

**REDUCTION OF ORGANIC NITROGEN COMPOUNDS  
WITH IRON(II) HYDROXIDE, III**  
**Microdetermination of Organic Nitrates with Silver Catalysis**

By

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The esters of nitric acid can be quantitatively reduced by iron(II) hydroxide in the presence of diamminesilver sulfate as catalyst, and the iron(III) salt formed in the reaction can be determined by titration with mercury(I) nitrate. The author investigated the reduction of nitroglycerine and erythritol tetranitrate. 8 moles of iron(II) are consumed per nitrate group in the reduction, and this favourable equivalent weight relation provides a possibility for the simple determination of micro and even ultramicro amounts.

Among organic compounds containing N—O bonds, the esters of nitric acid occupy a special place from the analytical point of view. The methods treated in the case of nitro compounds are either unsuitable or cannot be used directly for their determination.

The reduction of organic nitrates with titanium(III) salts does not take place in a clear-cut way: in part nitrogen monoxide, and in part an ammonium salt is obtained. According to some authors [1] 7.5 moles of titanium(III) are consumed per nitrate group, but according to other authors [2—4] this value is 6 moles. Reduction with iron(II) sulfate is most frequently used [5—8], but in this procedure (and in the titanometric method, too), the aerial oxidation of the nitrogen monoxide formed give rise to considerable error. (For example, as suggested by LEITHE [9], the neck of the flask has to be heated with another gas-burner while boiling the solution, in order to prevent the nitrogen monoxide from returning.) The so-called "transnitration" method, whether carried out on the basis of the Kjeldahl determination of the nitrosalicylic acid formed [10, 11] or on the basis of titanometric titration [12], is fairly lengthy. Colorimetric procedures and the so-called nitrometric procedure can be of service in routine analysis, but they do not give results of sufficient accuracy.

Data on the iron(II) hydroxide reduction of organic nitrates cannot be found in the literature. On the basis of our earlier nitrate determination [13], it could be expected that iron(II) hydroxide would also reduce organic nitrates, and it seemed probable that silver would catalyse the process.

*Experimental*

*Reagents* were as in the previous paper [14], while a solution of diamminesilver sulfate was used as catalyst. This was prepared as follows. A concentrated solution of 5 g p.a. silver nitrate was poured into 8—10 ml boiling dilute sulfuric acid, and the silver sulfate precipitated was washed 4—5 times by decantation with cold water. An approximately semisaturated solution was prepared from the silver sulfate by shaking it for 4—5 minutes with water, and to 4 volumes of this solution 1 volume of ca. 15% ammonia solution was added and stored in a dark bottle.

Alcoholic solutions of nitroglycerine and erythritol tetranitrate were used in the investigations.

*The procedure* was as described for nitro and nitroso compounds [14] (method A) with the difference that before the addition of the iron(II) sulfate 5 ml of diamminesilver sulfate solution was added to the boiling mixture. In the reaction 8 moles of iron(II) hydroxide are consumed per nitrate group.

*Experimental results*

The first experiments were carried out with nitroglycerine without a catalyst, and as can be seen from the data in Table I, and even in this case a reaction of considerable degree took place. The degree of the reduction was affected to a great extent by the rate of dripping-in of the solution. (The nitroglycerine solution was placed in a tap-funnel, diluted to 2—3 times its volume, and dripped through the reflux condenser into the flask at various rates.)

Table I

Nitroglycerine added, mg	Addition time, min.	0.05 N $\text{Hg}_2(\text{NO}_3)_2$ consumed, ml	Extent of reduction, %
2.01	3	3.20	75.3
	10	3.65	85.9
4.01	3	6.27	74.0
	10	6.85	80.8
	30	7.72	91.1
10.03	3	13.20	62.4
	10	16.40	77.6
	40	19.14	90.6

From this course of the reduction, the effectiveness of the silver catalysis could be expected. In fact, in the presence of diamminesilver sulfate a rapid reaction occurred. After adding the solution by pipette in just countable drops, the mixture can be immediately treated with acid. As can be seen from the data in Table II, the error of the determination is within 1%.

The nitroglycerine was reacted with the iron(II) hydroxide also by adding the iron(II) salt to the boiling alkaline solution. Approximately 6 equivalents of the

Table II

Compound	Amount added, mg	0.05 N Hg <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> consumed, ml	Amount found, mg	Relative error, %
Nitroglycerine	1.61	3.39	1.60	-0.4
		3.38	1.60	-0.7
		3.37	1.59	-1.0
	2.01	4.23	2.00	-0.4
		4.22	2.00	-0.7
		4.20	1.99	-1.1
	4.01	8.46	4.00	-0.2
		8.43	3.99	-0.5
		8.42	3.98	-0.7
	8.03	16.90	8.00	-0.4
		16.88	7.99	-0.5
		16.86	7.98	-0.7
Erythritol tetranitrate	1.523	3.21	1.515	-0.5
		3.20	1.511	-0.8
		3.18	1.501	-1.4
	3.047	6.41	3.026	-0.7
		6.38	3.012	-1.1
		6.37	3.007	-1.3
	5.332	11.26	5.316	-0.3
		11.22	5.297	-0.7
		11.20	5.287	-0.8
	8.379	17.70	8.355	-0.3
		17.64	8.327	-0.6
		17.63	8.322	-0.7

iron(II) salt per nitrate group were then consumed in the reaction. Under such conditions, a complex hydrolysis of the nitroglycerine, unelucidated so far in its details [15, 16], could take place before the reduction, and it was the hydrolysis products which were reduced. Such an interpretation of the reaction is also supported by the fact that, both in the presence and in the absence of the silver, identical results were obtained.

The end-point detection of the mercurimetric titrations was satisfactorily precise [17], and therefore the method permits the measurement even of ultramicro amounts, too.

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ВОССТАНОВЛЕНИЕ ОРГАНИЧЕСКИХ АЗОТСОДЕРЖАЩИХ  
СОЕДИНЕНИЙ ГИДРООКИСЬЮ ЖЕЛЕЗА(II), III

Микроанализ органических нитратов с помощью соединений серебра

*Л. Г. Барта*

Эфиры азотной кислоты могут быть количественно восстановлены гидроокисью железа(II) в присутствии диамин-сульфата серебра в качестве катализатора и образовавшаяся в результате реакции соль трёхвалентного железа определяется меркурометрическим титрованием. Автор изучал восстановление нитроглицерина и эритрол тетранитрата. Для восстановления одной нитро-группы расходуется 8 молей соли двухвалентного железа и в результате такого выгодного соотношения представляется возможность просто определить микро- и ультрамикро количества нитросоединений.