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THE REACTION OF GLUCOSE WITH AMMONIUM MOLYBDATE IN AQUEOUS SOLUTION

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ABSTRACT

There is an approach to this test. In this communication an alternative formation mode of the key intermediates, that are the same, is presented. Glucose, a carbon acid, forms the enol. This source of proton forms molybdic acid from ammonium molybdate, and also protonated molybdic acid, the reactive species. Nucleophilic reaction of glucose enolate with the reactive species affords an organic molybdate with concomitant separation of water. Another protonation, now in the inorganic moiety of the ester, gives rise to a concerted mechanism. Water and blue molybdenum dioxide are formed, whereas electronic apport from the second enol in the original enediol, gives 2-ketoglucose (glucosone) which is prone to hydration.

Chemical and stereochemical details concerning the nucleophilic reaction above mentioned are also given and are confirmed by 3D models.

Keywords: Ammonium molybdate; 2-Ketoglucose; Molybdenum blue; Molybdenum dioxide; Reactive intermediates; Redox reaction

1 INTRODUCTION

Glucose is an analyte, and thus, many tests for its detection have been advanced. Apart from its usefulness, it is very interesting to know what is happening in the test tube at molecular level, that is, the chemistry and the reaction mechanisms involved in each step.

In the present communication the interaction of glucose with ammonium molybdate in solution is studied, providing an alternative reaction route since there is a previous approximation, [1].

This paper is a follow up of our studies on reaction mechanisms, [2-6].

2 ANTECEDENTS

The test under study is due to Herman Hager (1816-1897) and the Polish chemist Gawalowsky, [7, 8]. The test is as follows: an aqueous solution of ammonium molybdate in contact with glucose gives a blue colour after heating.

There is a review about the reduction of ammonium molybdate in acid solution, [9].

3 DISCUSSION

The α-hydrogen to the aldehyde in glucose is acidic (carbon acid) and can form the enol. Phenol (phenic acid) and enols are sources of hydrions, hydronium ions in aqueous mediums. Thus, a metathesis between ammonium molybdate and an enol forms molybdic acid and ammonium enolate. Further protonation of molybdic acid yields the reactive species. Since enols are weak acids, the aqueous solution must be heated as in the Hager-Gawalowsky test.

Now let's see the exact reaction site for a nucleophilic attack to the protonated molybdic acid. Since each molybdenum-oxygen double bond creates a δ+ at the metal, the reaction site for a nucleophilic reaction by a glucose enolate must be between the two Mo=O groups, with concomitant elimination of a water molecule. The ligands in the molybdenum atom must rotate to the right. The Mo=O groups are now opposite between them, and the oxygen of the mixed ester and the remaining hydroxyl group in the molybdate must be linear. That these chemical and stereochemical considerations are correct were confirmed by the 3D structures showed in Figure 1.

