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Fundamentals of Wet Oxidation of Bayer-Process Liquor: Reactivity of Malonates

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The application of wet oxidation to the removal of organic impurities from Bayer-process liquors has the potential to deliver major benefits to the alumina industry. Previous work has identified the malonate anion as especially reactive under WO conditions, a property ascribed to its ability to form a carbanion in alkaline conditions. Understanding of the reaction mechanism involved in this effect is of importance to the development of improved WO technology. The current work confirms carbanion formation as the first step in the reaction. Deuterium exchange experiments and ¹³C NMR spectroscopy are used to demonstrate the weak acidity of the α -hydrogen atoms which leads to carbanion formation. The acidity of the α -hydrogen atoms in malonate is induced by the electron-withdrawing effect of the two adjacent carboxylate groups. Substituting an electron-donating group such as methyl or ethyl at the α -position reduces this effect, resulting in reduced oxidation rates for the substituted malonates. The role of the carbanion in the reaction mechanism is confirmed by analysis of the products and reaction kinetics.

1. Introduction

Alumina is refined by the Bayer process from bauxite, which generally contains small amounts of organic compounds due to the presence of humic substances and plant and animal residues. The first step of the Bayer process involves digestion of the bauxite in strong alkali to dissolve aluminum hydroxide and/or aluminum oxy-hydroxides. A proportion of the organics from the bauxite is also extracted and builds up in the process liquor. This results in a number of undesirable effects, including reduction of the overall productivity of the refinery process and emission of volatile organic compounds.^{1–5}

One method that has been used for removing organic impurities from Bayer liquor is wet oxidation (WO),^{6,7} in which gaseous oxygen or air is used to break complex organics down to simpler compounds, and ultimately to carbonate and water. Complete oxidation is generally only possible at high pressures and temperatures in the presence of catalysts using current technology.^{8,9}

The goal of this work is to improve the understanding of the complex reaction mechanisms involved as a basis for the development of technology for efficient WO at lower temperature and pressure and preferably without the need for a catalyst. A significant step has been taken by the discovery that compounds containing the malonate structural unit are unusually reactive, and can also facilitate the oxidation of certain other low-molecular-weight organics in alkaline solution at moderate temperatures.^{10–12} Understanding the reaction mechanism for the oxidation of malonate and malonate derivatives is an important step in determining how intermediates which are capable of initiating the oxidation of refractory compounds form. A greater understanding of the formation of such intermediates is of special interest to the development of current WO technology.

In this work the initial steps in the oxidation mechanism of malonate and malonate derivatives (methyl- and ethyl-malonate) in alkaline solution have been investigated. D-Exchange of the

α -hydrogen is demonstrated using ¹³C NMR.^{13–17} The products of reaction (analyzed by HPLC and ¹³C NMR), and the observed reaction kinetics, are shown to be consistent with formation of a carbanion as the first step in the reaction.

2. Experimental Section

2.1. Materials. 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 for WO tests and all samples for HPLC analysis.

2.2. Deuterium Exchange Experiments. A 5 mL portion of D₂O or NaOD (0.488 and 9.76 M) was added to a 20 mL Teflon bomb, followed by 5 mL of the organic compound of interest at a concentration of 0.72 M. The organic compounds were prepared from their acid forms and neutralized to pH 7 prior to addition. This procedure results in solutions containing 0.36 M of the organic compound and 0, 0.244, or 4.88 M NaOD in D₂O. The solution was then degassed with high purity nitrogen and the headspace was flushed with nitrogen prior to sealing the bomb. The solution was then brought to the desired temperature (200 °C in an oven or room temperature (25 °C)) and held at temperature for 2 h. The bomb was then cooled and the solution was collected for NMR analysis. A control experiment for each compound was also carried out in water and NaOH solutions (0.244 and 4.88 M) in the absence of O₂.

