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On the organic/inorganic mechanism of the oxidation of uric acid by means of potassium permanganate in alkaline medium

F. Sánchez-Viesca * and Luz Clarita

Department of Organic Chemistry, Faculty of Chemistry, National Autonomous University of Mexico, Mexico City (CDMX), Mexico

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Abstract

The chemical deportment of potassium permanganate at mechanistic level was cleared. Due to the marked difference existing in the electronegativities of manganese and oxygen, the permanganate anion act as having polarised one Mn=O double bond. This explains the electron receptivity of the manganese atom, as well as, the capture of a potassium cation by the negative oxygen, giving a molecule of potassium manganate and an oxidation step in the electron donor organic molecule, or oxidation of an inorganic ion. This is in accordance with the $3d^1$ electronic configuration of potassium manganate. Uric acid in alkaline medium (KOH) forms the potassium imidate, derived from the imido group present in this heterocycle. After reaction with $KMnO_4$ as above indicated, a free radical at nitrogen remains and couples with an electron of the C=C double bond. A cyclic ureido and an aziridinone are formed. Hydrolysis of the tensioned lactam gives acetylene di-urea with a carboxylate between the two rings. The radical at C-4 is removed by permanganate anion at any stage of the process. The carbonium ion thus formed is neutralised by water giving a double carbinolamide who is hydrolysed in acidic medium to 5-ureido-hydantoin.

Keywords: Cation capture; Electronegativity; Electron receptivity; Manganate anion; Polarization; Potassium permanganate

1. Introduction

Uric acid is a very interesting heterocyclic compound, both from the biomedical and organic chemistry points of view. It is an analyte who is estimated analytically as a routine procedure due to its importance as reference to the well function of kidneys, and also as indicator of balanced nutrition. Hyperuricemia leads to gout and renal calculi.

From the chemical point of view, uric acid has attracted attention of chemists since the 19th century. Many colour tests have been developed in order to detect this compound and also many reactions have been carried out, especially oxidations, both in acid and in alkaline mediums. Although the chemical structures of the final products are known, the reaction mechanism of each step of the route leading to the end product has not been described until very recently, [1-3].

In this communication the mechanism of uric acid oxidation by means of potassium permanganate in alkaline medium is given. This article is a follow-up of our studies on reaction mechanism, [4-8].

* Corresponding author: F. Sánchez-Viesca

2. Study Method and Process

This is an Organic Chemistry Theoretical Study. It is based on the chemical deportment of reagent and substrate. All is in accordance with the reaction medium and the catalyst present. The several steps leading to the final product are fully commented and the electron flow is also given.

3. Antecedents

Oxidation with potassium permanganate implies reduction of the reagent to potassium manganate, with Mn(VI). In order to understand how occurs this transformation let's see the electronic configuration of both anions:

MnO_4^- Mn(VII), [Ar] 3d°, 4s° MnO_4^{2-} Mn(VI), [Ar] $3d^1$, 4s°

In $KMnO_4$ (purple) In K_2MnO_4 (green)

As it can be seen, the reduced anion has gained one electron (free radical) and one potassium ion, [9, 10]. Obviously, the free radical comes from the organic substrate, as we will see in the next section.

Potassium permanganate has been used widely as oxidiser of many types of compounds, [11]. However, the mechanisms are missing. Books on mechanisms of oxidation of organic compounds contemplate a few examples with permanganate, [12].

4. Discussion

In the alkaline oxidation of uric acid, the first interaction is an acid-base reaction. A hydroxyl ion from KOH reacts with the acidic proton of the imido group present in the organic molecule. A water molecule and the potassium imidate are formed. The last anion transfers an electron to the intermediate coming from the polarization of one Mn=O double bond in $KMnO_4$, that is, to the Mn**+** formed in the polarization. Now the nitrogen atom is neutral, and the potassium ion goes to the so formed manganate ion. The electronegativity of manganese is 1.5, whereas in oxygen is 3.5, [13] This marked difference favours the polarization of the Mn=O double bond. Figure 1.

The free radical on nitrogen couples with one electron from the C=C double bond forming a 3-member ring, an aziridinone, as well as, a cyclic ureido. Figure 2. Basic hydrolysis of the tensioned lactam produces a symmetric intermediate with a carboxylate between the two rings. The remaining free electron at C-4 can be removed by a permanganate ion at any stage of the route, giving a carbonium ion which is neutralised by water. A double carbinolamide is formed whose hydrolysis in acidic medium yields a carbonyl at C-4.

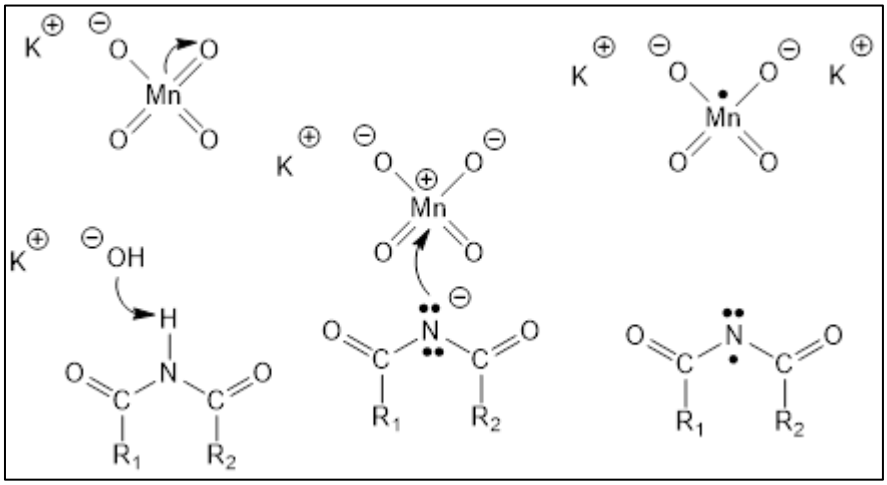

Figure 1 Electron transfer from the potassium imidate to the polarised permanganate anion.

