CXXVIII.—*The Estimation of Nitrites by means of Thiocarbamide, and the Interaction of Nitrous Acid and Thiocarbamide in the Presence of Acids of Different Strength.*

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In a recent communication (Werner, T., 1912, **101**, 2180) it was pointed out that when a nitrite is added to an acid solution of thiocarbamide, the reaction may proceed in two directions, dependent entirely on the relative strength or ionising power of the acid present.

Thus, in presence of a feeble ioniser, such as acetic acid, the change takes place almost entirely in accordance with the following equation:

$$(a)\quad CSN_2H_4 + HNO_2 = HSCN + N_2 + 2H_2O,$$

whilst if hydrochloric acid is present, the change is almost theoretically in agreement with equation (*b*):

$$(b)\quad 2CSN_2H_4 + 2HNO_2 = C_2S_2N_4H_6 + 2NO + 2H_2O.$$

In reaction (*a*) a small quantity of nitric oxide is always produced, and in reaction (*b*) the evolved gas contains a small proportion of nitrogen; this is of no importance so far as the estimation of nitrites is concerned, since the total volume of gas evolved is the same in both cases.

A few preliminary experiments seemed to indicate that thiocarbamide was likely to prove a useful substance for the estimation of various nitrites, and the results now recorded show beyond question that we have in this compound an admirable reagent for the simple, rapid, and accurate estimation of all nitrites by a gasometric method.

In carrying out these analyses, the following procedure was found to give very satisfactory results: a quantity of the nitrite, corresponding with a milligram-molecular proportion of nitrous acid together with 0·1 gram of thiocarbamide, was dissolved in 1 c.c. of water in the cup of the nitrometer, and introduced into the apparatus; an additional ½ c.c. of water was used to wash in the last traces from the cup; 1 c.c. of dilute acetic acid (20 per cent.) was then added. The reaction was completed in a few minutes. On account of the somewhat greater solubility of nitric oxide in water, as compared with nitrogen, it is preferable to use acetic acid.

A test experiment with pure silver nitrite gave a result in agreement with the theoretical; a sample of sodium nitrite gave for the mean of seven closely agreeing results a value equal to 96·76 per cent. of pure sodium nitrite; the same sample, when analysed by the well-known method, using ordinary carbamide, gave only 92·89 per cent. of pure sodium nitrite for the mean of three experiments, which were by no means so concordant as when thiocarbamide was used (Expts. 1—10).

An elegant volumetric method for the estimation of nitrites has been proposed by Rupp (*Zeitsch. anal. Chem.*, 1906, **45**, 690), based on the oxidation of the nitrite by a feebly alkaline solution of potassium permanganate, the excess of the latter, after five to ten minutes' heating on the water-bath, being determined by addition of potassium iodide, and after acidification, titrated with *N*/10-sodium thiosulphate. Two analyses of the sample of sodium nitrite by this method gave a mean value equal to 96·75 per cent. of pure nitrite, thus confirming the results obtained by the thiocarbamide method.

Estimations of ethyl nitrite in alcoholic solution have given results which appear to be more trustworthy than when the potassium iodide method is employed; with thiocarbamide, the values obtained were found to be always lower than those yielded by potassium iodide. This is due apparently to the presence of some nitric ester in the ethyl nitrite solution, which has a disturbing influence on the results obtained by the latter method, since a greater divergence was found in the values obtained from the analyses of an old specimen of the nitrous ester; the results of experiments 19 and 20 also appear to confirm this view.

The advantages which may be justly claimed for the estimation of nitrites by the aid of thiocarbamide are as follows:

(1) The accuracy of the results is not affected by the presence of nitrates, even when in large excess.

(2) The analysis can be completed in a few minutes, since no subsequent manipulation of the evolved gas is necessary, as in the case when ordinary carbamide is used; this also reduces the chances of experimental error.

