

MECHANISMS OF THE WET OXIDATION OF MALONATES AND CO-OXIDATION OF BENZOATE IN HIGHLY ALKALINE SOLUTION

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Abstract

Organic compounds in Bayer liquor cause significant reductions in alumina production and hence the development of processes for removing them from the liquor is of great interest to alumina refineries. Of the various organics removal processes known, wet oxidation has received significant interest. Further development of this technology requires an improved understanding of the underlying chemistry of the wet oxidation of Bayer organics. A significant step has been taken through the study of the oxidation mechanism of sodium malonate (a common Bayer organic). We have previously confirmed that the first reaction step in the wet oxidation of sodium malonate and malonate derivatives is the formation of a carbanion, as a consequence of the slight acidity of the α -hydrogen(s) in these compounds. In this study the subsequent reaction step, which has been proposed to involve the formation of alkyl and peroxy radicals via the reaction between the malonate carbanions and oxygen, is investigated. Consistent with this, the results show a linear dependence of the oxidation rate constant of the malonates on the oxygen partial pressure. The proposed mechanism is further supported by the reaction products identified, and by the effect of adding benzoate, a known free-radical scavenger. Malonate appears to catalyse the reaction of benzoate in the presence of oxygen, causing a co-oxidation effect, which is consistent with the presence of free radical intermediates in the overall mechanism.

1. Introduction

Organic compounds, which are extracted to the Bayer process liquor during bauxite digestion (Power and Loh, 2010), result in a variety of negative effects in the Bayer process for the production of alumina, mainly by reducing refinery productivity and causing emissions of volatile organic compounds (Guthrie et al., 1984, Eyer et al., 2002, Grocott and Rosenberg, 1988, Lever, 1978, Matyasi et al., 1986, Power, 1991, Smeulders et al., 2001, Coyne et al., 1994, Hind et al., 1999, Hind et al., 1997, Watling, 2000). The development of appropriate methods for removing organic impurities from the Bayer liquor is therefore of great interest to alumina refineries. Of the various types of organics removal methods that have been investigated, Wet Oxidation (WO), in which complex organics are oxidized to simpler compounds and ultimately to carbonate using oxygen or air, has received significant attention (Lalla and Arpe, 2002, Arnsward et al., 1991). Unfortunately, high pressures and temperatures are generally required to achieve full oxidation using current technology (Lin et al., 1996, Bhargava et al., 2006). To minimize the reaction pressures and temperatures required, greater understanding of the underlying reaction mechanisms of the organic compounds present in Bayer process liquors is needed.

Studies on the WO of sodium malonate (a common Bayer liquor impurity) have revealed that this dicarboxylate is unusually reactive under relatively mild wet oxidation conditions in highly alkaline solution and that it can also stimulate the oxidation of other Bayer organic compounds at moderate temperature and pressure in caustic solution (Tardio et al., 2004a, Tardio, 2002, Tardio et al., 2004b, Tardio et al., 2008). This "co-oxidation" effect has been attributed to the formation of reactive intermediates which can then react with other compounds that do not react with oxygen directly.

The first reaction step in the WO mechanism of sodium malonate and its methyl and ethyl derivatives in highly alkaline solution has previously been shown to be the formation of carbanion intermediates due to the slight acidity of the α -hydrogen(s) in these compounds (Dong et al., 2010). The subsequent reaction

step has been proposed to be the reaction of the carbanion with oxygen to form free radical intermediates (Tardio, 2002). In the current work the nature of the second reaction step is confirmed. The co-oxidation effects of the malonates were also investigated using sodium benzoate, a compound that is generally present in Bayer liquors (Power and Loh, 2010) and which is a known free radical scavenger (Harvath, 1979, Klein et al., 1975), as the target for oxidation. The effect is explained in terms of a mechanism in which malonates stimulate the oxidation of benzoate by producing free radicals.

