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Low-Temperature Wet Oxidation of Sodium Salts of Low Molecular Weight Mono- and Dicarboxylic Acids in Synthetic Bayer Liquor

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The wet oxidation of eight low molecular weight sodium salts of mono- and dicarboxylic acids that are usually present in alumina industrial liquor (Bayer liquor) has been investigated. The wet oxidation of the low molecular weight sodium salts was studied using a highly alkaline solution simulating that encountered in the alumina refining process. Wet oxidation experiments were conducted at relatively low temperature (165 °C) in a high-pressure reaction system. Two of the eight compounds studied, sodium formate and sodium malonate, underwent low-temperature wet oxidation in isolation. Sodium malonate was capable of co-oxidizing the six compounds that did not undergo wet oxidation in isolation.

1. Introduction

The removal of organic compounds from industrial waste or process streams by complete and/or partial oxidation (wet oxidation, WO) has received considerable attention over the last 3 decades. This is illustrated by the comprehensive review of Mishra et al.¹ The main goal of most industries conducting research into the removal of organic compounds is the production of more environmentally friendly waste streams. Some industries, such as the alumina refining industry, suffer from decreased productivity due to organic contaminants in their process liquors^{2–5} and therefore have an added incentive for removing organic compounds. The removal of organic contaminants is of great interest to industries that have multiple reasons for removing unwanted organic compounds.

The WO process, originally developed by Zimmermann over 50 years ago,⁶ removes organic compounds via complete oxidation (in the liquid phase) to carbon dioxide and water using an oxidizing gas such as oxygen or air. In most cases, high temperatures and pressures are required to completely oxidize all of the organic compounds present to carbon dioxide and water in a reasonable amount of time. When sufficiently high temperatures and/or reaction times are not used, a number of organic compounds are only partially oxidized to lower molecular weight compounds that are difficult to oxidize, such as acetic and propionic acids. Because low molecular weight compounds usually provide a barrier to achieving complete oxidation, the WO of this class of organic compounds has been studied extensively.^{7–15}

Although the WO of many low molecular weight organic compounds has been studied in the last 3

decades, the conditions (in particular, solution matrix) under which many compounds have been studied have varied significantly. This is due to the varying industries investigating organics removal via WO. The majority of studies conducted have utilized acidic or neutral solutions; hence, there has been a lack of studies conducted on the WO of low molecular weight compounds in alkaline solution, the solution that prevails in the alumina refining industry. In this study, low-temperature WO of eight low molecular weight organic compounds that have been identified in a Western Australia alumina process liquor¹⁶ has been investigated in a highly alkaline solution simulating that encountered in alumina refining.

2. Experimental Section

The highly alkaline solution simulating that encountered in alumina refining solution is hereafter referred to as synthetic Bayer liquor. The method for preparing 2.4 L batches of 4.4 M NaOH synthetic Bayer liquor was as follows: NaOH (422.40 g) was dissolved in ~1 L of Milli-Q water in a 2 L plastic beaker. Once dissolution of the NaOH was complete, Al(OH)₃ (366.95 g) was added slowly with heating (~100 °C) and stirring. In a separate beaker, Na₂CO₃ (101.76 g) was dissolved in ~500 mL of hot Milli-Q water and then added to the sodium aluminate solution (with continuous heating and stirring). NaCl (48.00 g), Na₂SO₄ (60.00 g), Na₃PO₄ (0.88 g), and silicic acid (2.56 g) were then dissolved as much as possible in ~500 mL of hot Milli-Q water in a separate beaker before being added to the sodium aluminate solution containing Na₂CO₃. The resulting synthetic liquor was then allowed to heat and stir continuously for ~1 h to ensure complete dissolution of all components. The synthetic Bayer liquor was then filtered (vacuum) while hot (~80 °C) through 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

