

Study of the Complexes of the Ascorbic Acid-Iron(III) System

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Ascorbic Acid-Iron(III) System

The blue complex of L-ascorbic acid with Fe^{3+} ions has been obtained and isolated. Various spectrographic and analytical techniques have been used to study this complex. A kinetic study was also carried out on L-ascorbic acid oxidation by Fe^{3+} by means of the stopped flow technique for rapid processes.

Introduction

The structure of ascorbic acid has been widely studied [1] and was found to correspond to the enol of 3-keto-D-gulofuranolactone, *i.e.* it has a lactone structure with an endiol group.

Biologically, the two acids, and in particular L-ascorbic acid, are used to counteract scurvy. In pharmaceuticals they are widely used [2, 3] and fulfill the function of an anti oxidizing agent in the food industry.

Dehydroascorbic acid is formed through the oxidation of ascorbic acid. This reaction has been studied using various oxidizing ions such as Co(III)^4 , Cu(II) [5, 6], $\text{Ti(III)-H}_2\text{O}_2$ [7] and Fe(III) [8]. Recently, the same reaction has been studied with electrochemical techniques [9]. Likewise, a kinetic study has been carried out on the hydrolysis products of dehydroascorbic acid [10].

Laurence and Ellis [11] detected, with the stopped flow technique, a blue intermediate in the oxidation of L-ascorbic acids by Fe^{3+} ions. They obtained the absorption spectrum in the visible range of this intermediate with a point by point measurement of maximum values of optical densities (absorbances) at various wavelengths. At around $\lambda = 560 \text{ nm}$ they found a wide band of maximum absorption and assumed that the intermediate was the ferric ascorbate complex AHFe^{++} . These authors worked with a highly acid medium ($\text{H}^+ = 0.2 \text{ M}$, *i.e.* $\text{pH} = 0.7$), and therefore the blue intermediate was obtained in solution for only a short period of time.

In the present paper, with a higher pH than that used by Laurence and Ellis the blue complex was

obtained in a relatively stable form in aqueous medium. It was, in fact, possible to precipitate the intermediate as a crystalline solid in ethanol.

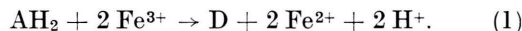
Experimental

Obtention of the blue complex

2.5 g of sodium propionate and 1 g of L-ascorbic acid are added to 50 ml of distilled water. The resulting solution is added to 200 ml of ethanol. To this solution, 0.25 g of ferric chloride is added and the complex precipitates. The precipitate is filtered and washed with ethanol. 0.65 g of the complex were obtained and were stored in vacuum.

Analytical and spectroscopic studies

The overall oxidation reaction of L-ascorbic acid (AH_2) with Fe^{3+} ions, producing dehydroascorbic acid D, is [12]

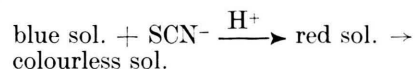


The disappearance of Fe^{3+} and the appearance of Fe^{2+} can be observed by adding L-ascorbic acid to a blue solution of Fe^{3+} in the presence of *o*-phenanthroline. The blue colour immediately changes to red, due to the Fe^{2+} formed.

In order to achieve a more complete understanding of the L-ascorbic acid oxidation by Fe^{3+} ions, we have carried out various experiments.

A solution of the blue complex was prepared by adding ferric chloride and excess of L-ascorbic acid to a sodium propionate solution.

a) Potassium thiocyanate and a few drops of HCl were added to the blue solution and this changed to red (due to the presence of Fe^{3+}), immediately losing colour (because of the reduction of Fe^{3+} to Fe^{2+}):



b) at room temperature, the blue solution gradually loses colour, becoming colourless after more

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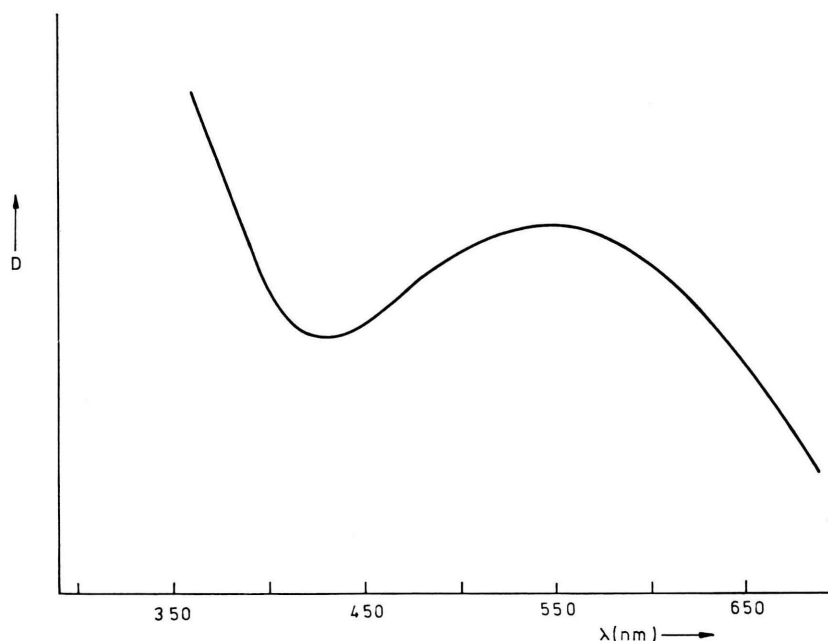


Fig. 1. Absorption spectrum of the blue compound obtained from AH_2 and Fe^{3+} .

than an hour. This process accelerates with increase in temperature. If *o*-phenanthroline is added to the colourless solution this once again goes red due to the presence of Fe^{2+} .

