REDUCTION OF ORGANIC NITROGEN COMPOUNDS WITH IRON(II) HYDROXIDE, II
Determination of Nitro and Nitroso Compounds

By

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A simple and rapid method was elaborated for the determination of nitro and nitroso compounds on the basis of their reduction with iron(II) hydroxide. The procedure is essentially as follows: addition of a measured amount of excess iron(II) salt and alkali, then after the reduction and the acidification of the mixture, mercurometric determination of the iron(III) salt formed. The reaction takes place at the boiling point, and so the aerial oxidation of the iron(II) hydroxide can be avoided.

The nitroso derivatives formed in the reduction of compounds containing hydroxy or amino groups as *ortho* or *para* substituents (and in the case of a nitroso compound the starting compound itself) tautomerize, and the quinone-type compounds thus formed are extremely volatile with water vapour. Some of these compounds cannot be determined with the accuracy required. The method can be used for the sucessful analysis of numerous compounds which cannot be determined by other methods, or only in a complicated way (tetryl, N-nitroso compounds, nitro derivatives of phenylhydrazine). The hydrazine group, too, takes part in the reduction of the nitro derivatives of phenylhydrazine: the N—N bond is reductively split. Similarly, reductive de-amination also occurs in the reduction of N-nitrosodiphenylamine.

Determination of the nitrogen-containing functional groups of nitro and nitroso compounds is most frequently achieved by quantitative reduction. Of the numerous procedures known, the reduction with titanium(III) salts is by far the most frequent. The determination was first described by KNECHT and HIBBERT [1], and, in spite of modifications suggested by other authors, the original procedure is the most commonly used [2, 3]. The tin(II) chloride method was the first of the reductometric methods [4]. Numerous modifications have been made to this method, too, and a procedure which leads to satisfactory results was recently described by TIWARI and SHARMA [5]. Much more vigorous conditions are required for quantitative reduction than with titanium(III) chloride: the mixture must be boiled for $1^1/_2$ hours. With chromium(II) salts the reduction proceeds rapidly even at room temperature, and thus in certain cases the determination can be carried out by direct titration [6]; nevertheless, it is generally more suitable to apply a back-titration method also in this case [7, 8]. Vanadium(II) and molybdenum(III) salts ([9, 10] and [11], respectively) have also been used as reductometric titrants. Gravimetric procedures based on the back-measurement of metallic tin [12] or copper [13] used for the reduction are known, too. The latter methods are very tedious, while the disadvantage of the reductometric procedures is the extreme sensitivity of the titrant to the oxygen

of the air. The storage of the solution and operations of the determination can only take place in a special apparatus, in a neutral gaseous atmosphere.

The iron(II) hydroxide reduction of nitro and nitroso compounds is frequently used in organic chemical practice, but no reference can be found to its analytical application. According to literature data, the condensation reaction between nitroso-benzene and phenylhydroxylamine or their derivatives occurs only rarely during iron(II) hydroxide reductions [14], and thus it seemed reasonable to make use of the reduction from an analytical point of view. The considerable sensitivity of iron(II) hydroxide towards aerial oxygen appears disadvantageous. However, as all operations during the reduction must be carried out with boiling, aerial oxidation of the iron(II) hydroxide cannot lead to a significant error.

Experimental

Reagents

15% iron(II) sulfate ($FeSO_4.7H_2O$) solution, containing 40 ml concentrated sulfuric acid per litre; 10% sodium hydroxide solution; 30% sulfuric acid solution; 0.05 N mercury(I) nitrate titrant solution (15 g $Hg_2(NO_3)_2.2 H_2O$ dissolved in 1 litre of 0.6 N perchloric acid); 40% ammonium thiocyanate solution.

The majority of the organic compounds examined were FLUKA or BDH products; they were used for the analyses without further purification, in alcoholic or aqueous solutions.

Procedure of the determination

100—110 ml water and 10 ml sodium hydroxide solution were added to a 250 ml flask equipped with a ground-glass neck. The solution was boiled for 4—5 minutes, and 10 ml iron(II) sulfate solution was then pipetted in at a rate that the boiling did not cease. A short reflux condenser was next fitted to the flask, and a solution containing 5—15 mg of the organic substance was pipetted dropwise into the flask through the condenser. The reduction took place already during the addition of the substance to be measured. Then 20 ml sulfuric acid was immediately added dropwise to the flask, and as a result the precipitate of Fe_3O_4 dissolved. After adding 10 ml of ammonium thiocyanate to the cooled solution, it was titrated with the 0.05 N mercury(I) nitrate titrant solution. As the colour of the solution began to fade, the titrant was added more slowly, dropwise, under continuous stirring, until the solution had completely lost its colour. A blank determination was made, and the result was calculated from the difference between the two titrations. The equivalent weights were for the nitro compound 1/6, and for the nitroso derivative 1/4 of the molecular weight, calculated for 1 functional group.