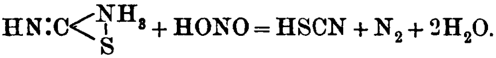
(3) The volume of gas evolved can be read off with great accuracy, since the operation is remarkably clean; even after a

large number of analyses the mercury remains quite untarnished, a result which is in marked contrast to that which occurs when potassium iodide is used after even a single operation.

(4) For the reasons given in (2) and (3), a much larger number of analyses can be made in a given time than by the other methods. For example, in the presence of sulphuric acid, the reaction is completed in about forty-five seconds; using acetic acid, it required only two minutes; in a comparative test, using carbamide in presence of sulphuric acid, the evolution of gas was not completed until after a lapse of twenty-eight minutes.

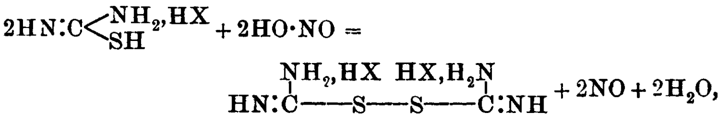
The Influence of Different Acids on the Composition of the Evolved Gas, when Nitrous Acid and Thiocarbamide interact.

The following results furnish interesting confirmatory evidence in support of the theory which has recently been put forward by one of us (Werner, *loc. cit.*) to explain the sharp difference in the behaviour of nitrous acid towards thiocarbamide under the two conditions already referred to. In a neutral solution the thiocarbamide molecule is in a state of fairly stable equilibrium, represented by the configuration $\mathrm{HN{:}C}{<}\begin{matrix}\mathrm{NH_3}\\ |\\ \mathrm{S}\end{matrix}$, which is not disturbed by the presence of a feeble ioniser, such as acetic acid, with the result that the nitrous acid exerts a direct oxidising action on the thiocarbamide in accordance with the equation:

(*a*) 

$$\mathrm{HN{:}C}{<}\begin{matrix}\mathrm{NH_3}\\ |\\ \mathrm{S}\end{matrix} + \mathrm{HONO} = \mathrm{HSCN} + \mathrm{N_2} + 2\mathrm{H_2O}.$$

When a strong acid is added, a salt of thiocarbamide is at once formed of the structure $\mathrm{HN{:}C}{<}\begin{matrix}\mathrm{NH_2,HX}\\ \mathrm{SH}\end{matrix}$, and oxidation by nitrous acid then takes place as follows:

(*b*) 

$$2\mathrm{HN{:}C}{<}\begin{matrix}\mathrm{NH_2,HX}\\ \mathrm{SH}\end{matrix} + 2\mathrm{HO{\cdot}NO} =$$
$$\mathrm{HN{:}}\overset{\mathrm{NH_2,HX}}{\overset{|}{\mathrm{C}}}\text{——}\mathrm{S}\text{——}\mathrm{S}\text{——}\overset{\mathrm{HX,H_2N}}{\overset{|}{\mathrm{C}}}\mathrm{{:}NH} + 2\mathrm{NO} + 2\mathrm{H_2O},$$

According to this view, the relative proportions of the two gases evolved should indicate the extent to which a particular acid was capable of reacting with thiocarbamide to form a salt, since interactions (*a*) and (*b*) will proceed simultaneously when both configurations of the thiocarbamide molecule are present in the solution.

In all the experiments, equal molecular proportions of thiocarbamide and sodium nitrite with two molecular proportions of the acid were allowed to interact in the same volume of solution;

the concentration of the thiocarbamide was therefore the same in each case; that of the acid varied somewhat according to the difference in molecular weight. For the latter reason it may be rightly argued that the experiments are not strictly comparable; still, the results recorded below prove conclusively that the direction of the change on the lines of equation (*b*) is directly proportional to the dissociation constant of the acid, a strong fact in support of the explanation just stated. The values in tables I and II have been calculated from the data given in the experimental part of this paper.

TABLE I.

