

XXI.—*The Nitrites of the Alkali Metals and Metals of the Alkaline Earths and their Decomposition by Heat.*

By PRAFULLA CHANDRA RÂY.

Barium Nitrite.—After I had completed my work on this salt, my attention was drawn to an elaborate paper on the subject by Arndt (*Zeit. anorg. Chem.*, 1901, **27**, 341), which also contains a full historical summary. I shall therefore confine myself to such information as is supplementary to this author's statements.

I am in a position to confirm Arndt as regards his inability to obtain pure barium nitrite by N. W. Fischer's method. Repeated crystallisations from alcohol gave a product which was always contaminated with 10 to 12 per cent. of the nitrate.

Barium nitrite was therefore prepared by double decomposition between silver nitrite and barium chloride in molecular proportions. As a solution of this salt has been found to be perfectly stable when heated to boiling or evaporated on the water-bath, the precautions adopted in the case of the preparation of mercuric nitrite (*Trans.*, 1904, **85**, 523) were quite unnecessary. Hot saturated solutions of the components were mixed together and vigorously agitated in a stoppered bottle in order to bring about the coagulation of silver chloride, the clear filtrate was evaporated nearly to dryness and allowed to crystallise, when clusters of glistening, faintly yellow needles slowly separated; these were pressed between folds of blotting paper and analysed in the usual way.

Found Ba = 55.42; $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ requires Ba = 55.46 per cent.

If the evaporation of the solution is carried further either on the water-bath or under diminished pressure over sulphuric acid, an efflorescent, white, granular mass is obtained. The whole of the water of crystallisation cannot be driven off even if the salt be powdered finely and dried in the steam oven. A sample thus dried gave

Ba = 58·91 per cent., the calculated amount for $\text{Ba}(\text{NO}_2)_2$ being 59·8, whilst that for $\text{Ba}(\text{NO}_2)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ is 57·56 per cent. Arndt's product, a "snow-white powder," was probably slightly dehydrated by the absolute alcohol used in its production, and this may account for the white, powdery appearance; his analysis also would seem to bear this out, as he found Ba = 56·86 per cent.

Calcium Nitrite.—This salt was prepared in a manner similar to that employed for its barium analogue. The solution could be evaporated on the water-bath without the salt becoming either decomposed or partially converted into nitrate. Owing to its highly deliquescent character, considerable difficulty was experienced in obtaining the salt in a form fit for analysis. When the concentrated solution was kept in a desiccator a yellow, pasty, crystalline mass was secured, which was found to contain rather more water than that required by the formula $\text{Ca}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$. When it was allowed to remain longer in the desiccator, the salt rapidly effloresced and ultimately turned into a hard lump, which did not lose in weight when heated on the water-bath; it gave off moisture, however, when heated in a bulb-tube, and yielded 27·03 per cent. of calcium, the theory for $\text{Ca}(\text{NO}_2)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ being 28·37. It is thus very probable that a semi-hydrated stable salt actually exists. The behaviour of the barium salt also points to the same conclusion.

Potassium and Sodium Nitrites.—These compounds were also prepared by double decomposition between silver nitrite and the respective chlorides. As already pointed out by Divers (Trans., 1899, 75, 86), solutions of the alkali nitrites can safely be evaporated on the water-bath. The nitrites were found to be free from nitrates. According to Lang (*J. pr. Chem.*, 1862, 86, 296), potassium nitrite crystallises with one molecule of water, whilst Divers found his crystals to be perfectly anhydrous. My own analyses go to confirm the latter chemist. I picked out small crystals, which were powdered and pressed between folds of blotting paper. An analysis gave 1·8 and 44·94 per cent. of moisture and potassium respectively, the calculated value for potassium nitrite being 45·88.