2.3. Wet Oxidation Tests. All WO experiments were conducted in a 1.2 L Inconel autoclave (Parr Instruments Co., USA), which was fitted with a magnetically driven stirrer with two six-vane impellers. The temperature in the autoclave and the stirrer speed were controlled automatically using a Parr 4843 controller. The pressure in the autoclave was monitored using a pressure transducer and controlled manually. WO tests were conducted by adding 400 mL of NaOH solution to the reaction vessel, followed by the acid form of the organic compound to be tested (0.03 M). The reaction vessel was then sealed and evacuated to remove oxygen in the headspace to avoid oxygen-induced oxidation during heat-up. 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 to a partial pressure of

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Table 1. Chemical Structure and Molecular Formula of the Malonates

Compound	Chemical Structure	Molecular Formula
Malonate		C ₃ H ₂ O ₄ ²⁻
Methyl-malonate		C ₄ H ₄ O ₄ ²⁻
Ethyl-malonate		C ₅ H ₆ O ₄ ²⁻

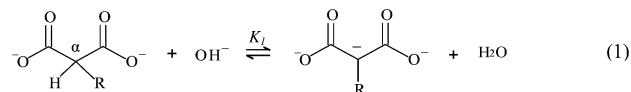
700 kPa, which was maintained throughout the reaction process. Samples were collected after reaction times of 0, 15, 30, 60, and 90 min. The same procedure was carried out for each compound under a nitrogen atmosphere to determine if any degradation occurred in the absence of oxygen.

2.4. Analytical Methods. The concentration of malonate and malonate derivatives was measured using a high-performance liquid chromatography (HPLC) instrument equipped with a Waters Associates 6000A solvent delivery system, a Waters Associates model 450 variable wavelength detector, and a Wakosil-II 5C18 RS column (4.6 × 150 mm I.D., particle size 5 μm, SGE). The mobile phases were as follows: A, 20 mM H₃PO₄–NaH₂PO₄ buffer (pH 2.5); B, 40% CH₃CN + 60% 10 mM KH₂PO₄–NaH₂PO₄ buffer (pH 3.0). Mobile phase A was used to analyze sodium malonate. Sodium methyl- and ethyl-malonate were analyzed using a combination of mobile phase A (80%) and B (20%). The flow-rate was 1.0 mL/min, and the wavelength for detection was 210 nm. The column was thermostatted at 25 °C. The injection volume was 20 μL. All samples were acidified and injected in triplicate. The internal standard used for sodium malonate and methyl-malonate was chloroacetic acid, and hexanoic acid was used for sodium ethyl-malonate.

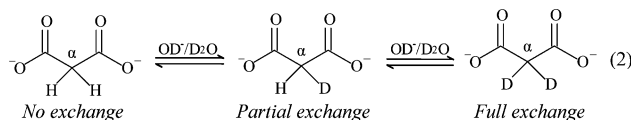
The ¹³C NMR spectra were obtained on a Bruker Advance 300 spectrometer, operating at a frequency of 300 MHz. Chemical shifts are reported relative to an external standard of sodium 3-trimethyl-silyl-1-propanesulfonate at 0 ppm.

3. Results and Discussion

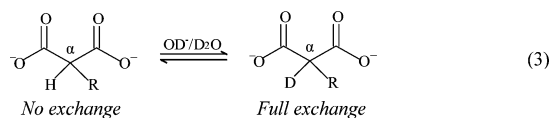
3.1. ¹³C NMR Studies of Malonate and Malonate Derivatives as a Function of Solution Alkalinity. According to the chemical structures of malonate and malonate derivatives shown in Table 1, the two –CO₂[–] electron-withdrawing groups on the malonate structure unit can potentially weaken the C–H bond on the central (α) carbon, imparting a slight acidity to the hydrogen(s) on the α-C (the electron withdrawing strength of the carboxylate group is lesser than a carboxylic group¹⁸ hence it is important to note that the induced acidity of the α-H(s) is less under alkaline conditions). The α-H(s) may therefore be abstracted by OH[–] in alkaline solution, leading to the formation of a carbanion intermediate in equilibrium with the malonates as shown in eq 1, in which R = H, CH₃, or CH₂CH₃ (the acidity of the α-H when R = CH₃ or CH₂CH₃ will be reduced due to the electron donating effect of these groups). This equilibrium has been proposed^{10,11} as the first step in WO of malonate in highly alkaline solution.



The reaction shown in eq 1 involves a dynamic exchange of protons between the malonate, water, and hydroxyl ions. This exchange can be observed by replacing the water and hydroxide by D₂O and OD[–] and detecting the formation of deuterated malonates by ¹³C NMR.¹³ Malonate has two exchangeable protons so it can potentially form mono- and/or di-deuterated species shown in eq 2.



The coupling patterns of the α-C present in the different malonate species are shown in Table 2. The absence of D-exchange results in a singlet, partial exchange provides a 3-way splitting giving a triplet with intensity ratios of 1:1:1, and full exchange results in a 5-way splitting producing a quintet with ratios of 1:2:3:2:1.¹⁹ The substituted malonates have only one exchangeable proton, so they can only form the monodeuterated species shown in eq 3, in which R = CH₃ or CH₂CH₃.