2. Experimental

All chemicals were obtained at the highest commercially available quality and were used without further purification. Milli-Q water was used to prepare the NaOH solutions used for WO tests and for the dilution of samples for analysis.

All WO experiments were conducted in a 1.2 L Inconel[®] autoclave (Parr Instruments Co. USA), which was fitted with a magnetically coupled stirrer with two six-vane impellers controlled at 300 RPM. The pressure in the autoclave was monitored using a pressure transducer and controlled manually. WO tests were conducted in 400 mL of NaOH solution at 200 °C under O₂ partial pressures (pO₂) from 0 to 1270 kPa gauge. The initial concentration of the NaOH solution was 2.4 M, which was chosen to be similar to the concentration of the 'free' hydroxide ion present in typical pregnant Bayer liquors (Tardio, 2002). The reaction vessel was then sealed and evacuated to remove oxygen in the headspace to avoid oxygen-induced oxidation while the solution was heated to 200 °C with stirring. The time at which this temperature was reached was assigned to be time zero, at which point oxygen was introduced to the reaction vessel and maintained at the desired partial pressure throughout the reaction. Samples were collected periodically for analysis.

The concentrations of the starting compounds (Figure 1) were measured using HPLC (Power et al., 2011) as described elsewhere (Dong et al., 2011). A standard solution containing sodium oxalate, formate, acetate, succinate, maleate, glyoxylate, glycolate and propionate was used for product identification.

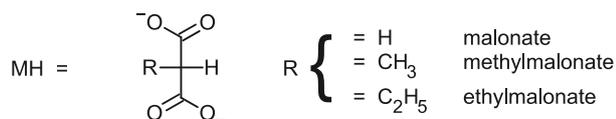


Figure 1. "MH" represents malonate and the substituted malonates as shown. The H on the central carbon atom is the α -H, which is slightly acidic because of the electron-withdrawing effects of the two adjacent carboxylate groups.

3. Results and Discussion

All of the WO experiments were carried out in pure NaOH solutions. Tests in this laboratory have demonstrated that the oxidation rate of sodium malonate under oxygen at 690 kPa in a synthetic Bayer liquor containing 4.4 M NaOH and 1.96 M $[\text{Al}(\text{OH})_4^-]$ is similar to the rate measured in a pure NaOH solution of the same "free hydroxide" concentration (2.4 M), consistent with the expectation that the influence of aluminate is primarily through its effect on the free hydroxide concentration. The complex mixture of organic compounds present in Bayer process liquors can be expected to provide the opportunity for a range of additional reactions, especially involving the free radicals, in addition to those described here.

Sodium malonate, methyl-malonate and ethyl-malonate were found to be stable in 2.4 M NaOH at 200°C under nitrogen. In the presence of oxygen however, all of these compounds react according to a pseudo-first order rate law, demonstrated by the linear relationship between $\ln(\text{concentration})$ and time observed at each oxygen partial pressure, as shown in Figure 2. The pseudo-first order rate constant was found to be directly proportional to the oxygen partial pressure, $p\text{O}_2$, in each case, as shown in Figure 3.

The first step in the oxidation reaction mechanism of malonate and the malonate derivatives has previously been confirmed as carbanion formation (Dong et al., 2010), as shown in Equation 1, in which MH represents malonate or a substituted malonate with an α -H, as shown in Figure 1.



The second step of the proposed mechanism is the formation of free radicals (M^\cdot and O_2^\cdot) as shown in Equation 2 (Tardio et al., 2004b, Tardio et al., 2004a):



Accordingly, the rate of reaction, r , of M-H is given by:

$$\begin{aligned} r &= k \times [\text{M}^-] \times [\text{O}_2] \\ &= k \times K_1 \times [\text{MH}] \times [\text{OH}^-] \times [\text{O}_2] \end{aligned} \quad (3)$$