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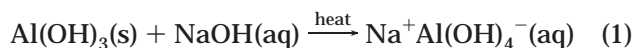
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Table 1. Composition (mol/L) of Synthetic Bayer Liquors

	liquor type						
	NaOH	Al	Na ₂ CO ₃	Na ₂ SO ₄	NaCl	Na ₃ PO ₄	Si
4.4 M NaOH	4.4	1.96	0.4	0.18	0.34	0.002	0.014
5.7 M NaOH	5.7	1.96	0.4	0.18	0.34	0.002	0.014
7.0 M NaOH	7.0	1.96	0.4	0.18	0.34	0.002	0.014

was then made up to 2.4 L with hot Milli-Q water and separated immediately into four equal portions. Synthetic Bayer liquors of 5.7 and 7.0 M NaOH were prepared as above except batches were only made up to 2.0 L and split into 4 × 500 mL portions. The final NaOH concentration required was achieved by adding 100 mL of a high-concentration NaOH solution just prior to use. The composition (Table 1) of synthetic Bayer liquors was confirmed using a variety of analytical methods. Although the amount of sodium hydroxide used to prepare synthetic Bayer liquors was the amount required to give a concentration of 4.4, 5.7, or 7.0 M, the actual "free" hydroxide ion concentration in the synthetic Bayer liquors used was significantly lower. This is due to the reaction between sodium hydroxide and aluminum hydroxide (reaction 1) to produce the sodium aluminate ion.



The following organic compounds were used without further purification: formic acid (CHCOOH, BDH Chemicals); acetic acid (CH₃COOH, BDH Chemicals); propionic acid (CH₃CH₂COOH, 98.0%, BDH Chemicals); butyric acid (CH₃(CH₂)₂COOH, BDH Chemicals); oxalic acid (HOCCOOH, 99.5%, May and Baker); malonic acid (HOCCCH₂COOH, 98.0+%, BDH Chemicals); succinic acid (HOOC(CH₂)₂COOH, 99.0+%, BDH Chemicals); and glutaric acid (HOOC(CH₂)₃COOH, 99.0%, Merck).

All reactions were conducted in a 1.2 L Inconel autoclave (Parr Instruments Co., Moline, IL). 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 setup also included a Parr 4843 controller to allow the 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.

All autoclave reactions 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. All organic compounds used were added in their acid form though it can be readily assumed that these were quickly converted to their sodium salt form in synthetic Bayer liquor based on the *pK_a* values of the organics studied and the pH of synthetic Bayer liquor (pH ≥ 14). The reaction vessel was then sealed and evacuated to -65 kPa to remove oxygen in the head-space area, to minimize 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 (Linde, minimum purity of 99.5%) was added at the partial pressure required (500 kPa). The oxygen partial pressure used was shown by preliminary tests to be sufficient for the organic concentrations used in

Table 2. Extent of Overall Compound Removal and TOC Removal of Individual Organic Compounds^a

compound	% TOC removal	% compound removal
sodium formate (HCO ₂ Na)	5.5	5.5
sodium acetate (H ₃ CCO ₂ Na)	<2	<2
sodium propionate (H ₃ CH ₂ CCO ₂ Na)	<2	<2
sodium butyrate (H ₃ CH ₂ CH ₂ CCO ₂ Na)	<2	<2
sodium oxalate (NaO ₂ CCO ₂ Na)	<2	<2
sodium malonate (NaO ₂ CH ₂ CCO ₂ Na)	7.6	18.5
sodium succinate (NaO ₂ CH ₂ CH ₂ CCO ₂ Na)	<2	<2
sodium glutarate (NaO ₂ CH ₂ CH ₂ CH ₂ CCO ₂ Na)	<2	<2

^a Conditions: reaction time = 2 h; *T* = 165 °C; *P*_{O₂} = 500 kPa; [initial organic] = 1.87 g/L (as C); 4.4 M NaOH synthetic Bayer liquor.

this study.¹⁷ The partial pressure of the added gas was maintained at the required amount throughout the course of the reaction. Samples were removed at predetermined times throughout the course of the reaction.

