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A kinetic study of the oxidation of L-ascorbic acid (vitamin C) in solution using an isothermal microcalorimeter

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Abstract

This paper reports the results of a microcalorimetric study of the oxidation of L-ascorbic acid in solution. The study of the oxidation reaction was carried out under varying conditions of pH, oxygen concentration, ascorbic acid concentration, temperature, addition of ethylenediaminetetraacetic acid (EDTA) and addition of a radical scavenger. From these results it is proposed that ascorbic acid is oxidised in solution by molecular oxygen via an ascorbic acid radical, formed from the interaction of ascorbic acid and free metal in solution. The oxidation product, dehydroascorbic acid, then goes on to form other products by hydrolysis. The change in enthalpy associated with the oxidation reaction was determined as $-130.9\,kJ\,mol^{-1}$ and the reaction has a first order rate constant, with respect to the oxygen concentration, of 1.8×10^{-4} s^{-1}. The rate of oxidation was found to increase with pH, oxygen concentration and concentration of metal in solution.

Keywords: Ascorbic acid; Isothermal microcalorimetry; Kinetic parameters; Mechanism of reaction; Thermodynamic parameters

1. Introduction

The mechanistic and kinetic study of the oxidation of L-ascorbic acid (vitamin C) has been, and still is, the subject of extensive investigation. Previous research into the oxidation of ascorbic acid in solution has relied on techniques such as chromatography [1], spectrophotometry [2,3], NMR [4] and isothermal calorimetry [5]. It is clear that, from the published literature, the rate of the oxidation step is dependent upon the

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pH of the solution [6], the concentration of metal ions in solution [7], the oxygen concentration in solution and the temperature [5]. However there is still some argument about the role that each of these parameters plays in the reaction mechanism, and so confusion in accounts of the pathway for the reaction.

The techniques employed to study the oxidation of ascorbic acid, such as NMR, HPLC, chromatography, spectrophotometry are all selective techniques, that is, they follow the fates of only instrumentally active reactants in the reaction system. Calorimetric techniques, however, are non-discriminating and follow the progress of a reaction by recording the time-dependent heat output for *all* reactions occurring. From this information the order, the rate constant and the change in enthalpy for the reaction can be calculated. By careful experimental design one can also gain insight into the sequence of complex reactions such as the oxidation of ascorbic acid.

Angberg et al. have described an isothermal microcalorimetric investigation of the oxidation of ascorbic acid in solution [5]. The data published suggested that this reaction could serve as a useful calorimetric chemical calibrant in addition to the usual method of the electrical substitution calibration (Digitam software manual). However, upon close study, by the use of the isothermal microcalorimeter, of the reactions they described, it was discovered that more, and important, kinetic and hence mechanistic detail could be obtained.

In order to investigate the reaction thoroughly, and in more detail than was done previously [5], the effects upon the reaction kinetics of variation in pH of the solution; oxygen concentration in solution; metal concentration in solution; concentration of ascorbic acid and temperature, have been systematically explored. Importantly too, the role of water in the system has been investigated, since, for the oxidative step in solution, water only serves as the transport medium, allowing the molecular oxygen in solution to diffuse to the ascorbic acid molecules. An investigation of the oxidation of ascorbic acid in limiting water concentrations, and hence, tending towards the solid state has been made, the results of which will be published separately.

2. Experimental

2.1. Equipment

The microcalorimetric system used to carry out these experiments was an isothermal microcalorimeter (TAM Thermometric, Sweden). This system has previously been described by Suurkuusk and Wadso [8]. The majority of the experiments were performed isothermally at 298.15 K, although a temperature study to determine activation energy was performed at temperatures of 291.15, 293.15, 295.15 and 298.15 K. Glass ampoules were used in most cases, but stainless steel ampoules and the LKB 2277-401/402 titration unit were also used. The ampoules were completely filled to avoid vapour space above the solution. Glass ampoules were sealed using Teflon-coated discs of rubber that were fitted to aluminium caps. Stainless steel ampoules were sealed with a Teflon disc fitted to the inside of the screw top.

The loaded ampoules were allowed to equilibrate for 30 min inside the calorimeter before data collection commenced. The heat flow from the reaction occurring within the ampoule was collected using the dedicated Digitam software [9].

The calorimeter was periodically calibrated using the electrical substitution method (supplying 300 W over a period of 60 min) at least once a week, and before a new batch of experiments was performed.

2.2. Materials

L-ascorbic acid was purchased from Aldrich Chemicals Ltd and was > 99% pure. This was stored in a sealed container in a vacuum desiccator at room temperature. Fresh solutions of ascorbic acid were made up for each experiment. Ascorbic acid solutions were prepared in ethanoic acid buffer at the appropriate pH and oxygen concentration. The usual concentration of ascorbic acid used was 3.5 mmol dm^{-3}, but other concentrations were studied: 4, 10, 15, 25 and 50 mmol dm^{-3}.

