

Determination and evaluation of the second-order rate constants for the oxidation of maleic and fumaric acid derivatives with alkaline potassium permanganate

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The second-order rate constants for the oxidation of maleic (*Z*-butenedioic) and fumaric (*E*-butenedioic) acid derivatives by potassium permanganate at pH 13 were determined. These constants varied by a factor of 10^4 . The results suggested that the rates of attack of the permanganate ion on the double bonds were largely governed by steric factors with electrostatic and electronic effects playing only a minor role.

Keywords: butenedioic acid, alkaline permanganate, oxidation, tartaric acid

With dilute alkaline permanganate solutions maleic and fumaric acids give *meso* and racemic tartaric acid respectively, showing that the addition of the two hydroxyl groups is *syn*. The oxidation of these acids (and other alkenes) by potassium permanganate in acidic and neutral conditions has been extensively studied,^{1–4} but there are many fewer data for oxidation under alkaline conditions. In alkaline solution, it is thought that there are two main steps in the reaction, leading to the formation of the *vic* diol.⁵



Earlier work with *E*-but-2-enoic acid⁵ had shown that the rate was first order with respect to permanganate and first order with respect to alkene if the reaction conditions were such that the first step was much slower than the second. In this work, the concentrations of the fumaric acid and maleic acid derivatives were chosen so that this was the case.

The $\text{MnO}_4^{2-}(\text{aq})$ ion was stable to disproportionation if $[\text{OH}^-(\text{aq})]$ was greater than 1 mol dm^{-3} ; at lower concentrations disproportionation took place, although this reaction was very slow at 0.5 mol dm^{-3} (pH ~13), which was the usual concentration used in this work.



High concentrations of $\text{OH}^-(\text{aq})$ ions promoted the following decomposition reaction.



These two competing effects were minimised by choosing $[\text{OH}^-(\text{aq})] = 0.5 \text{ mol dm}^{-3}$. At this concentration, the rate of disproportionation was very slow and could be neglected, while the decomposition rate was slow but measurable. The rate of decomposition was subtracted from the rates of reaction using alkene to make allowance for this accompanying reaction.

Results and discussion

It was established that 1.0 mol of alkene reacted quantitatively with 2.0 mol of permanganate. As the rate of the reaction was followed by the disappearance of the purple MnO_4^- ion, this gave the rate of the reaction in terms of $-\text{d}[\text{MnO}_4^-]/\text{dt}$. The overall stoichiometric equation was $2\text{MnO}_4^-(\text{aq}) + \text{C}=\text{C}=(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow -\text{COHCOH}=(\text{aq}) + 2\text{MnO}_4^{2-}(\text{aq})$.

Other workers who used acid or neutral conditions^{2,4} for the oxidation expressed their rate in terms of $-\text{d}[\text{alkene}]/\text{dt}$. In order to be able to compare rates under different conditions of alkalinity, the rates in terms of $-\text{d}[\text{MnO}_4^-]/\text{dt}$ rates were converted into rates in terms of $-\text{d}[\text{alkene}]/\text{dt}$ by dividing by two.

The pseudo first-order rate constant for the decomposition of permanganate (no alkene) in the presence of 0.5 mol dm^{-3} NaOH (an excess) was $0.0106 \pm 0.0006 \text{ s}^{-1}$. This value was subtracted from the pseudo first-order rate constants in the presence of alkene to give corrected rate constants.

The rates were measured by using a spectrophotometer set to 510 nm . At this wavelength the ratio of the absorbance of $\text{MnO}_4^-(\text{aq})$ to the absorbance of $\text{MnO}_4^{2-}(\text{aq})$ was ~6, a maximum value. The absorbances of $\text{MnO}_4^-(\text{aq})$ and $\text{MnO}_4^{2-}(\text{aq})$ were found to be linear with concentration up to a concentration of $5 \times 10^{-4} \text{ mol dm}^{-3}$ which was the upper concentration limit used; thus as the reaction took place there was a linear relationship between $[\text{MnO}_4^-(\text{aq})]$ and absorbance. In all experiments an excess of the alkene was used. Under these conditions $[\text{MnO}_4^-(\text{aq})]$ decreased exponentially with time showing a pseudo first-order relationship. A curve fitting program was used to find the rate constant for the reaction.

The order with respect to maleate is shown in Table 1.

The constancy of the second-order rate constant confirms that the reaction is first order in maleate.

The order of the reaction with respect to hydroxide ion is shown in Table 2, with [maleate] kept constant at $0.040 \text{ mol dm}^{-3}$.

