Determination of Nitrogen in Nitro and Oxime Compounds by the Iodic Acid Decomposition Method

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In the previous investigation[1] on the determination of nitrogen in organic compounds by the iodic acid decomposition method the author has found that for analyses of ammonium salts, amines, azo-compounds, pyrroles, thiazoles, etc., satisfactory results are obtained by means of this new method, but nitro and oxime compounds, etc. do not give good results.

The outline of this method is as follows. An organic compound containing nitrogen is decomposed by heating with a potassium iodate-strong phosphoric acid mixture in a special reaction vessel. By sending the liberated nitrogen with carbon dioxide into an azotometer, which is filled with potassium hydroxide solution, the nitrogen can be determined gas-volumetrically. The reason why the nitrogen in nitro and oxime compounds can not be directly estimated by this method may be due to the fact that the nitrogen in these compounds is already in an oxidized state and is liberated by the iodic acid decomposition, at least partially, merely as nitrogen monoxide, or dioxide, which is absorbed in potassium hydroxide solution in the azotometer.

The purpose of the present investigation is to extend this method to the determination of nitrogen in nitro and oxime compounds. It has previously been shown that the nitrogen in amine compounds can be easily determined by this method. Therefore, if the nitrogen of a nitro or oxime form could be reduced to an amine form by a somewhat simple treatment, it may be possible to determine the nitrogen in nitro or oxime compounds by the reduction and the subsequent iodic acid decomposition.

For this reason, the present study was mainly aimed at finding out the most suitable reducing agent against these compounds. From the results of the experiments described later, it was concluded that iron metal with diluted sulfuric acid is the best reducing agent for the present purpose.

In this paper the discussion of the reducing agents, the recommended procedure of this method, and the analytical results of several nitro and oxime compounds are described.

In the author's laboratory strong phosphoric acid has been used not only for the determination of nitrogen in organic compounds, but also for the determination[2] of the oxidation value of organic compounds and the determination[3] of elementary carbon such as active carbon and graphite. Since hitherto the property of strong phosphoric acid has not been stated in these papers, the specific gravity and the chemical composition of strong phosphoric acid used in these studies are also described complementally.

Reducing Agents

The reducing agent used in this method must have the following properties: A nitro or oxime radical is quantitatively reduced by it to an amino radical; the reduction should be done at temperatures lower than 100°C, because many nitro and oxime compounds are easily volatilized at higher temperatures; and after the reduction the remaining reducing agent does not interfere with the subsequent decomposition procedure of the reduced product and the estimation of nitrogen.

Since the decomposition process is carried out in a strong phosphoric acid medium, it seems to be convenient for the reduction process also to be done in the same medium. Therefore, at first, zinc metal in strong phosphoric acid was used as a reducing agent. But, using this agent, the analyses for *p*-nitroacetanilide and *α*-dinitrophenol gave low results. Probably it may be due to the fact that zinc metal does not easily dissolve in strong phosphoric acid at a relatively low temperature.

Next, tin(II)-strong phosphoric acid was tested, because it was found in the anthor's laboratory that this agent can reduce sulfates[4] or various organic sulfurs[5] to hydrogen sulfide. But it was

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[1] S. Ohashi. This Bulletin, 28, 177 (1955).

[2] S. Ohashi, This Bulletin, 28, 171 (1955).

[3] T. Kiba, S. Ohashi, T. Takagi and Y. Hirose, *Japan Analyst*, 2, 446 (1953).

[4] T. Kiba, T. Takagi, and Y. Yoshimura, Presented at the Symposium of Analytical Chemistry at Kinki University, October 30, 1954.

[5] S. Ohashi, I. Kishi, Presented at the same Symposium described above.

not favorable, as it produces, when heated, a certain gas, probably hydrogen, which can not be absorbed in potassium hydroxide solution in the azotometer.

Glucose was used by J. Noguchi[6] as a buffer agent in the micro-Dumas method for the analyses of nitro compounds. Accordingly as an example α-dinitrophenol was decomposed with iodic acid-strong phosphoric acid in the presence of glucose, but the test also failed, because too much iodine was liberated by the oxidation of glucose and the sample.