Ethanoic acid 0.1 mol dm^{-3} and NaOH 0.1 mol dm^{-3} were made up in freshly distilled and deionised water before each experiment. The pH of the buffer solution was adjusted to the appropriate value using the 0.1 mol dm^{-3} NaOH solution prior to use.

The oxgyen content of the ascorbic acid solution was adjusted by purging the buffer solution with nitrogen gas. The nitrogen gas was first passed through a solution of potassium thiosulphate to remove soluble particles and traces of oxygen and also to saturate the gas with water, and then through a 0.2 μm membrane filter to remove insoluble particles. The oxygen concentration in the buffer solution was monitored using a Griffin oxygen meter, model 40 (Griffin and George, Loughborough, UK). Concentrations of oxygen in solution used in these experiments were 0.075, 0.087, 0.125, 0.137, 0.187 and 0.25 mmol dm^{-3}.

Metal ions were unavoidably introduced into these experiments as contaminants present in trace quantities in the deionised water used. It was assumed that the concentration of the metal contamination remained constant throughout the time period of this work. Experiments in which rates of oxidation were determined were carried out in batches, the buffer solution used being common to all the experiments in the batch. This was to ensure, specifically, that the metal ion concentration remained constant for these experiments. 0.15 mmol dm^{-3} ethylenediaminetetraacetic acid (EDTA supplied by Aldrich 99% pure) was added to buffer solutions to remove free metal ions from solution, when this was appropriate.

The effects of radical quenching was investigated using 7,8-benzoquinoline (Aldrich, 98% pure). 0.5 mmol dm^{-3} benzoquinoline was made up in ethanoic buffer before the addition of ascorbic acid.

2.3. Hydrogen peroxide assay

0.1 mol dm^{-3} ascorbic acid was dissolved in 100 ml ethanoic acid buffer at pH 6 in a conical flask and incubated at 298.15 K. Air saturated with water was passed through the solution for up to 10 h. At hourly intervals 10 ml of the solution was removed. The sample was purged with nitrogen to remove dissolved oxygen and an oxygen probe was introduced into the solution and the sample vessel sealed. A solution of catalase enzyme (Sigma, 0.5 g (5 ml^{-1}) degassed buffer) was then introduced into the ascorbic acid solution. The increase in oxygen in solution, caused when the catalase enzyme

catalysed the decomposition of hydrogen peroxide to oxygen and water, was monitored using the Griffin oxygen meter. The concentration of hydrogen peroxide that had been produced could then be estimated from the concentration of oxygen in the solution.

2.4. Determination of rate constants for the reaction

The first order rate constants were determined by a graphical method, plotting (ln) heat flow versus time. The rate constant was then calculated from the slope of the line. A more precise mathematical method of analysis has recently been developed [10] that allows determination of the rate constant, order and change in enthalpy for the reaction. It has been found that by using this mathematical procedure the calculated rate constant and change in enthalpy was, within experimental error, consistent with the conventional method of analysis.

3. Results

Fig. 1 shows a typical calorimetric power–time curve (dq/dt in watts vs time) for the oxidation of 3.5 mmol dm^{-3} ascorbic acid (in ethanoic buffer pH 3.9 and at an oxygen

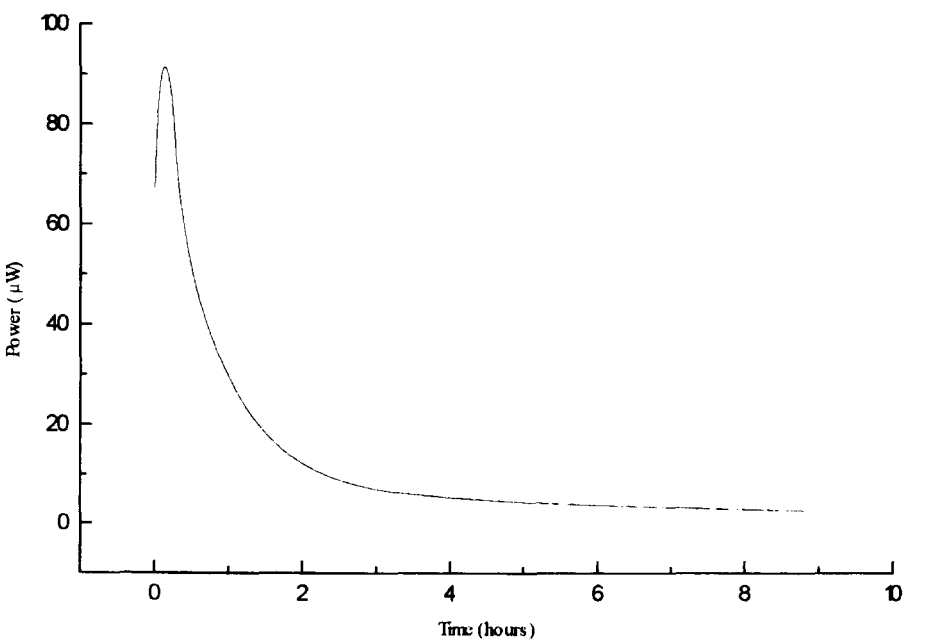


Fig. 1. A typical power–time profile for the oxidation of 3.5 mmol dm^{-3} ascorbic acid in ethanoic acid buffer at pH 6, and an oxygen concentration in solution of 0.25 mmol dm^{-3}. The data for the first 30 min of this power–time curve have been excluded to allow thermal equilibrium to be established in the calorimeter.