From these observations it is deduced that:

- 1) In the loss of colour, Fe^{3+} is reduced to Fe^{2+} .
- 2) In a propionate medium, the ferric complex is fairly stable at room temperature.
- 3) In an acid medium, the complex immediately decomposes, the Fe^{3+} is freed and almost instantaneously reduces to Fe^{2+} .

According to Laurence and Ellis [11], the blue complex is formed in an acid medium in two rapid stages prior to the reduction of Fe^{3+} .

Visible spectroscopy

Fig. 1 gives the absorption spectrum of the blue complex, using a DB-GT Beckman Spectrometer and a 1006 Recorder. A wide maximum absorption band is observed at $\lambda_{\text{max}} = 540\text{--}550\text{ nm}$ and a minimum at $\lambda_{\text{min}} = 430\text{ nm}$.

Mössbauer spectroscopy

Fig. 2 gives the Mössbauer spectrum for the solid blue complex at room temperature. The chemical shift is $\delta = 0.51 \pm 0.01\text{ mm/s}$ referred to potassium ferrocyanide, and the quadrupolar split is $\Delta E_{\text{q}} = 0.76 \pm 0.02\text{ mm/s}$.

Fig. 3 gives the spectrum at liquid nitrogen temperature, with $\delta = 0.44 \pm 0.01\text{ mm/s}$ and $\Delta E_{\text{q}} = 0.67 \pm 0.02\text{ mm/s}$.

A Co^{54} source diffused in 25 mCiPd was used together with an Inter technique Didac 800 Multichannel Analyser, a Kr- CO_2 Renter-Stockes Proportional Counter and an Elscint-Am 30 Spectrometer.

In both spectra δ and ΔE_{q} are small, which is typical of high spin Fe(III) compounds. The very little variation in the quadrupolar split with temperature also confirms this, as for these compounds $q_{\text{val}} = 0$, with only q_{lattice} existing, independent of the temperature.

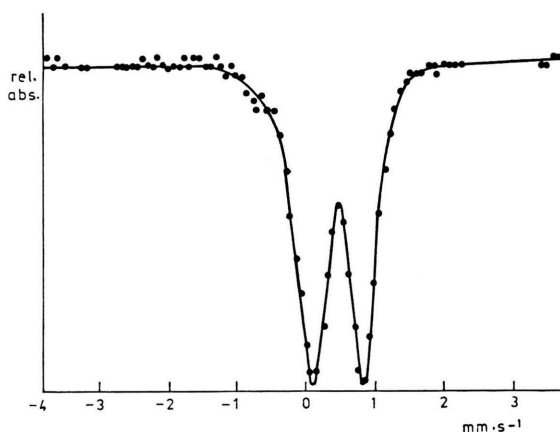


Fig. 2. Mössbauer spectrum of the solid blue compound at room temperature ($\delta = 0.51\text{ mm} \cdot \text{s}^{-1}$, $\Delta E_{\text{q}} = 0.76\text{ mm} \cdot \text{s}^{-1}$).

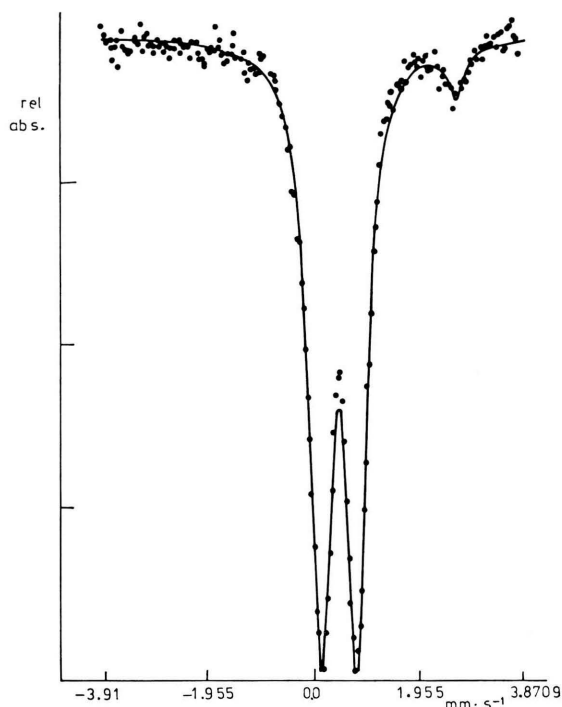


Fig. 3. Mössbauer spectrum of the solid blue compound at N_2 liquid temperature ($\delta = 0.44$ mm/seg, $\Delta E_Q = 0.67$ mm/seg).

