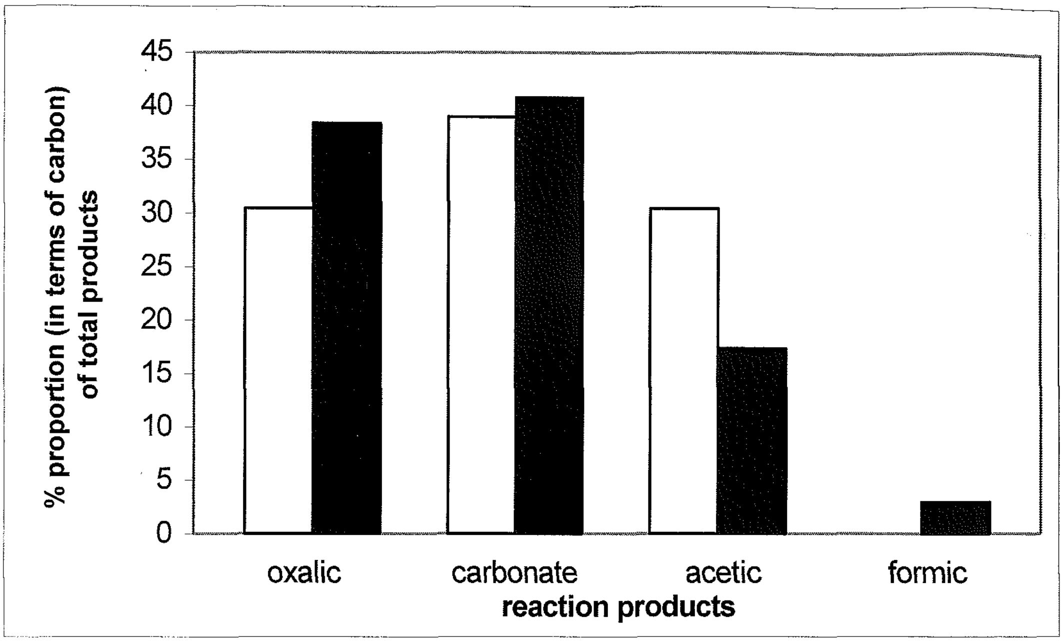


Figure 5.9 *Distribution of reaction products for uncatalysed (open bars) and CuO catalysed WO (closed bars) of malic acid.*

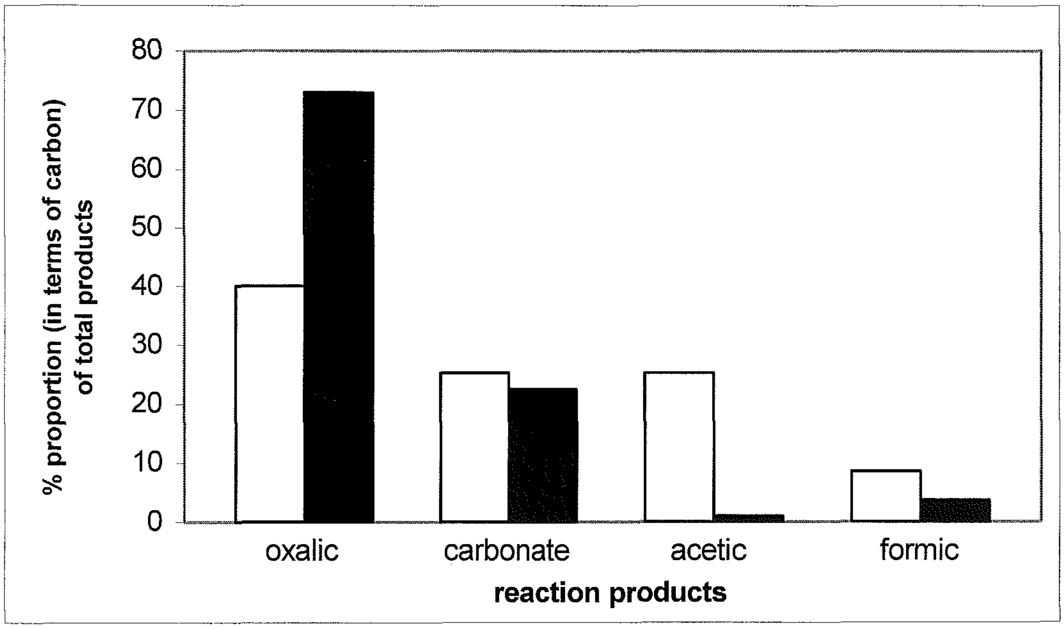


Figure 5.10 *Distribution of reaction products for uncatalysed (open bars) and CuO catalysed WO (closed bars) of tartaric acid.*

5.4.2.2.3 Type of catalytic reaction mechanism – ionic or free radical.

Based on the results discussed in sections 5.4.2.2.1- 5.4.2.2.2 it was decided to investigate the type of catalysis occurring for CuO catalysed WO of citric, lactic, malic and tartaric acids in highly alkaline solution. Although the experimental data for uncatalysed WO of the hydroxy carboxylics studied did not support a free radical chain type mechanism occurring it was decided to investigate the possibility of dissolved CuO species to initiate a free radical mechanism via generation of a copper superoxo species (Reaction scheme 3.5), and/or to propagate any free radical intermediates produced. The co oxidation method was used to determine if free radical intermediates were being produced during CuO catalysed WO of citric, lactic, malic and tartaric acids. Succinic acid was used to detect the possible presence of free radical intermediates as it was not identified as a product for CuO catalysed WO of the hydroxy carboxylics studied. The initial concentrations used for the CuO catalysed hydroxy carboxylic co oxidation tests were the same as those used in the analogous uncatalysed tests (refer to Table 5.6).

The results of the co oxidation tests for CuO catalysed WO of the hydroxy carboxylic acids are presented in Table 5.10. All the hydroxy carboxylics were capable of co oxidising succinic acid. The extent of co oxidation observed however is significantly low compared to malonic acid co oxidation when taking into account the amount of each compound oxidised. Based on the relatively low extent of co oxidation achieved by each of the hydroxy carboxylics CuO does not catalyse the WO of the hydroxy carboxylic acids tested predominantly via a free radical mechanism. The low extent of co oxidation achieved by each of the hydroxy carboxylic acids is most likely due to the formation of a low amount of free radical intermediates capable of co oxidation, though the length of the chain of these reactions is extremely short.

Table 5.10 *CuO catalysed hydroxy carboxylic induced co oxidation of succinic acid.*

Organic	Extent of succinic oxidation (co oxidation) (%)	Extent of hydroxy acid oxidation (%)
Citric	13.2 (9.05)	33.5
Lactic	3.6 (<2)*	56.5
Malic	6.7 (<2)*	42.4
Tartaric	4.0 (<2)	52.7^{+}

Corresponding uncatalysed WO results in parentheses.
*Uncatalysed tests conducted in 7.0M NaOH synthetic Bayer liquor
$^{+}$Amount of oxalic acid produced exceeded solubility limit, only dissolved oxalate was measured

5.4.2.2.4 Complexation initiated reaction - soluble copper levels during CuO catalysed WO of citric, lactic, malic and tartaric acids.

The possibility of a complexation based reaction mechanism occurring during CuO catalysed WO of citric, lactic, malic and tartaric acids was considered based on the increased level of soluble copper observed in the CuO catalysed hydroxy carboxylics mixture test compared to the analogous tests using mono and di carboxylic acids (Figure 5.11). Based on the soluble copper data obtained for the CuO catalysed bulk hydroxy carboxylics test it was assumed that one or more of the hydroxy carboxylic acids were forming intermediate copper-organic complexes which were more susceptible to oxidation than the free organic compound(s).