The ionic strength of the solution was kept at 2.0 mol dm^{-3} with sodium perchlorate. Because the rate of decomposition of the MnO_4^- ion varied with $[\text{OH}^-]$, it was necessary to

Table 1 Rate constants when [maleate] was varied

[Maleate]/ mol dm^{-3}	Corrected pseudo first-order rate constants/ s^{-1}	Second-order rate constant / $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
0.01	0.060 ± 0.001	3.0 ± 0.1
0.015	0.085 ± 0.003	2.9 ± 0.2
0.02	0.117 ± 0.006	2.9 ± 0.3

ionic strength = 0.5 mol dm^{-3} , $[\text{OH}^-] = 0.46\text{--}0.48 \text{ mol dm}^{-3}$, Temperature = 25.0°C .

Table 2 Rate constants when $[\text{OH}^-]$ was varied.

$[\text{OH}^-]$	Corrected pseudo first-order rate constant/ s^{-1}
0.5	0.049
1.0	0.042
1.5	0.044
2.0	0.048

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allow for this by subtracting a different constant from each measured rate constant to give the corrected rate constant. The [maleate] was $0.040 \text{ mol dm}^{-3}$; thus the second-order rate constant was $0.046/(0.040 \times 2) = 0.57 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, a value 1/6th of that determined when the ionic strength was 0.5 mol dm^{-3} . This decrease in rate as the ionic strength was increased was consistent with the attack of a negatively charged MnO_4^- ion at a region of high electron density.

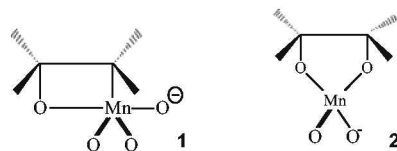
The second-order rate constants for a variety of maleic and fumaric acid derivatives were determined by this method; each determination was repeated several times in order to check for consistency in the results. The results are given in Table 3.

Temperature = 25°C . Ionic strength = 0.50 mol dm^{-3} . The rate was independent of $[\text{OH}^-]$ but was kept within the range $0.4\text{--}0.5 \text{ mol dm}^{-3}$ to minimise side reactions.

The most obvious feature of these results is the slowness of the rates with maleic acid derivatives compared to the equivalent fumaric acid derivatives (about 200 times). It has been suggested that the slow rates of reaction with maleic acid derivatives are due to repulsion between the carboxyl groups as they are forced closer together when the sp^2 hybridised carbon atoms change to sp^3 hybridisation while the intermediate is being formed.¹ In alkaline conditions, this repulsion could be either electrostatic or steric in origin. Such repulsion is absent with fumaric acid and the rates of its derivatives will be considered first.

The rates of reaction with fumaric acid derivatives and with propenoate and *E*-but-2-enoate are very similar. If electronic effects played a significant part in determining the rate, then there would have been a marked difference between the rate with *E*-but-2-enoate and with the rates with fumaric acid derivatives which contain an extra carboxyl group. This suggests that the initial attack showed no strong electrophilic or nucleophilic activity. Such behaviour is consistent with the initial formation of a cyclic organometallic complex **1**, as has been suggested when the reaction was carried out at pH 6.86.³

This complex can either be directly converted into the *vic* diol or could go via the cyclic diester **2**; there is some evidence that more than one oxygen is transferred from the permanganate to the double bond, which would support the formation of the cyclic diester.⁶



The structure of the manganese complex formed is still uncertain although some computational methods suggest,^{7,8} that **2** is preferred over **1**.

The principal difference in these results at pH 13 to those obtained by other workers in acid or neutral conditions^{2,4} is that their measured rates of reaction with maleic acid derivatives were very much faster than those found here. It may be that at a lower pH, some isomerisation to the more stable fumaric derivative had taken place which would have a big effect on the reaction rate. The only other work that has been done at pH 13 was on the ethyl esters in 25% ethanol; this showed that the fumaric ester reacted 50 times as fast as the maleic ester⁹ which is much nearer to the value obtained here (200 times). This big difference in rates emphasised the importance of the repulsion of the carboxyl groups in the transition state of maleic acid derivatives.

The results suggest that the repulsion of the carboxyl groups and the ester groups in the maleic acid derivatives is similar, showing that the repulsion is largely steric, rather than electrostatic, in nature. Substituents adjacent to the double bond slowed down the rate of reaction, irrespective of whether they were electron donating (methyl group) or electron withdrawing (bromine atom). The reduction in rate was most pronounced with the introduction of the large phenyl group (3 times) and the second bromine atom (40 times).