Sodium hydroxide, sodium carbonate, and aluminum concentrations were measured using an automated potentiometric titration system. Total organic carbon (TOC) concentrations were measured using an OI-Analytical TOC analyzer. Gas chromatography was used for sodium formate, acetate, butyrate, oxalate, malonate, succinate, and glutarate analyses (as methyl esters).^{18–21} Sodium propionate could not be analyzed directly because it eluted with the solvent. Sodium chloride and sodium sulfate were analyzed using capillary electrophoresis. Phosphorus was analyzed using inductively coupled plasma atomic emission spectrometry.

3. Results and Discussion

Extent of the Overall and Complete WO and Reaction Products. The WO of sodium formate, acetate, propionate, butyrate, oxalate, malonate, succinate, and glutarate was investigated for each compound individually. The results of these tests are presented in Table 2. Of the eight compounds studied, only sodium formate and malonate underwent appreciable WO (>2% conversion to carbon dioxide and other low molecular weight compounds) under the reaction conditions used. Neither of these compounds underwent thermal degradation in the absence of oxygen.

WO of sodium formate did not produce any organic reaction products. There was, however, a decrease in the organic carbon concentration, which coincided closely with the decrease in the sodium formate concentration (in terms of carbon). This indicates that sodium formate is completely oxidized to carbon dioxide (which, in turn, is converted into carbonate in an alkaline solution). Two low molecular weight organic compounds were produced from the WO of sodium malonate in a highly alkaline solution: sodium oxalate and sodium formate. A significant amount of sodium malonate was also converted to carbon dioxide (carbonate) based on TOC measurements.

Effect of the Sodium Hydroxide Concentration. On the basis of the results presented in Table 2, it was

Table 3. Effect of the NaOH Concentration on WO of Individual Organic Compounds^a

compound	% compound removal at varying [NaOH] (% TOC removal)		
	4.4 M NaOH	5.7 M NaOH	7.0 M NaOH
sodium formate	5.5 (5.5)	8.5 (8.5)	14.2 (14.2)
sodium acetate	<2	<2	<2
sodium propionate	<2	<2	<2
sodium butyrate	<2	<2	<2
sodium oxalate	<2	<2	<2
sodium malonate	18.5 (7.6)	29.6 (12.7)	39.5 (15.0)
sodium succinate	<2	<2	<2
sodium glutarate	<2	<2	<2

^a Conditions: reaction time = 2 h; $T = 165\text{ }^{\circ}\text{C}$; $P_{\text{O}_2} = 500\text{ kPa}$; [initial organic] = 1.87 g/L (as C); 4.4–7.0 M NaOH synthetic Bayer liquor.

decided to determine why only sodium formate and sodium malonate underwent appreciable WO under the reaction conditions used. On the basis of the -OH -initiated WO reaction mechanisms in a highly alkaline solution proposed by Wakabayashi and Okuwaki²² and Furuya et al.,²³ it was hypothesized that sodium formate and sodium malonate may have undergone WO because they contain noncarboxylic hydrogen atoms that could be more acidic than the noncarboxylic hydrogen atoms on the other compounds studied. The assumption of the comparatively higher acidity of the noncarboxylic hydrogen atoms on sodium formate and sodium malonate was also partly supported by literature on the effects of the positioning of carboxylate functional groups²⁴ on the acidity of noncarboxylic hydrogen atoms (refer to Table 2 for the structural formulas of compounds studied). On the basis of the above hypothesis, it was decided to investigate the effect of the NaOH concentration on sodium formate and sodium malonate WO.