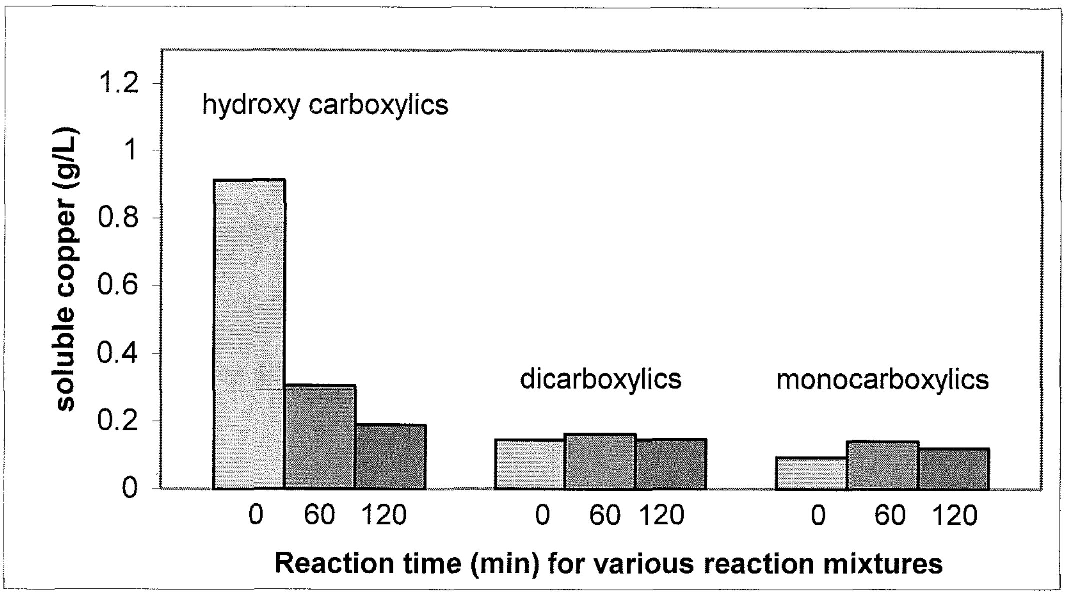


Figure 5.11 *Soluble copper throughout reaction period for CuO (5.0 g/l) catalysed WO of different classes of organic compounds.*

Analysis of the soluble copper data obtained for the individual CuO catalysed tests (initial organic concentration of 1.87 g OC/L) revealed that during the tartaric acid test a very high level of soluble copper was present at time zero (0.73 g/l). This was expected due to the well-known formation of copper tartrate complexes in highly alkaline solution (Fehlings solution) [Atkins 1989]. The level of soluble copper then decreased significantly throughout the course of the test (0.21 g/L @ 30 min, 0.18 g/L @ 60 min and 0.13 g/L @ 120 min.). The soluble copper data for the other three hydroxy carboxylics also showed increased levels of soluble copper, though the same trend observed for the bulk hydroxy organics test, a decrease in soluble copper over the course of the reaction was not observed. However, the levels of soluble copper in the other three hydroxy organics tests were not a great deal higher (~0.04 g/L) than the equilibrium level of soluble copper in an organics free synthetic Bayer liquor (~0.11 g/L). Therefore, it was decided to investigate the concentration of soluble copper for all the hydroxy organics using a higher initial organic concentration in an attempt to increase the level of soluble copper (if complex formation) was occurring and consequently reduce the effects of the background concentration. The results of the tests using a higher initial organic concentration are presented in Figure 5.12. In all cases the level of soluble copper is significantly higher at the beginning of the test, and decreases throughout the course of the reaction.

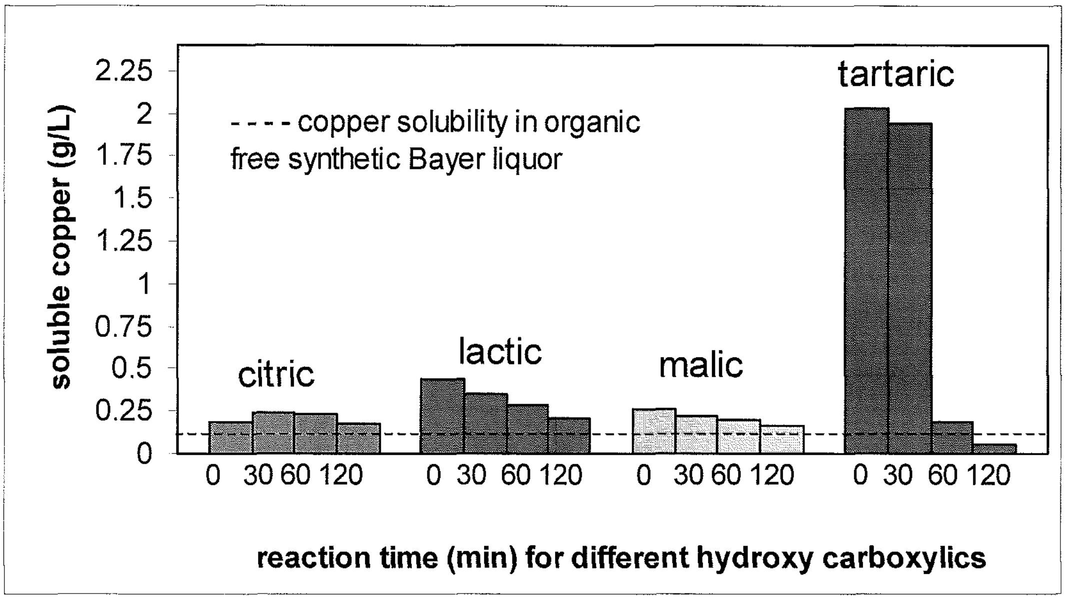


Figure 5.12 *Soluble copper concentration throughout course of reaction for CuO catalysed individual WO of citric, lactic, malic and tartaric acids.*

5.4.2.2.5 Relationship between catalytic activity and degree of complexation.

Figure 5.13 shows a strong correlation between the degree of complexation (which is assumed to be proportional to the level of soluble copper) and catalytic activity for the different hydroxy carboxylic acids. The order for degree of complexation at time zero;

tartaric > lactic > malic > citric is identical to the order of catalytic activity. Hence, the experimental data supports a complexation-based mechanism occurring for the hydroxy carboxylics studied.

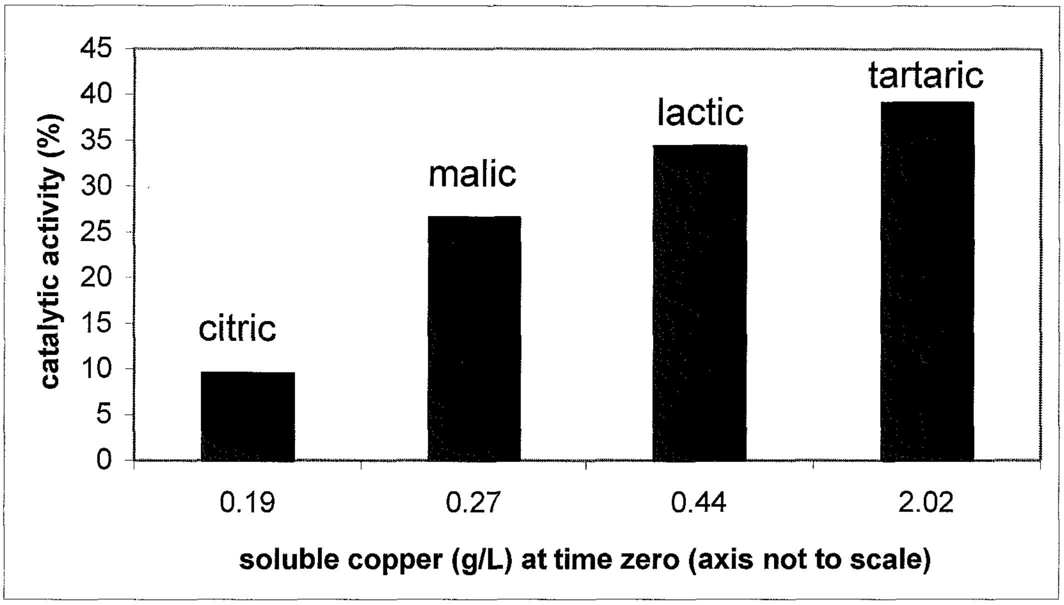


Figure 5.13 *Relationship between soluble copper at time zero (degree of complexation) and catalytic activity.*