Hypophosphorous acid in strong phosphoric acid was not suitable for the present purpose, since it liberates, when heated, phosphine, which can not be absorbed in alkali solution in the azotometer.

In view of the above facts the reduction methods using strong phosphoric acid were given up. Then the reduction in diluted mineral acids was investigated.

Iron metal powder in hydrochloric acid was tested, since it has been commonly used to reduce nitro compounds. The results for picric acid gave values which were almost correct. But it was not favorable, because the liberated chlorine reacts with iodine and mercury in the azotometer to produce iodine chloride and mercuric chloride, which block the capillary of the azotometer.

Finally it was found that iron metal powder in diluted sulfuric acid does not possess the various defects described above and is the most suitable reducing agent.

Apparatus and Reagents

The same apparatus described in the previous paper[7] was used. Only the reaction vessel is illustrated in Fig. 1.

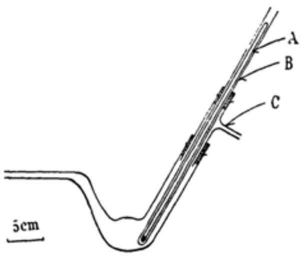

Fig. 1. Reaction vessel
A: Thermometer
B: Thermometer-protecting Tube
C: Gas-introducing Tube

The following reagents were the same ones that were used in the foregoing paper[8]; strong phosphoric acid, potassium iodate, carbon dioxide, and potassium hydroxide solution. Acetone, 6 N sulfuric acid, and iron metal powder were all of extra pure grade.

Procedure

Weigh accurately a 10 to 30 mg. sample, depending upon its nitrogen content, into a small weighing tube; choose the sample weight so that the volume of the nitrogen formed will be 1 to 5 ml. Place the weighing tube containing the sample in the reaction vessel, add 1 to 1.5 ml. of acetone, and dissolve the sample in it. Next, add 50 to 60 mg. of iron metal powder and 1 ml. of 6 N sulfuric acid. Gently heat the mixture on a water bath. By this treatment the nitro or oxime compound is reduced to the corresponding amine compound and at the same time the excess of iron is dissolved in sulfuric acid. Continue heating on the water bath until all the acetone and the greater part of the water are expelled. At the end of this time the dissolution of the iron is almost always complete.

After cooling the contents of the vessel, add 3 to 5 ml. of strong phosphoric acid and two or three times as much of the theoretically required amount of potassium iodate in it.

Now insert a gas-introducing tube, a thermometer, and a thermometer-protecting tube into the reaction vessel, and connect the vessel with a carbon dioxide generator and a calcium carbonate-filled guard tube. After removing the air present in the reaction vessel, connect it to an azotometer.

Heat the mixture in the vessel on a small electric heater at 200°C to 250°C. After the complete decomposition of the sample, transfer the gas in the vessel into the azotometer and carbon dioxide is then allowed to be introduced. Read the volume of the nitrogen, the room temperature, and the atmospheric pressure at this time and calculate the percentage of the nitrogen by using these values.

Results of Analyses and Discussion

Analyses of various known nitro and oxime compounds were carried out by this method. These results are summarized in Table I. As shown in Table I analyses for *p*-nitrophenol, α-dinitrophenol, picric acid, *p*-nitroacetanilide, sodium hexanitrodiphenlyamine, *m*-nitro-*o*-anisidine, dimethylglyoxime, cyclohexanone oxime, and α-oxime of phenylpropionic acid gave satisfactory results. In the case of *p*-nitroacetanilide, sodium hexanitrodiphenylamine, and *m*-nitro-*o*-anisidine, the total nitrogen contents of both the nitro and amino radicals were determined.

The accuracy of the results obtained is within ±2%. The time required for an analysis is fifty minutes.

It is necessary for a rapid and complete reaction between a sample and a reducing agent that the sample be homogeneously dissolved in acetone.

If the quantity of sulfuric acid to be added is deficient, the reduction can not be carried out completely and if it is in too excess, after the reduction, strong phosphoric acid is so much diluted that the sample can not be decomposed perfectly.

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[6] J. Noguchi, Scientific Papers from the Osaka University, No. 22, February 1951.

[7],[8] S. Ohashi, This Bulletin, 28, 177 (1955).