This group enhances decarboxylation and 5-ureido-hydantoin (allantoin) is formed. The steps of this route are confirmed because allantoin results when uric acid is oxidised in alkaline medium, [14, 15].

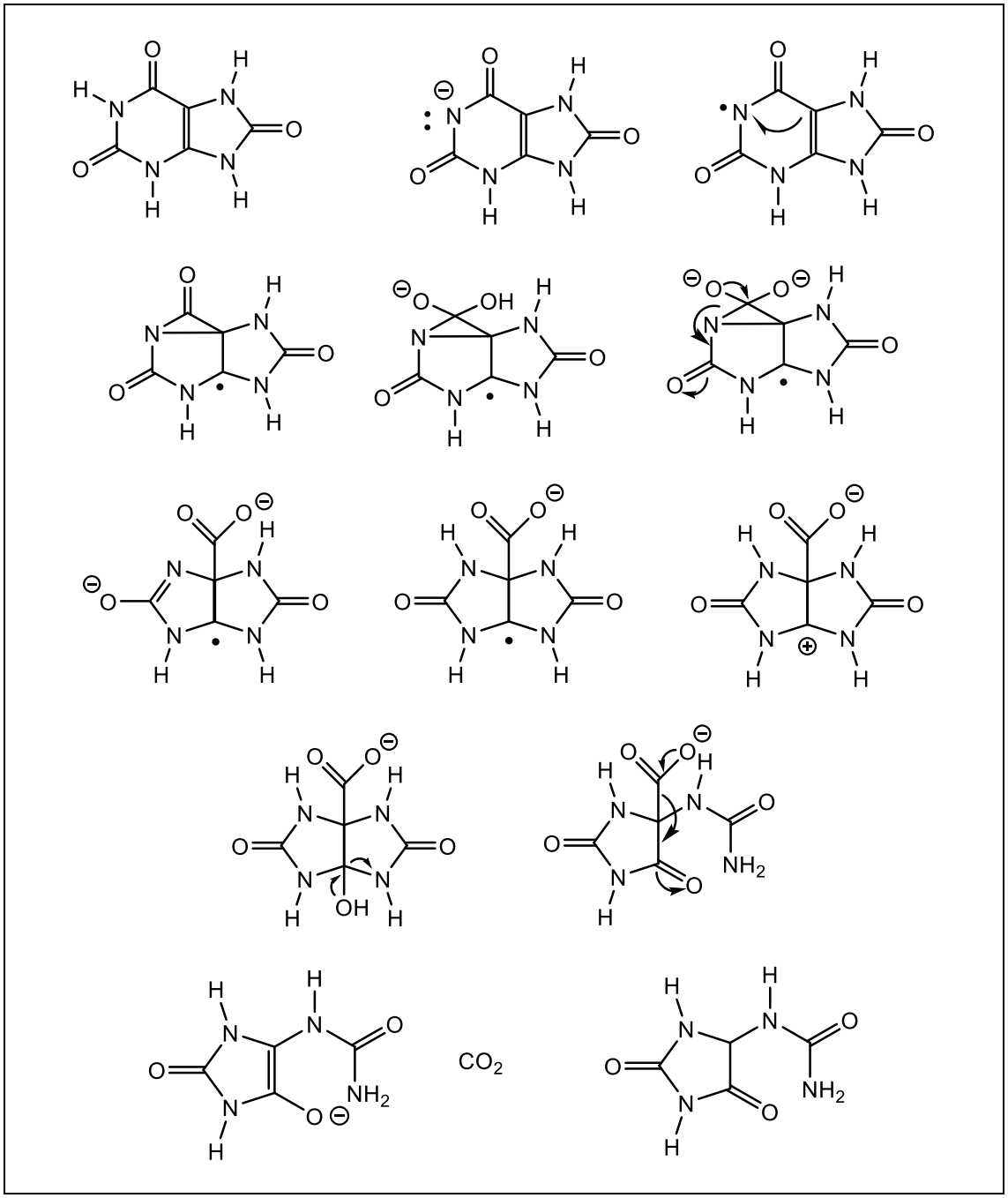

Figure 2 Reaction route from uric acid to 5-ureido-hydantoin by $KMnO_4$ oxidation

5. Conclusion

The chemical deportment of potassium permanganate has been cleared. It operates as having polarised one Mn=O double bond. This explains its electron caption capability, as well as, the formation of bi-negative manganate anion. This is in accordance with the electronegativities and with electron configuration. The organic sequence has been treated in the Discussion.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

There is no conflict of interest to declare

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