Based on the results obtained supporting a complexation-based mechanism for CuO catalysed WO of the hydroxy carboxylic acids studied it was decided to investigate the effect that varying the degree of complex formation had on catalytic activity for the different hydroxy carboxylics. Various methods were considered to attempt the above-mentioned investigation. The first method used involved varying the extent of complexation by varying [OH^-]. This method was based on bench tests that showed the extent of complexation to be dependant on [OH^-]. Uncatalysed and CuO catalysed tests were conducted in simple 2, 4 and 6 M NaOH solutions (2M NaOH synthetic Bayer liquor could not be prepared as complete dissolution of the required amount of $Al(OH)_3$ was not possible) to investigate the relationship between the extent of complex formation and catalytic activity. A significant assumption was also made for these tests. It was assumed that the rate of breakdown of copper-organic complexes would not be significantly effected by $[OH^-]$ and/or the level of dissolved oxygen present, which is also dependant on $[OH^-]$. Figure 5.14 shows the relationship between the degree of complexation (soluble copper due to complexation) at time zero for the different hydroxy carboxylics at varying $[OH^-]$ and the amount of each compound catalytically oxidised. The amount of both malic and lactic acids catalytically oxidised increased significantly when the degree of complexation increased. The same trend however was not observed for citric acid, a compound which does not undergo a high degree of complexation with copper under the conditions used. Citric acid was found to undergo the highest degree of complexation with copper in 4M NaOH solution however the highest amount of catalysis was observed in the 2M NaOH test. Hence CuO catalysed WO of citric acid either does not occur predominantly via a complexation based mechanism or the rate at which copper-citric complexes undergo oxidation is significantly effected by $[OH^-]$ and/or the amount of soluble oxygen present. The data for tartaric acid was not included in Figure 5.14 due to this compound undergoing > 90 % overall oxidation in all catalytic tests over the concentration range used. As studying the relationship between complexation and catalytic activity for tartaric acid would have required the use of low alkalinity solutions, not relevant to this study, this was not investigated further.

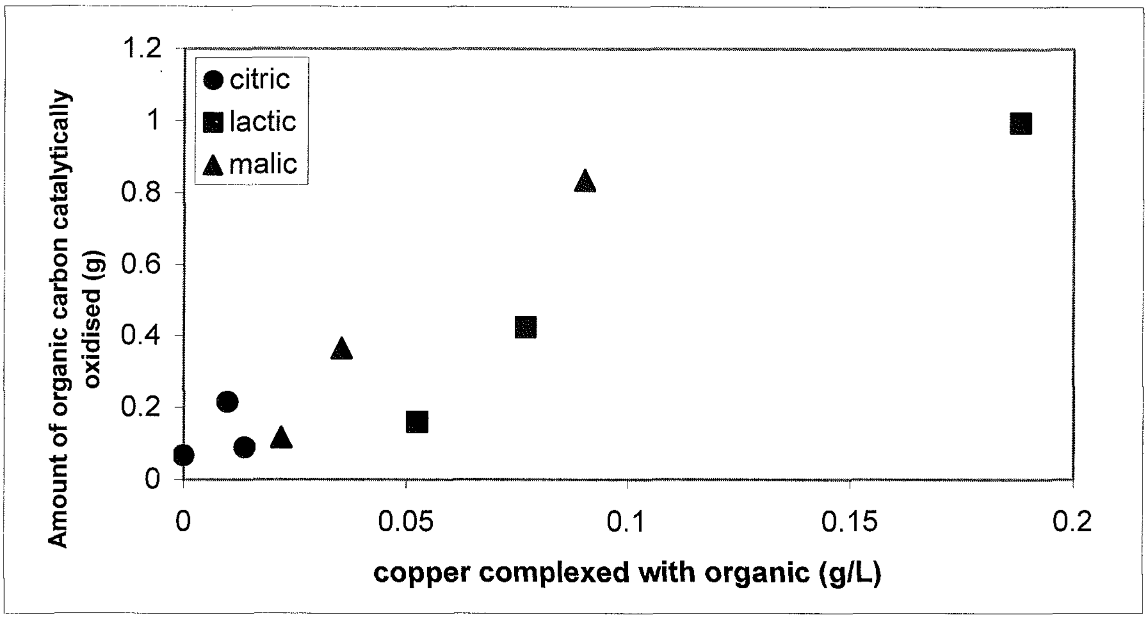


Figure 5.14 *Relationship between soluble copper at time zero (degree of complexation) and amount of citric, lactic, and malic acids catalytically oxidised at varying [NaOH] in simple alkaline solution. Data given in Appendix 4.*

5.4.2.2.6 Copper complexes of citric, lactic, malic and tartaric acids.

The other method used to investigate the mechanism occurring during CuO catalysed WO of citric, lactic, malic and tartaric acids involved the use of the actual copper complexes of each of the hydroxy carboxylic acids. WO tests were conducted using the actual copper complexes of the hydroxy carboxylics as the initial form of the respective organic compounds. These tests were conducted based on the assumption that if CuO catalysed WO of these compounds occurred predominantly via a complexation-based mechanism then WO of the actual copper complexes of each of the organics would give similar results as the CuO catalysed tests (in terms of extent of oxidation and product distribution). It was acknowledged that the amount of the copper complexes present at time zero in both the copper salt and CuO catalysed tests would be similar as the equilibrium solubility of the copper complexes would be reached before time zero in both systems under the reaction conditions used. The main goal of these tests was however to establish similar results (extent of WO and product distribution) for both systems.

The extent of oxidation results for the copper complex WO tests are given in Table 5.11. The extent of oxidation which occurred was higher when the hydroxy carboxylic acids were used in their copper complex form for all of the hydroxy carboxylic acids excluding citric acid. The soluble copper data obtained for the copper complex tests (Figure 5.15) was similar to that observed for the corresponding CuO catalysed tests, indicating that a similar mechanism occurs in both cases.

Table 5.11 *Comparison of extent of oxidation for copper complex and CuO catalysed tests.*

Organic	Extent of oxidation (%)	
	Copper salt	CuO catalysed
Citric	56.4	59.8
Lactic	53.0	43.0
Malic	43.0	32.2
Tartaric	91.2	90.1

The extent of oxidation result obtained for the copper complex of citric acid agrees with the previous data obtained investigating the mechanism of CuO catalysed WO of citric acid, which did not support a complexation-based mechanism predominating. CuO catalysed WO of citric acid most likely occurs partially via a free radical mechanism due to free radical intermediates produced from the generation of malonic acid as an intermediate and partially via a minor complexation-based mechanism.