Magnesium Nitrite.—An aqueous solution of this salt was prepared by double decomposition between barium nitrite and magnesium sulphate; it could not, however, be evaporated on the water-bath, as it was found that nitric oxide was evolved with consequent formation of a basic nitrate. The solution was therefore concentrated under diminished pressure over sulphuric acid, when a crystalline, very faint yellow crust was obtained, which was pressed between folds of blotting paper in order to remove the adhering mother-liquor. The substance dissolved to a clear solution, and, on analysis, gave $\text{Mg} = 14·72$; the formula $\text{Mg}(\text{NO}_2)_2 \cdot 3\text{H}_2\text{O}$ required $\text{Mg} = 14·12$ per cent.

If this salt, instead of being removed at the above stage, is allowed to remain in the desiccator, it loses its lustre, and is converted into a hard, efflorescent, white mass. As the exact composition of this substance has been a matter of some controversy, three distinct preparations were undertaken, the properties and the analyses of which are given below.

1st Preparation.—In this case, complete solution of the substance in water was not obtained, but there was a slight residue: 0.345 gave 0.238 $\text{Mg}_2\text{P}_2\text{O}_7$ from the soluble, and 0.0115 $\text{Mg}_2\text{P}_2\text{O}_7$ from the insoluble portions; whence $\text{Mg} = 14.92$ and 0.72 per cent. respectively, the theoretical value for $\text{Mg}(\text{NO}_2)_2 \cdot 2\text{H}_2\text{O}$ being 15.78.

2nd Preparation.—The substance dissolved with a faint opalescence. Analysis gave $\text{Mg} = 16.30$; $\text{N} = 18.46$; the calculated values being $\text{Mg} = 15.78$, $\text{N} = 18.42$ per cent. respectively.

3rd Preparation.—The salt dissolved just as above, and gave $\text{Mg} = 16.27$ per cent.

The nitrogen, as estimated by the Crum-Frankland method, was the same in amount as when measured by the "urea" process.

Magnesium nitrite, like the foregoing nitrites, is a deliquescent salt; it crystallises with 3 mols. of water, of which it loses only 1 mol. if it is not removed from the desiccator at this stage. The dehydration cannot be carried further, and in this form it has been found to be stable, whereas the crystalline salt, when it is stored in a stoppered bottle, slowly decomposes, evolving nitrous fumes. In this respect, magnesium nitrite bears a marked analogy to mercuric nitrite (*Trans.*, 1904, 85, 524).

It is thus evident that the experiences of Lang, who analysed only the crystalline variety (*J. pr. Chem., loc. cit.*), and of Hampe, who examined it in the dehydrated form only (*Annalen*, 1863, 125, 334), are fully borne out, whereas Vogel (*Zeit. anorg. Chem.*, 1903, 35, 398) appears to be partially correct when he states that the salt, when dehydrated as above, undergoes slight decomposition like the chloride.

Divers has already drawn attention to the fact that a solution of the alkali nitrites can safely be evaporated even at the boiling temperature without decomposing or oxidising it (*Trans.*, 1900, 75, 86). Not only has this observation been found to hold good as regards the sodium and potassium nitrites, but it can be extended equally to solutions of barium and calcium nitrites. It is often stated that a solution of sodium nitrite gradually absorbs oxygen from the air.* I have, however, allowed solutions of this compound to evaporate spontaneously in a flat dish for two months at temperatures varying from 25° to 30° , and have tested them from time to time without being able to detect any appreciable oxidation to the nitrate. Even the

* "Nimmt langsam in Lösung Sauerstoff auf" (Lang, *loc. cit.*, p. 296).

crystalline crust which was deposited has been found to be a pure nitrite. Sodium and potassium nitrites are distinctly, although faintly, yellow, and give markedly yellow concentrated aqueous solutions (compare Divers, Proc., 1900, 16, 70).

Both Arndt and Vogel agree in stating that a concentrated solution of barium nitrite has a yellow tint, whilst the latter also makes the same observation with regard to calcium nitrite solution; but these chemists seem not to have noticed that these nitrites in the solid form also have a distinct pale yellow colour. They prepared the salts by precipitation from concentrated solution by alcohol, and thus obtained them as "white powders," but this appearance was probably due to the fine state of division in which these compounds were produced.