There were several advantages in carrying out the oxidation at pH 13 rather than at a lower pH. The first was that the degree of ionisation of the carboxyl groups was known (approaching 100%); the second was that there was much less likelihood of the oxidation being carried beyond the *vic* diol stage; the third that there was less likelihood of isomerisation of the maleic acid derivatives and fourthly measurement of the absorption of a homogeneous solution was likely to show more consistent results than measurement of the absorption of a solution containing colloidal manganese dioxide.

Experimental

All the chemicals were obtained from Sigma-Aldrich and glass distilled water was used for the solutions. The solutions of maleic acid, bromomaleic acid and dichloromaleic acid were made from the anhydrides which minimised the possibility of fumaric acid impurities. The esters and halogeno acids were made up an hour before the rates were carried out and there was no measurable hydrolysis during that time. There was also no measurable hydrolysis during the few minutes when they were mixed with the sodium hydroxide in the cuvette.

The stoichiometry of the permanganate/fumarate reaction was found by adding 10.0 cm^3 of $0.0020 \text{ mol dm}^{-3}$ potassium permanganate to 10.0 cm^3 of $0.0010 \text{ mol dm}^{-3}$ fumaric acid in 10 cm^3 of 1.0 mol dm^{-3} NaOH. Extra permanganate was then added until the green solution became tinged with purple. This corresponded to a stoichiometry of 2.08 to 1. When allowance was made for the decomposition of permanganate as it was mixed with the sodium hydroxide, this result indicated that the reaction quantitatively gave the diol.

The rate experiments were carried out in a CamSpec M301 spectrophotometer. The reaction vessel was a cuvette (path length 1 cm), kept at 25°C by circulating water from a thermostatically controlled bath. The output was fed to a PicoScope ADC100 analogue to digital converter and hence to a computer. In a typical run, 200 results were recorded, each one being the average of several thousand readings from the spectrophotometer. The resulting results were analysed with a curve fitting program which showed that a good fit (to at least four half-lives) with an exponential plot. With maleic acid derivatives the rate was slow enough for the reactants to be mixed

Table 3 Values for second-order rate constants for some maleic and fumaric acid derivatives

Alkene	Corrected second-order rate constant/ $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
Maleic acid derivatives	
$\text{O}_2\text{CCH}=\text{CHCO}_2^-$	2.9 ± 0.3
$\text{O}_2\text{CCMe}=\text{CHCO}_2^-$	2.6 ± 0.1
$\text{MeO}_2\text{CCH}=\text{CHCO}_2\text{Me}$	1.7 ± 0.05
$\text{O}_2\text{CCBr}=\text{CHCO}_2^-$	1.8 ± 0.2
$\text{O}_2\text{CCPh}=\text{CHCO}_2^-$	0.87 ± 0.03
$\text{O}_2\text{CCBr}=\text{CBrCO}_2^-$	0.070 ± 0.004
$\text{O}_2\text{CCCl}=\text{CClCO}_2^-$	0.16 ± 0.01
Fumaric acid derivatives	
$\text{O}_2\text{CCH}=\text{CHCO}_2^-$	610 ± 30
$\text{O}_2\text{CCMe}=\text{CHCO}_2^-$	480 ± 20
$\text{MeO}_2\text{CCH}=\text{CHCO}_2\text{Me}$	470 ± 20
$\text{MeO}_2\text{CCH}=\text{CHCO}_2^-$	630 ± 50
Others	
$\text{CH}_2=\text{CHCO}_2^-$	560 ± 30
$\text{MeCH}=\text{CHCO}_2^-$	520 ± 20

manually before starting the computer; the initial concentration of the maleic acid derivatives varied between 0.01 and 0.5 mol dm⁻³ which was always in excess of the initial [MnO₄⁻] which was 5 × 10⁻⁴ mol dm⁻³. With fumaric acid derivatives a modified technique was used; 1.0 cm³ of the 0.5 mol dm⁻³ alkali and 1.0 cm³ of 0.0010 mol dm⁻³ alkene were mixed together in the cuvette, the computer started and then 100 µL of 0.0020 mol dm⁻³ MnO₄⁻ rapidly injected just below the surface from a Hamilton syringe, fitted with a ptfe plunger. This resulted in thorough mixing of the MnO₄⁻ ion in less than 0.5 s and allowed determination of rate constants with a half life of ~1 s without having to use a stopped-flow reactor. The initial concentrations of the MnO₄⁻ was 2.0–2.1 × 1.0 × 10⁻⁴ mol dm⁻³ and that of the alkene 2.0–2.1 × 5.0 × 10⁻⁴ mol dm⁻³. This was effectively a 10-fold excess of alkene because the stoichiometry of the reaction was 2 : 1.

Received 16 October 2008; accepted 28 December 2008

Paper 08/0234 doi: 10.3184/030823409X424867

Published online: 6 April 2009

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