To establish the role of the condensation reaction and to determine the extent of its effect, experiments were also carried out with the substance to be determined already in the alkaline reaction mixture at the beginning of the procedure. The iron(II) sulfate was then added through the condenser to the boiling mixture, as the final component.

Standardization of the mercury(I) nitrate titrant can be achieved with either (a) potassium dichromate (by means of iron(II) sulfate) [15] or (b) with potassium iodate [16].

(a) Approximately two-fold excess of iron(II) sulfate solution is added to 20.0 ml potassium dichromate solution, and the iron(III) ions formed are titrated with the titrant in the presence of ammonium thiocyanate.

(b) 20 ml 0.05 N potassium iodate solution is acidified with 5 ml 4 N perchloric acid, 5 ml of 10% potassium iodide is added, and the solution is thoroughly mixed. After addition of 10 ml ammonium thiocyanate, the solution is diluted to about 60 ml, and the iodine titrated with the titrant up to the appearance of a pale yellow colour. The titration is completed in the presence of starch solution. In the vicinity of the end point the titrant is added dropwise, with an interval of about 20—25 seconds between each drop.

The iron(II) sulfate is present in about 2.5-fold excess. About 0.3 g $FeSO_4.7 H_2O$, equivalent to 20 ml 0.05 N mercury(I) nitrate was necessary for the stoichiometric reduction of the nitro compound. Since the iron(III) hydroxide produced reacted with the excess iron(II) hydroxide to form iron(II) iron(III) oxide according to the equation:

$$Fe(OH)_2 + 2 Fe(OH)_3 = Fe_3O_4 \cdot 4 H_2O,$$
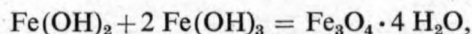
3 mole of iron(II) hydroxide were consumed; further, since the iron(II) oxide content of the iron(II) iron(III) oxide fluctuates considerably [17], about twice the stoichiometrically calculated iron(II) sulfate had to be used. In fact, two and a half times the amount thus calculated was employed for the determination.

Suitable boiling stones were necessary in the boiling of the precipitate mixture. Pieces of sinter-glass of medium porosity were used for this purpose.
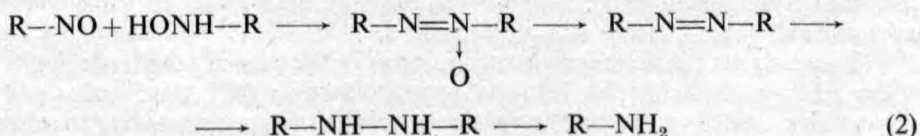

Experimental results and discussion

The data given in the Tables I and II are marked by A and B, according to the two methods applied. In the case of both methods the number of measurements varied between 9 and 12 (Tables I and II).

It can be seen from the Tables that in some cases the reduction with method A and with method B took place in a different way. To interpret the results, we set out from the fact that under optimum experimental conditions (method A) the reduction of the overwhelming majority of the nitro and nitroso compounds proceeded quantitatively according to the reaction scheme:

$$R—NO_2 \longrightarrow R—NO \longrightarrow R—NHOH \longrightarrow R—NH_2 \qquad (1)$$

However, in cases in which a smaller or larger negative error was found in the results of the determination, it was assumed that a condensation reaction of the nitroso and hydroxylamine derivatives took place, the products of which could not be reduced quantitatively by iron(II) hydroxide to the amine, according to the scheme:

$$R—NO + HONH—R \longrightarrow R—N{=}N—R \longrightarrow R—N{=}N—R \longrightarrow$$
$$\underset{O}{\downarrow}$$

