

A complete and sustained organic/inorganic reaction mechanism of Baeyer's test

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Abstract

The Baeyer's test for unsaturation has been used in Qualitative Organic Analysis for a long time. However, if an alkaline reagent is used, compounds having an active hydrogen (carbon acids) also give a positive test with potassium permanganate, detracting the test for unsaturation. The first steps of the reaction sequence have been described but the next stages are missing. These are very important because they involve the formation mode of the observed end product, brown manganese dioxide.

In this communication, a complete and sustained reaction mechanism is provided for both reaction mediums, neutral and alkaline. It is in accordance with observed experimental facts. The missing steps are a redox reaction between hypomanganate and permanganate ions, and a second cyclic intermediate now formed with manganate ion. The instability of this intermediate leads directly to manganese dioxide and alkalization of the neutral medium, as observed experimentally.

Keywords: Carbon acids; Cyclic hypomanganate ester; Molecular scission; Qualitative Organic Analysis; Redox reaction; Test for unsaturation

1. Introduction

The Baeyer test for unsaturation (alkenes and alkynes) or functional groups that can be oxidized (aldehydes and some alcohols) has been used for a long time in Organic Qualitative Analysis. Baeyer's reagent is an aqueous potassium permanganate solution and it can be in neutral or alkaline medium. The last form is a potent oxidizing agent.

Although there is ample experimental information about this tests, a complete and sustained reaction mechanism involving both the Organic and the Inorganic Chemistry in both mediums, is missing. Now the theoretical part is provided is this communication.

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

2. Antecedents

The test for unsaturation under study is due to Professor Adolf von Baeyer (1835-1917). He proposed the correct formula for indole and achieved the synthesis of indigo. He also prepared barbituric acid, the parent compound of the sedative-hypnotic barbiturates.

Let's see first the reaction for unsaturation in neutral medium. Dissolve 4 drops or 40 mg of sample in 1 ml of ethanol or 1,2-dimethoxyethane. Add three drops of the deep purple 1% KMnO_4 aqueous solution. Mix the test tube with

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agitation, and allow it to sit for a minute, A positive result is the appearance of a brown colour or precipitate of MnO_2 , [6]. If the reaction mixture is heated there is cleavage of the carbon chain, giving two carboxylic acids. Acetylenic linkages are cleaved and yield acids.

A 3% KMnO_4 solution is also employed. Olefinic or acetylenic bonds produce instant decolouration, [7].

Others consider that Baeyer's reagent is an alkaline solution of cold KMnO_4 , a potent oxidizing reagent [8], a test for unsaturation or functional groups that can be oxidized, such as aldehydes and some alcohols, [9]. The test for glucose has been mentioned in a book of chemical tests, [10, 11], but it is not used to detect sugar in urine, [12]. The substance is shaken with dilute sodium carbonate solution, and dilute permanganate solution is added dropwise. The colour will be discharged and a brown precipitate of manganese dioxide will appear, [13].

The preparation of the alkaline Baeyer's reagent is as follows: dissolve 1 gramme of KMnO_4 in 100 ml distilled water, add 10 g of anhydrous sodium carbonate, and shake the stoppered vial until fully dissolution, [14].

Some remarks on manganese compounds. The common oxidation states of manganese are +2, +4, and +7, but the less common states, +3, +5, and +6 are easily prepared, [15]. Manganous compounds are +2, like MnCl_2 ; whereas a manganic derivative is Mn_2O_3 , a sesquioxide, [16, 17].