	NO, per cent.	N_2, per cent.
Hydrochloric acid	95·95	4·05
Oxalic acid .... (K=10)	88·66	11·34
Tartaric acid .... (K=0·108)	58·01	41·99
Malonic acid .... (K=0·163)	51·88	48·12
Malic acid .... (K=0·0395)	39·68	60·32
Lactic acid .... (K=0·0147)	35·91	64·09
Glycollic acid........... (K=0·0152)	32·51	67·49
Succinic acid .... (K=0·00655)	19·37	80·63
Acetic acid .... (K=0·0018)	12·55	87·45
Propionic acid .... (K=0·0013)	11·60	89·40

TABLE II.

	NO, per cent.	N_2, per cent.
o-Bromobenzoic acid ...	31·77	68·23
m-Bromobenzoic acid.. (K=0·01307)	18·16	81·84
p-Bromobenzoic acid ...	0·0	100·00
o-Nitrobenzoic acid ... (K=0·616)	25·98	74·02
m-Nitrobenzoic acid ... (K=0·035)	12·48	87·52
p-Nitrobenzoic acid ... (K=0·039)	4·35	95·65

With the above derivatives of benzoic acid, it was necessary to use a certain amount of alcohol to help the solution of the acids, and in the case of the *p*-derivatives a larger volume was required than for the *o*- and *m*-compounds; the ionisation being thereby greatly diminished all round, the change has been diverted in the direction of equation (*a*) out of proportion to the dissociation constants of the acids. The larger volume of alcohol required in the case of *p*-nitrobenzoic acid, as compared with the meta-derivative, is no doubt the cause of the wide difference in the two results, which is also magnified by the influence of concentration, a factor the effect of which has yet to be studied. The result with *p*-bromobenzoic acid is remarkable as the only case in which nitrogen only was obtained; no record of its dissociation constant could be found.

Difference in concentration is probably also responsible for the order of the values obtained for malonic and tartaric acids, although the difference in constitution may also have some effect. It is intended to carry out further experiments to test these points.

EXPERIMENTAL.

Estimation of Nitrites by means of Thiocarbamide.

In order to establish the accuracy of the method, a specimen of freshly prepared silver nitrite, purified by recrystallisation from hot distilled water, was analysed, with the following result:

Silver nitrite (M.W. 153·9: 0·07695 gram) and thiocarbamide (0·1 gram) were introduced into the nitrometer with 2 c.c. of water, and 1 c.c. of acetic acid (20 per cent.) was added.

Vol. of gas evolved = 12 c.c. at 16·7° and 769·8 mm. = 11·24 c.c. (dry) at 0° and 760 mm.

Theoretical volume at N.T.P. = 11·18 c.c.

One gram of hydrogen, at N.T.P. = 11·18 litres, has been taken as the standard throughout all the experiments.

Analyses of Sodium Nitrite alone, and in the presence of Different Proportions of Sodium Nitrate.

A sample of commercial pure fused sodium nitrite was used. 0·069 Gram of the sample and 0·1 gram of thiocarbamide were dissolved in 2 c.c. of water, and having been introduced into the nitrometer, 1 c.c. of dilute acetic acid (20 per cent.) was added. The reaction was completed in a few minutes. Theoretical volume of gas at N.T.P. = 22·36 c.c.:

	Vol. at N.T.P. in c.c.	$NaNO_2$, per cent.
Expt. 1 :		
Gas evolved 23·5 c.c. at 17·4° and 758·82 mm.......	21·64	96·84
Expt. 2 :		
Gas evolved 23·5 c.c. at 16·6° and 757·5 mm.	21·66	96·87
Expt. 3. 0·2 gram $NaNO_3$ present :		
Gas evolved 23·8 c.c. at 17·6° and 750·5 mm.	21·66	96·87
Expt. 4. 0·3 gram $NaNO_3$ present :		
Gas evolved 23·4 c.c. at 16·7° and 760·35 mm.......	21·65	96·82
Expt. 5. 0·4 gram $NaNO_3$ present :		
Gas evolved 23·9 c.c. at 18·8° and 750·55 mm.......	21·61	96·64
Expt. 6. 0·6 gram $NaNO_3$ present, also in Expt. 7 :		
Gas evolved 23·2 c.c. at 14·6° and 757·9 mm.	21·61	96·64
Expt. 7 :		
Gas evolved 23·4 c.c. at 15·9° and 756·7 mm.	21·62	96·69