If $[\text{OH}^-]$ is constant and $[\text{O}_2]$ obeys Henry's Law, Equation 3 can be rewritten as:

$$r = k' \times K_1 \times [\text{MH}] \times p\text{O}_2 \quad (4)$$

If oxygen is in excess and is maintained at a constant partial pressure, Equation 4 may be integrated as follows:

$$\ln[\text{MH}] = -k'' \times t + \ln[\text{MH}]_0 \quad (5)$$

in which k'' is a pseudo-first order rate constant containing $[\text{OH}^-]$ and $p\text{O}_2$, according to Equation 6:

$$k'' = K_1 \times [\text{OH}^-] \times p\text{O}_2 \quad (6)$$

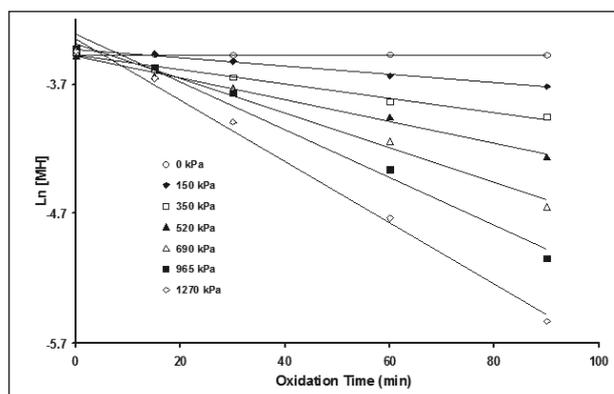


Figure 2. Kinetics of WO of malonate for a range of oxygen partial pressures ($T = 200^\circ\text{C}$; $[\text{OH}^-] = 2.4 \text{ M}$; starting $[\text{malonate}] = 0.03 \text{ M}$)

The pseudo-first order kinetics of the WO of the malonates and the linear dependence of the rate constants on $p\text{O}_2$ shown in Figures 2 and 3 are consistent with Equation 5 and 6, which indicates that O_2 is involved in the rate determining step of the reaction, consistent with the proposed mechanism (Equations 1 and 2). The reactivity sequence malonate > methyl-malonate > ethyl-malonate is the same as previously observed in the study of hydroxide dependence (Dong et al., 2010), and is similarly consistent with the reactivity sequence of the α -Hs of these compounds.

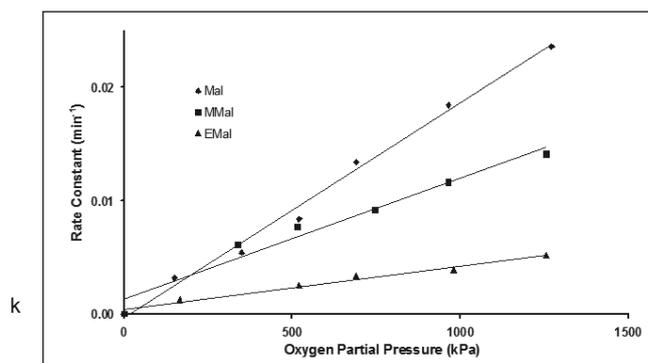


Figure 3. Effect of oxygen partial pressure on WO rate constant for the degradation of malonates ($T = 200^\circ\text{C}$; $[\text{OH}^-] = 2.4 \text{ M}$; starting $[\text{organic}] = 0.03 \text{ M}$. Mal = malonate, MMal = methyl-malonate, EMal = ethyl-malonate)

