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Der Pharma Chemica, 2012, 4(4):1440-1444
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Reductimetric Determination of Nitroso Compounds With Iron(II)

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ABSTRACT

A simple accurate and convenient reductimetric titration method has been developed for the determination of two nitroso compounds namely: I -Nitroso 2 Napthol (α-Niraso β –Napthol) and 2-Nitraso 1-Napthol (β-Nitroso α-Napthol) using iron(II) as a reducing agent in a phosphoric acid medium. The method consists in titrating the solutions of these compounds against iron(II) in about 9 M (or above) phosphoric acid medium and in presence of a small amount of resorufin (RSF) which acts as a catalyst as well as redox indicator. The color transition of the indicator at the end- point (from red to bluish green) is sharp, reversible and no indicator correction need to be applied. The two nitroso compounds in the range 5 -20 mg have been determined with an accuracy of ±0.06 %. The precision of the method is found by computing pooled standard deviation and 95% confidence limits. The two nitroso compounds are found to be reduced by iron(II) to their corresponding amino compounds each in a four electron reduction step. The indicator RSF is reduced to its bluish green semi quinone by iron(II) in one electron reduction step. The formal redox potentials of the two oxidant systems ([nitroso compound]/[amino compound] couple) and the reductant system ([iron(III)] /[iron(II)] couple) and the transition potential of the indicator RSF have been measured in 9-12 M phosphoric acid medium. Based on these potentials data, the conditions needed in the titrations have been explained.

Key words: I-Nitroso 2-Napthol, 2-Nitraso 1-Napthol, Iron(II), Resorufin, Phosphoric Acid Medium.

INTRODUCTION

1-Nitroso 2-napthol and 2- Nitroso 1-napthol belong to the nitrso group of dyes and are generally utilized in calico printing. However, they find numerous applications in analytical chemistry[1-10] for the detection (boron, cobalt, iron, copper, molybdenum, nickel, palladium, vanadium, zirconium .etc) and determination (cobalt, copper, palladium and zirconium etc.) of several inorganic ions present in real samples such as steel, varnishes and similar materials. Recently, utilizing these nitroso compounds, some spectrophotometric methods for the determination of microgram quantities of nickel, iron, cobalt, copper etc. present in some real samples have also be reported [11,12]. In spite of their numerous applications in analytical chemistry, the existing methods for assay or determination of these two compounds are found to be a few in numbers. These methods utilize the reductant like hydrazine[13], titanium(III) [14,15], iodide[16] ,hydriodicacid[17], chromium(II)[18] iron(II) in high phosphoric acid[19] medium etc.

However, these methods are not entirely satisfactory. For example, in the method using hydrazine as a reductant, the collection of nitrogen gas from the nitroso compounds is tedious and time consuming. The reductants such as titanium(III) and chromium(II) are highly unstable towards oxygen of the air and thus require the use of a special storage apparatus. Further, these titrations have to be carried out at elevated temperatures. The reduction of the nitroso compounds with potassium iodide is very slow and requires about 20minutes for the completion of the reaction in a dark place. Moreover, the method is less accurate (± 5%). In the hydroiodic acid method the nitroso compound solutions must be heated in a sealed tube for 100 to 300^{0}C. The method utilizing iron(II) as a reluctant in phosphoric acid medium takes about 20 minutes for the completion of the reaction. Further, the detection of end-point (yellow to colorless) in the method is difficult and it is less accurate.

In view of the above mentioned disadvantages associated with earlier methods, we have now developed a convenient reductimetric titration method for the determination of the above mentioned two nitroso compounds using iron(II) as a reductant in phosphoric acid medium employing resorufin (RSF) as a catalyst as well as a redox indicator. In this method, the reduction of the nitroso compounds by iron(II) is instantaneous, the color transition at the end-point is sharp and the method accurate.

MATERIALS AND METHODS

All the chemicals were the analytical regent grade unless and otherwise stated and all solutions were prepared in distilled water.

Iron(II) solution: - A 0.05 M solution of iron(II) is prepared from iron(II) sulphate hexahydrate in 1N sulphuric acid medium and standardized [20] by titrating against a standard solution of dichromate in the usual way.

1-Nitroso- 2-Napthol and 2- Nitroso-1 –Napthol solutions:-0.01M solutions of the compounds are prepared in glacial acetic acid medium and standardized [15] by titrating against a standard solution of titanium (III) chloride (0.01 N) in 1M hydrochloric acid medium at about60^{0}C.

Resorufin solution (RSF solution):- An approximately 0.05% (50 mg in 100 ml) solution of resorufin (Aldrich U.S.A) is prepared in 0.05M sodium hydroxide medium.

A digital potentiometer with a bright platinum rod (as indicator electrode) and a saturated calomel electrode (as reference electrode) has been used for potential measurements.