The presence of nitrates therefore does not materially affect the accuracy of the method, even when present to the extent of ten times the amount of the nitrite. This result is of importance in connexion with the use of thiocarbamide as a reagent for the estimation of nitrous esters, such as ethyl and amyl nitrites, which are liable to contain some of the corresponding nitric ester.

Comparative Analyses of the same sample of Sodium Nitrite by means of Carbamide.

0·069 Gram of the sample of nitrite and 0·1 gram of carbamide were dissolved in 2 c.c. of water, and 1 c.c. of dilute sulphuric acid (1 in 7) was added; after absorption of the carbon dioxide by 1 c.c. of 30 per cent. potassium hydroxide solution, the following results were obtained:

	Volume of gas (N_2).	Vol. at N.T.P. in c.c.	$NaNO_2$, per cent.
Expt. 8.	22·9 c.c. at 13·2° and 733 mm.	20·74	92·75
Expt. 9.	22·6 c.c. at 14·6° and 749·6 mm.	20·81	93·07
Expt. 10.	23·0 c.c. at 14·1° and 733·5 mm.	20·76	92·84

Mean of thiocarbamide results = 96·76 per cent. $NaNO_2$.
,, carbamide ,, = 92·89 ,, ,,

The results obtained with carbamide are beyond doubt too low, and this method is not trustworthy, as proved by the following analysis of the sodium nitrite by Rupp's method (*loc. cit.*).

Expt. 11.—0·069 Gram of sodium nitrite was dissolved in 40 c.c. of *N*/10-potassium permanganate solution, to which a few small crystals of sodium carbonate were added. The solution was warmed on the water-bath for fifteen minutes, cooled, acidified with dilute sulphuric acid, and excess of potassium iodide then added; the liberated iodine was titrated with *N*/10-sodium thiosulphate.

20·7 c.c. *N*/10-$Na_2S_2O_3,5H_2O$ required. Hence 40 − 20·7 = 19·3 c.c. *N*/10-$K_2Mn_2O_8$ required for oxidation of the nitrite. (1 c.c. = 0·00345 $NaNO_2$) = 96·5 per cent. $NaNO_2$.

Another experiment gave as a result 97 per cent. $NaNO_2$, thus confirming the accuracy of the experiments with thiocarbamide.

Analyses of Ethyl Nitrite in Alcoholic Solution.

A dilute solution of ethyl nitrite was prepared according to the method described in the British Pharmacopœia, which yields a product containing as nearly as possible 2·5 per cent. of the pure ester. One c.c. of this solution should give, when analysed by the well-known method using potassium iodide, 7 c.c. of gas (NO) at 15·5° and 760 mm.

Results using thiocarbamide, 1 c.c. of ethyl nitrite solution, 0·1 gram of thiocarbamide, dissolved in 1 c.c. of water, 1 c.c. of dilute acetic acid:

	Gas evolved.	Vol. (c.c.) at 15·5° and 760 mm.
Expt. 12.	6·9 c.c. at 11·7° and 758 mm...............	6·88
Expt. 13.	6·9 c.c. at 12·1° and 758 mm.	6·87

Estimated by the potassium iodide method, 1 c.c. of 10 per cent. potassium iodide solution, 1 c.c. of dilute sulphuric acid:

Expt. 14.	7 c.c. at 11·2° and 758 mm.	6·99

In order to obtain a further comparison of the two methods, a specimen of "sweet spirits of nitre" several months old was analysed, with the following results (2 c.c. of the sample were taken in each experiment):

A.—Thiocarbamide Method.