concentration of 0.25 mmol dm^{-3}). The features of this curve, noting that for the first 30 min of the reaction the power–time profile cannot be observed (see experimental section), are:

(a) an early time signal whose order cannot be accurately evaluated;
(b) an apparent first order period from 30 min to ca 2.3 h;
(c) another apparent first order period with a different rate constant that occurs from 2.3 h (for solutions at 100% oxygen saturation) up to 90 h.

3.1. *The oxidation of ascorbic acid as a function of the oxygen concentration*

The rate of ascorbic acid oxidation is dependent on the concentration of oxygen in the buffer solution. Fig. 2 and Table 1 show that as the concentration of oxygen in solution is increased from 0.075 to 0.25 mmol dm^{-3}, the rate of oxidation, measured in terms of dq/dt, increases. A plot of ln q vs time gave a linear relationship, indicating that the oxidation reaction was first order with respect to the concentration of oxygen. This first order process continues for a period of up to 3 h, where experimentally it has been shown that all the oxygen in the buffer solution has been consumed (see Fig. 3).

3.2. *The oxidation of ascorbic acid as a function of pH*

Within experimental error, the pH of the buffer solution does not affect the reaction mechanism, hence the rate constants for the reaction remain constant with respect to

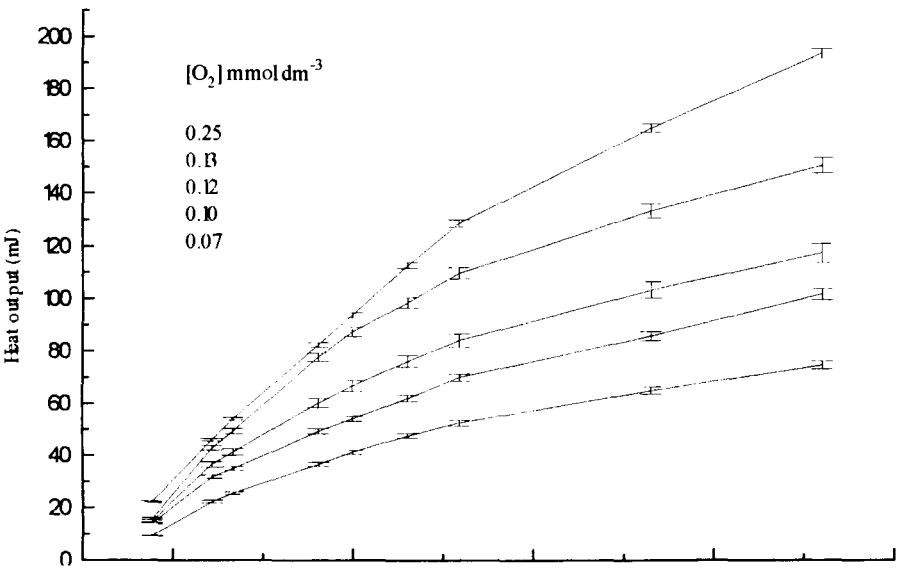


Fig. 2. The increase in rate of oxidation of 3.5 mmol dm^{-3} ascorbic acid in ethanoic acid buffer at pH 5 as a function of oxygen concentration in solution. It shows the rate of oxidation increasing as the concentration of oxygen is increased.

Table 1
The oxidation of 3.5 mmol dm^{-3} ascorbic acid in ethanoic acid buffer (initial oxygen concentration in solution of 0.25 mmol dm^{-3}) as a function of pH of the solution

Solution pH	First order rate constant/s^{-1}	Rate of reaction/dq/dt
1.0	$4.41 \times 10^{-5} (\pm 3.2 \times 10^{-5})$	4.16×10^{-3}
2.0	$5.52 \times 10^{-5} (\pm 8.8 \times 10^{-5})$	1.38×10^{-4}
3.9	$1.22 \times 10^{-4} (\pm 2.2 \times 10^{-5})$	2.26×10^{-2}
5.0	$1.77 \times 10^{-4} (\pm 2.1 \times 10^{-5})$	2.43×10^{-2}
9.5	$2.16 \times 10^{-4} (\pm 6.0 \times 10^{-5})$	1.01×10^{-2}
Average rate constant for 11 experiments	$1.29 \times 10^{-4} \pm 6.06 \times 10^{-5}$	

The oxidation of 3.5 mmol dm^{-3} ascorbic acid in ethanoic acid buffer pH 5, as a function of the initial concentration of oxygen in the buffer solution