Summarising the results, it may be laid down that, in the first and second groups of the periodic system, the higher the atomic weight of the element the more pronounced is the colour of its nitrites. Mercurous nitrite stands at the head of the series, being markedly yellow, while silver nitrite occupies an intermediate position between this compound and the nitrites of sodium and potassium. In the second group also, although the colour is much less developed than in the first, barium nitrite stands at the head of the series, calcium nitrite comes next, whilst magnesium nitrite occupies the lowest place.*

As regards stability also, magnesium nitrite ranks lowest in position in the present series. This might be expected from the feebly basic properties of the magnesium oxide; in fact, this element forms a connecting link, as it were, between barium, strontium, and calcium on the one hand, and cadmium and zinc on the other.

A dilute solution of magnesium nitrite was kept for six months in a stoppered bottle, which was opened from time to time; the salt was found to remain perfectly stable. The solution, however, cannot be evaporated on the water-bath, as it undergoes partial decomposition, even at 60°, with evolution of nitric oxide.

Decomposition of the Nitrites by Heat [with ATUL CHANDRA GAṄGULI, B.A.].

The substance was placed in a combustion tube of Jena glass which was attached to a glass spiral, 1½ metres in length, packed close

* Strictly speaking, mercury occupies a two-fold position in the Periodic System. On account of the close similarity in properties between mercurous nitrite and its silver analogue, as has been pointed out in some of my previous communications, these two metals should be placed side by side. But mercuric nitrite, on the other hand, strongly resembles magnesium nitrite, justifying the position assigned to it by Mendeleef, and it is interesting to note that it has a pale yellow colour, more pronounced than that of the barium compound.

with glass beads which had been previously soaked in a strong caustic potash solution free from nitrite or nitrate. The apparatus, which in fact was a modified and improved form of that used in a similar experiment with mercuric nitrite (Trans., 1904, 85, 525), was then exhausted with the aid of the mercury pump. The heating was effected with a Bunsen burner in two distinct stages, which are termed the "initial" and the "final" stages respectively. In the first stage, the salt was heated slowly and gently for about 15 minutes, keeping the temperature, as far as practicable, a little above the fusion point; for instance, in the case of the barium nitrite, the temperature was between 250° and 300° , the melting point of this salt being about 220° (Arndt). At the end of the operation, the temperature was much lowered, so that no more gas was evolved. In the second stage, a far stronger heat was applied, the temperature rising to 450° and 500° . The gases which were absorbed by the caustic potash, either as nitrite or nitrate or both, were analysed, as were also those which collected in the reservoir of the mercury pump.

Barium Nitrite.—Expt. I. The substance (0.341 gram) turned distinctly yellow and remained so as long as the heating was continued and effervesced with intumescence. No nitrous fumes were noticed; the gas consisted of 19.2 c.c. of nitric oxide* and 5.0 c.c. of nitrogen. Besides baryta, the residue contained a mixture of nitrate and nitrite, the total nitrogen being 21.0 c.c., of which 13.3 c.c. was in the form of nitrite. The caustic potash of the glass beads yielded 1.8 c.c. of nitrogen in the form of pure nitrite.

The sum total of nitrogen in the salt (in the moist state) at 33° and 752 mm. was thus made up of the following: as gas, 14.6 c.c.; in the residue, 21.0 c.c.; in the caustic potash, 1.8 c.c.; the total being 37.4 c.c., whence the nitrogen found was 0.0397, the calculated amount being 0.040. It would thus appear that the method of analysis was fairly trustworthy, and that nearly 25 per cent. of the nitrogen in the salt was given off as nitric oxide. The ratio in volume of the nitrogen in the residue as nitrate to nitrite was as 1:1.73.

Expt. 2. Salt taken, 0.255 gram.

1st Stage. $\text{NO} = 19.6$ c.c.; $\text{N} = 3.4$ c.c.; $t = 30^{\circ}$; $p = 759$ mm., whence N as $\text{NO} = 0.0105$ gram, the total nitrogen in the salt being 0.03 gram; thus 29.28 per cent. of the nitrogen was given off as nitric oxide.