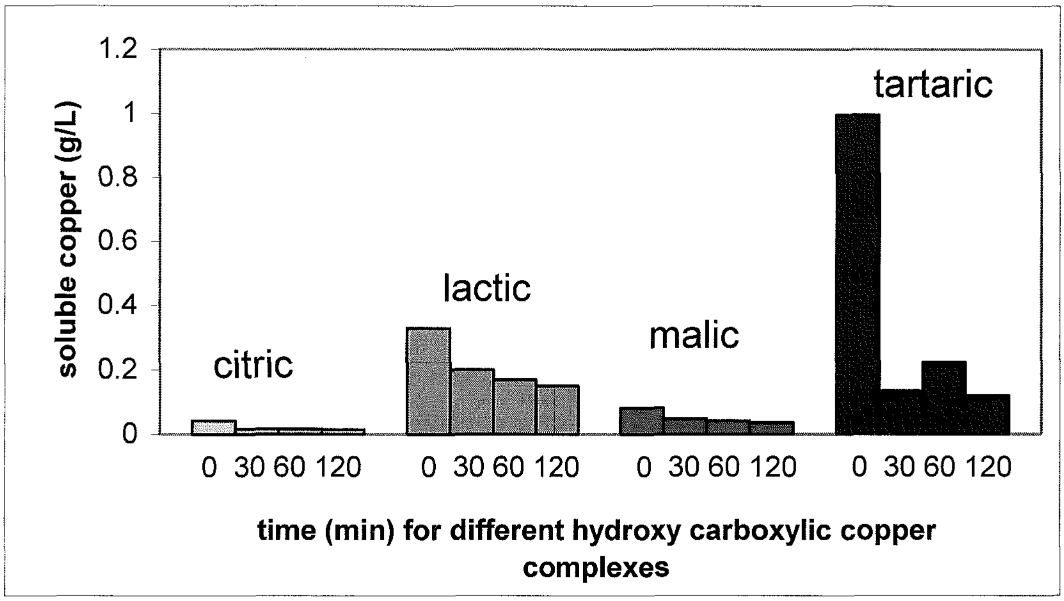


Figure 5.15 *Amount of soluble copper during WO of copper salts of citric, lactic, malic and tartaric acids.*

The type of reaction products identified for the copper complex tests were identical to the reaction products identified for the corresponding CuO catalysed tests (Figures 5.16 – 5.19). The distribution of reaction products obtained for WO of the copper complex of citric acid was more similar to the uncatalysed reaction then the CuO catalysed reaction. This is most likely due to the lower level of soluble copper available in the copper complex test (stoichiometric amount in copper citrate – 3.3 g/l as Cu) compared to the CuO catalysed test (4.0 g/l as Cu) and the type of reaction mechanism occurring. Based on the previous results obtained for CuO catalysed WO of citric acid, which indicated that the predominant mechanism was not complexation based and more likely via generation of free radical intermediates from formation of malonic acid as an intermediate, it is possible that propagation of free radicals in the copper complex test was restricted due to the lower amount of soluble copper available.

The distribution of products obtained for WO of the copper complex of lactic acid were very similar to those obtained for the CuO catalysed test, hence the reaction mechanism occurring in both cases is also very similar. There was however a slight decrease in the proportion of carbonate produced and a corresponding slight increase in the amount of oxalic acid produced. As there is most likely a small amount of co oxidation of reaction products occurring during CuO catalysed WO of lactic this could be due to a slight decrease in co oxidation of the oxalic acid produced into carbonate occurring during WO of the copper complex. The predicted lower amount of copper catalysed co oxidation could be due to the lower amount of soluble copper available in the copper complex test. Overall, however the experimental data supports that CuO catalysed WO of lactic acid occurs predominantly via a complexation-based mechanism.

The distribution of products obtained for the WO of the copper complex of malic acid differed significantly to the products obtained for CuO catalysed WO of malic acid. The proportion of acetic acid formed was considerably higher for the copper complex test while the reverse trend occurred for carbonate. The proportion of oxalic acid formed was however very similar. This indicates that acetic acid and carbonate are most likely formed via the same intermediate compound during malic acid oxidation and that in the copper complex test (and the uncatalysed test) oxidation/degradation of this compound leads to a higher proportion of acetic acid and lower proportion of carbonate compared to the CuO catalysed test. This could be due to the oxidation of this intermediate compound also being catalysed by soluble copper and there is insufficient soluble copper available in the copper complex test to significantly catalyse this reaction. This is supported by the product distributions observed for CuO catalysed WO of malic acid at 2.0, 4.0 and 6.0 M NaOH, where a higher proportion of acetic acid and lower proportion of carbonate was observed for the 2.0 M test which contained the lowest level of soluble copper (refer to Appendix 4). Based on the soluble copper and extent of oxidation data obtained for the various copper catalysed WO tests conducted using malic acid it is proposed that CuO catalysed WO of malic acid occurs predominantly via a complexation-based mechanism.

The product distribution data obtained for WO of the copper complex of tartaric acid was very similar to that observed for CuO catalysed WO of tartaric acid. A slightly higher proportion of oxalic acid and lower proportion of carbonate was however produced in the copper complex test. The same difference in product distribution also occurred for the corresponding lactic acid tests. Hence, the slight differences in product distribution which occurred for the copper catalysed tartaric acid tests are most likely due to the same reason given for the lactic acid tests.

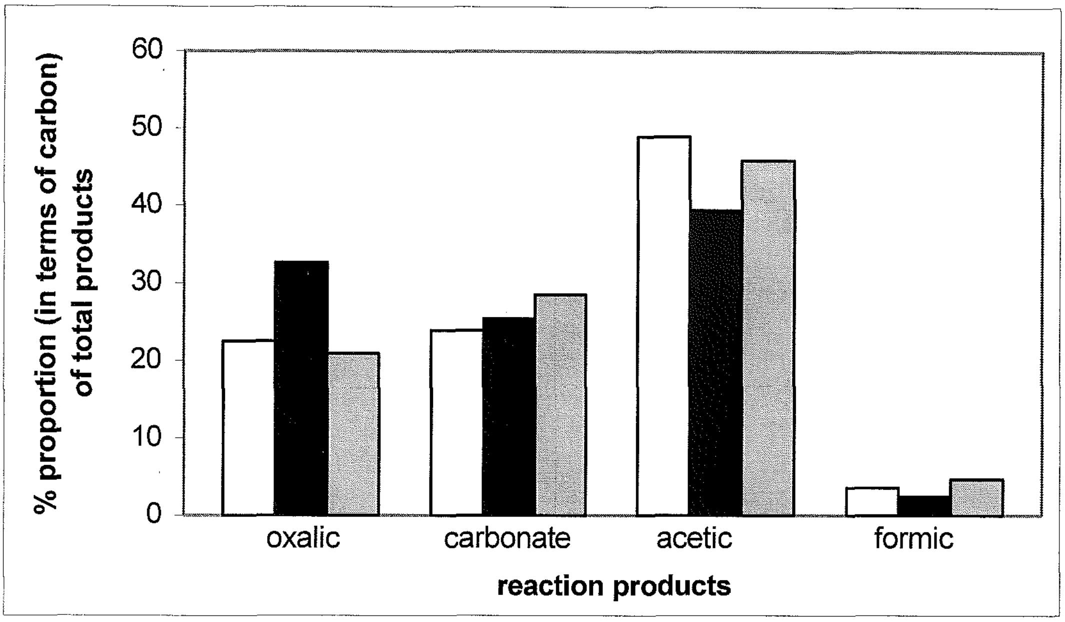


Figure 5.16 *Comparison of product distribution for uncatalysed (open bars), CuO catalysed (closed bars) and WO of copper complex form (shaded bars) of citric acid.*