Oxygen in solution/(mmol dm^{-3})	First order rate constant/s^{-1}	Rate of reaction/dq/dt
0.08	$1.95 \times 10^{-4} (\pm 2.0 \times 10^{-5})$	
0.09	$8.83 \times 10^{-5} (\pm 8.2 \times 10^{-5})$	2.40×10^{-3}
0.13	$1.97 \times 10^{-4} (\pm 3.5 \times 10^{-5})$	
0.14	$1.96 \times 10^{-4} (\pm 5.8 \times 10^{-5})$	1.98×10^{-2}
0.19	$3.19 \times 10^{-4} (\pm 8.5 \times 10^{-5})$	2.15×10^{-1}
0.24	$1.08 \times 10^{-4} (\pm 7.6 \times 10^{-5})$	3.36×10^{-2}
0.25	$1.57 \times 10^{-4} (\pm 1.3 \times 10^{-5})$	
Average value for 16 experiments	$1.82 \times 10^{-4} \pm 6.04 \times 10^{-5}$	

pH (see Table 1). The rate of the reaction however tends to increase with increasing pH (see Fig. 4). From a pH of 0.6 to pH 4, the results indicate that there is a large increase in the rate of oxidation. Above pH 4, the rate increases steadily to a maximum at pH 9.

3.3. The oxidation of ascorbic acid as a function of the ascorbic acid concentration

The rate of ascorbic acid oxidation is independent of the concentration of ascorbic acid in solution. Table 2 shows that, within experimental error, increasing the ascorbic acid concentration from 0.25 to 50 mmol dm^{-3} has no effect on the reaction rate.

3.4. The effect of EDTA *on the oxidation of ascorbic acid*

The oxidation of ascorbic acid was found to require trace quantities of transition metals to initiate the reaction. It was found (Pfizer Limited, Central Research, Sand-

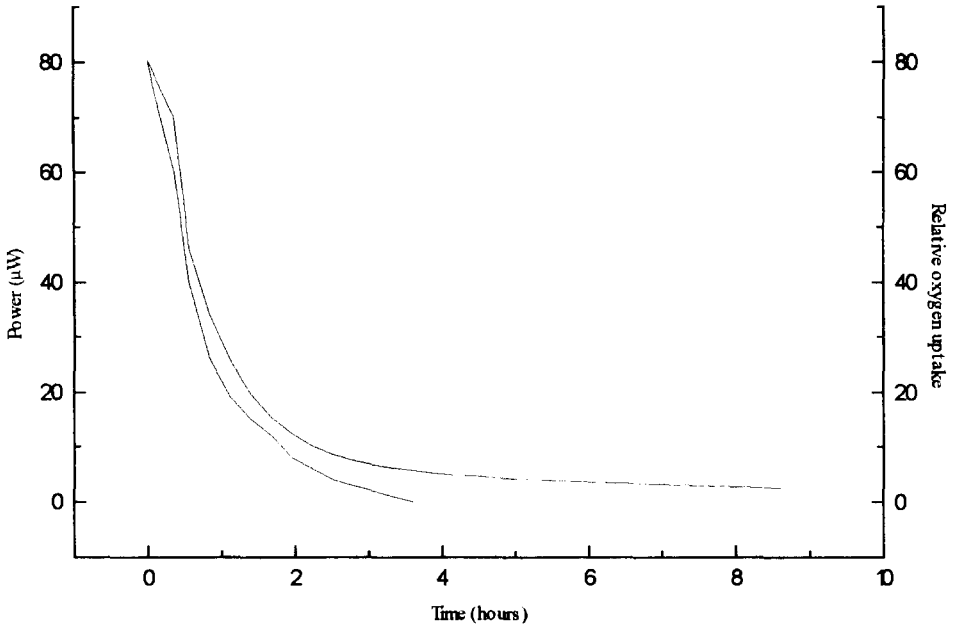


Fig. 3. The time when there is a change in reaction rate constant for the oxidation of 3.5 mmol dm^{-3} ascorbic acid in ethanoic acid buffer at pH 5 and an oxygen concentration in solution of 0.25 mmol dm^{-3}, (upper curve) is shown to coincide with the time when the concentration of oxygen in solution has been essentially totally depleted (lower curve).