The effect of the NaOH concentration is presented in Table 3. The WO of sodium formate and sodium malonate was significantly affected by the NaOH concentration, with both compounds undergoing increased WO with increasing NaOH concentration. This result supports the hypothesis that these two compounds undergo WO via the abstraction of a slightly acidic hydrogen atom by NaOH, similar to the mechanism proposed²² for sodium acetate WO in a highly alkaline solution. None of the other compounds investigated underwent appreciable WO over the NaOH concentration range studied (4.4–7.0 M). This is most likely due to either NaOH not being a strong enough base to abstract the slightly acidic hydrogen atoms on the other compounds tested (excluding sodium oxalate) or the temperature used in this study not being sufficiently high for this reaction to take place at a significant rate. Because the main aim of this study was to investigate relatively low temperature WO, the possibility of an energy barrier was not investigated further. On the basis of the previously reported results²² on the high-temperature ($250\text{ }^{\circ}\text{C}$) WO of sodium acetate in a highly alkaline solution, the lack of WO undergone by sodium acetate in this study is most likely due to the low temperature used.

Mechanism Studies. The type of reaction mechanism (free radical or ionic) predominantly occurring during the WO of sodium formate and sodium malonate was investigated using an indirect method because the reaction conditions of interest did not readily allow for a direct method to be used. To determine if free-radical intermediates were produced during the WO of sodium

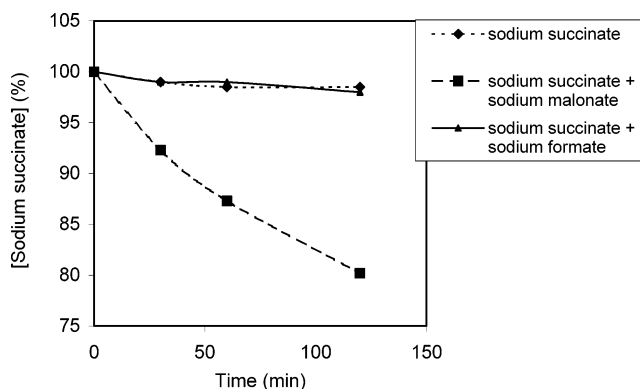


Figure 1. Effect of sodium malonate and sodium formate on the WO of sodium succinate. Conditions: reaction time = 2 h; $T = 165\text{ }^{\circ}\text{C}$; $P_{\text{O}_2} = 500\text{ kPa}$; 4.4 M NaOH synthetic Bayer liquor (sodium malonate + sodium succinate); 7.0 M NaOH (sodium formate + sodium succinate), which is a test conducted in 7.0 M NaOH synthetic Bayer to increase the extent of sodium formate WO.

formate and sodium malonate, both compounds were wet oxidized in the presence of sodium succinate, a compound shown earlier to undergo no appreciable WO under the same reaction conditions (Table 2). This method was used based on the hypothesis that if any free-radical intermediates were being produced, they could possibly co-oxidize other compounds that are otherwise stable. Sodium succinate was selected as the stable compound for use in the co-oxidation tests because of it not being produced as a product in the WO of sodium formate or sodium malonate and because of its intermediate molecular size.

The results of the co-oxidation tests are presented in Figure 1. Sodium malonate clearly produces free-radical intermediates during WO that are capable of co-oxidizing sodium succinate, a compound shown earlier to undergo no appreciable WO under the same reaction conditions when in isolation. Hence, the WO of sodium malonate in a highly alkaline solution occurs predominantly via a free-radical reaction mechanism. Sodium formate, however, did not produce free-radical intermediates capable of co-oxidizing sodium succinate (Figure 1). Hence, the WO of sodium formate does not occur predominantly via a free-radical reaction mechanism, or the free-radical intermediates produced during sodium formate WO are not stable or reactive toward sodium succinate. Because WO of sodium formate can only lead to the formation of methyl-type free-radical intermediates, which are more unstable than the ethyl- and/or butyl-type radicals²⁵ that could form during sodium malonate WO, it was decided to investigate the stability of free-radical intermediates produced during sodium formate WO.