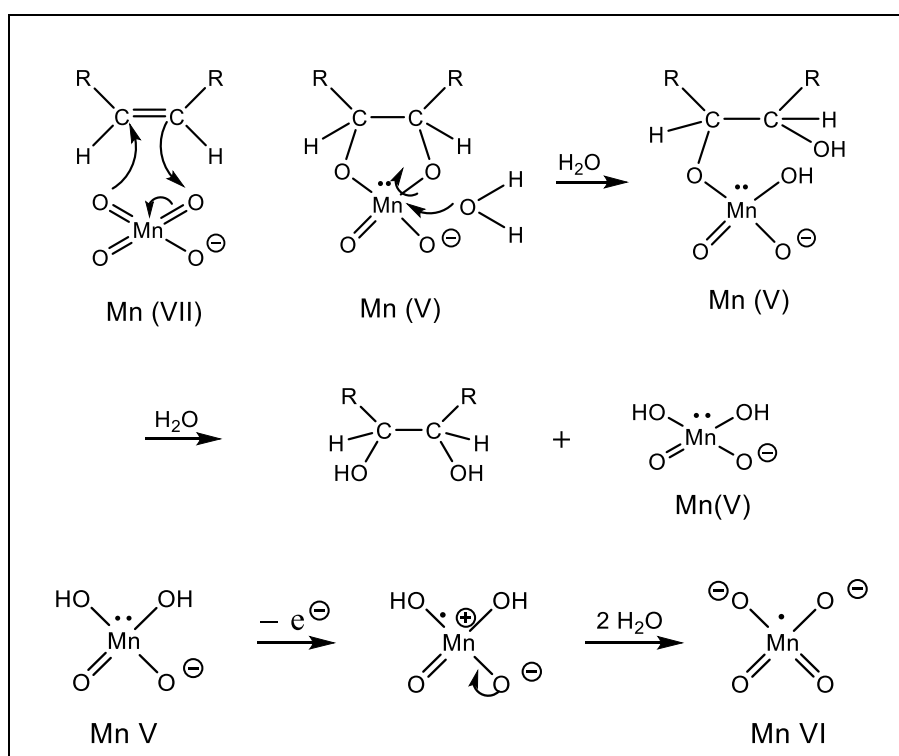
3. Discussion

Only the first steps of the reaction mechanism of the Baeyer's test have been described, the next steps are missing.

The initial step is cis addition of permanganate ion to the double bond to give a cyclic ester. Figure 1. This 5-member ring adduct, a derivative of manganese-V, is hydrolysed by solvolysis to a glycol, [18].

Although potassium permanganate reacts readily with any ethylenic linkage holding one hydrogen atom in each sp^2 carbon atom, or only one hydrogen in this system, it rarely reacts with completely substituted olefins, [19]. This reactivity is due to the increasing steric hindrance in the above-mentioned compounds.

The short-lived hypomanganate ion (Mn-V) [20] is oxidised to manganate ion (Mn-VI) by one-electron transfer to a permanganate ion (Mn-VII) which is reduced to a second manganate ion. This redox reaction involves a radical-ion from the hypomanganate ion which is neutralised internally to manganic acid, whereas polarised permanganate receives the transferred electron.



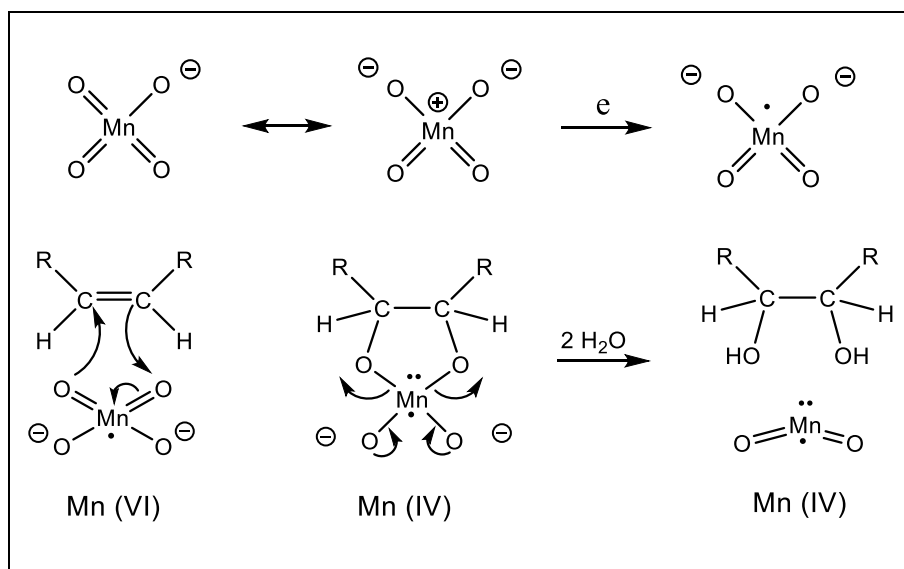


Figure 1 Complete reaction mechanism of Baeyer's test

Elimination of the double bond during formation of the cyclic manganese ester, reduces the Mn-VII atom to Mn-V by two-electron transfer. Thus, if MnO_2 (Mn-IV) is formed as final inorganic product, it must become from a VI to IV reduction; that is, from a ring adduct formed with a manganate ion instead of a permanganate one. The cyclic reactive intermediate yields MnO_2 and two alkoxides which are neutralised by water, with elimination of two hydroxyl ions. This reaction mechanism is in accordance with the experimental observation that the neutral reaction medium becomes alkaline as the reaction proceeds [21], and with the stoichiometry, [22]:



As we have seen above, from three alkene molecules, one reacted with permanganate, and the other two with manganate ions which produce a different cyclic adduct, each giving a manganese dioxide molecule and hydroxyl ions.

