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(RESEARCH ARTICLE)

Mechanism of the interaction of formaldehyde, o-diketone, and 1,2-dinitro benzene

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Abstract

The mechanisms in the reaction sequence of the interaction of formaldehyde, o-diketone, and 1,2-dinitrobenzene in alkaline medium, have been provided. The different points of view regarding the mechanism of the Cannizzaro reaction have been discussed.

A cross Cannizaro reaction between formaldehyde and o-diketone occurs. The resulting α-ketol is the key intermediate since the entering hydride ion is now an acidic hydrogen which reacts with the anion of the zwitter ion in a nitro group. Then is reaction with a hydride ion yielding a nitroso group after dehydration. A further reduction to o-nitro-phenylhydroxylamine and rearrangement to a dibasic o-quinone di-imine salt gives the violet salt observed in the test. That is, the hydroxylamine is oxidised to the salt of iso-nitroso group, and the nitro group is reduced to nitronate.

Keywords: o-Diketone; Formaldehyde; α-Ketol; o-Nitro-phenylhydroxylamine; o-Quinone-di-imine derivative; Halochromism

1. Introduction

Feigl proposed a colour test for o-diketones and quinones by catalytic acceleration of the formaldehyde-o-dinitro benzene reaction, [1, 2].

That is an empirical study without reaction mechanism and there is no explanation of how this acceleration is produced. Besides, the violet alkali salt observed in the test is considered due to the aci-form of nitroso-nitrobenzene. However, nitroso-benzene cannot have aci-form since there is no hydrogen atom vicinal to the nitroso group.

In the present communication the reaction mechanisms are provided and there are not lacks or errors.

This paper is a follow up of our studies on reaction mechanism, [3-7].

2. Antecedents

There are no antecedents to the test under study. The present communication is an Organic Chemistry Theoretical Study based on the chemical deportment of reagent and substrate. All is in accordance with the reaction medium. The steps leading to the final product are entirely commented as well as the reaction mechanism.

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3. Discussion

The use of formaldehyde in alkaline medium means the Cannizzaro reaction in which there is a hydride transfer (hydrogen anionotropy), Beyer [8]. Formaldehyde is not a hydrogen donor (Feigl). The concept of nascent hydrogen is obsolete.

The mechanism of this disproportionation reaction (Bonner [9], has been considered in a simple manner, that is, a hydroxyl group adds to the aldehyde and the electron return displaces a hydride ion, Alexander [10], Sykes [11], with some variants like hydrogen bond with the second aldehyde molecule, Leffler [12], or consideration of the second aldehyde molecule as completely polarised, as a carbonium oxide, Isaacs [13]. Figure 1.

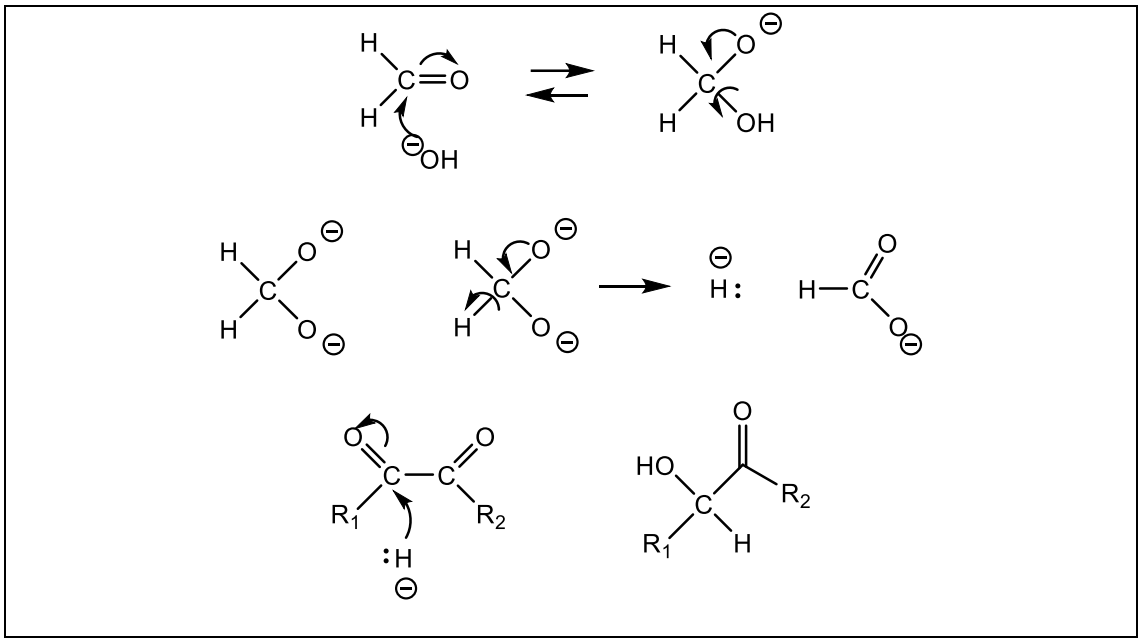
Return of the electrons from the alkoxide and displacement of a hydride ion in the presence of a hydroxyl in the same carbon atom is not correct since the hydroxyl ion is a better leaving group than a hydride ion. Thus, formation of a dialkoxide can explain the elimination of a hydride, Packer [14], and Denney [15].