$$\longrightarrow R—NH—NH—R \longrightarrow R—NH_2 \qquad (2)$$

However, if the results obtained with the two methods are subjected to a closer

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Table I

Compound	Average relative error, %		Relative standard deviation %
	A	B	A
Nitrobenzene	−1.2	−4.5	0.4
o-Nitroaniline	−4.7	−12	0.8
p-Nitroaniline	−1.0	−5.2	0.3
m-Nitroaniline	−1.8	−2.5	0.5
o-Nitrophenol	−2.2	−6.8	0.5
p-Nitrophenol	−1.2	−4.1	0.4
m-Nitrophenol	−1.3	−2.4	0.4
o-Nitrobenzoic acid	−1.1	−1.5	0.4
p-Nitrobenzoic acid	−1.3	−1.5	0.3
o-Nitrotoluene	−1.0	−1.4	0.3
o-Nitrobenzenesulfonic acid	−1.6	−1.8	0.4
p-Nitrobenzaldehyde	−2.2	−2.4	0.4
m-Nitrobenzaldehyde	−2.3	−2.6	0.3
m-Nitroacetophenone	−2.0	−2.4	0.4
o-Nitrobenzaldehyde hydrazone	−2.4	−2.5	0.3
m-Nitrobenzaldehyde hydrazone	−2.2	−2.3	0.4
p-Nitrophenylhydrazine[1]	−1.2	−1.5	0.3
3-Nitrophthalic anhydride	−2.6	−3.2	3.2
2-Chloro-4-nitroaniline	−2.1	−2.3	0.4
2-Chloro-4-nitrobenzoic acid	−1.8	−2.0	0.4
p-Nitrobenzoyl chloride	−1.8	−2.2	0.4
2-Nitrophenol-4-arsonic acid	−2.3	−2.5	0.5
2-Hydroxy-5-nitropyridine	−1.6	−2.0	0.4
2,4-Dinitrobenzoic acid	−1.3	−2.3	0.5
m-Dinitrobenzene	−2.6	−20	0.6
2,4-Dinitrophenol	−1.9	−6.3	0.5
2,4-Dinitrophenylhydrazine[2]	−2.1	−10	0.5
1,6-Dinitro-2-naphthol	−28	−37	
3,5-Dinitrobenzoyl chloride	−2.0	−3.1	0.5
1,3,5-Trinitrobenzene	−2.4	−45	0.6
Picric acid	−2.2	−25	0.5
Tetryl (nitramine)	−2.1	−12	0.5

[1] The reduction takes place with the uptake of 8 electrons.
[2] The reduction takes place with the uptake of 14 electrons.

study, it becomes obvious that the differences cannot be explained in every case by the occurrence of the condensation reaction. It is striking for example that of the first seven compounds in Table I the two *ortho* and the two *para* derivatives give low results with method B, whereas the *meta* derivatives of the same compounds are reduced quantitatively with this method.

These results are all the more surprising as in the case of other reducing systems these compounds behave in just the opposite manner [18]; thus, *ortho*- and *para*-nitroaniline and the corresponding nitrophenols are reduced according to scheme (1) even in strongly basic medium, while the "bimolecular" steps develop according to scheme (2) only in the reduction of the *meta* derivatives. As an explanation, it

Table II

Compound	Average relative error, %		Relative standard deviation, %
	A	B	A
Nitrosobenzene	−3.5	−15	0.8
p-Nitroso-N,N-dimethylaniline	−1.2	−4.5	0.4
p-Nitroso-triphenylamine	−1.4	−4.4	0.4
p-Chloronitrosobenzene	−2.0	−5.2	0.5
8-Hydroxy-5-nitrosoquinoline	−3.6	−8	0.6
3,4-Dichloronitrosobenzene	−2.2	−5.6	0.4
1-Nitroso-2-naphthol	−70	−85	
Nitroso-R salt	−20	−30	
N-Nitrosodiphenylamine[1]	−1.6	−2.5	0.3
N-Nitrosocarbazole	−2.2	−2.8	0.4

[1] The reduction takes place with uptake of 6 electrons

was assumed that in the cases of the *ortho* and *para* derivatives the nitroso compound formed reacts further in tautomeric form, as quinone imine monoxime or quinone monoxime:
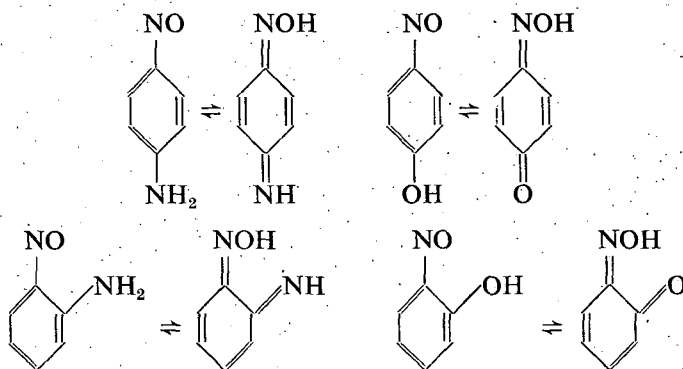
The compounds of quinoid character formed are easily reduced to amines. The *meta* derivatives, however, are not able to develop a quinoidal structure, so the hidroxylamine derivative can take part in a condensation reaction with the still unchanged nitroso compound, under formation of an azoxy compound.