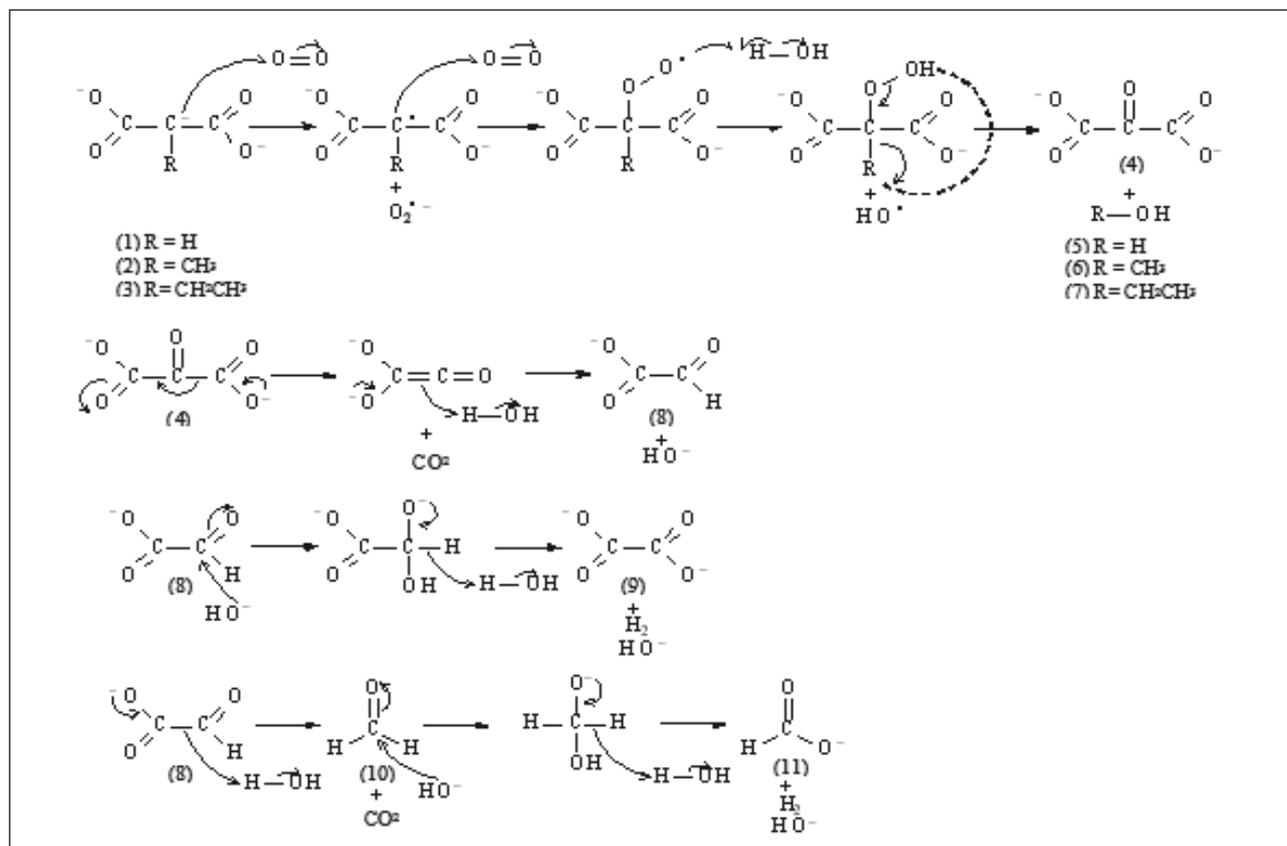
(1)

The reaction products determined by HPLC analysis are summarized in Table 1. In the presence of oxygen, all of the malonate compounds produce oxalate and formate as the main organic products. The formation of oxalate and formate is consistent with the oxidation products of malonate obtained through an initial reaction of oxygen with a carbanion (formation of the alkyl free radical), as suggested by Tardio (2002). The proposed oxidation mechanism for the carbanions in alkaline solution resulting in the formation of oxalate and formate is shown in Scheme 1, which is based on the mechanisms suggested previously by Tardio (2002) and Loh et al (2010). Methanol (6) and ethanol (7), which are formed in the proposed reaction pathway, have been identified in the VOC emissions from an alumina refinery (Galbally, 2008). Glyoxylate (8) which is formed according to pathway (A) and can react in two ways – either through the addition of a hydroxyl group to the carbonyl carbon to form oxalate (9) and hydrogen, or by decarboxylation to formaldehyde (10) as an intermediate species leading to formate (11) and hydrogen. Hydrogen has previously been observed from the alkaline degradation of formaldehyde (Ashby et al., 1993, Bi et al., 2010, Kapoor et al., 1995, Kapoor and Naumov, 2004). The production of hydrogen gas, which is a product of base-catalyzed oxidation by water (Loh et al., 2010), has also been detected

under wet oxidation conditions (Brown, 1989, The et al., 1985). In addition to oxalate and formate, oxidation of methyl-malonate and ethyl-malonate also forms small amounts of acetate and propionate, respectively, as the final products. A second common pathway in parallel with the main mechanism has been proposed to account for this (Dong et al., 2011).

