

Summary

The dipole moments have been determined in benzene solution for diphenyl sulfide, diphenyl sulfoxide and diphenyl sulfone. The sulfoxide and sulfone have a very large moment.

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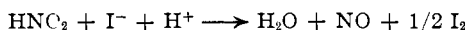
THE REACTION BETWEEN NITRITE AND IODIDE AND ITS APPLICATION TO THE IODIMETRIC TITRATION OF THESE ANIONS

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The reaction between nitrous acid and iodide



occurs only in acid medium. In the presence of oxygen the nitric oxide is oxidized to nitrogen dioxide which partly reacts with water, forming nitrous and nitric acid. With regard to the application of the reaction between nitrite and iodide to the iodimetric determination of these components, it was desirable to know at which hydrogen-ion concentration the reaction between the two takes place with a measurable speed. Moreover, it was of importance to study the reaction between iodide, dissolved oxygen and nitric oxide at various *P_H* values.

To 10 ml. of Clark's buffer solutions, known amounts of potassium iodide and sodium nitrite were added and after definite times of standing the iodine was titrated with thiosulfate. Some results obtained at room temperature are given in Table I.

TABLE I
REACTION BETWEEN NITRITE AND IODIDE AT VARIOUS *P_H*

<i>P_H</i> of buffer, 10 cc.	Concn. I ⁻ molarity	Concn. NO ₂ ⁻ molarity	Time of standing, in minutes	0.1 <i>N</i> thiosulfate, cc.
3.4	0.2	0.2	5	2
4.0	.2	.2	5	1.5
4.0	.4	.2	5	2.5
5.0	.2	.2	5	0.4
5.0	.4	.2	5	.7
5.6	.2	.2	5	.05
5.6	.2	.2	30	.20
5.6	.4	.2	5	.10
5.6	.4	.2	30	.40
6.0	.4	.2	5	.04
6.0	.4	.2	240	.09
7.0	.4	.2	30	.00

From the results in Table I it may be concluded that under practical conditions at a P_H larger than six, the reaction between nitrite and iodide takes place with a negligibly slow speed. This is not true for the reaction between nitric oxide, iodide and oxygen. Solutions of nitric oxide in buffers of various P_H were treated with iodide in the presence of air. Even at a P_H of 9.0 a trace of iodine is liberated very quickly; if the latter is titrated after five minutes no further reaction takes place upon standing. The same is true at P_H values between 6 and 9, and the amounts of iodine liberated are relatively small even at a P_H of 6. It should be mentioned, however, that the amount of iodine formed is not only dependent upon the P_H , but also on the type of buffer used; in borate buffers more iodine is formed than in phosphate solutions of the same P_H . Further studies for a better understanding of the reaction are in progress. Anyhow, the results obtained at P_H values between 6 and 9 show definitely that the reaction between nitric oxide, iodide and oxygen at these low acidities cannot be interpreted by the hydrolysis of the oxidation product, nitrogen dioxide, to give nitrite and nitrate, since traces of nitrite do not react with iodide at a P_H larger than 6. Therefore, it must be assumed that the nitrogen dioxide formed by the oxidation of nitric oxide reacts with iodide to liberate iodine. Even in stronger acid medium this kind of reaction must take place as it is impossible to interpret the results of the nitrite-iodide reaction on the sole assumption that the nitrogen dioxide formed by oxidation of the nitric oxide hydrolyzes to give nitrous and nitric acids.

For the analytical application of the reaction between nitrite and iodide it is of importance to know under what conditions nitrous acid and nitric oxide can be removed from the solution by addition of urea. In acetic acid medium the reaction is very incomplete even after a long time of standing. The best conditions are obtained if the solution contains at least 0.2 N hydrochloric or sulfuric acid and a large excess (1-2 g. was generally used) of urea. After fifteen minutes' standing no iodine is liberated on addition of potassium iodide.

On the basis of these preliminary experiments procedures were developed for the iodimetric titrations of iodide and nitrite.

Determination of Iodide.—Pure substances were used and the solutions standardized according to reliable methods of volumetric analysis.