2nd Stage. Nitrous fumes were noticed and 4.6 c.c. of gas were collected; these were almost completely absorbed by an alkaline solution of pyrogallate.

For the sake of comparison, a blank experiment was made by heating barium nitrate directly at about 500° for two minutes;

* A strong solution of ferrous sulphate was used as the absorbent for this gas.

2 c.c. of gas were collected, which proved to be oxygen. It should not, however, be supposed that the reaction in this case is so simple as that represented by the equation: $\text{Ba}(\text{NO}_3)_2 = \text{Ba}(\text{NO}_2)_2 + \text{O}_2$. On examining the liquid in the worm receiver, a small quantity of a mixture of nitrate and nitrite was obtained. Here also the reactions as detailed below probably take place, only in the reverse order.*

Calcium Nitrite.—Expt. 1. Salt = 0.1386 gram.

1st Stage. $\text{NO} = 25.2$ c.c.; $\text{N} = 1.8$ c.c. at 29° and 756 mm.

2nd Stage. Gas = 3 c.c. (completely absorbed by alkaline pyrogallate). The residue was found to be only lime, free from nitrite or nitrate. Analysis of the liquid distillation gave: total $\text{N} = 11.2$ c.c.; as nitrite = 8.05 c.c.

The total nitrogen in the salt is thus made of 3 parts: as $\text{NO} = 12.6$ c.c.; as $\text{N} = 1.8$ c.c.; in the alkaline liquid = 11.2 c.c.; whence N (found) = 0.02772 gram; N (calc.) = 0.0277 gram.

It will be seen that nearly 50 per cent. of the nitrogen was evolved as nitric oxide.

Sodium Nitrite.—Expt. 1. Salt = 0.484 gram.

In the first stage, 7.4 c.c. of nitric oxide and 4.0 c.c. of nitrogen were obtained at 31° and 755 mm., or 8.4 per cent. of the nitrogen in the substance taken. On examining the alkaline liquid, only a trace of absorbed gas was found.

This experiment is of importance in establishing conclusively that in the earlier stages it is nitric oxide more or less mixed with nitrogen that is given off.

Expt. 2. Substance = 0.47 gram.

In the first stage, 27 c.c. of gas ($t = 31^\circ$; $p = 755$ mm.) were collected; a second nitrometer was then employed; after about 2 c.c. more of the gas had been collected, the surface of the mercury lost its lustre and became coated with mercurous nitrate, and the gas assumed a reddish-brown colour, thus proving that oxygen was being eliminated. Once more the nitrometer was changed, this time 9 c.c. of gas were collected, of which 5 c.c. were absorbed by alkaline pyrogallate, the unabsorbed portion being nitrogen.

Magnesium Nitrite.—The stable variety, $\text{Mg}(\text{NO}_2)_2 \cdot 2\text{H}_2\text{O}$, was used, 0.1052 gram being taken. Even at 60° , minute quantities of gas began to be evolved. The decomposition, however, was chiefly effected

* In a recent paper entitled "Über die Zersetzung des Baryum-nitrates in der Hitze" (*Chem. Zeit.*, 1904, **28**, 356), Gottlieb points out that, when the heating is rapid and not gradual, so as to allow the salt to decompose suddenly before it fuses, the largest amount of nitrous fumes is obtained; but when the temperature is gradually raised, the nitrous fumes, acting on the molten mass, undergo dissociation. Gottlieb's object was the regeneration of nitric acid from the barium nitrate. In our investigation, the temperature was always raised slowly and gradually.

at 120°. A slight evolution of nitrous fumes was distinctly perceptible at the outset.