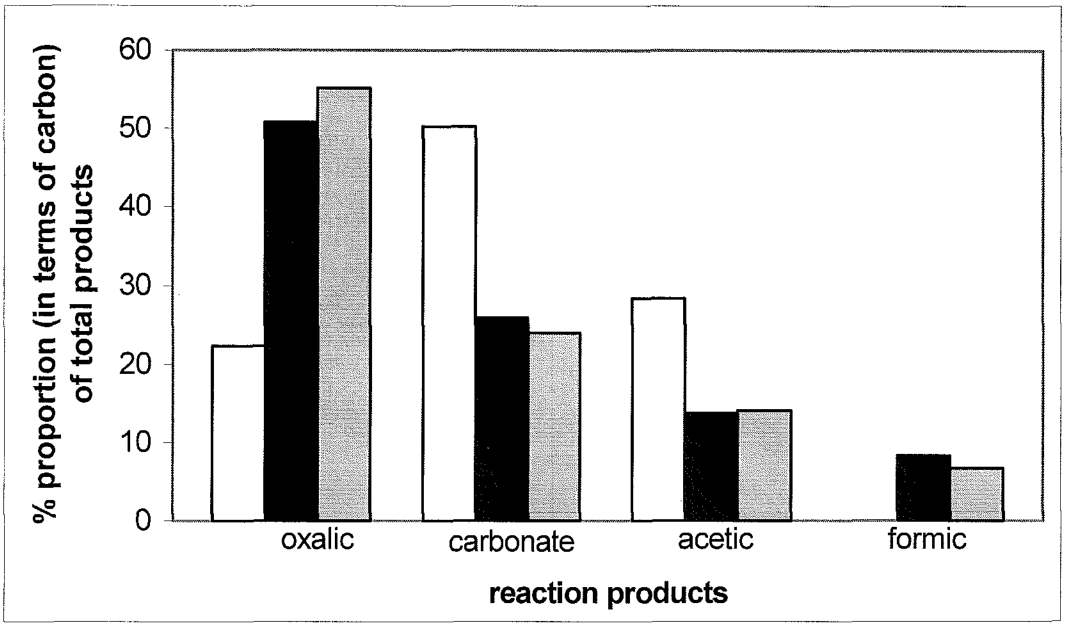


Figure 5.17 *Comparison of product distribution for uncatalysed (open bars), CuO catalysed (closed bars) and WO of copper complex form (shaded bars) of lactic acid.*

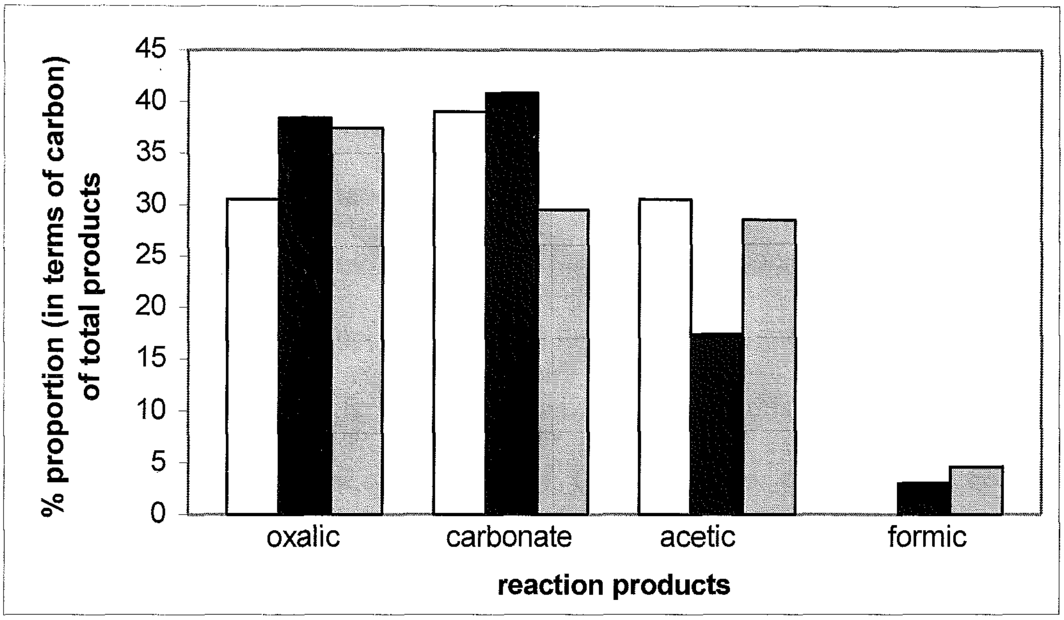


Figure 5.18 *Comparison of product distribution for uncatalysed (open bars), CuO catalysed (closed bars) and WO of copper complex form (shaded bars) of malic acid.*

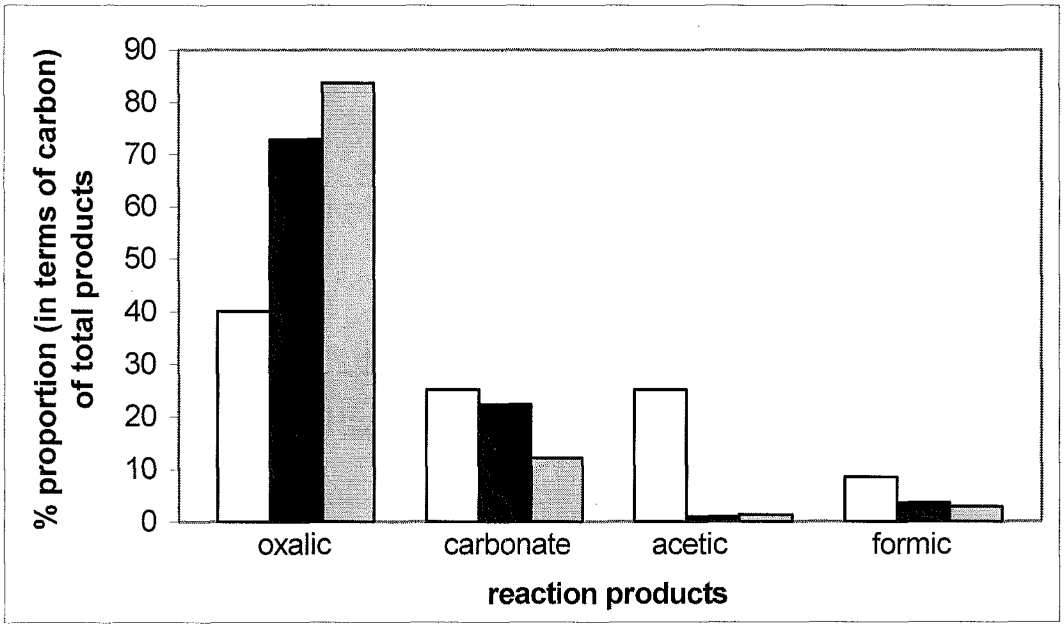


Figure 5.19 *Comparison of product distribution for uncatalysed (open bars), CuO catalysed (closed bars) and WO of copper complex form (shaded bars) of tartaric acid.*

5.4.3 Proposed reaction mechanisms for CuO catalysed WO of citric, lactic, malic and tartaric acids.

5.4.3.1 Complexation-based reaction mechanism.

To assist with the determination of the mechanisms occurring during CuO catalysed WO of citric, lactic, malic and tartatric acids in highly alkaline solution an attempt was made to determine the types of copper complexes formed in the highly alkaline solution used in this study using FTIR-ATR spectroscopy. Unfortunately this was unsuccessful due to formation and subsequent adsorption of $Cu(OH)_2$ onto the ATR crystal causing considerable (and expensive) damage to the crystal surface. Due to conjecture over the structure of copper hydroxy carboxylic complexes in general (five different cupric tartrate salts have been proposed for cupric tartrate trihydrate [Kirschner and Kiesling 1959]), a general complexation-based reaction mechanism is proposed for CuO catalysed WO of the hydroxy carboxylics studied based on the experimental results obtained and relevant literature.

Based on the experimental results discussed in sections 5.4.2.2.4 – 5.4.2.2.5 it is proposed that the initial reaction in CuO catalysed WO of citric, lactic, malic and tartaric acids in highly alkaline solution is complex formation between copper hydroxy species' of the general form $[Cu(II)_x(OH)_y]^{(2x-y)}]$ (based on the studies of Baes and Mesmer the predominant form of soluble copper present at the pH used in this study is $[Cu(II)(OH)_4]^{2-}$). Although the actual structures of the copper hydroxy carboxylic complexes formed in highly alkaline solution is not known, it is assumed that the same types of bonds that occur in solid copper hydroxy carboxylic complexes (copper-hydroxy and copper-carboxyl, refer to Figure 5.20) also form during complex formation in highly alkaline solution.