Procedure.—The iodide solution is introduced into a 250-cc. glass-stoppered Erlenmeyer flask; about 1 g. of urea, 5 cc. of 0.5 molar sodium nitrite and 5 cc. of 4 N sulfuric acid are added. The flask is stoppered and allowed to stand with frequent shaking for about ten minutes, thereupon 1-2 g. of potassium iodide is added and the solution titrated with 0.1 N thiosulfate.

NOTE: 1. The amount of sodium nitrite given in the procedure is satisfactory for the oxidation of 25 cc. of 0.05-0.2 N iodide. It was found that in the presence of oxygen the nitrite will oxidize twice the theoretical amount of iodide. A large excess of nitrite is not harmful, provided urea has been added.

2. Since part of the nitric oxide formed is present in the gas phase, frequent shaking

is recommended to allow of all this gas reacting with urea. If at the end of the titration the color quickly comes back, the nitrogen oxide was not completely removed and the procedure must be repeated.

3. For the determination of very dilute solutions (25 cc., 0.01 to 0.001 *N*), 0.5 g. of urea, 1 cc. of 0.2 molar nitrite, 5 cc. of chloroform and 5 cc. of 4 *N* sulfuric acid were used and the liberated iodine titrated (after addition of some iodide) after thirty minutes' standing in the stoppered flask. Even in very dilute solutions accurate results are obtained (see Table II). It may be mentioned here that the iodide-nitrous reaction has already been applied by Grange¹ and later by Fresenius² to the determination of traces of iodide. The iodine is shaken out in carbon disulfide. Various authors have examined the method, but it cannot be recommended for the determination of traces of iodide, the chief reason being that the excess of nitrous acid or the nitrogen oxide formed interferes more or less. It was found by the present authors that the procedure is improved if the excess of nitrite and the nitrogen oxide formed are removed by urea. The iodine can be shaken out in chloroform, carbon tetrachloride, carbon disulfide, benzene, etc., and no difficulties are encountered.

4. Chlorides do not interfere with the iodide determination. Too high results are found if more than the equivalent amount of bromide is present. Improvement is obtained if the sulfuric acid is added in portions of 1 cc. at five-minute intervals (compare results in Table II).

5. Recently H. Szancer³ applied the nitrite-iodide reaction to the determination of iodide. After the liberation of the iodine, the acid solution is neutralized with a slight excess of sodium bicarbonate and the iodine titrated with thiosulfate or arsenious-

TABLE II
TITRATION OF IODIDE ACCORDING TO RECOMMENDED PROCEDURE

Potassium iodide, cc.	Addition, g.	Thiosulfate used, cc.	Thiosulfate, theoretical, cc.	Deviation in, %
25		24.80 0.1 <i>N</i>	24.80 0.1 <i>N</i>	0.0
25		24.75 0.1 <i>N</i>	24.80 0.1 <i>N</i>	-.2
25		24.83 0.1 <i>N</i>	24.80 0.1 <i>N</i>	+.1
25		24.83 0.1 <i>N</i>	24.80 0.1 <i>N</i>	+.1
25	1 NaCl	24.67 0.1 <i>N</i>	24.70 0.1 <i>N</i>	-.1
25	2 NaCl	24.65 0.1 <i>N</i>	24.70 0.1 <i>N</i>	-.2
25	0.26 NaBr	25.50 0.1 <i>N</i>	24.70 0.1 <i>N</i>	+3.2
25	.26 NaBr	25.65 0.1 <i>N</i>	24.70 0.1 <i>N</i>	+3.8
25 ^a	.26 NaBr	24.85 0.1 <i>N</i>	24.70 0.1 <i>N</i>	+0.6
25 ^a	.26 NaBr	24.75 0.1 <i>N</i>	24.70 0.1 <i>N</i>	+.2
25 ^a	.26 NaBr	24.75 0.1 <i>N</i>	24.70 0.1 <i>N</i>	+.2
25 ^a	.52 NaBr	25.20 0.1 <i>N</i>	24.70 0.1 <i>N</i>	+2.0
10		9.85 0.01 <i>N</i>	9.84 0.01 <i>N</i>	+0.1
10		9.82 0.01 <i>N</i>	9.84 0.01 <i>N</i>	-.2
10		9.81 0.01 <i>N</i>	9.84 0.01 <i>N</i>	-.3
10 ^b		9.58 0.001 <i>N</i>	9.44 0.001 <i>N</i>	+1.4
10 ^b		9.50 0.001 <i>N</i>	9.44 0.001 <i>N</i>	+0.6