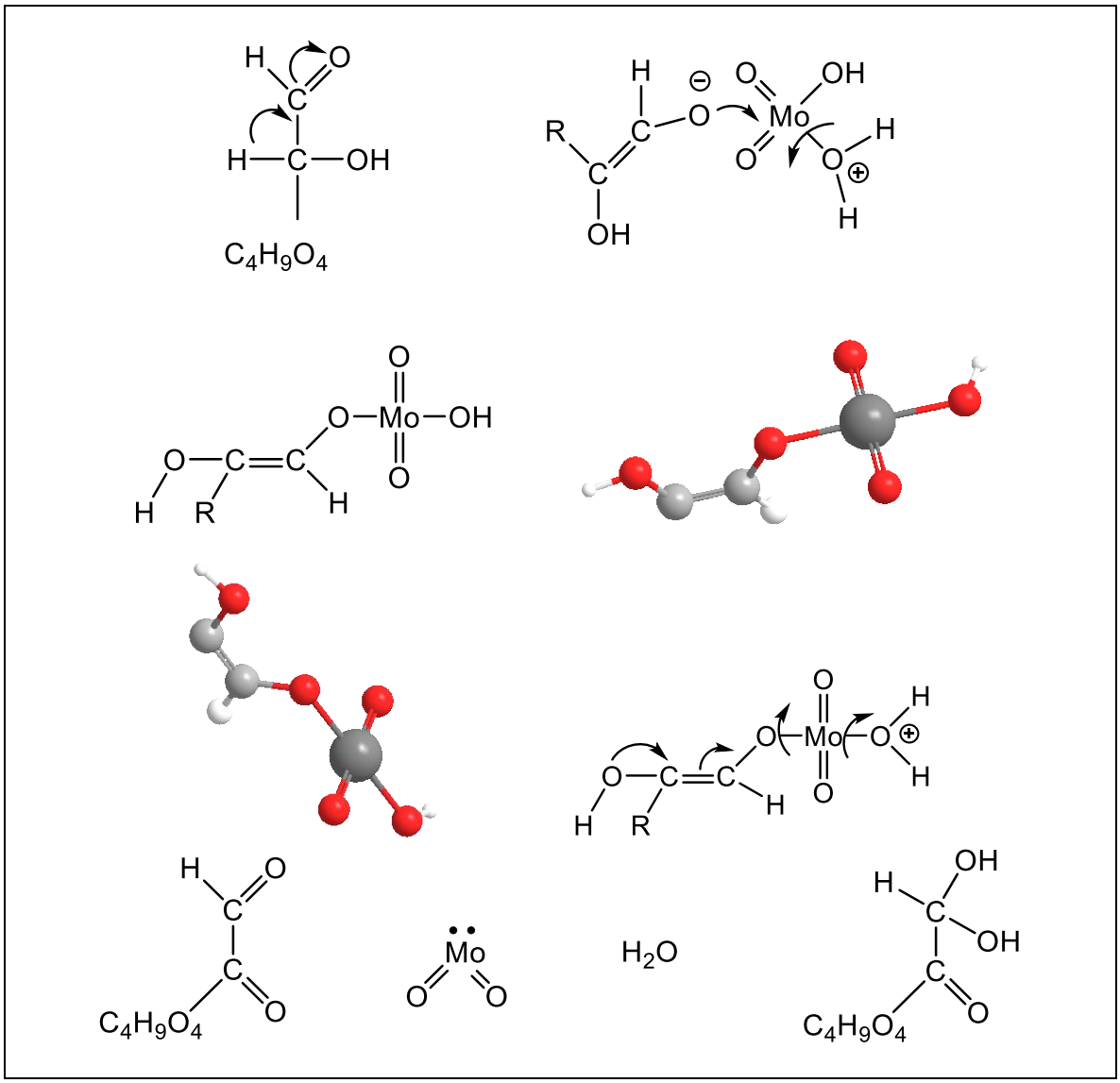

Figure 1: Reaction route of the interaction of glucose with ammonium molybdate

The next step is reaction of a hydrion at the remaining hydroxy group in the inorganic moiety. A push-pull mechanism takes place. That is, a concerted mechanism via four electron-shifts. A water molecule is eliminated, as well as, blue molybdenum dioxide (reduction step to Mo-IV). The electron push comes from the remaining enol of the original enediol. This way 2-ketoglucose (glucosone) is formed (oxidation step). This keto aldohexose is prone to be hydrated at C-1, forming a gem diol.

This route is in accordance with the blue colour observed in the test. Two other blue compounds are derivatives of MoO_2 [10, 11].

4 CONCLUSION

The chemistry and the reaction mechanism of the interaction of glucose with ammonium molybdate in aqueous solution has been cleared. The enolic form of glucose is a source of protons which form molybdic acid from ammonium molybdate. The reactive species is protonated molybdic acid, attracting glucose enolate. A molybdate is formed, with separation of water. Protonation of the molybdate produces s synchronous reaction mechanism: water, blue molybdenum dioxide, and 2-ketoglucose (glucosone) are formed.

STATEMENTS ON COMPLIANCE WITH ETHICAL STANDARDS

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Disclosure of conflict of interest

There is no conflict of interest to declare.

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