The stability of sodium formate free-radical intermediates was investigated by testing the effect that sodium formate had on the WO of sodium malonate. This test was based on the hypothesis that if free-radical intermediates produced during the WO of sodium formate were unreactive toward other compounds, then any sodium formate molecules co-oxidized by malonate free-radical intermediates would effectively terminate the malonate chain reaction and hence cause a decrease in the amount of sodium malonate undergoing WO. The results of this test are presented in Figure 2. Sodium formate clearly hinders the WO of sodium malonate, hence supporting the hypothesis that free-radical intermediates formed from sodium formate are highly unstable and therefore incapable of co-oxidizing other

Table 4. Sodium Malonate Induced Co-oxidation^a

co-oxidized compound	initial concn (acid form) of co-oxidized compound (g/L)	initial concn (acid form) of sodium malonate (g/L)	% co-oxidized compound removal in the presence of sodium malonate
sodium formate	1.86 (0.038 M)	20.25 (0.195 M)	9.6 (4.1) ^b
sodium acetate	2.27 (0.038 M)	20.27 (0.195 M)	9.1
sodium propionate	3.05 (0.041 M)	20.24 (0.195 M)	24.6
sodium butyrate	3.43 (0.039 M)	20.27 (0.195 M)	18.0
sodium oxalate	2.28 (0.027 M)	19.77 (0.190 M)	5.3
sodium succinate	4.33 (0.037 M)	19.10 (0.184 M)	19.5
sodium glutarate	5.02 (0.038 M)	19.71 (0.189 M)	16.4

^a Conditions: reaction time = 2 h; $T = 165\text{ }^{\circ}\text{C}$; $P_{\text{O}_2} = 500\text{ kPa}$; 4.4 M NaOH synthetic Bayer liquor. ^b Extent of co-oxidation in parentheses.

Table 5. Products of Sodium Malonate Induced Co-oxidation

co-oxidation test	products
sodium malonate (blank)	oxalate, carbonate, formate
sodium malonate + sodium formate	oxalate, carbonate, (formate)
sodium malonate + sodium acetate	oxalate, carbonate, formate
sodium malonate + sodium propionate	oxalate, carbonate, formate, acetate
sodium malonate + sodium butyrate	oxalate, carbonate, formate, acetate
sodium malonate + sodium oxalate	oxalate, carbonate, formate
sodium malonate + sodium succinate	oxalate, carbonate, formate, acetate, fumarate, malonate
sodium malonate + sodium glutarate	oxalate, carbonate, formate, acetate, fumarate, malonate

compounds such as sodium succinate and sodium malonate under the reaction conditions used in this study.

Effect of Sodium Malonate WO on Sodium Acetate, Oxalate, Propionate, Butyrate, and Glutarate. On the basis of the finding that free-radical intermediates produced during sodium malonate WO in a highly alkaline solution were capable of co-oxidizing sodium succinate, a compound shown to be stable to WO in a highly alkaline solution, it was decided to investigate the ability of sodium malonate to co-oxidize the other compounds, which were shown earlier to be stable (Table 2). The results of these tests are presented in Table 4. Free-radical intermediates produced during sodium malonate WO are clearly capable of co-oxidizing the compounds studied. The order of the extent of co-oxidation was as follows: propionate > succinate > butyrate > glutarate > acetate > oxalate > formate. The extent of co-oxidation undergone by the above compounds would most likely be reliant upon a number of factors, such as molecular size, number of reactive sites (functional groups), and number and reactivity of intermediates formed.