Recommended procedure: - To an aliquot (3 to 10 ml) of a nitroso compound solution taken in a150 ml beaker fitted with a three- holed rubber stopper (one of which is intended for introducing the jet of a burette and the other two for accommodating the inlet and out let tubes for circulation of carbon dioxide gas) required volume of ortho phosphoric acid is added to get an acid strength of about 9-10 M near the end- point. The solution is diluted to about 50 ml, followed by the addition of 0.2 - 0.3 ml of 0.05% resorufin solution. Purified nitrogen gas is now passed through the solution for about 3-4 minutes to expel any dissolved oxygen. The solution is then titrated against a 0.05M iron (II) solution with the help of a magnetic stirrer to the color change of the indicator from red to bluish green. Carbon dioxide atmosphere is maintained throughout the titration to prevent the aerial oxidation of reduced nitroso compounds (or amino compounds). Some of the typical results obtained by the method are shown in Table – 1.

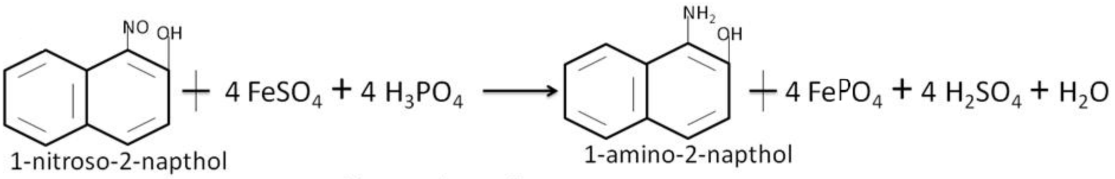
RESULTS AND DISCUSSION

The concentration of phosphoric acid must about 9.0M or above for a rapid reduction of the nitroso compounds with iron(II). The accuracy of the method is found to be $\pm$ 0.6%. The precession of the method is determined by computing the pooled standard deviation and 95% confidence limits [21] to the mean $\bar{x}$ and these values are included in same table.

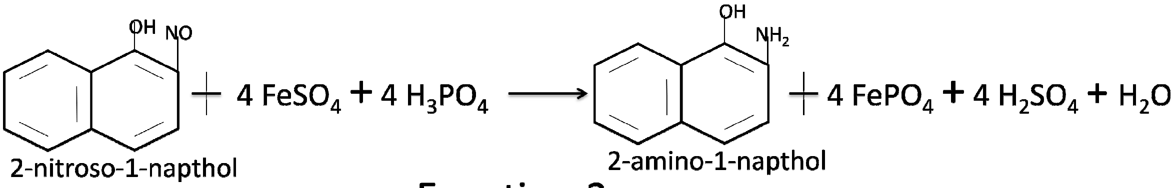
Table-1: Determination of 1-Nitroso- 2-Napthol and 2- Nitroso-1 –Napthol with Iron(II) in Phosphoric Acid Medium:

Nitroso compound found*		Pooled standard deviation Sg, mg	$1.96\times Sg/\sqrt{n}$ mg	95% confidence limits $\bar{X}\pm 1.96\times Sg/\sqrt{n}$ mg
Standard method [15] mg	Author's method mg			
1-Nitroso-2-Napthol				
5.19	5.22			5.20 to 5.24
8.66	8.71			8.69 to 8.73
12.12	12.06	0.03	0.02	12.04 to 12.08
15.58	15.51			15.49 to 15.53
17.32	17.39			17.37 to 17.41
2-Nitroso-1-Napthol				
5.88	5.84			5.81 to 5.87
6.93	6.97			6.94 to 7.00
9.52	9.47	0.04	0.03	9.44 to 9.50
13.85	13.92			13.89 to 13.95
16.45	16.53			16.50 to 16.56
*Average of six determinations				

In the present method two nitroso compounds are reduced to their corresponding amino compounds in a four electron reduction step according to the fallowing equations 1&2.

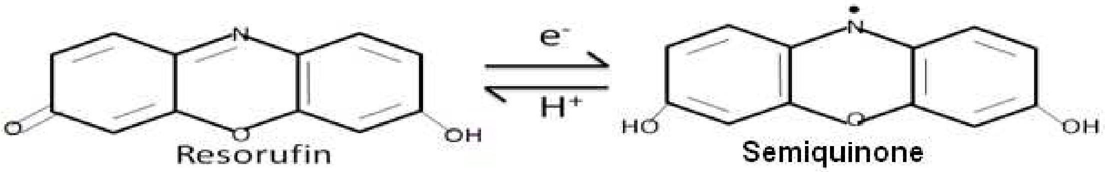


Equation-1



Equation-2

At the end-point, however, the indicator (RSF) (red in color) is reduced by iron(II) to its bluish green semiquinone form in one electron reduction step as for the fallowing equation(Eqation-3) as elucidated earlier[22,23].