These two species only produce a singlet or a triplet peak for the α-C when no deuteration or full deuteration occurs, respectively. The presence of both patterns together indicates partial exchange.

To test for the occurrence of the exchange reactions, malonates were dissolved in D₂O and D₂O/NaOD solutions. The solutions were held at temperature for 2 h and then analyzed by ¹³C NMR at room temperature without further treatment. Two NaOD concentrations (0.244 and 4.88 M) and two temperatures (25 and 200 °C) were used. Examples of the ¹³C NMR spectra of malonate obtained are shown in Figure 1. The main features and interpretation of the NMR spectra of all the malonates for all reaction conditions are summarized in Tables 3 and 4.

According to Figure 1 and Table 3, the splitting patterns of the malonate α-C observed in D₂O at 25 °C is an asymmetric quintet. This pattern can be explained as a combination of the overlapping of a quintet, triplet, and singlet due to the presence

Table 2. Overview of the Coupling Patterns Based on One ¹³C Nucleus with 0, 1, and 2 D Atoms (Assuming Equal Coupling Constants)

Number of D	Coupling Pattern	Multiplicity
0		Singlet
1		Triplet
2		Quintet

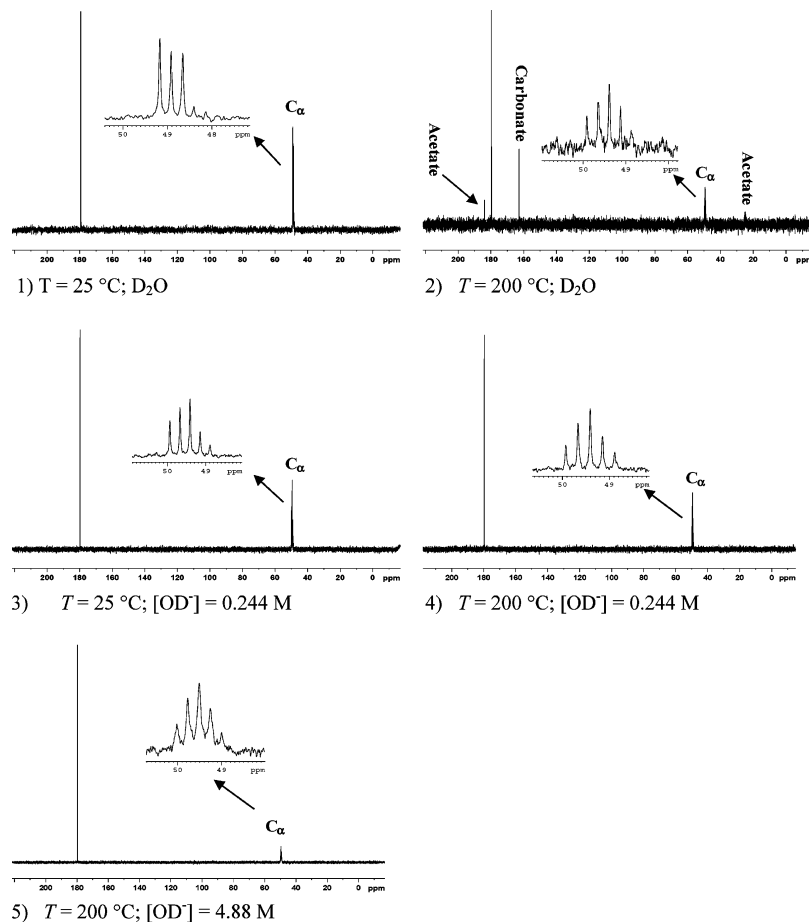


Figure 1. ^{13}C NMR spectra of malonate (reaction time = 2 h; [malonate] = 0.36 M; nitrogen atmosphere).