^a Sulfuric acid added in fractions of 1 cc.; *cf.* Note 4 in discussion. ^b This solution contained only 1.25 mg. of iodide.

¹ Grange, *J. prakt. Chem.*, **55**, 167 (1852).

² Fresenius, "Anleitung zur quantitativen Analyse," **1875**, Vol. II, p. 482.

³ H. Szancer, *Arch. Pharm.*, **268**, 263 (1930).

trioxide. Under these conditions the nitrite does not react any more with iodide. However, in the slightly alkaline medium the iodine-thiosulfate reaction gives somewhat erratic results owing to a slight oxidation to sulfate. The results obtained by us with Szancer's method for this reason were 2 to 3% low. Probably the As_2O_3 titration will give better results; we have not tried it. Presence of bromide has the same effect in Szancer's method as in the procedure proposed by the authors.

Some results obtained are reported in Table II. The figures have been recalculated on the basis of a normality of the thiosulfate of exactly 0.1 *N* (0.01 *N* and 0.001 *N*, respectively).

Determination of Nitrite.—C. P. sodium nitrite was recrystallized twice from water and dried at 110°. Qualitative tests indicated its purity. The nitrite content was determined gravimetrically by treating with silver bromate and weighing as silver bromide.⁴ The results indicated that the sodium nitrite contained 99.9–100.3% $NaNO_2$. Previous authors⁵ have made use of the reaction between nitrous acid and iodide for the evaluation of nitrites. B. S. Davisson⁶ has tested the various methods, but did not find them very satisfactory. He developed a method giving results accurate to within -1.5 and +2.5%. F. Dienert⁷ described another elaborate procedure which, however, is no more accurate than to about 2% for 3 mg. of nitrite nitrogen. No experimental figures are given in his paper.

Proposed Procedure.—Ten to twelve grams of sodium bicarbonate, 3 g. of potassium iodide, 0.5 to 1 cc. of amyl alcohol and 25 cc. of water are introduced into a 250-cc. glass-stoppered Erlenmeyer flask, whereupon a measured volume of the nitrite solution is added. The contents of the flask are well mixed by shaking. After most of the sodium bicarbonate has settled, about 4 cc. of glacial acid is added from a pipet in such a way that the acid is well distributed through the solution, without shaking the flask. The latter is loosely stoppered and after the evolution of the carbon dioxide has nearly ceased gently rotated. After the sodium bicarbonate has settled, 6 to 7 cc. of 20 *N* sulfuric acid is added quickly without shaking the flask. The latter is loosely stoppered again, and after evolution of most of the carbon dioxide has ceased gently rotated to allow thorough mixing. The stopper is rinsed with water and the solution titrated with standard thiosulfate, using starch as an indicator.

After the end-point has been reached the stoppered flask is allowed to stand for ten minutes. If more than 0.1 to 0.2 cc. of 0.1 *N* iodine is formed (titration with thiosulfate), the procedure should be repeated.

NOTE: 1. A large excess of bicarbonate has to be used in order to remove all nitric oxide with the carbon dioxide during the reaction between nitrite and iodide. Potassium bicarbonate cannot be substituted for the sodium salt since the former is too easily soluble.

2. Since the presence of oxygen is very harmful during the reaction between iodide and nitrous acid, the air has to be removed from the reaction mixture before the strong acid is added. This is done by the addition of glacial acetic acid. At the low hydrogen-ion concentration in the acetate buffer formed no, or a very slight, reaction between nitrite and iodide takes place.