Nuclear magnetic resonance

NMR- ^{13}C spectra were recorded with proton noise decoupling by using a Varian Spectrometer, model XL-100.

In the acid pH zone (≈ 2), with addition of $FeCl_3$ to the ascorbic acid solution, no formation of complex is observed as there is no increase in line width nor any variation in the chemical shifts. Around $pH \approx 6$, with addition of $FeCl_3$ to the ascorbic acid solution, an increase in line width is observed, in particular those corresponding to carbons 2, 3 and 4 (Fig. 4). There is also a shift to low field of 0.4, 1.0 and 0.5 ppm. Similar effects are also observed at $pH \approx 9$ with shifts of 0.4, 0.6 and 1.2, respectively.

The above data show that the central $Fe(III)$ ion basically affects the ring (see L-ascorbic acid formula in Fig. 4) but does not affect the molecular segment $-CHOH-CH_2OH$. Furthermore, and as the L-ascorbic acid in a propionate medium is fundamentally in its anionic state AH^- , it follows that the complex formed is a chelate between the AH^- anion and the Fe^{3+} cation, as seen in Fig. 4. There is, effectively, a chemical shift of C_3 to low field by 20.5 ppm with the change from acid to neutral medium, as corresponds to the deprotonation of the $HO-C_3$ group.

Quantitative Analysis of the Blue Complex

The quantitative analysis of the solid blue complex was carried out in the Department of Edaphology of this Faculty and the Section of Analysis, Department of Organic Chemistry, of the Consejo Superior de Investigaciones Científicas, Madrid. The following average weight percentage as were obtained: Fe - 13.2, C - 33.1, H - 3.3.

These results show that the blue complex is primarily composed of a bichelate of ascorbic acid with an Fe cation of the $(AH)_2FeOH$ type. The theoretical weight percentages of this bichelate, with the formula $C_{12}H_{15}O_{13}Fe$, are: Fe - 13.2, C - 34.0, H - 3.5, whilst the theoretical values for the monochelate $(AH)Fe(OH)_2$ would be: Fe - 21.1, C - 27.2, H - 3.4 and those for the trichelate $(AH)_3Fe$: Fe - 9.6, C - 37.2, H - 3.6.

Solubility of the blue complex

In the various solubility tests made on different solvents, it was demonstrated that the complex is

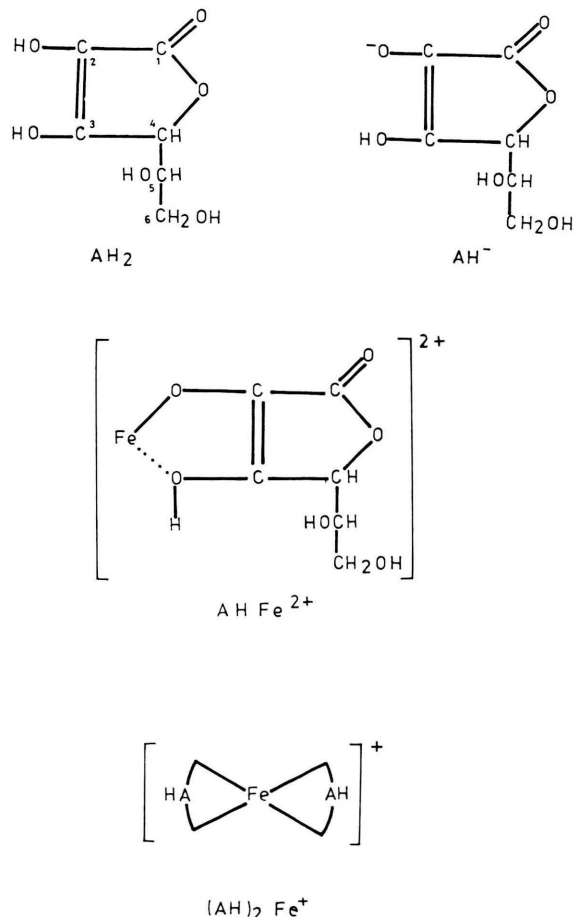


Fig. 4. Scheme of species involved in the complexation of L-ascorbic acid with Fe^{3+} ion.

completely insoluble in acetone, ether, benzene, chloroform, ethanol, carbon tetrachloride and is very soluble in water giving rise to the typical blue colour. The high solubility in water is probably due to the dissociation of the ferric ascorbate complex according to the equilibrium:



All products used were from Merck p.a.

Kinetics

The kinetic studies, by means of the stopped flow technique, of the L-ascorbic acid oxidation by Fe^{3+}

ions in acid medium (HClO_4) and $I = 3 \text{ M}$, give rise to the following rate equation:

$$v = - \frac{d(\text{Fe}^{3+})}{dt} = k (\text{Fe}^{3+})(\text{AH}_2)(\text{H}^+)^{-1} \quad (3)$$

The value we obtained at 20°C was: $k = 3.6 \times 10^2 \text{ s}^{-1}$. Further studies are at present being carried out.

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