Moreover, the manganese dioxide molecule formed in the provided mechanism shows three external electrons, in accordance with the electronic configuration [23] of manganese in MnO_2 ; $[\text{Ar}] 4s^2 3d^1$.

This way, a complete and sustained reaction mechanism of Baeyer's test for unsaturation has been provided.

Now let's see the reaction in alkaline medium. The step of solvolysis is now an alkaline hydrolysis, and of course the alkalinization observed in the neutral conditions cannot be detected.

The alkaline Baeyer's reagent is a stronger oxidant compared to the neutral one since in basic conditions compounds having an active hydrogen (carbon acids) also react. Even in neutral conditions aldehydes are oxidised to carboxylic acids. This is a drawback in analysis but useful in organic preparations. In Figure 2 the reaction with glucose is depicted. This carbon acid forms a carbanion at C-2 which is stabilised to enolate in an enediol system. A nucleophilic reaction with permanganate takes place. The resulting negative charged oxygen at the manganese moiety reacts with water. The electrodotic property [24] of the second enolate yields 2-ketoglucose (glucosone) with concomitant formation of hypomanganate ion via elimination of a hydroxyl ion from manganese.

Gluconic acid results by a Cannizzaro reaction of the α -ketoaldehyde.

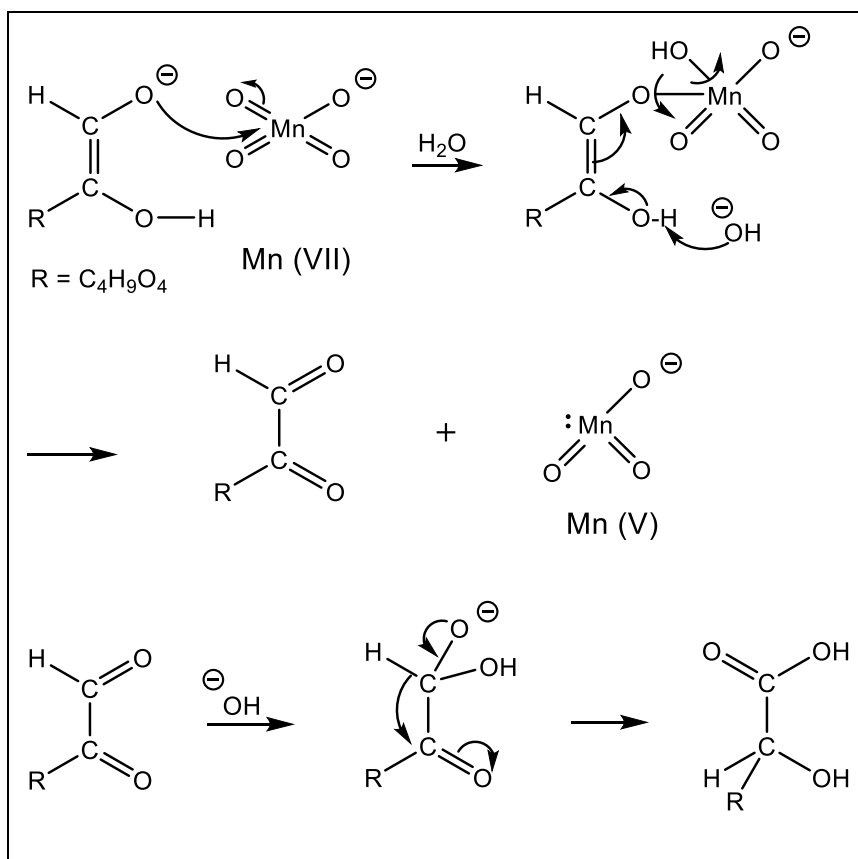


Figure 2 Mechanism of glucose oxidation by alkaline permanganate

Finally, manganese dioxide is formed by reaction of glucose enolate with manganate ion, which is obtained in the redox reaction between hypomanganate and permanganate, as described before.

4. Conclusion

We have found that the end product of this test, the observed brown manganese dioxide, doesn't come from the original alkene/permanganate complex, but from a second 5-member ring derived from alkene and manganate ion, the last being formed by disproportionation of hypomanganate and permanganate ions. The provided reaction mechanism is complete, and involves both the organic and inorganic parts, and it is in accordance with experimental observation, with stoichiometry, and with the electronic configuration of manganese subshells in manganese dioxide.

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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