3. The addition of amyl alcohol is not essential, but is strongly recommended as it prevents overfoaming of the liquid during the evolution of carbon dioxide.

⁴ Busvold, *Chem.-Ztg.*, **38**, 28 (1914).

⁵ Comp. L. W. Winkler, *ibid.*, **23**, 545 (1899); **25**, 586 (1901); *Z. Unt. Nahr. Gen.*, **29**, 107 (1915); Meisenheimer and Heim, *Ber.*, **38**, 3834 (1905); F. Raschig, *ibid.*, **38**, 3911 (1905).

⁶ B. S. Davisson, *THIS JOURNAL*, **38**, 1683 (1916).

⁷ F. Dienert, *Ann. chim. anal. chim. appl.*, [2] **1**, 4 (1919).

4. If the air is not removed completely the blue color returns after the end-point has been reached. To test the reliability of the result it is necessary to titrate the liquid ten to fifteen minutes after having reached the end-point. If more than 0.1 to 0.2 cc. of thiosulfate is then used, the result should not be accepted and the determination should be repeated.

5. Very dilute nitrite solutions can be titrated according to the recommended procedure. The accuracy is about 0.5%. (See Table III.)

6. Good results are obtained in the presence of no more than 2-3% of ethyl alcohol and of amyl alcohol. Therefore the procedure seems well adapted for the determination of nitrites in the presence of these organic substances (*e. g.*, in amyl nitrite, spirit of ethyl nitrite U. S. P.) where the permanganate method cannot be applied.

TABLE III
IODIMETRIC TITRATION OF NITRITE

Nitrite, cc.	Addition, cc.	Thiosulfate, cc.	Thiosulfate, theoretical, cc.	Deviation in, %
10		9.82 0.1 <i>N</i>	9.82 0.1 <i>N</i>	0
10		9.80 0.1 <i>N</i>	9.82 0.1 <i>N</i>	- .2
10		9.81 0.1 <i>N</i>	9.82 0.1 <i>N</i>	- .1
25		24.55 0.1 <i>N</i>	24.55 0.1 <i>N</i>	0
25		24.55 0.1 <i>N</i>	24.55 0.1 <i>N</i>	0
25		24.50 0.1 <i>N</i>	24.55 0.1 <i>N</i>	- .2
40		39.30 0.1 <i>N</i>	39.28 0.1 <i>N</i>	+ .05
40		39.30 0.1 <i>N</i>	39.28 0.1 <i>N</i>	+ .05
25	5 Ethyl alcohol	24.10 0.1 <i>N</i>	24.55 0.1 <i>N</i>	-1.8
25	5 Ethyl alcohol	24.20 0.1 <i>N</i>	24.55 0.1 <i>N</i>	-1.4
25	5 Ethyl alcohol	24.20 0.1 <i>N</i>	24.55 0.1 <i>N</i>	-1.4
25	2 Ethyl alcohol	23.50 0.1 <i>N</i>	23.55 0.1 <i>N</i>	-0.2
25	1 <i>Sec.</i> -amyl alcohol	23.60 0.1 <i>N</i>	23.55 0.1 <i>N</i>	+0.2
25	1 <i>Sec.</i> -amyl alcohol	23.60 0.1 <i>N</i>	23.55 0.1 <i>N</i>	+ .2
25		24.65 0.01 <i>N</i>	24.55 0.01 <i>N</i>	+ .4
25		24.60 0.01 <i>N</i>	24.55 0.01 <i>N</i>	+ .2
25		24.62 0.01 <i>N</i>	24.55 0.01 <i>N</i>	+ .3
25		24.60 0.01 <i>N</i>	24.55 0.01 <i>N</i>	+ .2

Summary

The reaction between iodide and nitrite and nitric oxide, respectively, has been investigated at various P_H values.

The optimum condition for the reaction between urea and nitrite and nitric oxide, respectively, has been determined.

Applications have been made to the iodimetric determination of iodide and nitrite, respectively. The Fresenius method for the determination of iodides has been improved.

The procedure described for the determination of nitrite can also be used in the presence of alcohols.

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