Table 1. Products of WO of malonates under O₂ in caustic solution (T = 200 °C; pO₂ = 150, 350, 520, 690, 965 and 1270 kPa; starting [organic] = 0.03 M; [OH⁻] = 2.4 M)

Compound	Oxidation Products
Malonate	oxalate, formate, carbonate
Methyl-malonate	oxalate, formate, acetate, carbonate
Ethyl-malonate	oxalate, formate, propionate, carbonate

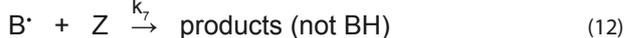
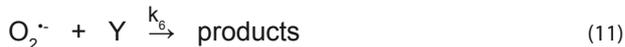
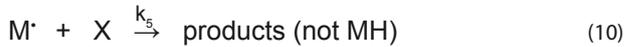


Scheme 1. Proposed oxidation mechanisms of carbanions from malonate (1), methyl-malonate (2) and ethyl-malonate (3) in alkaline solution involving free radical formation (Tardio et al., 2004b, Tardio et al., 2004a) and base-catalyzed oxidation by water (Loh et al., 2010) to form oxalate (9) and formate (11).

The existence of radical species was investigated by observing the effect of adding benzoate, a known radical scavenger, to the reaction mixture. Sodium benzoate by itself was found to be stable in 2.4 M NaOH at 200 °C in the presence of oxygen, up to the highest partial pressure investigated (1270 kPa). However, in the presence of malonate, benzoate reacts and the rate of consumption of malonate is lower than in the absence of benzoate. Both of these effects are shown in Figure 4. Similar behaviour (Tardio, 2002) is observed with methyl- and ethyl-malonate, but to a lesser degree. The magnitude of this "co-oxidation" effect is in the same order as the reactivity of the malonates themselves, i.e. malonate > methyl-malonate > ethyl-malonate. These observations support the hypothesis that free radicals are the means of propagating the degradation reactions of both malonates and benzoate, but there is no direct proof of what particular radicals are involved. The reaction scheme below is proposed as a reasonable overall mechanism that provides a good fit to the observed kinetics; however it is not claimed to be unique or complete. Nonetheless, it appears to provide a reasonable explanation for the main aspects of the observations, in particular the co-oxidation effect.

In order to model the kinetics of degradation of malonate and benzoate together, reactions (7) to (12) were considered. In these equations, BH represents benzoate, B[•] represents a mono-dehydrogenated benzoate radical, and X, Y and Z are other

unspecified reactants which may include water, but which do not include benzoate, malonate or oxygen species.



Malonate WO experiments were carried out with and without benzoate present, and the data were fitted using this model by solving the kinetic equations using the PolyMath Professional Version 6.1 numerical analysis package. According to this model, benzoate reacts rapidly with the malonate radical to form benzoate radicals and re-form malonate according to equation (7). This equation represents one aspect of the co-oxidation effect, which proposes that malonate acts as a catalyst in the degradation of benzoate. Co-oxidation may also occur as a result of the presence of peroxy radicals, assuming that they attack benzoate according to equation (8). It was not possible to fit the observed reaction curves with equations (7) and (8) alone

however; in particular, it was necessary to include the reformation of benzoate, for example by the reaction of the benzoate radical with water (9). On the other hand, the observed kinetics were not sensitive to the rates of reactions (10), (11) or (12).