TABLE I

DETERMINATION OF NITROGEN IN VARIOUS NITRO AND OXIME COMPOUNDS

Substance	Nitrogen Content %	Sample Weight mg.	Nitrogen Content	
			Found %	Deviation %
p-Nitrophenol $C_6H_4(OH)NO_2$	10.01	13.1	9.9_9	-0.0_2
		13.7	9.9_8	-0.0_3
		11.1	10.0_9	$+0.0_8$
		14.5	10.0_7	$+0.0_6$
		10.8	10.0_2	$+0.0_1$
		10.9	10.1_1	$+0.1_0$
a-Dinitrophenol $C_6H_3(OH)(NO_2)_2$	15.19	14.9	15.3_0	$+0.1_1$
		13.3	15.3_3	$+0.1_4$
		12.9	15.1_5	-0.0_4
		11.1	15.2_3	$+0.0_4$
		11.5	15.2_0	$+0.0_1$
		13.9	15.2_0	$+0.0_1$
		13.0	15.1_4	-0.0_5
Picric acid $C_6H_2(OH)(NO_2)_3$	18.34	7.8	18.3_0	-0.0_4
		11.4	18.3_2	-0.0_2
		10.3	18.4_9	$+0.1_5$
		11.0	18.3_6	$+0.0_2$
		7.7	18.2_1	-0.1_3
		9.1	18.0_4	-0.3_0
p-Nitroacetanilide $C_6H_4(NO_2)NHCOCH_3$	15.55	13.3	15.5_5	0.0_0
		15.7	15.5_8	$+0.0_3$
		14.6	15.6_3	$+0.0_8$
		15.0	15.6_9	$+0.1_4$
		14.3	15.6_9	$+0.1_4$
		13.9	15.7_4	$+0.1_9$
Sodium hexanitrodiphenylamine $NaN(C_6H_2(NO_2)_3)_2$	21.26	10.5	21.2_1	-0.0_5
		11.4	20.9_5	-0.3_1
		12.4	21.2_5	-0.0_1
		10.1	21.1_4	-0.1_2
		10.9	21.2_7	$+0.0_1$
		11.1	21.0_7	-0.1_9
m-Nitro-*o*-anisidine $C_6H_3(NO_2)(NH_2)(NH_2)OCH_3$	16.66	11.4	16.5_8	-0.0_8
		8.1	16.6_6	0.0_0
		14.8	16.6_0	-0.0_6
		16.7	16.4_5	-0.2_1
		11.2	16.6_2	-0.0_4
Dimethylglyoxime $HON(CH_3)C\cdot C(CH_3)NOH$	24.13	12.6	24.1_6	$+0.0_3$
		12.1	24.2_0	$+0.0_7$
		23.3	24.0_8	-0.0_5
		16.7	24.2_2	$+0.0_9$
		16.4	24.0_4	-0.0_9
		20.4	24.1_4	$+0.0_1$
Cyclohexanone oxime $C_6H_{10}NOH$	12.38	24.7	12.3_7	-0.0_1
		28.0	12.2_7	-0.1_1
		24.6	12.3_3	-0.0_5
		26.5	12.3_6	-0.0_2
		24.3	12.4_0	$+0.0_2$
		24.0	12.4_0	$+0.0_2$
a-Oxime of phenylpropionic acid $C_6H_5CH_2C(NOH)COOH$	7.82	26.4	7.67	−0.15
		28.6	7.85	+0.03
		22.6	7.66	−0.16
		23.9	7.86	+0.04
		26.1	7.97	+0.15
		28.4	7.77	−0.05
		28.6	7.79	−0.03

On many occasions excess iron metal powder is all dissolved in sulfuric acid by means of the above mentioned procedure. If it remains, the hydrogen formed by the reaction between iron and strong phosphoric acid may be transferred with nitrogen to the azotometer and gives a serious error. Therefore, in such a case, before the addition of potassium iodate the remaining iron powder should be dissolved by heating with strong phosphoric acid.

Strong Phosphoric Acid

The strong phosphoric acid used in the experiments below was prepared from common 89% orthophosphoric acid by using an apparatus shown in Fig. 2. About 18 g. of the orthophosphoric acid was dehydrated by heating until the temperature of the liquid attained various points, ranging from 200° to 320°C at intervals of about 20°C.