Table 3. Summary of the Main Features and Interpretation of the ^{13}C NMR Spectra of the Malonates Observed in D_2O (pH = 6.8)

compound	T ($^{\circ}\text{C}$)	chemical shift of $\alpha\text{-C}$ (ppm)	multiplicity ^a	degree of exchange
malonate	25	49.17	S	P
		48.66 – 49.17	T	
		48.13 – 49.17	small Q	
methyl-malonate	200	48.88 – 49.91	Q	F
		53.58	S	
		53.73 – 54.25	T	
ethyl-malonate	25	54.37	small S	N
		61.48	S	
	200	62.00 – 62.52	T	P
		62.67	small S	

^a Multiplicity: S = singlet; T = triplet; Q = quintet. Degree of exchange: N = no exchange; P = partial exchange; F = full exchange.

of all three possible species shown in eq 2, indicating full exchange of one of the $\alpha\text{-H}$ atoms with D from the D_2O , and partial exchange of the second $\alpha\text{-H}$. By contrast, the $\alpha\text{-Cs}$ on methyl-malonate and ethyl-malonate produce only singlets, which demonstrates that there is no $\alpha\text{-H}$ exchange for these compounds under these conditions. In D_2O at 200 $^{\circ}\text{C}$, malonate shows full exchange on the $\alpha\text{-C}$, which is observed as a symmetric quintet. Partial exchange occurs for the substituted malonates under these conditions, indicated by the combination of one symmetrical triplet and one small singlet.

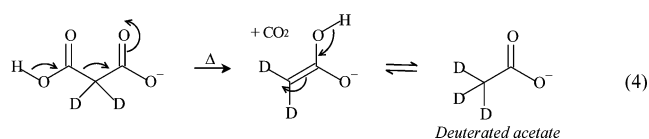
In addition to the deuterium exchange, each of these malonates reacts to form the corresponding monoacid anion with one less carbon atom, that is, acetate, propionate or butyrate, respectively, at 200 $^{\circ}\text{C}$. This is consistent with the results of Belsky and Maiella, who found that malonate undergoes decarboxylation in water at 200 $^{\circ}\text{C}$.^{20,21} Given the exchange-

Table 4. Summary of the Main Features and Interpretation of the ^{13}C NMR Spectra of the Malonates Observed in NaOD Solution

compound	[NaOD] (M)	T ($^{\circ}\text{C}$)	chemical shift of $\alpha\text{-C}$ (ppm)	multiplicity ^a	degree of exchange
malonate	0.244	25	48.89 – 49.93	Q	P
			49.41 – 49.93	T	
			49.41	small S	
methyl-malonate	4.88	200	48.88 – 49.93	Q	F
			49.00 – 50.02	Q	
	0.244	25	54.39	S	N
			53.76 – 54.29	T	
			54.39	small S	
ethyl-malonate	4.88	200	53.39 – 53.89	T	P
			54.00	small S	
	0.244	25	65.86	S	N
			65.35 – 65.74	T	
	4.88	200	65.86	small S	P
			61.71 – 62.16	T	
			62.33	small S	

^a Multiplicity: S = singlet; T = triplet; Q = quintet. Degree of exchange: N = no exchange; P = partial exchange; F = full exchange.

ability of the $\alpha\text{-Hs}$, this results in the formation of deuterated acetate from malonate in D_2O according to eq 4. Deuterated propionate and butyrate may be formed in the same way from the corresponding substituted malonates.



At pH 7, about 7% of malonate is present as the monoacid anion ($\text{p}K_{\text{a}2} = 5.7$), so decarboxylation can proceed according

to eq 4. The observed lack of acetate formation in strongly alkaline solution is consistent with the absence of the monoacid species under those conditions.

Comparison of the NMR spectra shows that the α -Hs on malonate exchange more readily than those on the substituted malonates because (1) the α -Hs exchange at 25 °C in both D₂O and NaOD for malonate but not for the substituted malonates and (2) the extent of H-exchange is greater for malonate than for the malonate derivatives at 200 °C in both D₂O and NaOD.

The different reactivities of the malonates are consistent with the electron-donating nature of the $-\text{CH}_3$ and $-\text{CH}_2\text{CH}_3$ substituent groups causing the α -Hs to be less acidic.²¹

3.2. Analysis of Product of Reaction at 200 °C. Autoclave tests were conducted in NaOH solution at 200 °C under N₂ and O₂ for 90 min at OH[−] concentrations of 0.244, 0.488, 2.44, and 4.88 M. The acid forms of the malonates were used as the starting materials, which were converted directly to the dianions by reaction with OH[−] resulting in final [OH[−]] concentrations of 0.184, 0.428, 2.38, and 4.82 M. The reaction products determined by HPLC analysis are summarized in Table 5.

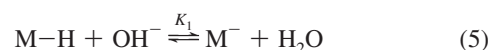
The HPLC results show that no decarboxylation or other reaction occurs for any of the malonates under N₂ at 200 °C over the full range of alkalinities, consistent with the ¹³C NMR results. With the addition of O₂, all of the compounds undergo significant oxidation within 90 min to produce oxalate and formate as the major products.