Formation of a dialkoxide in sodium carbonate solution can be explained since the reaction goes better than in strong alkali. The possibility of hydrogen bond formation between two aldehyde molecules, already mentioned, must be taken into account.

Then occurs a trans Cannizzaro reaction with the ortho-diketone and an α-ketol is formed. The chemical deportment of this compound is of utmost importance since the hydrogen atom that entered as a hydride is now acidic because it is in α-position to the second carbonyl group.

So, the oxide in the zwitterionic nitro group in 1,2-dinitrobenzene reacts with the acidic hydrogen in the α-ketol, leaving a naked positive charge at the nitrogen. This cation is much more reactive than the neutral zwitter ion and attracts hydride ions coming from the formaldehyde. An unstable intermediate with ten external electrons results which is dehydrated to aromatic nitroso group with the ordinary octet.

This way, the catalytic effect of o-diketones in the reaction of 1,2-dinitrobenzene with formaldehyde has been explained.



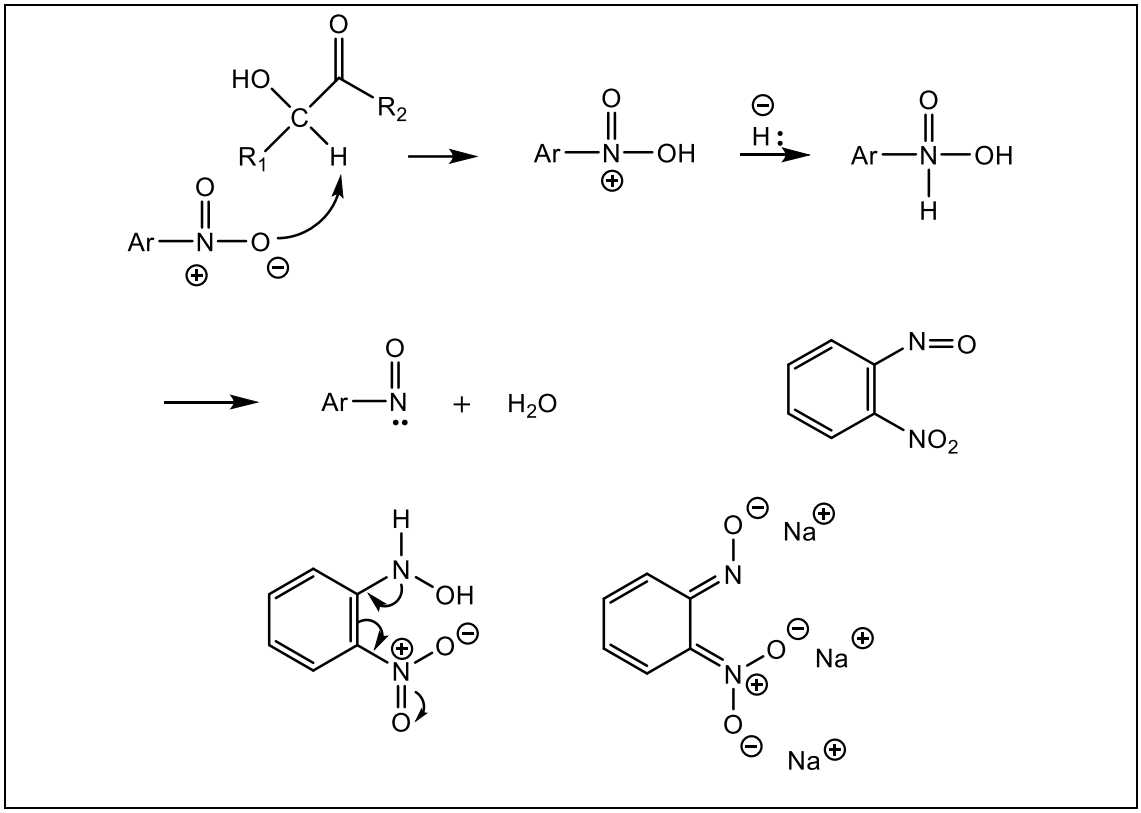


Figure 1 Mechanistic sequence of the interaction of formaldehyde, o-diketone, and 1,2-dinitrobenzene

Now let's see the colour observed in the test. Feigl states that it is the violet alkali salt of the aci-form of o-nitroso-nitrobenzene. However, an aromatic nitroso group has no aci-form since there is no hydrogen vicinal to it,

On the other hand, o-nitro-phenylhydroxylamine in the presence of alkali hydroxide yields blue-violet water-soluble alkali salts. The structure is a dibasic nitrogen-ortho-quinoidal alkaline salt, [16]. That is, the hydroxylamine donates an electron pair and is oxidised to the anion of iso-nitroso group, and the nitro group is reduced to nitronate, [17]. As it is obvious, the observed colour is due to halochromism, [18, 19].

So, another reduction step was missing in the Feigl sequence to the final product.

4. Conclusion

The mechanisms in the reaction sequence of the interaction of formaldehyde, o-diketone, and 1,2-dinitrobenzene in alkaline medium, have been provided. The different points of view regarding the Cannizzaro reaction have been discussed.

A cross Cannizaro reaction between formaldehyde and o-diketone occurs. The resulting α-ketol is the key intermediate since a hydride ion is now an acidic hydrogen which reacts with a nitro group and then with a hydride ion yielding a nitroso group. A further reduction to o-nitro-phenylhydroxylamine and rearrangement gives the violet salt observed in the test.

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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