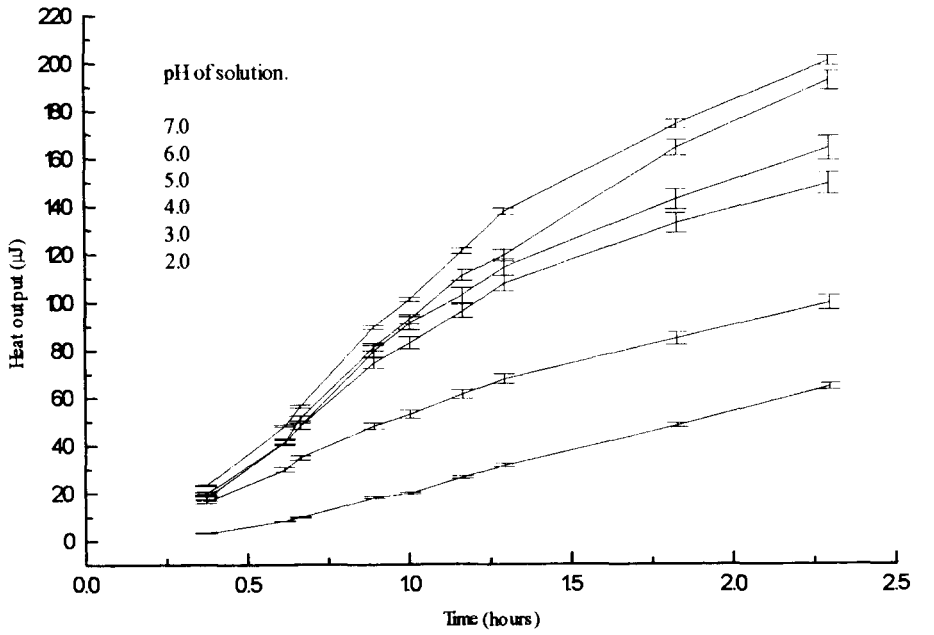


Fig. 4. The increase in rate of oxidation of 3.5 mmol dm^{-3} ascorbic acid in ethanoic acid buffer at an oxygen concentration of 0.25 mmol dm^{-3}. It shows the rate of oxidation increases with an increase in the pH of the solution.

Table 2
The oxidation of ascorbic acid in ethanoic acid buffer, pH 5 and at an oxygen concentration in solution of 0.25 mmol dm^{-3} as a function of the initial concentration of ascorbic acid in solution

Ascorbic acid concentration (mmol dm^{-3})	First order rate constant/s^{-1}	Rate of reaction/dq/dt
0.25	$1.37 \times 10^{-4} (\pm 3.2 \times 10^{-5})$	1.56×10^{-2}
1.00	$1.56 \times 10^{-4} (\pm 4.3 \times 10^{-5})$	1.66×10^{-2}
3.50	$1.44 \times 10^{-4} (\pm 5.5 \times 10^{-5})$	2.58×10^{-2}
4.00	$1.50 \times 10^{-4} (\pm 3.4 \times 10^{-5})$	1.86×10^{-2}
10.00	$1.43 \times 10^{-4} (\pm 3.1 \times 10^{-5})$	1.70×10^{-2}
15.00	$1.33 \times 10^{-4} (\pm 1.1 \times 10^{-5})$	1.56×10^{-2}
25.00	$5.00 \times 10^{-4} (\pm 3.2 \times 10^{-5})$	3.97×10^{-2}
50.00	$1.63 \times 10^{-4} (\pm 2.2 \times 10^{-5})$	1.86×10^{-2}
Average rate constant for 11 experiments	$2.18 \times 10^{-4} \pm (8.8 \times 10^{-5})$	

wich, Kent) that the deionised water supply contained significant quantities of metals, especially copper, in solution. Fig. 5 shows that by incubating the buffer solution with 0.15 mmol dm^{-3} EDTA for 30 min, the oxidation reaction was greatly reduced.

3.5. *The effect of benzoquinoline on the oxidation of ascorbic acid*

Incubating a solution of ascorbic acid with the addition of 0.2 mmol dm^{-3} benzoquinoline for 30 min also reduced the rate of the oxidation of ascorbic acid, see Fig. 5.

3.6. *The calculation of the change in enthalpy for the oxidation of ascorbic acid*

The change in enthalpy for the oxidation reaction was calculated for different oxygen concentrations. This was done by evaluation of the area under the power–time curve for the oxidation step. Assuming all of the oxygen had reacted (see Fig. 3) the area under the power–time curve represents the total heat output for the reaction, q_T.

For a first order reaction, the total heat output from the reaction, $(q_T) = A.H$, where A = the initial number of moles of oxygen in solution. Therefore the change in enthalpy $H = q_T/A$.

A recent and more precise mathematical procedure was used to calculate the H [10]. This method gave values for H that agreed with the values from the above method of calculation.

Table 3 shows the change in enthalpy for the oxidation step as a function of oxygen concentration in solution. This was found to be in agreement with the theoretical change in enthalpy, calculated from the appropriate gas phase bond enthalpies [11]. The titration unit was used (see experimental section) to determine the heat output (q) for the oxidation reaction using an unlimited supply of oxygen. The change in enthalpy was then calculated, assuming that all the ascorbic acid had oxidised.

