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Organometallic intermediates in Böttger test for glucose in urine

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Abstract

The reaction mechanism in organometallic chemistry is not always correctly understood or it is missing. In this communication the reaction route in the Böttger test for glucose is provided. The reagent can be bismuth subnitrate or bismuth meta-hydroxide (also called hydrated oxide of bismuth), since in alkaline medium (sodium carbonate) the nitrate ion is displaced by hydroxyl. The basic medium is essential in order to activate the glucose molecule. The reaction goes through a series of organometallic intermediates in a redox process. Finally, elemental bismuth separation occurs via one electron transfer in a bimolecular reaction. The white insoluble solid formed in situ blackens since it is covered by metallic bismuth.

Keywords: Bismuth meta-hydroxide; Bismuth subnitrate; Organometallic chemistry; Reaction mechanism; Reactive intermediates; Redox process

1. Introduction

Glucose is the most widely used aldohexose in most living organisms. Reaction of glucose with the amino group of proteins —glycation— impairs or destroys the function of many proteins.

Thus, glucose is an analyte. Glycosuria —glucose in urine— can result from hyper-glycemia because the kidneys are working to get rid of some of the excess sugar circulating in the blood. So, a urinalysis is very important. In this article we describe the route and the mechanism of the Böttger test for glucose, not previously advanced. The electron flow is given in each step and the reaction fully commented. It is important and interesting to know what is happening during the test, not only its application.

This communication is a follow up of our studies on reaction mechanism, [1-5].

2. Study Method and Process

This is a Theoretical Organic and Inorganic Chemistry Study. It is based on the chemical deportment of reagents and substrate. All is in accordance with the reaction medium, the nature of the oxidizer and catalyst employed. The several steps leading to elemental bismuth and 2-ketoglucose (Glucosone) are fully commented and the electron flow is given in each reaction.

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3. Antecedents

The test under study is due to Professor Rudolph Böttger (1806-1881). He published his test in a chemical Journal [6], and in a Polytechnical Journal [7]. There is a brief account of the test,[8]. The test has been recorded in books on analytical chemistry [9-11].

The test is as follows**:** Boil dilute glucose solution, or diabetic urine, with an equal volume of sodium carbonate (made from 3 parts of water and one part of crystallised sodium carbonate), then add some bismuth subnitrate (a knife tip), or bismuth meta-hydroxide [12], that is, bismuthyl hydroxide, BiO.OH [13]. This product is formed on boiling the ortho-hydroxide, [14]. Reduction causes blackening of white suspended bismuth salts. Apart from glucose, no other substance occurring in the urine, both organic and inorganic, has the property of deoxygenating the bismuth salt to metallic bismuth. On the other hand, uric acid has a reducing effect on copper hydroxide.

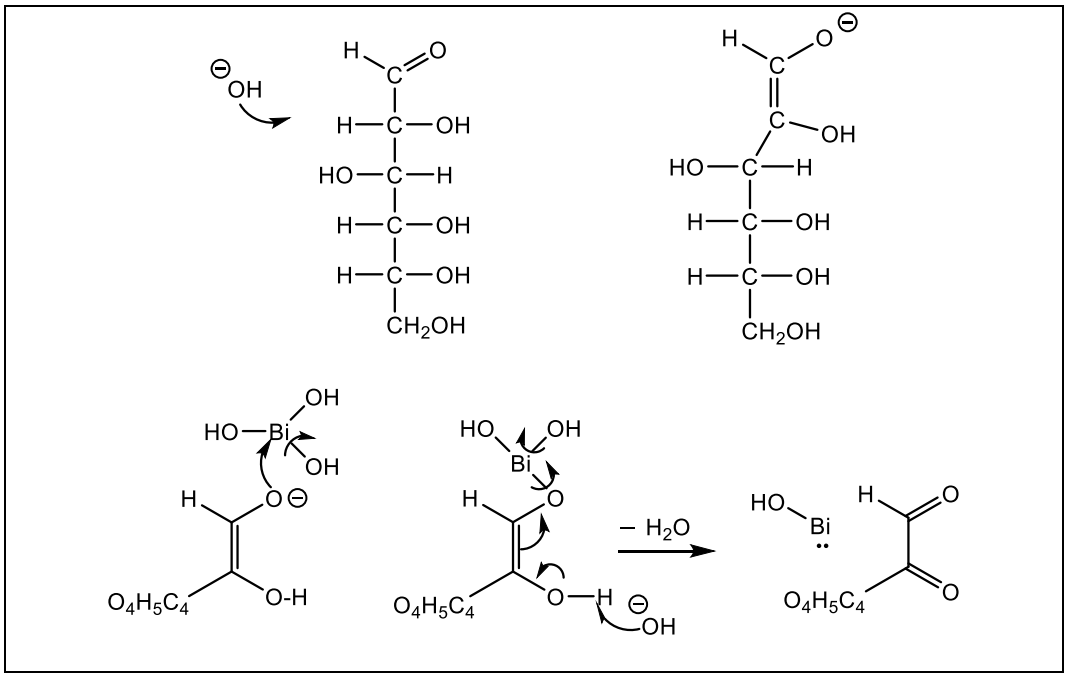
Bismuth is a post-transition metal having 83 electrons in six shells, [15]. The electron configuration is [Xe] $4f^{14}5d^{10}6s^{2}6p^{3}$, [16]. Thus, bismuth is trivalent.

