

Classroom



In this section of *Resonance*, we invite readers to pose questions likely to be raised in a classroom situation. We may suggest strategies for dealing with them, or invite responses, or both. “Classroom” is equally a forum for raising broader issues and sharing personal experiences and viewpoints on matters related to teaching and learning science.

A Closer Look at the Mulliken–Barker Test An Improvisation for Nitro Compounds Having Acidic Functionality

Qualitative analysis of unknown organic compounds is an essential part of the core curriculum for BSc and MSc students in chemistry. The functional group detection is a significant component of qualitative analysis. The present work describes the reason for the failure of Mulliken–Barker test for nitro compounds having carboxylic acid functionality and suggests a possible remedy.

Introduction

Qualitative analysis of single organic compounds and mixtures [1, 2] constitutes an important laboratory chemistry assignment for graduate and post-graduate students. Detection of particular functional group(s) present in a given sample is an essential part of this analysis. Among the nitrogenous functional groups, $-\text{NO}_2$ (aromatic or aliphatic nitro) is an important one. Usually two tests are carried out for detection of this group. They are:

Dye test: This involves reduction of the nitro group by a metal such as Sn or Zn and concentrated HCl and the resulting amine is detected by diazo coupling [2].

Kaushik Basu¹,
Suchandra Chakraborty² and
Chandan Saha³

¹ Department of Chemistry
St Paul's Cathedral Mission
College
Kolkata 700 009, India.
Email: kb.spcmc@gmail.com

^{2,3} Department of Clinical and
Experimental Pharmacology
School of Tropical Medicine
Kolkata 700 073, India.
Email:

²suchandra82@gmail.com

³katichandan@yahoo.co.in

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Mulliken–Barker test: In this test the nitro group is reduced by $\text{Zn-NH}_4\text{Cl}$ or Zn-CaCl_2 to hydroxylamine which is detected by Tollens' reagent [3, 4]. A blank test with the original sample must be performed to ensure that it does not reduce the Tollens' reagent.

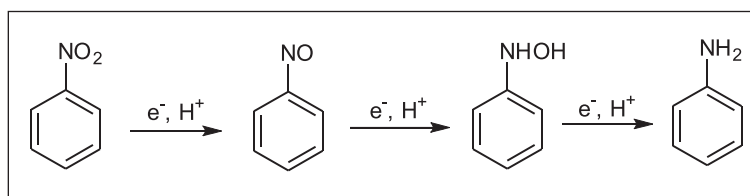
The two tests are not complementary. Generally both tests should be performed to confirm the presence of nitro group in a sample that does not have amino group. If amino group is present originally diazo coupling obviously works. Nitrophenols and aliphatic nitro compounds which do not give the dye test, give a positive Mulliken Barker test. This procedure works well for most of the nitro-containing compounds such as nitrotoluenes, 1,3-dinitrobenzene, and nitroanilines. But in case of nitrobenzoic acids, students often fail to get silver mirror/precipitate with Tollens' reagent. However, we have found that a simple modification of the procedure gives the desired result without fail.

The Chemistry of Nitro Group Reduction

To explain failure in the Mulliken–Barker test with nitrobenzoic acids, one needs to take a closer look at the reduction sequence of nitro group. The reaction is sensitive to the pH of the medium, as the products formed depend on the reducing agent used. In strong acidic medium like Sn-HCl or Zn-HCl , the reaction proceeds via the intermediates nitroso and hydroxylamine to finally give amine (*Scheme 1*) [5].

In the so-called 'neutral' reaction condition, such as with $\text{Zn-NH}_4\text{Cl}$ or Zn-CaCl_2 , the reduction stops at hydroxylamine which reduces Tollens' reagent. A point to note is that NH_4Cl or CaCl_2 is the salt of a strong acid (HCl) and weak base. Though the

Scheme 1. Reduction sequence of nitrobenzene.



textbooks [2,5] refer to the Mulliken–Barker reaction condition as a neutral one, it is actually feebly acidic (pH ~ 6.8) at the start of the reaction. The pH of the aqueous alcoholic solution (1:1 v/v) of 0.5 g of *p*-nitrobenzoic acid was measured to be ca. 3.6, which drops down to 2.9 on addition of 0.5 g of NH₄Cl. Under such fairly strong acidic condition it is perhaps difficult to stop the reaction at the hydroxylamine stage, and the reduction proceeds to give amine, which was corroborated by the fact that the filtrate obtained from the Zn-NH₄Cl reduction of *p*-nitrobenzoic acid gave positive diazo coupling test, confirming the presence of amine in the medium. The occasional success of Mulliken–Barker test with nitrobenzoic acid by the conventional procedure can be attributed to variations in conducting the test, such as using smaller quantities of NH₄Cl than is actually prescribed or heating the reaction medium for a shorter period of time than recommended. In any case, the test fails (i.e., no Ag-mirror/precipitate) more often than not, which is puzzling.

This failure can be successfully overcome by preventing the reaction medium from becoming too acidic. This is achieved if the test is carried out by omitting NH₄Cl. The nitro-substituted acid itself is enough to maintain the slightly acidic pH required for the partial reduction of nitro group. This was indeed found to be the case.

Modified Mulliken–Barker Test for Nitrocarboxylic Acids

The sample (0.5 g) was dissolved in 10 ml of 50% ethanol, and 0.5 g of zinc powder was added. After boiling the mixture for 5 min, it was cooled and filtered into Tollens' reagent. An immediate black or grey precipitate or a silver mirror appeared indicating the presence of the hydroxylamine group, the result of partial reduction of the –NO₂ group.

The procedure shows negative results with samples containing –NO₂ group but without any acidic functionality, such as 4-nitrotoluene, 1,3-dinitrobenzene and nitroanilines for which the conventional Mulliken–Barker's method has to be followed. An interesting

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Nitrocarboxylic acids		Nitrophenols	Nitrosophenols
2-nitrobenzoic acid	2-nitrocinnamic acid	2-nitrophenol	2-methyl-4-nitrosophenol
3-nitrobenzoic acid	3-nitrocinnamic acid	3-nitrophenol	4-nitrosothymol
4-nitrobenzoic acid	4-nitrocinnamic acid	4-nitrophenol	
4-nitrophenylacetic acid	5-nitrosalicylic acid	3-methyl-4-nitrophenol	
3-nitrophthalic acid			

Table 1. Compounds responding to the modified Mulliken–Barker test.

The modified method is successful in case of samples with acidic functionality such as $-\text{CO}_2\text{H}$ and phenolic $-\text{OH}$ group, but fails in the absence of these groups.

point to note is that the modified method works well in case of nitrophenols and nitrosophenols, as these substances are also acidic enough to maintain the slightly acidic pH required for the reduction, even without the presence of NH_4Cl . Table 1 gives the list of nitro compounds that we have successfully tested with our modified procedure.

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Conclusion

Mulliken–Barker test used to detect $-\text{NO}_2$ group was found to fail for nitro compounds containing acidic functionality. This modified method which omits NH_4Cl in the reduction procedure works well with nitro-substituted aromatic acids, can also be extended to cases of nitrophenols and nitrosophenols. In addition, the chemistry behind this improvisation is elegant, yet simple enough to be adopted for undergraduate laboratory.

Suggested Reading

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