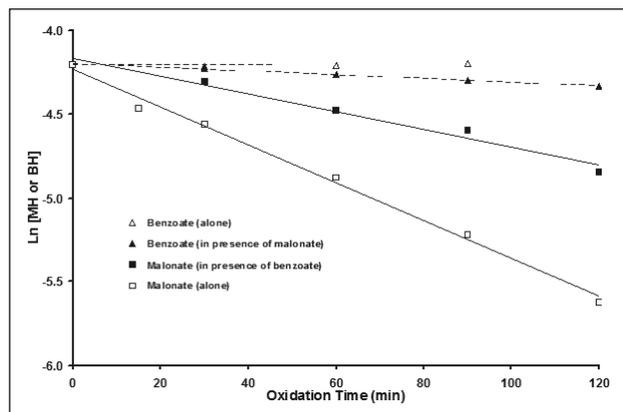


Figure 4. Kinetics of WO of benzoate and malonate, individually and together. ($T = 200\text{ }^{\circ}\text{C}$; $[\text{OH}^-] = 2.4\text{ M}$; starting concentrations = 0.015 M ; $p_{\text{O}_2} = 690\text{ kPa}$).

Figure 5 shows the fit of this model to the experimental data for malonate degradation with and without benzoate. Similar fits to the results have been achieved at different oxygen pressures. Based on this, Figure 6 provides an indication of the evolution of the relative concentrations of the main assumed radical species as a function of time. As expected, the concentrations of M^{\cdot} and $\text{O}_2^{\cdot-}$ initially rise rapidly followed by the appearance and subsequent removal of B^{\cdot} . The concentrations of all three radicals then decline monotonically as the reactions proceed. The most prevalent radical appears to be the peroxy radical, followed by the malonate radical and then the benzoate radical.

In the absence of benzoate, the dependence of the degradation rate constant on p_{O_2} is stronger for malonate than for the malonate derivatives, as shown by the slopes of the plots in Figure 3. This reactivity sequence, malonate > methyl-malonate > ethyl-malonate, is the same as previously observed in the study of hydroxide dependence (Dong et al., 2010). The same order of reactivity is found in the co-oxidation reaction with benzoate. These observations are consistent with the order of acidity of the α -H in the malonates in combination with the mechanism described above. The reactions assigned to benzoate are consistent with previous observations of its behavior as a free radical scavenger (Harvath, 1979, Klein et al., 1975).

The apparent decrease in the measured rate of decrease of the concentrations of the malonates in the presence of benzoate is most likely a direct consequence of their re-formation by the reaction of the corresponding malonate radical with benzoate (Equation 7), while the primary degradation of the malonate according to Equations (1) and (2) is unaffected.

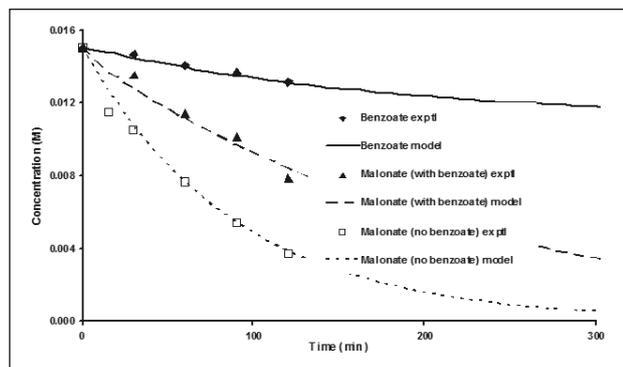


Figure 5. Co-oxidation of malonate and benzoate compared to oxidation of malonate alone, showing experimental data (points) and curves generated by the simulation model proposed. Conditions: Initial malonate and benzoate concentrations 0.015 M ; NaOH concentration 3.88 M ; $p_{\text{O}_2} = 690\text{ kPa}$; temperature $200\text{ }^{\circ}\text{C}$.