The next step in the reaction mechanism undoubtedly involves either reaction and/or degradation of the copper-hydroxy carboxylic complex. The type(s) of reactions that occur during this step will depend on the types of copper- hydroxy carboxylic bonds that form during complexation, as the type of bonds formed will alter the reactivity of various sites on the hydroxy carboxylic ligand. Based on the assumption that the types of bonds present in solid copper-hydroxy carboxylics also exist in copper-hydroxy carboxylic complexes in highly alkaline solution, the complexes formed could undergo a number of reactions under the reaction conditions used in this study. These reactions include: a one electron transfer between bridging copper atoms leading to a reduced form of copper which would be re oxidised readily under the oxidising atmosphere used in this study; removal of an alcoholic proton by hydroxide ion from a hydroxyl group complexed to copper; and copper complexation inducing decarboxylation. Similar reactions could also occur for intermediates formed from either uncatalysed initiated WO or CuO catalysed initiated WO.

It is proposed that the above mentioned possible reactions of the copper-hydroxy complexes of citric, lactic, malic and tartaric acids lead to direct products of CuO catalysed WO and/or to intermediates compounds which may also be catalysed by CuO. As the products detected in CuO catalysed WO tests are a combination of both uncatalysed and CuO catalysed WO as well as CuO catalysed WO of intermediates formed from uncatalysed WO, it is not possible to determine the exact type and distribution of products for purely CuO catalysed WO, hence detailed reaction pathways were not attempted.

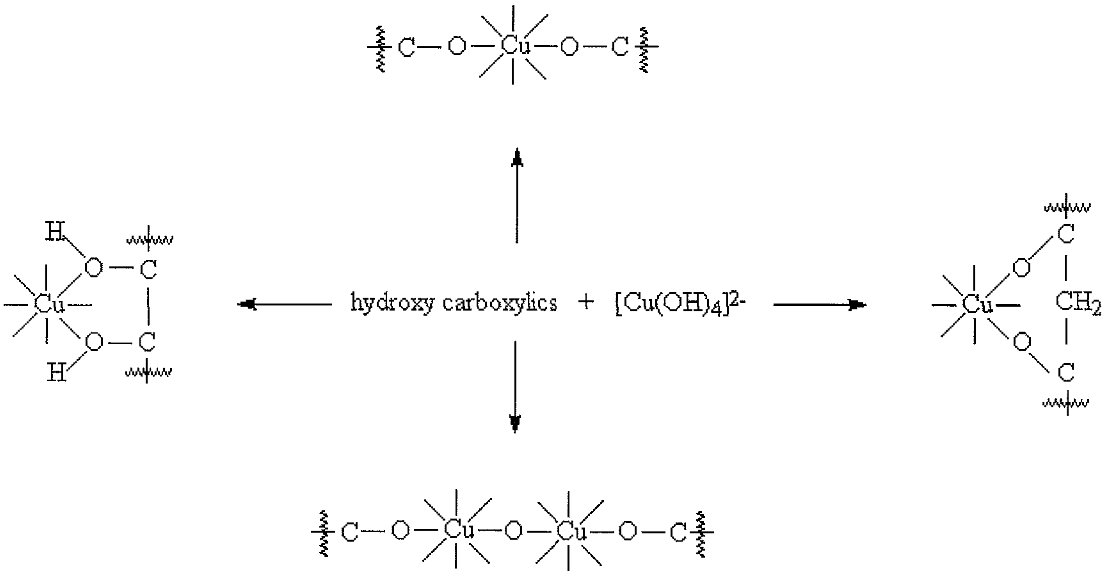


Figure 5.20 *Examples of types of copper-hydroxy carboxylic bonds that may form during copper complexation of citric, lactic, malic and tartaric acids in highly alkaline solution.*

5.4.3.2 Free radical reaction mechanism.

Although the experimental results obtained implied that CuO catalysed WO of citric, lactic, malic and tartaric acids occurs predominantly via a complexation-based reaction mechanism there was some experimental evidence to suggest that CuO catalysis does increase the number of free radial intermediates produced during WO of citric, lactic, malic and tartaric acids (Table 5.10). It is proposed that CuO increases the number of free radicals generated via the decompostion of alkyl hydroxperoxide intermediates formed

(Reaction scheme 3.5). This is however proposed to be only a minor reaction occurring during CuO catalysed WO of citric, lactic, malic and tartaric acids.

5.5 Conclusions.

The chemistry of low temperature (165 °C) WO and CuO catalysed WO of citric, lactic, malic and tartaric acids in highly alkaline solution has been studied in detail to the best of the authors' knowledge for the first time. The following conclusions were reached from the above-mentioned study:

Citric, lactic, malic and tartaric acids all undergo appreciable low temperature (165°C) WO in highly alkaline solution under the standard reaction conditions used in this study (4.4 M NaOH, 500 kPa PO_2, 2 h). These compounds are however only partly removed (completely oxidised to carbonate) as they also undergo partial oxidation. The two major compounds formed from partial oxidation of these compounds are oxalic and acetic acids, these compounds do not undergo low temperature WO unless in the presence of co oxidising free radicals.

The WO of citric, lactic, malic and tartaric acids occurs predominantly via ionic reactions in highly alkaline solution. Some minor free radical reactions do occur, however the lengths of the free radical chains are extremely short.

WO of citric, lactic, malic and tartaric acids is significantly affected by $[OH^-]$. The extent of overall oxidation (complete plus partial) undergone by each of these compounds increases significantly with increasing [OH^-] (over the [OH^-] range studied). The distribution of reaction products from hydroxide ion accelerated WO of citric, lactic and malic acids are significantly affected by [OH^-]. The proportional increase in overall oxidation achieved by hydroxide ion accelerated WO does not lead to the same proportional increase in complete oxidation (and hence complete removal).

Citric, lactic, malic and tartaric acids are all catalytically wet oxidised by CuO in highly alkaline solution at low temperature. CuO catalyses (increases) the extent of removal (complete oxidation) of each of these compounds, CuO also significantly catalyses (increases) the partial oxidation of each of these compounds.

CuO catalysed WO of citric, lactic, malic and tartaric acids occurs predominantly via a homogenous mechanism in highly alkaline solution. Copper hydroxy species of the general form, $[Cu(II)_x(OH)_y]^{2x-y}]$, formed from the dissolution of CuO, are proposed to be responsible for the catalysis that occurs via a complexation-based reaction mechanism. However, some minor free radical reactions were also catalysed by dissolved CuO during CuO catalysed WO of these compounds.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Low molecular weight mono, di and hydroxy carboxylic acids that contain weakly acidic hydrogen atoms undergo low temperature (165°C) WO in highly alkaline solution in isolation. Six such compounds that were identified in this study include malonic, formic, citric, lactic, malic and tartaric acids. Each of these compounds can be partly removed (converted to carbonate) by low temperature WO. All of these compounds also undergo some partial oxidation (excluding formic acid which is only converted to carbonate). The major compounds formed from partial WO of these compounds are oxalic and acetic acids. Neither of these compounds undergo low temperature WO in isolation in highly alkaline solution.

Mono, di and hydroxy carboxylic acids undergo low temperature WO in highly alkaline solution by both free radical and ionic reaction mechanisms. Malonic acid undergoes WO predominantly via a free radical chain reaction mechanism. Formic acid most likely undergoes WO predominantly via a free radical mechanism. Citric, lactic, malic and tartaric acids undergo WO predominantly via an ionic reaction mechanism.

Compounds that do not undergo low temperature WO in highly alkaline solution in isolation (such as oxalic, succinic, glutaric, acetic, propionic and butyric acids) can be co oxidised by free radical intermediates produced during low temperature WO of malonic acid. To the author's best knowledge interaction between organic compounds (such as co oxidation) during WO and CWO has not been investigated and/or discussed in detail in the open literature. The only reference discovered that discusses the interaction of organic compounds is a brief discussion in Ingale *et al* [1996]. These authors state:

> *"The destruction of acetic acid is influenced by the presence of other free radicals. Shende and Mahajani have independently seen that although acetic acid alone is refractory below 215°C, the presence of other compounds undergoing wet oxidation has resulted in acetic acid destruction even at 200°C."*

These authors however include no data to support their statement, and the reference included in the above quote (Shende and Mahajani) is to unpublished work.