4. Discussion

The Böttger test for glucose takes place in alkaline medium in order to activate the glucose molecule, since it is a carbon acid. Thus, this aldose forms a very reactive enolate. On the other hand, the reagent, bismuth subnitrate (*Magisterium bismuthi*) forms in alkaline medium insoluble bismuth hydroxide. Nevertheless, the oxido-reduction reaction goes on and the white hydroxide blackens since it is covered by elemental bismuth. Figure 1.

The glucose enolate reacts with bismuth hydroxide, a hydroxyl group is eliminated with concomitant formation of an organometallic intermediate. A second enolate is formed in this molecule, and a concerted mechanism takes place. 2-Ketoglucose (glucosone) and reduced Bi(I) hydroxide are formed via four electron-shifts.

A second glucose enolate reacts with Bi-OH giving a salt of bismuth(I). Reaction of the second enolate in this intermediate eliminates an unstable negatively charged bismuth atom which cedes an electron to another Bi-OH intermediate and hydroxyl displacement. This way two atoms of elemental bismuth result plus a molecule of glucosone.



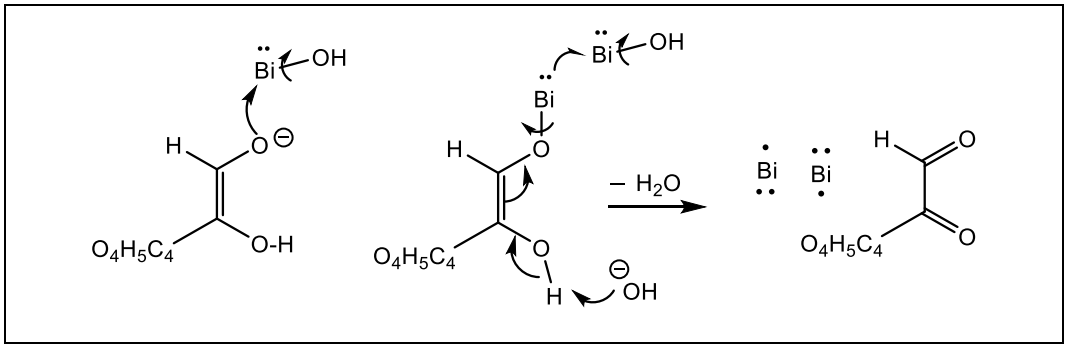


Figure 1 Organometallic intermediates in Böttger test for glucose

Thus, the electrodotic property [17] of glucose enolate is the driving force for deoxygenation (reduction) of bismuth hydroxide into black elemental bismuth.

5. Conclusion

The chemistry of the Böttger test for glucose detection in diabetic urine has been cleared. It is a redox process initiated by the sodium enolate of glucose formed in alkaline medium (aqueous carbonate solution), displacing the hydroxyl ions of the bismuth hydroxide formed in situ. Several organometallic intermediates are formed and finally two atoms of metallic bismuth result in a bimolecular reaction between two key intermediates.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

There is no conflict to declare

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