Table 3
The calculated and theoretical changes in enthalpy for the oxidation of ascorbic acid in solution (3.5 mmol dm^{-3}, pH 5)

Initial oxygen conc. in solution/(mmol dm^{-3})	Total heat output for the reaction (q_T)/mJ	Exp. change in enthalpy/(kJ mol^{-1})	Theoret. change in enthalpy/(kJ mol^{-1})
0.25	88.8	111	128.75
0.14	68.0	155	128.75
0.13	52.0	130	128.75
0.1	40.9	127	128.75
0.08	26.9	112	128.75
With unlimited oxygen supply	1980	150	128.75

3.7. *The calculation of activation energy for the oxidation of ascorbic acid*

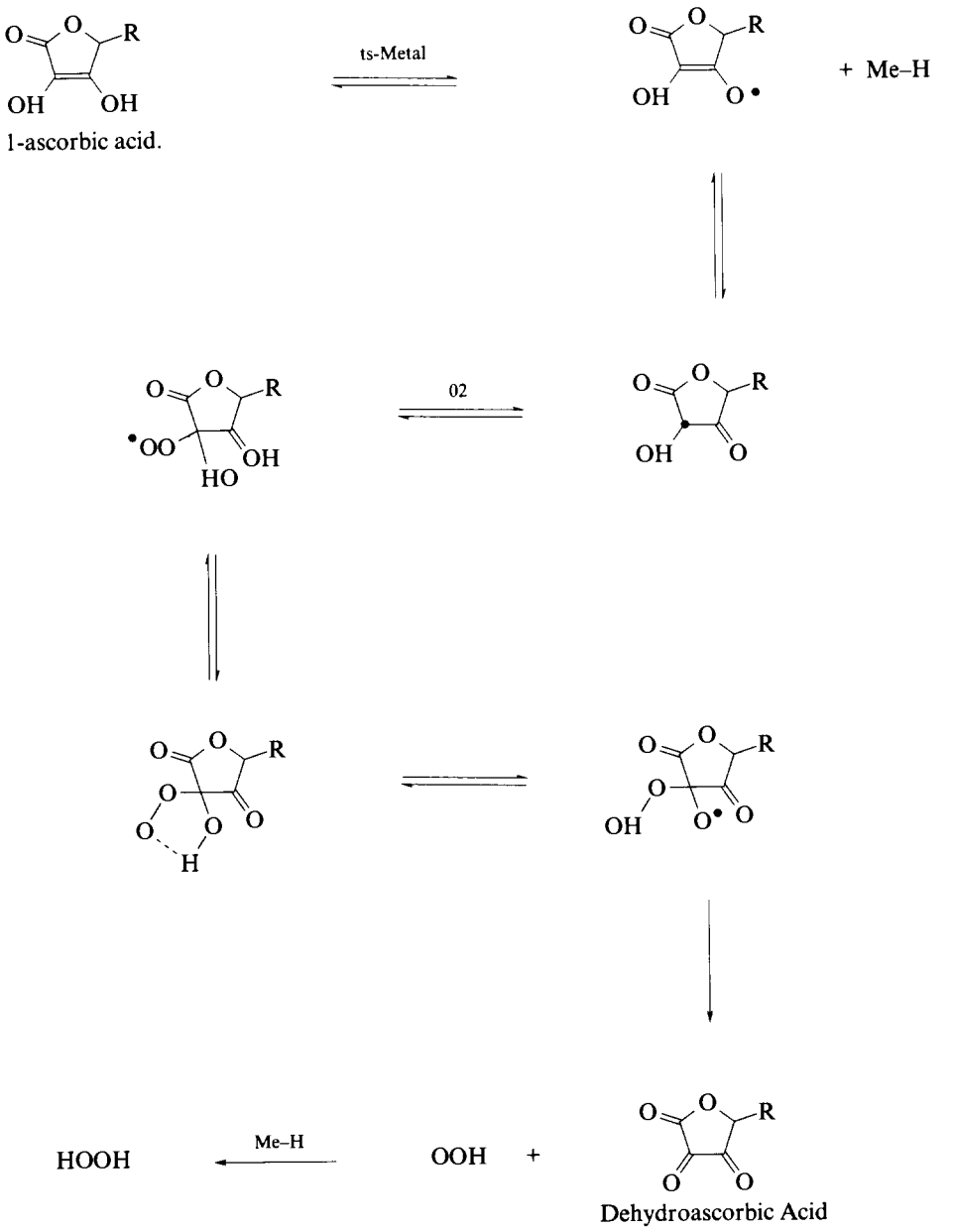
A temperature study of the oxidation of ascorbic acid under identical conditions (3.5 mmol dm^{-3}, in ethanoic acid buffer pH 3.9, with an oxygen concentration of 2.5 mmol dm^{-3}) was carried out at 291.15, 293.15, 295.15 and 298.15 K. From an Arrhenius plot of ln k vs 1/K, a straight line (linear regression coefficient of 0.99) was obtained. From this an activation energy of 41 kJ mol^{-1} $\pm$ 2 kJ mol^{-1} was calculated.

3.8. *The hydrolysis of dehydroascorbic acid*

The oxidation of ascorbic acid yields dehydroascorbic acid. The lactone ring of the dehydroascorbic acid is then hydrolysed to products, the nature of which depends on the reaction conditions, e.g. pH [12]. This step was found to be pseudo first order with respect to the concentration of dehydroascorbic acid and independent of water concentration as this is in excess at all times.