CuO catalyses low temperature WO of some low molecular weight di and hydroxy carboxylic acids in highly alkaline solution. Five such compounds that were identified in this study include; malonic, citric, lactic, malic and tartaric acids. CuO catalyses the extent of complete and partial oxidation of these compounds. The products formed from CuO catalysed partial WO of these compounds are similar to those formed from uncatalysed WO, namely oxalic and acetic acids.

The catalytic activity of CuO observed in highly alkaline solution is predominantly due to soluble copper hydroxy complexes of the general form, $[Cu(II)_x(OH)_y]^{2x-y}$, produced from partial dissolution of the oxide. Hence, CuO catalysed WO of malonic, citric, lactic, malic and tartaric acids occurs predominantly via a homogenous mechanism.

Copper hydroxy complexes of the general form, $[Cu(II)_x(OH)_y]^{2x-y}$, can catalyse the WO of di and hydroxy carboxylic acids in highly alkaline solution by two different reaction mechanisms. These complexes catalyse the free radical chain reactions occurring during malonic acid WO. They also catalyse the WO of citric, lactic, malic and tartaric acids predominantly via a complexation-based mechanism.

Compounds that do not undergo CuO catalysed WO in isolation (such as formic, acetic, propionic, butyric, oxalic, succinic and glutaric acids) can be indirectly catalytically wet oxidised by CuO via the increased number of free radical intermediates produced during CuO catalysed WO of malonic acid.

Further investigation into the species' produced during low temperature WO of malonic acid WO in highly alkaline solution that are capable of co oxidising compounds such as acetic, oxalic and succinic acids would be of great interest. Of even more interest would be ways of generating a substantial amount of this species economically. Generation of such a species' economically (and without any other adverse side effects to the Bayer process, such as those that would be caused by generating this species' with malonic acid i.e. a substantial amount of oxalic acid would be produced as a by product) would enable a high extent of organics removal from highly alkaline solution at low temperature.

Types of organic compounds that are present in Bayer liquor that can potentially shorten the length of free radical chain reactions in highly alkaline solution, such as formic acid, also require further investigation. Removal of such compounds could also lead to a significant increase in removal of other compounds in solution via co oxidation.

The ability of basic catalysts to catalyse WO of organics in highly alkaline solution would be of interest based on the strong dependency of WO in highly alkaline solution on $[OH^-]$. The most likely major difficulty which would need to be overcome is that this type of catalyst would also most likely remove hydrogen from water.

The discovery of malonic acid as a compound capable of co oxidising other organic compounds in highly alkaline solution, in the presence of oxygen, could be of significance to the production of valuable pre-cursor compounds and fine chemicals. Malonic acid and oxygen, in highly alkaline solution at relatively low temperature, could be a potentially cheap and clean powerful oxidising agent used to oxidise difficult-to-oxidise reactants into sought after organic compounds.

CHAPTER 7

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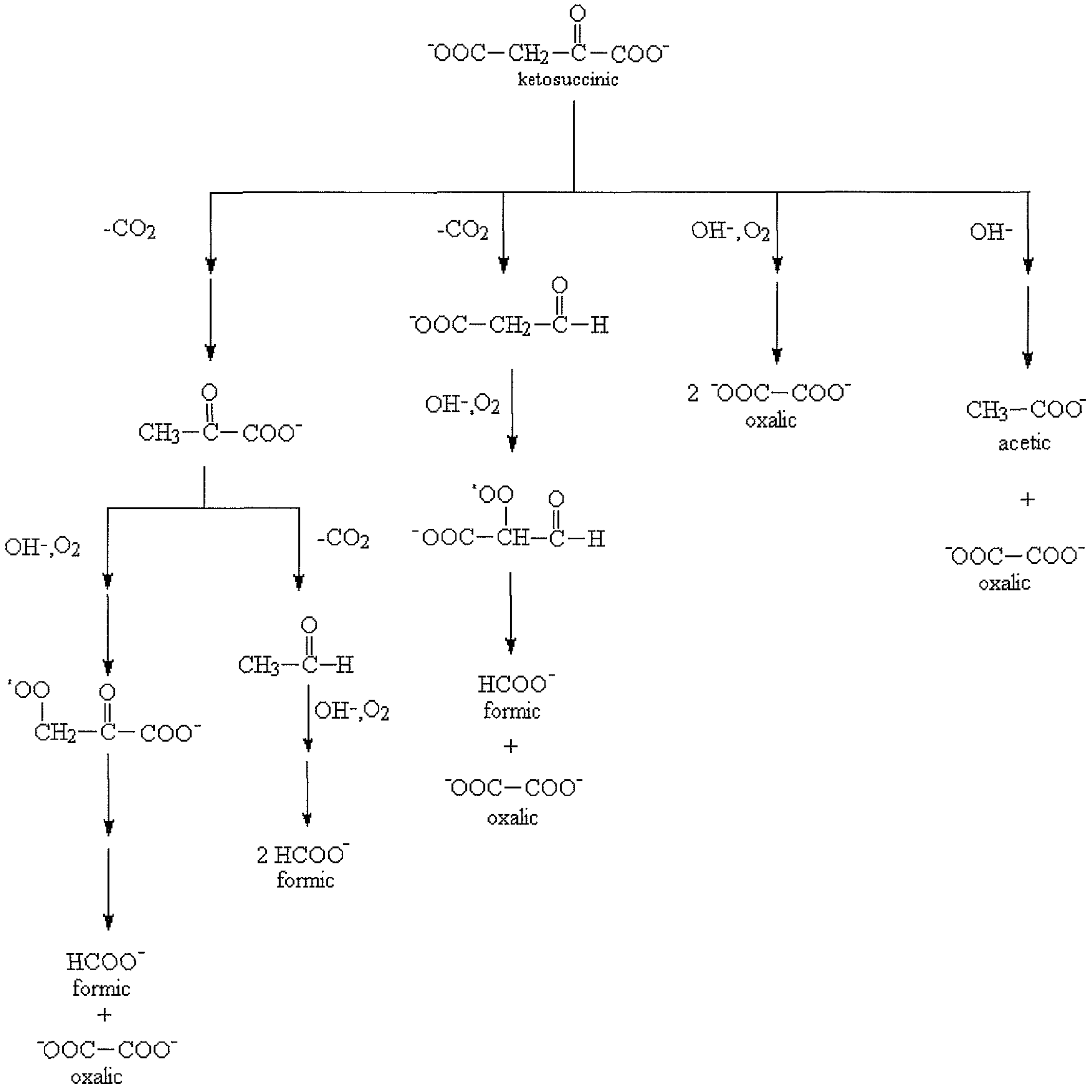
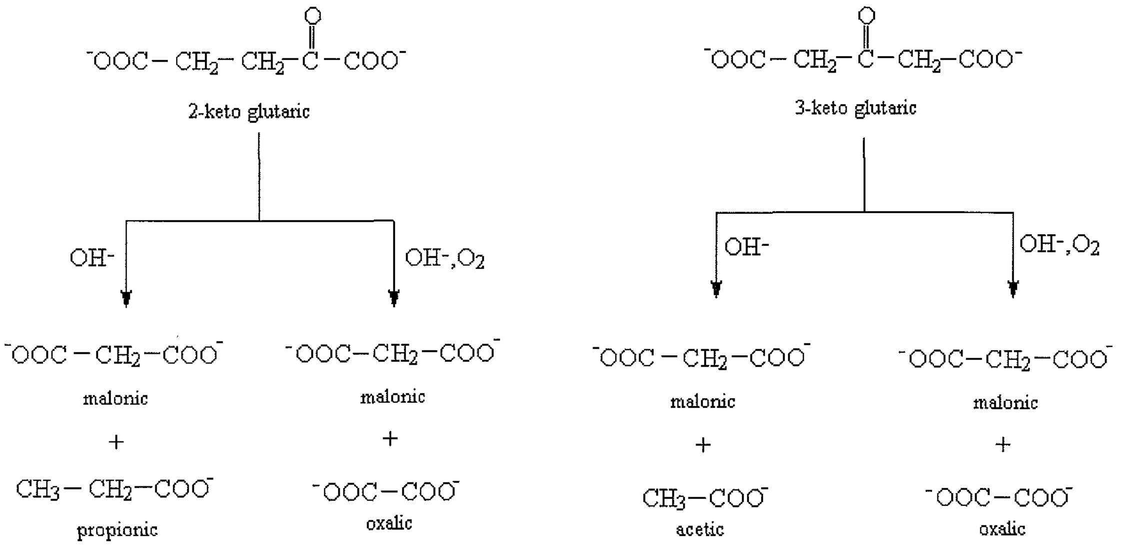
CHAPTER 9