The formation of oxalate and formate is consistent with the oxidation occurring through an initial reaction of oxygen with a carbanion, as suggested by Tardio et al.¹¹ No decarboxylation products (i.e., acetate from malonate, propionate from methyl-

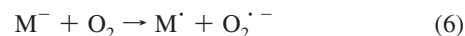
malonate, or butyrate from ethylmalonate) were observed under any of the conditions studied, consistent with the ¹³C NMR observations.

3.3. Kinetic Studies of the WO of Malonates in Alkaline Solution. The kinetics of the degradation of the malonates is approximately first order for all of the conditions studied here. This is illustrated for malonate itself by the linearity of the plots of ln[malonate] vs time especially at the lower [OH[−]] concentrations shown in Figure 2. Similar behavior (but slower rates) was found for the substituted malonates. The dependence of rate constant on [OH[−]] is shown in Figure 3. The [OH[−]] dependence is strongest for malonate and weakest for ethyl-malonate. This reactivity trend is in the same direction as the order of acidity of the α -H atoms observed by ¹³C NMR.

The observed first-order reaction kinetics and linear dependence of the rate constant on [OH[−]] are consistent with the mechanism shown below, in which the first step is an equilibrium between the malonate α -H and OH[−] in solution (M–H represents a malonate or substituted malonate with an α -H attached; note that eq 5 is equivalent to eq 1).



In the presence of O₂, the carbanion intermediate may react to form carbon- and oxygen-based free radicals as shown in eq 6:^{10,11}



Assuming that these radicals have short lifetimes and rapidly react to form other species, the rate of disappearance of M–H may be written as

$$r = k \cdot [\text{M}^-] \cdot [\text{O}_2] \quad (7)$$

If O₂ is in excess and can be considered to be constant, eq 7 can be rewritten as

$$r = k' \cdot K_1 \cdot [\text{M-H}] \cdot [\text{OH}^-] \quad (8)$$

Table 5. Products of Reaction of Malonates under N₂ and O₂ in Caustic Solution^a

compound	products	
	N ₂	O ₂
malonate	no products	oxalate, formate, carbonate
methyl-malonate	no products	oxalate, formate, acetate, carbonate
ethyl-malonate	no products	oxalate, formate, propionate, carbonate

^a Conditions: *T* = 200 °C; *P*_{O₂} = 700 kPa; starting [organic] = 0.03 M; [OH[−]] = 0.184, 0.428, 2.38, and 4.82 M.

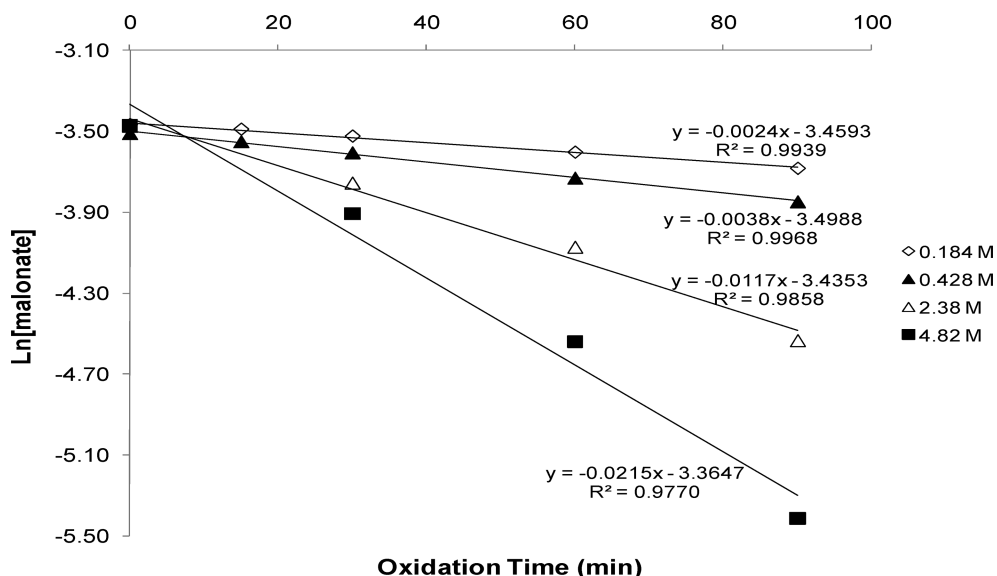


Figure 2. Kinetics of WO of malonate for a range of alkalinities (*T* = 200 °C; *P*_{O₂} = 700 kPa; starting [malonate] = 0.03 M; [OH[−]] = 0.184, 0.428, 2.38, and 4.82 M).