We have explained the iron(II) hydroxide reduction of the above compounds on the basis of the transformations of this tautomer. Under the experimental conditions employed, the iron(II) hydroxide reduction of the quinone oximes formed tautomerically does not proceed quantitatively, because this process is much slower than the reduction of the nitroso derivative, and in addition the quinones are extremely volatile in water vapour and so, part of the compound is to be found in the vapour phase where it is not reduced. At the same time, this tautomerism cannot develop in the case of the *meta* derivatives, and the quantitative reduction of these

compounds is in accordance with our experience that with such a method no condensation reaction occurs in the iron(II) hydroxide reduction [14].

Among the compounds studied, we find many others containing hydroxy or amino groups in *ortho* or *para* positions which behave in a similar way. The question is important, because the effect of the tautomerism mentioned is also found for certain compounds in the experiments using the method A. This effect is particularly marked in the cases of the nitro and nitrosonaphthols. The reductions of 1-nitroso-2-naphthol and nitroso-R salt provide an interesting comparison (Table II). The former gives much lower results, and the difference can be brought into good relation with the presumably considerable difference in volatilities of the quinones formed from the tautomers.

In addition to the substances capable of reacting as tautomers, also the behaviour of the polynitro compounds deserves attention. These compounds are not reduced quantitatively with method B. The explanation of this fact is undoubtedly the successive reduction of the nitro groups, from which a possibility for the formation of the "bimolecular" condensation products results.

In the same way it is possible to explain our experimental observation that with the compounds not reduced quantitatively with 6 electrons, the results obtained with the method B are the lower the greater the amount of substance taken (Table III). This tendency can be clearly discerned with some of the compounds even in the results of the trials with method A, and therefore it seemed advisable, primarily in the case of the polynitro compounds, to carry out the measurements with smaller amounts of the compounds, most suitably with 0.2—0.4 millimoles.

A similar phenomenon is also found in connection with polarographic reductions. For example, in a study of nitrobenzene two steps can be observed. The second of these corresponds to the conversion of phenylhydroxylamine to aniline. In alkaline medium this step gradually stretches out, and its height is no longer proportional to the concentration. From this, it was concluded by STOCESOVÁ [19] that, in addition to the direct reduction, also dimerisation occurs, the product of which cannot be reduced quantitatively to aniline. This process is the more pronounced the more concentrated is the nitrobenzene solution to be polarographed.

Table III

Compound	Amount taken (millimoles)	Average relative error, %	
		A	B
2,4-Dinitro-phenol	0.088	− 1.5	− 4.7
	0.176	− 1.8	− 6.4
	0.352	− 2.6	− 7.8
	0.433	− 3.2	− 9.2
m-Dinitro-benzene	0.126	− 1.5	− 16
	0.252	− 2.2	− 19
	0.631	− 3.1	− 25

This interpretation differs from that for the reductions taking place in alkaline medium according to scheme (2) only in so far as here the condensation reaction of the nitroso and hydroxylamine derivatives is assumed as the starting point of the scheme. The result is, however, the same: the reduction by this route leads to reaction products which are not quantitatively reduced by every reducing agent to the amine; for example, with iron(II) hydroxide the system does not attain the amine derivative by this means.

At the same time, with method A the majority of the compounds are reduced

quantitatively according to scheme (1). Here, in contrast with method B, the combined effect of the following three factors can be established from a consideration of the results.

(*i*) The rate of the condensation reaction is much lower in neutral medium than in alkaline medium [20].

(*ii*) Because of the dropwise addition in the case of procedure A, the concentration of the organic compound is extremely small during the entire reaction.

(*iii*) In neutral medium the reducing power of iron(II) hydroxide is substantially higher than in the presence of excess alkali. This was demonstrated in our earlier studies in connection with the reducibility of the nitrate ion [21]. The most active precipitate is formed between about pH 6 and pH 8. As is evident from the results, the formation of the bimolecular products can be successfully avoided with method A in all cases.