APPENDICES

Appendix 1. Other possible product determining reactions for co oxidation of succinic acid.



Other possible product determining reactions for co oxidation of glutaric acid.



Appendix 2. Data for bulk dicarboxylic acids catalyst screening tests.

Table 9.1 *Individual compound data for bulk dicarboxylic acids catalyst screening tests.*

	Extent of oxidation of dicarboxylic acids (%), 2 h			
Catalyst	Malonic	Succinic	Glutaric	Oxalic
none	13.1	7.6	11.9	(+6.6)
CuO	95.1	21.8	33.9	(+33.8)
Ni_2O_3	87.5	6.7	6.9	(+38.0)
Co_2O_3	29.9	13.0	21.4	(+13.1)
MnO_2	46.0	<2	2.5	(+18.8)
Fe_2O_3	12.0	6.1	10.8	(+6.8)

Table 9.2 *TOC reduction for bulk dicarboxylic acids catalyst screening tests.*

Catalyst	TOC removed (%)	TOC removed (g/L)	Sum of TOC removed (g/L) from corresponding individual tests	% Increase in TOC removal achieved by wet oxidising dicarboxylic acids in the same solution
None	1.9	0.14	0.14	0.0
CuO	22.5	1.69	0.72	134.4
Ni_2O_3	13.0	0.98	Individual tests not conducted	Individual tests not conducted
Co_2O_3	13.1	0.98	"	"
MnO_2	6.4	0.48	"	"
Fe_2O_3	3.0	0.23	"	"

Table 9.3 *Individual compound data for bulk dicarboxylic acids CuO loading tests.*

	Extent of oxidation of dicarboxylic acids (%), 2 h			
CuO loading (g/L)	Malonic	Succinic	Glutaric	Oxalic
0.0	13.1	7.6	11.9	(+6.6)
0.05	92.5	22.5	34.8	(+18.7)
0.25	95.2	23.1	34.8	(+30.3)
0.50	96.3	22.7	34.9	(+33.6)
0.75	96.1	22.9	34.9	(+41.0)
1.0	96.5	22.7	34.8	(+40.8)
5.0	95.1	21.8	33.9	(+33.8)
15.0	95.3	20.0	31.7	(+34.8)

Table 9.4 *TOC reduction for bulk dicarboxylic acids CuO loading tests.*

CuO loading (g/L)	TOC reduction (%)
0.0	1.9
0.05	24.2
0.25	26.8
0.50	22.3
0.75	20.6
1.0	19.5
5.0	22.5
15.0	21.7

Appendix 3. Data for bulk hydroxy carboxylic acids catalyst screening tests.

Table 9.5 *Product data for bulk hydroxy carboxylic acids catalyst screening tests.*

	Reaction products (g OC/L), 2 h				
Catalyst	Formic	Acetic	Oxalic	Malonic	Carbonate
None	0.14	0.73	0.50	0.01	1.12
CuO	0.19	0.59	2.17	0.02	1.60
Co_3O_4	0.39	0.65	0.63	0.02	0.93
Fe_2O_3	0.18	0.68	0.49	0.01	0.88
MnO_2	0.52	0.77	0.31	0.08	1.56
Ni_2O_3	0.43	0.80	0.42	0.00	0.80

Table 9.6 *Product data for bulk hydroxy carboxylic acids CuO loading tests.*

	Reaction products (g OC/L), 2 h				
CuO loading (g/L)	Formic	Acetic	Oxalic	Malonic	Carbonate
None	0.14	0.78	0.53	0.01	1.12
0.05	0.19	0.78	1.30	0.01	1.24
0.25	0.15	0.60	1.90	0.03	1.35
0.50	0.16	0.64	2.00	0.02	1.40
0.75	0.18	0.67	2.12	0.02	1.47
1.00	0.18	0.69	2.25	0.02	1.58
5.00	0.20	0.63	2.30	0.02	1.57
15.00	0.15	0.49	1.77	0.02	1.45

Appendix 4. Data for hydroxy carboxylic acid tests in simple alkaline solution.

Table 9.7 *Extent of uncatalysed and CuO catalysed WO and TOC reduction for citric, lactic, malic and tartaric acids in simple alkaline solution (NaOH-H_2O).*

		Extent of oxidation (%), 1 h		TOC reduction (%), 1h	
Organic	[NaOH] (M)	WO	CuO catalysed WO	WO	CuO catalysed WO
Citric	2.0	10.2	22.3	5.8	12.6
Citric	4.0	31.8	35.8	9.1	10.6
Citric	6.0	62.6	65.3	9.2	12.1
Lactic	2.0	3.3	12.8	2.6	6.6
Lactic	4.0	5.4	28.5	3.2	8.1
Lactic	6.0	17.2	68.0	8.1	19.6
Malic	2.0	5.3	7.5	4.3	2.4
Malic	4.0	7.0	21.9	5.3	8.7
Malic	6.0	9.6	51.3	2.4	12.3
Tartaric	2.0	18.7	90.3	10.3	24.7
Tartaric	4.0	71.1	96.8	26.7	19.7
Tartaric	6.0	90.6	98.4	23.2	19.8

Table 9.8 *Reaction products for uncatalysed and CuO catalysed WO of citric, lactic, malic and tartaric acids in simple alkaline solutions.*

		Reaction products (g OC/L), 1 h							
Organic	[NaOH] (M)	Formic		Acetic		Oxalic		Carbonate	
		WO	CuO catalysed WO	WO	CuO catalysed WO	WO	CuO catalysed WO	WO	CuO catalysed WO
Citric	2.0	0.01	0.02	0.06	0.11	0.01	0.05	0.11	0.24
Citric	4.0	0.03	0.02	0.29	0.27	0.11	0.18	0.17	0.20
Citric	6.0	0.03	0.03	0.62	0.56	0.35	0.40	0.17	0.23
Lactic	2.0	nd	0.02	0.01	0.06	nd	0.04	0.05	0.12
Lactic	4.0	nd	0.03	0.03	0.13	0.01	0.22	0.06	0.15
Lactic	6.0	0.01	0.05	0.10	0.19	0.06	0.61	0.15	0.37
Malic	2.0	0.01	0.02	0.01	0.04	nd	0.04	0.08	0.04
Malic	4.0	0.01	0.03	0.01	0.09	0.01	0.13	0.10	0.16
Malic	6.0	0.01	0.04	0.06	0.31	0.06	0.38	0.05	0.23
Tartaric	2.0	0.07	0.24	0.02	0.01	0.07	0.98	0.19	0.46
Tartaric	4.0	0.33	0.08	0.08	0.01	0.42	1.35	0.50	0.37
Tartaric	6.0	0.29	0.07	0.17	0.03	0.79	1.37	0.44	0.37