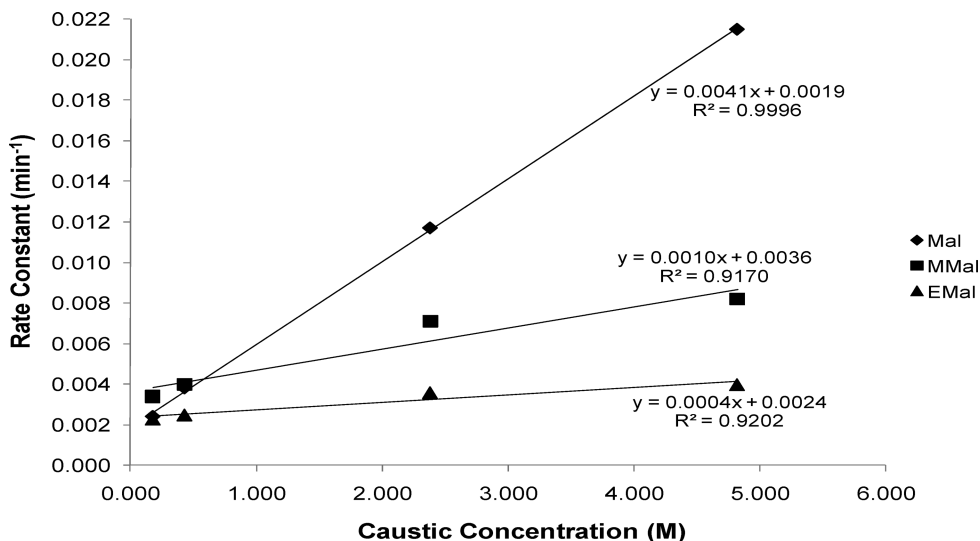


Figure 3. Effect of caustic concentration on WO rate of the malonates ($T = 200\text{ }^{\circ}\text{C}$; $P_{\text{O}_2} = 700\text{ kPa}$; starting [organic] = 0.03 M ; $[\text{OH}^-] = 0.184, 0.428, 2.38, \text{ and } 4.82\text{ M}$. Mal = malonate, MMal = methyl-malonate, EMal = ethyl-malonate).

Provided that $[\text{OH}^-]$ is constant and $\gg [\text{M-H}]$, this results in a pseudo-first-order rate law, the integrated form of which is

$$\ln[\text{M-H}] = -k'' \cdot t + \ln[\text{M-H}]_0 \quad (9)$$

In which k'' is a pseudo-first-order rate constant containing $[\text{OH}^-]$ and $[\text{O}_2]$. The linear $\ln[\text{M-H}]$ vs t plots shown in Figure 2 are consistent with eq 9. In addition, the pseudo-first-order rate constant should be a linear function of $[\text{OH}^-]$:

$$k'' = k' \cdot K_1 \cdot [\text{OH}^-] \quad (10)$$

Hence, if carbanion formation is the first step of the reaction mechanism, the observed rate constants can be expected to have a linear dependence on $[\text{OH}^-]$. As shown in Figure 3, such a linear dependence is clearly shown in the case of malonate. However the dependence is less strong for the substituted malonates. This indicates that oxidation via a carbanion intermediate becomes less favorable as electron-donating groups are added to the α -C, consistent with the conclusions of the ^{13}C NMR work. The reaction rates at neutral pH, and a degree of nonlinearity in the k'' vs $[\text{OH}^-]$ plots for the substituted malonates are indicative of a second (slower) reaction path in parallel with the carbanion-based oxidation mechanism.

4. Conclusion

The first direct evidence of the formation of a carbanion as the first step in the oxidation mechanism of malonate and malonate derivatives in highly alkaline solution is presented. Exchange of α -protons, which is necessary for the formation of carbanions, was observed using ^{13}C NMR. The reaction kinetics and products observed are consistent with carbanion formation as the first step in the reaction.

Carbanion formation is most pronounced in the case of malonate itself. Substituting electron-donating groups at the α -position significantly reduces carbanion formation, resulting in lower reaction rates.

The unusual reactivities of malonate and related compounds during alkaline wet oxidation, and trends in reactivity among structurally related compounds, are explained on the basis of carbanion formation as the first step in the reaction mechanism.

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