The products formed from the sodium malonate induced co-oxidation tests are given in Table 5. To determine the products formed from the co-oxidized compound, it is necessary to assume that the type and distribution of products formed from WO of sodium malonate in the presence of an added compound are identical with those produced in isolation. The above

Table 6. Effect of Added Compounds on Sodium Malonate WO^a

co-oxidized compound	sodium malonate removal (%)
none (sodium malonate) ^b	16.6
sodium formate	8.3
sodium acetate	15.9
sodium propionate	12.6
sodium butyrate	10.2
sodium oxalate	14.2
sodium succinate	19.2
sodium glutarate	10.1

^a Conditions: reaction time = 2 h; $T = 165\text{ }^{\circ}\text{C}$; $P_{\text{O}_2} = 500\text{ kPa}$; 4.4 M NaOH synthetic Bayer liquor. For organic concentrations, refer to Table 4. ^b Initial sodium malonate concentration (acid form) = 19.80 g/L (0.190 mol/L).

assumption was used to determine the extent of co-oxidation undergone by sodium oxalate because it was not possible to differentiate between the sodium oxalate added at the beginning of the test and the sodium oxalate produced from WO of sodium malonate. This assumption was, however, not used to determine the type and distribution of products formed exclusively from the co-oxidized compound because of the inherently high degree of uncertainty in using such an assumption for calculating the quantities of multiple compounds.

Effect of Added Compounds on WO of Sodium Malonate. The effect that sodium acetate, oxalate, succinate, propionate, butyrate, and glutarate had on the WO of sodium malonate is given in Table 6. The effect of the above-mentioned compounds on the WO of sodium malonate, in order of decreasing hindrance, was glutarate > butyrate > propionate > oxalate > acetate > succinate. The degree to which each of the compounds studied hindered the WO of sodium malonate would most likely be due to a number of factors. The most important factors are most likely the ability of the intermediates formed from the co-oxidized compound to propagate sodium malonate co-oxidation and the number of reactive sites (functional groups) on the co-oxidized compound. The number of reactive sites (functional groups) would determine the extent to which the co-oxidized compound can compete with unreacted sodium malonate for free-radical intermediates.

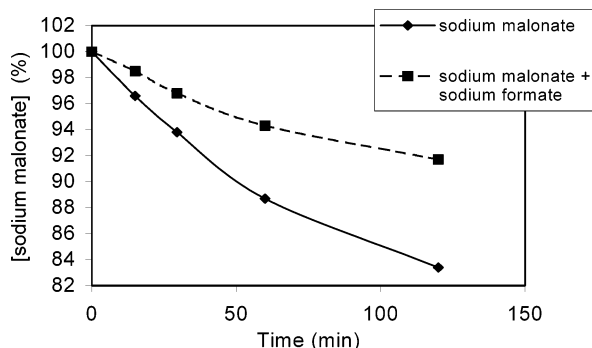
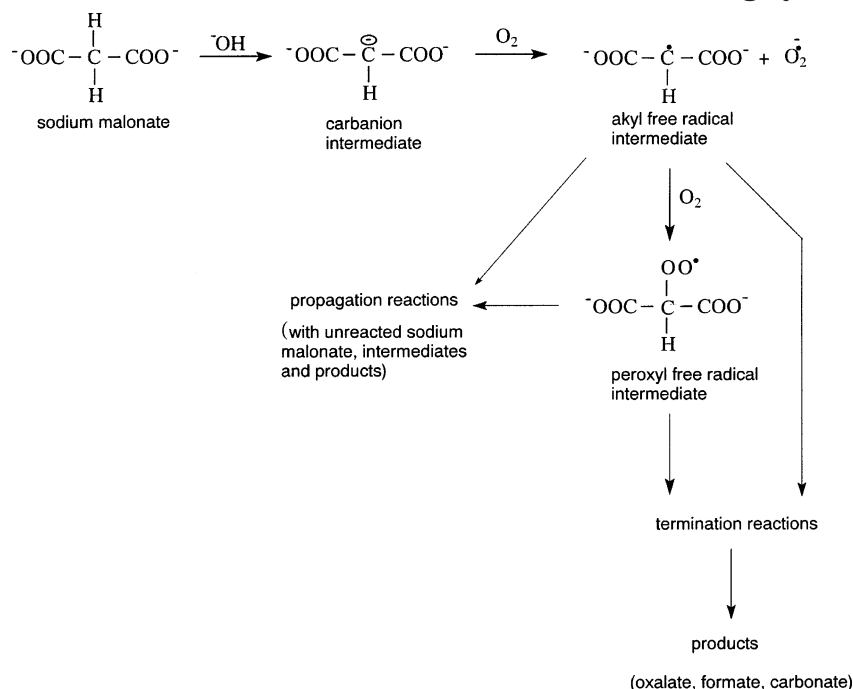
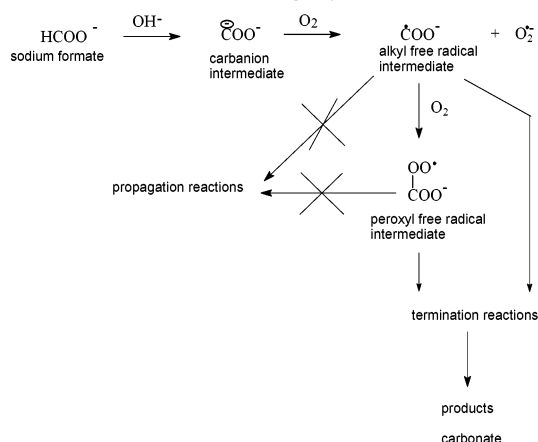