4. Discussion

The oxidation of ascorbic acid has been the subject of extensive investigation using various techniques to monitor the formation of product or the depletion of ascorbic acid. Until now, no other published work has proposed an internally consistent and complete account of a mechanism for the oxidation of ascorbic acid in solution. Our experimental data and reaction scheme (see Scheme 1) was found to be consistent with the conclusions from previously published data. The study of the oxidation of ascorbic acid using an isothermal microcalorimeter has already been attempted by Angberg et al. [5]. On using the experimental procedure outlined by Angberg as a means for a chemical calibration experiment for our calorimeter, it was found that the conclusions that were drawn from Angberg's results, although consistent with the experimental data, were not as reported, solely due to the process of oxidation, but related to



Scheme 1. A mechanism for the oxidation of L-ascorbic acid.

a physical process of oxygen diffusion through the solution. This is because of the way in which the reported experiments were constructed: The experimental procedure adopted allowed a considerable headspace above the ascorbic acid solution in the sealed ampoules. The kinetics therefore appear, for the process being observed, to be

limited by the rate at which oxygen could diffuse from a stagnant headspace into solution. For the experimental procedure that we adopted the ampoules were completely filled so that the headspace was negligible and thus the oxidation process was limited solely by the oxygen present in solution. The oxygen concentration was then controlled (see experimental section) to allow study of the effects of variation of oxygen concentration on the rates of oxidation.

We have determined that metals in solution are important for the oxidation reaction. The use of EDTA, although producing a modest change in the ionic strength of the buffer solution, has a profound effect on the rate of oxidation which far outweighs the effect of changing ionic strength, see Fig. 5. EDTA is a very efficient chelating agent and the addition of EDTA essentially removes free metal from solution and so inhibits the oxidation process. This is consistent with the conclusions of Angberg et al. [5]. We suggest that the role of metals in solution is to initiate the oxidation reaction by abstraction of a hydrogen atom from the ascorbic acid forming the ascorbic acid radical (Scheme 1). This initial step is comparatively fast and, due to the operational procedure of the calorimeter, cannot be accurately evaluated using the microcalorimetric procedures adopted in this work (see experimental section).

El-Zaru et al. demonstrated that ascorbic acid radicals are formed from the reaction of ascorbic acid and transition metal complexes [13]. Cabelli et al. also studied radical

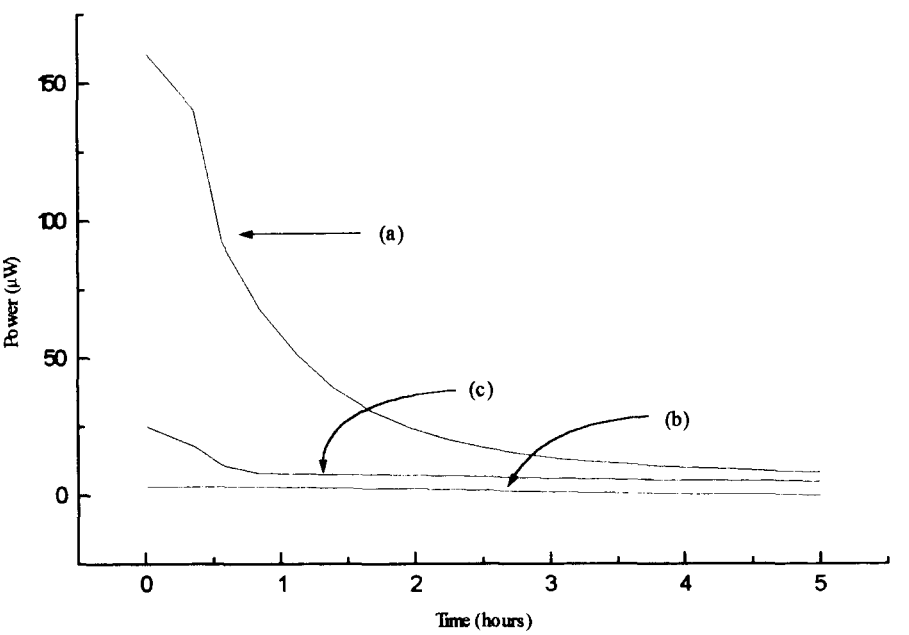


Fig. 5. A power–time curve for the oxidation of 3.5 mmol dm^{-3} ascorbic acid in ethanoic acid buffer at pH 4 and an oxygen concentration in solution of 0.25 mmol dm^{-3}. (a) The power–time curves (b) and (c) show the effects on the oxidation when 0.15 mmol dm^{-3} EDTA or 0.5 mmol dm^{-3} benzoquinoline, respectively, is added.

formation and demonstrated that the formation of the ascorbic acid radical is an important step that precedes oxidation [14]. This is consistent with our mechanistic intermediate (Scheme 1). We confirmed that the formation of radicals is an important process that precedes oxidation by the addition of benzoquinoline to the reaction solution. It was found that benzoquinoline scavenges the ascorbic acid radicals and so inhibits the oxidation process.