Equation-3

The intense bluish green color observed at the end-point is attributed to the free electron that is present in the semiquinone.

Rukmini and Kavitha [19] earlier stated that the reaction between nitroso compounds and iron(II) in phosphoric acid medium is slow and takes about 20 minutes for the completion of the reaction. The present authors also made the same observation but found that the reaction is quite rapid in presence of a small amount of RSF. Thus, it has been observed RSF is no doubt catalyzing the present redox reactions and simultaneously acting as an indicator to detect the end-point of the titration.

The mechanism of catalysis of RSF may be explained as fallows: Earlier authors observed[19] that the reaction between the nitroso compounds iron(II) is slow in phosphoric acid medium, while that between resorufin and iron(II) in the same acid medium is quite rapid [23]. Therefore, it is a assumed that, when the nitroso compounds are titrated against iron(II) In phosphoric acid medium and in presence of RSF, first of all RSF is reduced to its semi quinone from which contains a free electron (equation-3). The free electron may be readily transferred to the nitroso compounds leading to their rapid reduction (catalyzing the reaction) to their corresponding amino compounds.

In order to explain the feasibility of the reaction between the two nitroso compounds and iron(II) in phosphoric acid medium and in presence of RSF as a catalyst, the authors have determined the formal redox potentials of the two nitroso compounds or oxidant systems ([1-nitroso- 2-napthol]/[1-amino -2-napthol], and [2-nitroso -1-napthol]/[2-amino -1-napthol]), & those of iron or reductant system [iron(III)]/[iron (II)] at different phosphoric acid concentrations. The potentials of the former couples (nitroso compound systems) have been measured adopting the procedure of Murthy and Murthy [24] while those of the latter by the procedure of Rao and Dikshitulu [25]. The potentials data thus obtained have been recorded in Table-2.

Table-2: Formal Redox Potentials of Oxidant systems (nitroso compound systems) and Reductant System (iron system) in 9-12 M H_3PO_4 Medium.

Sl No.	Concentration of Phosphoric, M	Conditional redox potentials NHE*, mV±5 mV		
		1-Nitroso-2-napthol system	2-Nitroso-1-naptol system	Iron system
1	9.0	687	689	429
2	10.0	695	698	419
3	11.0	705	707	409
4.	12.0	710	715	388

* *Normal Hydrogen Electrode*

From these potentials data it may be seen at the formal potentials of the two nitroso compound systems increase while those of iron(III) / iron(II) couple decrease with increase in phosphoric acid concentration from 9-12 M. Further, it is evident from these data that the difference in potentials between the oxidant and reductant systems (nitroso compound system and iron system) is about 255 to 320 mV under the optimum titration conditions i.e in 9-12 M phosphoric acid medium. This difference in potentials is sufficient for rapid reduction of the nitroso compounds to their corresponding amino compounds in a four electron reduction step. Thus, these potentials data neatly explained the conditions for the rapid reduction of the nitroso compounds by iron(II) in phosphoric acid medium in presence of RSF as a catalyst.

In order to explain the suitability of RSF as a redox indicator, the author has determined transition potentials of the indicator RSF adopting the procedure of Belcher et.al. [26] under optimum titration conditions and compared them with those of the oxidant and reductant systems recorded above in Table-2. The transition potentials of RSF indicator has been found to be 560 ±10mV and 552 ±10mV in the titration of 1-Nitroso-2-napthol and 2-Nitros-1-napthol respectively. From these potentials data it is evident that the observed transition potentials (552 - 560mV) of RSF are in the useful intermediate range between the formal potentials of the oxidant systems (range 687-715 mV) and those of the reductant system (range 429-388 mV). Thus, these potentials data are helpful in explaining the feasibility of a RSF as a redox indicator in the present redox reactions.

Recently, we reported the use of iron(II) as a reductimetric reagent in buffer medium & in presence of oxalate for the determination of vanadium(v)[27]. We found however, that this reagent is futile in reducing the nitroso compounds. We further noticed that methylene blue [28], a thiazine dye , which is similar in characters to those of resorufin could not catalyse the present redox reaction and attempts to develop redox methods for these compounds using potassium ferro or ferricyanides[29] did not succeed.

CONCLUSION

The two nitroso compounds (1-Nitroso-2-Naphthol and 2-Nitroso-1-Nsphthol) can accurately be determined by titrating the solutions of these compounds against a standard iron(II) solution in about 9M or above phosphoric acid medium and in presence of small amount of resorufin which acts as a catalyst as well as a redox indicator. In this method, however, chloride, sulfate, acetate, manganese(II), zinc(II) and aluminum(III) do not interfere. Nitrate and nitrite ions interfere at all conditions.

Acknowledgment
The authors express their grateful thanks to Dr.G.D.Sudhakar for his valuable suggestions in preparing this manuscript.

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