

**REDUCTION OF ORGANIC NITROGEN COMPOUNDS
WITH IRON(II) HYDROXIDE, I
The Factors Affecting the Reduction**

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The authors summarize their earlier observations concerning the reduction of the nitrate ion, and on this basis find that with suitable experimental conditions iron(II) hydroxide is a convenient reagent for the quantitative reduction and determination of nitro and nitroso compounds and of nitric acid esters. Among the factors affecting the reduction, the condensation reaction of the nitroso and hydroxylamine derivatives deserves the most attention, because the azoxy derivative thus formed is not reduced quantitatively to the amine by iron(II) hydroxide. Since the participation of this reaction in the reduction is the least in neutral medium, its effect can be avoided if somewhat less alkali than the equivalent is used for the precipitation of the iron(II) salt applied. In the same way, the order of mixing the reacting substances also exerts an effect.

The reduction of organic compounds containing nitrogen-oxygen bonds is an intensively studied process in both organic and analytical chemical practice. For analytical purposes the most frequently used reductants are titanium(III) and chromium(II) salts, while iron(II) salts are more common in the case of organic nitrates:

On the basis of our nitrate determination [1], elaborated earlier, iron(II) hydroxide appeared to be a suitable reductant for the reduction and determination of nitro and nitroso compounds and organic nitrates.

Compared with the use of iron(II) salts in acidic medium, the analytical applications of iron(II) hydroxide are of secondary importance, without doubt because of its sensitivity towards aerial oxygen. However, it can be well employed when the reaction product formed as a result of the reduction can be measured after separation. Iron(II) hydroxide has been used successfully, among others, for the determination of the nitrite and nitrate ions by means of the distillation of the ammonia formed in the reduction [2, 3]. The reduction proceeds quantitatively only in strongly alkaline solution, after prolonged distillation, but the reaction can be catalysed by silver ions [4].

In the reaction, 8 moles of iron(II) hydroxide are consumed for the reduction of 1 mole of nitrate, and this equivalence ratio gave us the idea of elaborating a

redox determination which promised advantages in the multiplication procedures. In principle, two routes seemed suitable: to measure (i) the excess iron(II) salt, or (ii) the iron(III) salt formed. On the basis of the well-known iron(II) methods [5, 6], the measurement of the iron(II) salt excess was selected, and in accordance with the above principles, a permanganometric method was elaborated for the determination of nitrate [1].

In the course of our studies it turned out that, in addition to silver, copper ions catalyse the process, too [7]. The advantage of using copper is the fact that the catalysis is disturbed only by the presence of antimony salts, while the catalytic effect of silver is completely destroyed by numerous metal ions and several anions, even in amounts of a few tenths of a milligram [8].

In this connection, it is worth while mentioning that BARKER and VOLK [9] describe the presence of silver ions to be without effect on the iron(II) hydroxide reduction of nitrate. They criticize the method of VARNER *et al.* [10] who, on the basis of our studies, elaborated a procedure for the determination of the nitrogen of ammonium, amide, nitrite and nitrate in the presence of each other.

Their experiences with the considerable sensitivity of the silver catalysis can be understood and therefore in both of these works [9, 10] it would have been more favourable to use copper sulfate as catalyst.

Although iron(II) hydroxide is extremely sensitive to aerial oxygen oxidation of the iron(II) ions, this effect can practically be eliminated by carrying out the operations under boiling.

To establish the extent of aerial oxidation, four permanganate titrations were carried out on solutions of iron(II) sulfate to which 10 ml 30% sodium hydroxide had

Table I

I	II
28.74	28.63
28.74	28.61
28.72	28.60
28.73	28.60
Mean value 28.73 ml	Mean value 28.61 ml

been added, the mixtures boiled for 10 minutes and then acidified, and four were carried out by direct titration. According to the results given in Table I, the consumption of the titrant is on average only 0.12 ml lower in the case of the solution boiled with alkali. (In Table I, column I gives the volumes of 0.1 *N* potassium permanganate solution consumed in the direct titration of the iron(II) sulfate solution, while column II gives the volume consumed in the titration of the solution which had been treated with alkali and boiled for 10 minutes.)

By applying a blank test, this very small degree of oxidation causes a completely negligible error.

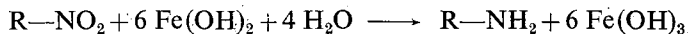
In the determination of the organic substances, permanganometry or other oxidimetric methods could not be applied because of the presence of the amine formed in the reduction. At the same time, the measurement of the iron(III) salt produced by the use of a reducing titrant promised greater precision: in this case a difference of 0.01 ml in the added iron(II) salt causes a difference of 0.05 ml in the consumption of 0.1 *N* titrant; the iron(II) sulfate applied consumes about 50 ml 0.1 *N* potassium permanganate.

A solution of the very stable mercury(I) nitrate seemed most suitable as titrant. This reagent was used by BRADBURY and EDWARDS [11] for direct titration of iron(III)

ions; more recently it was proposed by BELCHER and WEST [12], and its use was extended by TARAJAN [13] to the direct titration of other oxidants, too. In the presence of sufficient thiosulfate the reaction is stoichiometric, and because of the extremely stable nature of the titrant it is more suitable than all other reductants for the determination of iron(III) ions.