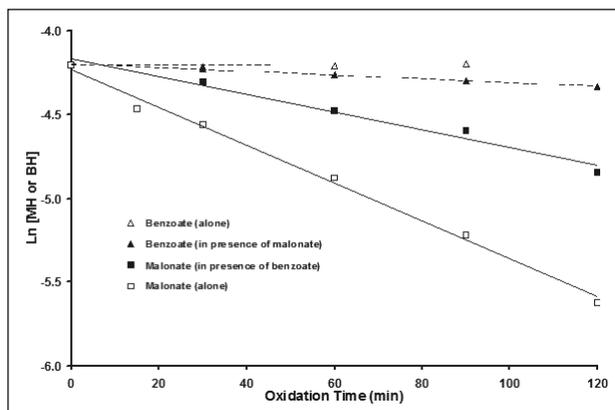


Figure 6. Simulated evolution of radicals in co-oxidation of malonate and benzoate according to the model. Conditions: Initial malonate and benzoate concentrations 0.015 M ; NaOH concentration 3.88 M ; $p_{\text{O}_2} = 690\text{ kPa}$; temperature $200\text{ }^{\circ}\text{C}$.

The overall co-oxidation reaction proposed on the basis of these observations is shown schematically in Figure 7, from which it can be seen that it consists of a catalytic cycle in which the alkyl radical attacks the benzoate while the corresponding malonate is re-formed, and an additional reaction in which the benzoate is attacked by the peroxy radicals that were formed in the reaction of oxygen with the original malonate.

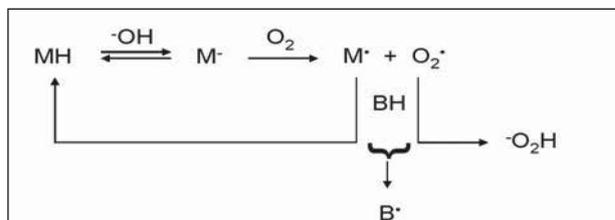


Figure 7. Schematic representation of the mechanism proposed for the co-oxidation of benzoate (BH) by malonate (MH).

4. Conclusions

In this study, the rate-determining step in the WO of malonate and its derivatives in alkaline solution has been confirmed to involve the reaction of oxygen with malonate carbanions to form alkyl and oxygen-based (presumably peroxy) free radicals. This builds on previous confirmation of the formation of a malonate carbanion as the first step in the reaction. Accordingly, the reaction follows pseudo first order kinetics in which the oxygen partial pressure is a factor in the pseudo first order rate constant.

The products observed indicate the existence of two distinct reaction pathways following the formation of radicals. The dominant pathway leads to the formation of formate and oxalate for each of the starting materials, whereas the minor pathway leads to formate, acetate or propionate for malonate, methyl-malonate and ethyl-malonate, respectively.

The "co-oxidation" effect of malonate in stimulating the oxidation of benzoate, which is often used as a "radical scavenger", has been explained by demonstrating that benzoate reacts with both the alkyl and peroxy free radicals that are formed in the reaction of malonate with oxygen. The reaction of benzoate with the alkyl radicals reforms the parent malonate, which leads to a net decrease in the rate of malonate consumption, while the underlying degradation rate of the malonate remains unchanged. Malonate therefore acts in this aspect as a catalyst in the oxidation of benzoate.

Methyl- and ethyl-malonate also stimulate the degradation of benzoate, but to a lesser extent than malonate. The order of reactivity reflects the lower the acidities of the α -Hs on the substituted malonates due to the electron-donating effects of the substituent groups.

These observations highlight the roles of weakly acidic hydrogen atoms and free radical reactions in the oxidative degradation of organic compounds in highly alkaline solutions. The ability of certain compounds, in particular malonate and its derivatives, to form free radicals and stimulate the degradation of other compounds, has been observed and a general mechanism for such "co-oxidation" has been proposed. This understanding points the way for future research into the nature of organic reactions in Bayer process liquors and the improvement of the wet oxidation process for their removal.

5. Acknowledgements

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