Hughes et al. published results demonstrating that the rate of oxidation was dependent on the pH of the solution [6].

Our results (see Table 1) also indicate that on increasing pH the rate of oxidation increases.

Hughes et al. also derived from spectrophotometric studies at different temperatures, an activation energy for the oxidation process of 50 kJ mol^{-1} [6]. In our temperature study (see experimental section) we determined an activation energy for this reaction to be 42 kJ mol^{-1}. This activation energy is consistent with that for the diffusion of molecular oxygen through water [15].

The change in enthalpy for the oxidation reaction was determined (see experimental section). This experimental change in enthalpy is due to the sum of all reactions occurring within the time period of the oxidation step. However, assuming that the oxidation of ascorbic acid radicals has the most important contribution to the change in enthalpy within this time period, the theoretical change in enthalpy (calculated from Scheme 1 via gas phase bond enthalpies) was found to be consistent with the experimental change in enthalpy (see Table 3). The oxidation of ascorbic acid results in the formation of dehydroascorbic acid. Kurimura et al. reported the detection of quantities of hydrogen peroxide in the end products of the reaction between ascorbic acid and ruthenium ion complexes [2]. We also found that hydrogen peroxide was being produced during the oxidation of ascorbic acid and an attempt was made to quantify the amounts (see experimental section).

Considering all the above findings, we conclude that overall the oxidation process has an apparent first order dependency with respect to the concentration of oxygen. We deduce from our results that the formation of ascorbic acid radicals is dependent on the concentration of metal in solution. The oxidation of ascorbic acid radicals is thus pseudo first order with respect to the concentration of oxygen in solution and zero order with respect to the ascorbic acid radicals (as the concentration of ascorbic acid radicals remains constant). This is presumably because the kinetics of the radical formation reaction are much faster than those of the oxidation process. As soon as hydrogen peroxide radicals are formed, they react with the metal hydrides, abstracting a hydrogen atom leaving the metal free to react with another molecule of ascorbic acid. Peroxide radicals may also extract hydrogen atoms from ascorbic acid in a radical chain.

After a time period (about 2.3 h for solutions at 100% oxygen saturation) all the oxygen in solution has been consumed (see results section). The subsequent slow reaction is assumed to be the hydrolysis of dehydroascorbic acid. This is a pseudo first order reaction with respect to the concentration of dehydroascorbic acid because in an aqueous solution, the relative concentration of water is always in excess.

The role of water in the oxidation process has also been studied. We decreased the amount of water in the ampoules to an extent that essentially we were studying solid

state oxidation, with water playing the role of a medium for the movement of gases to and products away from the surface of the ascorbic acid. The results of this study will be published at a later date.

5. Conclusion

The oxidation of ascorbic acid in solution is a more complex reaction than it first appears. By using a careful experimental procedure, and analysis of the power–time curve, it was possible to obtain more detailed mechanistic information about the reactions than other studies of this kind have previously produced [5]. We found that there were three individual parts to the power–time curve, each with a different rate constant.

The first part was the initiation step where metals in solution cause the formation of ascorbic acid radicals. This was followed by the oxidation of ascorbic acid radicals to dehydroascorbic acid. The final part was the slow hydrolysis of dehydroascorbic acid. From our experimental results of the study of the rate of ascorbic acid oxidation with variation in temperature, pH, oxygen concentration, ascorbic acid concentration, addition of EDTA chelating agent and addition of benzoquinoline radical scavenger, we have proposed a reaction pathway (see Scheme 1). This reaction pathway is initiated by the formation of ascorbic acid radicals by the abstraction of a hydrogen atom by metals in solution. The ascorbic acid radical then reacts with molecular oxygen and a process of rearrangement with the elimination of hydrogen peroxide radical forms the more stable dehydroascorbic acid. There is a second possible pathway for this reaction where the metal hydride reacts with molecular oxygen and then the metal hydroxide reacts with ascorbic acid resulting in the same product. The dehydroascorbic acid undergoes slow hydrolysis to various products depending on the reaction conditions such as pH. This reaction pathway has also been shown to be consistent with the findings from independent research.

The change in enthalpy for the oxidation step was determined as 131 kJ mol^{-1} $\pm$ 18 kJ mol^{-1}. This was found to be consistent with the theoretical change in enthalpy calculated from gas phase bond energies from Scheme 1. The activation energy for the oxidation process was determined as 42 kJ mol^{-1}, consistent with the activation energy for the diffusion of oxygen through water at 298.15 K. The kinetics for the oxidation step were found to be first order with respect to the oxygen concentration. The first order rate constant was determined as $1.824 \times 10^{-4}\ s^{-1} \pm 6.04 \times 10^{-5}$. This is consistent with the time that it took for all the oxygen to be consumed. The kinetics for the hydrolysis of dehydroascorbic acid were found to have an apparent first order with a rate constant of $3 \times 10^{-6}\ s^{-1} \pm 2 \times 10^{-6}$.

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