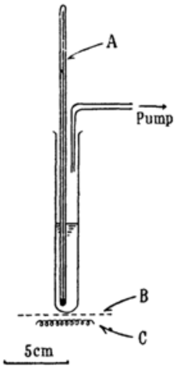

Fig. 2. Dehydration Apparatus
A: Thermometer
B: Wire Gauze
C: Electric Heater

The specific gravity of the strong phosphoric acid obtained in this manner at 15°C was estimated by means of a specific gravity bottle.

Since some phosphoric acid is expelled with water during the dehydration, a percentage of phosphorus pentoxide in the prepared strong phosphoric acid can not be calculated from the decrease of the total weight of the sample. As pyro- or triphosphoric acid is not completely converted into orthophosphoric acid even by heating with water for thirty minutes, it is undesirable to use a direct titrimetric method with a standard sodium hydroxide solution for the determination of the total phosphorus pentoxide. Therefore it was determined gravimetrically as magnesium pyrophosphate.

From the obtained percentage of phosphorus pentoxide and the diagram reported by R. N. Bell[9], which shows the relation between the content of phosphorus pentoxide and the chemical composition of strong phosphoric acid, the content of ortho-, pyro-, and triphosphoric acid in the sample can be estimated respectively.

All of the above-mentioned results are shown in Table II. According to R. N. Bell strong phosphoric acid is defined as phosphoric acid containing more than 72.4% phosphorus pentoxide, which corresponds to the phosphorus pentoxide content of 100% orthophosphoric acid. According to this definition, in Table II, only the acids having a specific gravity higher than 1.882 are the true strong phosphoric acid.

If the dehydration condition changes, a different strong phosphoric acid is formed, even though heated to the same temperature. For example, when 400 g. of 89% orthophosphoric acid is dehydrated until its temperature reaches 300°C, the resulting strong phosphoric acid has a specific gravity of 1.932, which is greater than that obtained in the above-mentioned experiments. This is probably due to the fact that, when the larger amount of the acid is used, the dehydration takes place more effectively than in the case of the smaller amount. The so-called "300°C strong phosphoric acid" used in the author's laboratory has a specific gravity of about 1.93.

Summary

(1) The iodic acid decomposition method for the determination of nitrogen in organic compounds, which has been reported already by the author, was extended to analyses of nitro and oxime compounds.

TABLE II

SPECIFIC GRAVITY AND CHEMICAL COMPOSITION OF VARIOUS STRONG PHOSPHORIC ACIDS

Dehydration Temp. °C	Initial Weight g.	Final Weight g.	Remains Weight %	Specific Gravity at 15°C	P_2O_5 %	H_3PO_4 %	$H_4P_2O_7$ %	$H_5P_3O_{10}$ %
202	17.574	16.570	94.28	1.805	69.23	95.6	—	—
218	17.684	16.276	92.04	1.833	70.52	97.4	—	—
241	17.657	15.971	90.46	1.865	72.21	95	1	4
259	17.910	15.969	89.18	1.882	72.97	90	5	5
281	17.974	15.767	87.72	1.909	74.15	82	12	6
300	17.315	15.022	86.78	1.925	74.63	76	18	6
320	17.873	15.274	85.51	1·948	75.75	65	28	7
300	400	—	—	1.932	—	—	—	—

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[9] R.N. Bell, *Ind. Eng. Chem.*, 40, 1464 (1948), L.F. Audrieah, "Inorganic Syntheses, Volume III", McGraw-Hill Book Company, Inc., New York, (1950), p. 89.

(2) In a reaction vessel, a samplew as dissolved in acetone, reduced with a reducing agent to the corresponding amine, and then decomposed by heating with a mixture of iodic acid and strong phosphoric acid. The liberated nitrogen was determined by means of an azotometer.

(3) After testing many reducing agents it was concluded that a mixture of iron metal powder and diluted sulfuric acid was the best.

(4) For various nitro and oxime compounds satisfactory results were obtained by means of this modified method.

(5) The specific gravity and the chemical composition of strong phosphoric acid prepared in the various conditions have been described complementally.

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