Figure 2. Effect of sodium formate on the WO of sodium malonate. Conditions; reaction time = 2 h; $T = 165\text{ }^{\circ}\text{C}$; $P_{\text{O}_2} = 500\text{ kPa}$; 4.4 M NaOH synthetic Bayer liquor.

Scheme 1. Proposed Reaction Mechanism for WO of Sodium Malonate in a Highly Alkaline Solution**Scheme 2. Proposed Reaction Mechanism for WO of Sodium Formate in a Highly Alkaline Solution**

Proposed Reaction Mechanisms. Proposed reaction mechanisms for WO of sodium malonate and sodium formate are given in Schemes 1 and 2. On the basis of the effect of the NaOH concentration on the extent of WO undergone by the aforementioned compounds, it is proposed that the initial reaction step in the WO of both compounds involves reaction with OH^- and subsequent formation of a carbanion intermediate. The carbanion intermediates would then most likely react with oxygen to form alkyl free-radical intermediates, which could subsequently react further with oxygen to form peroxy free-radical intermediates. The majority of alkyl/peroxy intermediates formed during WO of sodium formate do not take part in propagation reactions based on the results obtained in this study and hence predominantly undergo termination reactions, leading to the only product identified (carbonate). The alkyl/peroxy intermediates formed during WO of sodium malonate, however, do most likely undergo propagation reactions based on the results obtained in this study and hence an auto-oxidation step is included in the proposed reaction mechanism. The free-radical

intermediates formed during WO of sodium malonate also undergo termination reactions, leading to the formation of the products identified (formate, carbonate, and oxalate).

4. Summary

Sodium malonate and sodium formate undergo appreciable WO in a highly alkaline solution at relatively low temperature (165°C). Both of these compounds undergo WO in a highly alkaline solution because they contain slightly acidic noncarboxylic hydrogen atoms that can react with NaOH. The WO of sodium malonate occurs predominantly via a free-radical chain reaction mechanism in a highly alkaline solution. The WO of sodium formate also most likely occurs via a free-radical reaction mechanism in a highly alkaline solution. The free-radical intermediates that form during WO of sodium formate are, however, highly unstable, and therefore the WO of sodium formate does not occur via a chain reaction mechanism. Free-radical intermediates that form during sodium malonate WO in a highly alkaline solution are capable of co-oxidizing low molecular weight organic compounds that are stable under the same reaction conditions in isolation. Free-radical intermediates formed during the WO of sodium malonate can co-oxidize sodium acetate, propionate, butyrate, oxalate, succinate, and glutarate.

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