	Gas evolved.	Vol at N.T.P. in c.c.
Expt. 15.	4·6 c.c. at 14·6° and 751 mm.	4·24
Expt. 16.	4·5 c.c. at 14·6° and 751 mm.	4·15

B.—Potassium Iodide Method.

Expt. 17.	4·9 c.c. at 14·6° and 771·7 mm.	4·65
Expt. 18.	4·9 c.c. at 14·7° and 760·85 mm.	4·58

The greater divergence in the results by the two methods with the old specimen of the nitrite solution suggests that the accuracy of the potassium iodide method is probably affected by the presence of some ethyl nitrate in the sample, and the following results of the analysis of sodium nitrite in presence of some sodium nitrate appear to confirm this view.

0·069 Gram of sodium nitrite and 0·138 gram of sodium nitrate (that is, double the weight of the nitrite) were dissolved in 2 c.c. of water; 2 c.c. of potassium iodide solution were added, and having been introduced into the nitrometer, 2 c.c. of dilute sulphuric acid were added:

	Gas evolved.	Vol. at N.T.P. in c.c.	$NaNO_2$, per cent.
Expt. 19.	23·3 c.c. at 15·3° and 765·35 mm.	21·84	97·6
Expt. 20.	23·4 c.c. at 16·2° and 762·8 mm.	21·78	97·4

The mean result of these two determinations, namely, 97·5, is thus 0·74 per cent. higher than that obtained for the same specimen of sodium nitrite when analysed by the aid of thiocarbamide (see after Expt. 10), or by Rupp's method (*loc. cit.*). An alcoholic solution of commercial pure amyl nitrite was also found to give a somewhat higher result when analysed by means of potassium iodide, as compared with the thiocarbamide method.

Analyses of the Gases Evolved when Nitrous Acid and Thiocarbamide interact in the presence of Acids of Different Strength and Constitution.

In all the following experiments a milli-molecular proportion of thiocarbamide (0·076) and two milli-molecular proportions of the acid were dissolved in about 2 c.c. of water and introduced into the nitrometer; 0·072 gram of sodium nitrite (equivalent to 0·069 of the pure salt) dissolved in 1 c.c. of water was then added.

After the evolution of gas had ceased, the volume was read off, and the nitric oxide was then absorbed by means of a fresh saturated solution of ferrous sulphate; the residual nitrogen was measured after complete absorption of the nitric oxide was ensured. Since the object in these experiments was merely to determine the relative proportions of the two gases evolved, the volume results obtained, corrected to the normal temperature and pressure, are alone given. The theoretical volume of the mixed gases is 22·36 c.c.:

Expts. 21—36.	Vol. at N.T.P. in c.c.	Vol. of NO.	Vol. of nitrogen.
Hydrochloric acid	22·37	21·47	0·9
Oxalic acid	22·41	19·87	2·54
Malonic acid	21·36	11·08	10·28
Succinic acid	22·16	4·29	17·87
Malic acid	22·25	8·83	13·42
Tartaric acid	22·36	12·97	9·39
Acetic acid	22·39	2·88	19·51
Propionic acid	22·42	2·60	19·82
Glycollic acid	22·49	7·30	15·19
Lactic acid	22·39	8·04	14·35
o-Nitrobenzoic acid	21·21	5·51	15·70
m-Nitrobenzoic acid	22·04	2·75	19·29
p-Nitrobenzoic acid	18·42	0·80	17·62
o-Bromobenzoic acid	21·06	6·69	14·37
m-Bromobenzoic acid	20·03	3·69	16·63
p-Bromobenzoic acid	22·63	0·00	22·63

In the experiments with the derivatives of benzoic acid, 2 c.c. of alcohol were used as solvent for the *o*- and *m*-compounds, and 4 c.c. for the *p*-compounds, on account of the sparing solubility of these acids in water; even then the reactions were not quite completed. The evolution of gas was very slow; twenty-four hours were required in the case of *p*-bromobenzoic acid. The results, however, show sufficiently the effects of these acids on the direction of the change.

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