With certain compounds, the reduction of the nitro group also initiates the reduction of other groups in the molecule. In the iron(II) hydroxide reduction of *p*-nitrophenylhydrazine the hydrazine group is reduced by bond splitting:

$$O_2N-C_6H_4-NH-NH_2 \xrightarrow{+\ 8e\ +\ 8H} H_2N-C_6H_4-NH_2 + NH_3$$
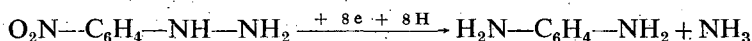
The N—N bond similarly splits in the case of 2,4-dinitrophenylhydrazine, too.

A similar reductive bond splitting in the case of titanium(III) chloride reductions was first reported by ROBINSON [22], likewise in connection with *p*-nitrophenylhydrazine, and his studies were later confirmed by ZIMMERMANN and LIEBER [23]. These authors also attempted the titanium(III) chloride determination of the nitro derivatives of phenylhydrazine, but the determination was not accurate: the consumption of titrant only approached the 8 equivalents, and in the case of the dinitro derivative the 14 equivalents. The iron(II) hydroxide reduction proceds quantitatively in the case of both compounds.

Phenylhydrazine itself does not react with iron(II) hydroxide, and thus it seems that the reduction accompanying the bond splitting in the hydrazine group is induced by the reduction of the nitro group.

The iron(II) hydroxide reduction of N-nitrosodiphenylamine is similarly accompanied by splitting of the N—N bond:
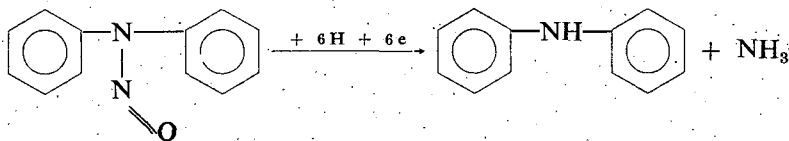
There are no data in the literature on the titanium(III) chloride reductions of this latter compound and of N-nitrosocarbazole. Moreover, no generally applicable analytical procedure for the determination of N-nitroso compounds is known [24]. Namely, these compounds are converted to amines on the action of acids:

$$R_2N-NO \xrightarrow[\text{acid}]{\text{water}} R_2NH + HNO_2.$$
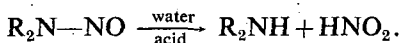
Because of the decomposition of the nitrous acid formed, this transformation makes the determination in acidic medium completely hopeless.

There is a further compound in Table I which could not be successfully reduced with titanium(III) chloride: tetryl (2,4,6-trinitrophenylmethylnitramine). Its determination with iron(II) hydroxide gives good results.

As can be seen from the data in the Table, the determination is of sufficient accuracy in most cases. The accuracy of the determinations of some compounds is affected by the tautomerism of the nitroso derivatives, and therefore the method cannot be used in the case of the nitro and nitroso derivatives of naphthol.

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ВОССТАНОВЛЕНИЕ ОРГАНИЧЕСКИХ АЗОТСОДЕРЖАЩИХ СОЕДИНЕНИЙ ГИДРООКИСЬЮ ЖЕЛЕЗА(II), II

Определение нитро- и нитрозосоединений

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Разработан простой и быстрый метод для определения нитро- и нитрозосоединений на основании их восстановления гидроокисью железа(II). Существо метода заключается в добавлении избыточных количеств соли железа(II) и щелочи, затем после восстановления и подкисления раствора, в меркурометрическом определении образовавшейся соли железа(III). Реакция проходит при температуре кипения и, таким образом, можно избежать окисление кислородом воздуха гидроокиси железа(II).

Нитрозопроизводные, образующиеся при восстановлении соединений содержащих гидроксильную или аминную группу в орто- или пара-положении (а в случае нитрозосоединения непосредственно исходное вещество), таутомеризуются и образовавшиеся соединения хинонного типа легко улетучиваются с парами воды. Некоторые вещества такого типа не могут быть определены с требуемой точностью. Используя описанный метод, удалось осуществить анализ ряда соединений, которые другими методами не могут быть определены или определяются весьма сложно (фенил-гидразин нитропроизводные тетрил—N—нитрозосоединения). Гидразинная группа принимает участие в восстановлении нитро-производных фенилгидразина: связь N—N реактивно разрывается. Аналогично происходит редуктивное отщепление амина при восстановлении N-нитрозо-дифениламина.