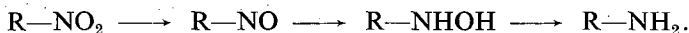
For the preparation of a 0.05 *N* mercury(I) nitrate titrant solution, the descriptions to be found in literature use nitric acid. The prepared solution must be freed from nitrogen oxides with a current of air, because otherwise nitrosyl thiocyanate is formed from the ammonium thiocyanate added to the solution to be titrated. The colour of ammonium thiocyanate is so similar to the red colour of the iron(III) thiocyanate that the detection of the end-point becomes practically impossible because of its constant re-formation [14]. In our experience, the formation of nitrosyl thiocyanate frequently occurs even if the solution has previously been boiled, whereas not even the slightest disturbing effect appears if the solution of mercury(I) nitrate is prepared with perchloric acid.

The experiments for iron(II) hydroxide reduction of organic compounds were originally carried out as in the determination of nitrate. An iron(II) sulfate solution was measured into a boiling, alkaline solution of the organic compound, and after the reduction the acidified and cooled solution was titrated for iron(III) ions with a standard solution of mercury(I) nitrate. With this method, however, satisfactory results could not be obtained with the vast majority of the nitro and nitroso compounds. When calculations were made on the basis of the reaction

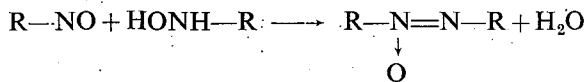


low results were very frequently obtained. From the similarly considerable differences (5—20%) in the results obtained for a given sample, it could also be established that the reaction does not take place in a clear-cut manner, even assuming the transfer of a number of electrons different from that mentioned above.

The results could be explained by a deviation from the Haber mechanism [15]:



HABER himself pointed out that under different experimental conditions a number of side-reactions may take place in the three-step reduction of nitrobenzene. The most important of these is the reaction between nitrosobenzene and phenylhydroxylamine:



The participation of this reaction in the overall process is quite significant, particularly in alkaline medium.

BRANDT and MAHR [16] studied the rate of the reaction between nitrosobenzene and phenylhydroxylamine and found the following relations with regard to the effect of the medium. If the reaction rate in neutral medium was taken as unity, then in a medium of 0.005 *M* HCl, 0.01 *M* HCl, 0.0025 *M* KOH or 0.005 *M* KOH, the rate was found to be 2, 3, 200 and 300, respectively.

The investigations of HINSHELWOOD *et al.* [17] showed that the reaction between hydrazobenzene and phenylhydroxylamine plays an important role in the titanium(III)-chloride reduction of nitrobenzene and its derivatives, in spite of the fact that the direct reductions of these two compounds are fast processes.

Thus, the reason of the failure of iron(II) hydroxide reduction of the nitro compounds to give analytically useful results with the given procedure in the case of numerous compounds was that considerable amounts of azoxy compounds were formed during the reaction, and the iron(II) hydroxide was not able to reduce these to amines.

Considering the above, the subsequent experiments were carried out in such a way that the alkaline medium should have no effect on the side-reaction mentioned. For this purpose the addition of the iron(II) sulfate was now made to a boiling but neutral solution of the compound, and finally a solution containing an amount of sodium hydroxide, almost equivalent to the iron(II) sulfate, was introduced into the mixture. With this method it was possible to attain or to approximate very well the six-electron reduction with the vast majority of the compounds studied. In most cases, however, even better results could be obtained by adding the reagents to each other in yet another sequence: adding first the iron(II) sulfate solution to the boiling solution of sodium hydroxide, and then the solution of the nitro compound to this reaction mixture.

After working out the most suitable method, the reaction was also carried out in every case with the original sequence of adding the reagents. Although the data so obtained were not of use from an analytical point of view, valuable conclusions could be drawn with regard to the course of the reduction, the extent of the participation of the side-reactions, and the transformations of certain compounds in the course of the reaction.

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ВОССТАНОВЛЕНИЕ ОРГАНИЧЕСКИХ АЗОТСОДЕРЖАЩИХ
СОЕДИНЕНИЙ ГИДРООКИСЬЮ ЖЕЛЕЗА(II), I

Факторы, влияющие на реакцию восстановления

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Авторы подводят итоги ранее полученным данным, относящимся к восстановлению нитрат-иона, и на основании этого показывают, что при соответствующих экспериментальных условиях гидроокись железа(II) является подходящим реагентом для количественного восстановления и определения нитро- и нитрозосоединений и эфиров азотной кислоты. Среди факторов, влияющих на реакцию восстановления, заслуживает наибольшее внимание реакция конденсации нитрозо- и гидроси-аминопроизводных потому, что образовавшееся производное азоксисоединения, под влиянием гидроокиси железа(II) не восстанавливается количественно. Вследствие того, что участие этой реакции в восстановлении наименьшее в нейтральной среде, её влияние может быть устранено при применении меньших количеств щелочи, чем необходимо для осаждения соли железа(II). К аналогичному результату приводит и соответствующий порядок введения реагентов.