The temperature was now raised to 172–175° for half an hour, but no more gas was evolved, as was proved by the fact that the “click” of the pump was persistent. The collected gas consisted of 9.2 c.c. of nitric oxide and 1.8 c.c. of nitrogen. The alkali in the worm yielded 2.4 c.c. of nitrogen as nitrite at 31° and 755 mm. pressure. The stable residue on examination was found to be a pure nitrate and gave 0.0166 Mg and 0.10 N, whence the

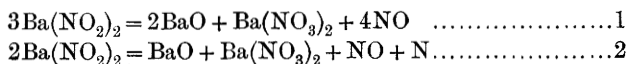
ratio of $\text{Mg} : \text{N} = \frac{0.0166}{24} : \frac{0.10}{14} = 0.007 : 0.00715 = 1 : 1$. It thus had

the composition $2\text{MgO}, \text{N}_2\text{O}_5$ or $\text{MgO}, \text{Mg}(\text{NO}_3)_2$. The simplest reaction yielding this compound would be: $2\text{Mg}(\text{NO}_2)_2 = \text{MgO} + \text{Mg}(\text{NO}_3)_2 + \text{NO} + \text{N}$. This, however, would require the nitrogen as nitric oxide to be equal in amount to that in the free state, whereas the quantity of the former is actually $2\frac{1}{2}$ times that of the latter. It would thus appear that by far the larger proportion of the salt decomposed according to the equation: $3\text{Mg}(\text{NO}_2)_2 = 2\text{MgO} + \text{Mg}(\text{NO}_3)_2 + 4\text{NO}$. But neither of these equations serves to account for the formation of a considerable amount of nitrite in the alkali of the worm.

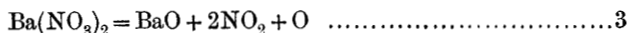
Interpretation of the Results.

It will be seen that, in the first stage, when the heating is slow and cautious, nitric oxide is the main gaseous product of decomposition, and that a portion of the salt is converted into nitrate; whilst in the second stage it is nitrate which undergoes decomposition, giving off oxygen. As a matter of fact, several reactions go on side by side, some of which, again, probably overlap, so that no sharp line of demarcation can be laid down between them. Taking barium nitrite as the type, we have the following reactions:

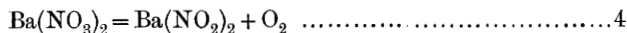
Initial.



Final.



whilst intermediate between these we have also,



In the earlier stages, it is the nitric oxide and nitrogen, with only traces of oxygen, that pass on through the worm, the oxygen and a

corresponding portion of nitric oxide being absorbed by the caustic potash in the form of nitrite, thus : $2\text{KOH} + 2\text{NO} + \text{O} = 2\text{KNO}_2 + \text{H}_2\text{O}$.

Later on, as a much larger proportion of oxygen begins to be evolved, a mixture of nitrate and nitrite is formed in the glass worm. In the final stage, owing to increased heat, the evolution of oxygen begins to preponderate, and this time it is all the nitric oxide with only its equivalent of oxygen, together with the nitric peroxide, which is absorbed by caustic potash to form varying quantities of nitrate and nitrite. Thus it is oxygen which is collected in the reservoir of the mercury pump.

As the salts were heated in glass tubing, the results might have been slightly vitiated, owing to secondary reactions due to the corrosion of the glass, but in the experiments with calcium and magnesium nitrites the glass was not in the least attacked, and, in this case, the results are in perfect harmony with those obtained from barium and sodium nitrites. It will also be noticed that calcium and magnesium nitrites yielded very little free nitrogen, whereas the barium and sodium salts gave considerable amounts.

It may here also be suggested as a working hypothesis that, as a result of the purely thermal decomposition, a portion of the salts breaks up into the peroxide and nitric oxide, but as the former is unstable, especially under diminished pressure at the temperature at which the scission takes place, it parts with its oxygen both to the nitric oxide and also to the remaining portion of the undecomposed salt in a state of fusion, and that it is in this way that the internal oxidation and reduction are brought about. It may be urged in support of this view that sodium peroxide absorbs nitric oxide forming the nitrite.

Moreover, this kind of self-oxidation and reduction also goes on when an alkali nitrite is heated just above the fusion point in an open crucible and kept in that state for a minute or two; bubbles of nitric oxide are given off and a considerable portion of the nitrite is changed into nitrate.

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE
CALCUTTA.
