On the Electrolysis of Liquid Ammonia Solution
of Alkali Nitrates

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Synopsis

When a liquid ammonia solution of sodium nitrate is electrolysed, a violent explosion occurs at a certain condition. The following experiments have been conducted for making the mechanism clear.

(1) By examining the reaction between liquid ammonia solutions of ammonium nitrate and metallic sodium, it was clarified that the reaction product changed according to the magnitude of the molar ratio of sodium to the nitrate.

(2) From the reaction between sodium nitrate and sodium, the above reaction mechanism was proved to be correct.

(3) In the above reaction, the formation of sodium hyponitrite was confirmed, although the amount was small.

(4) The reaction between ammonium nitrate and calcium was more slow and mild than that of sodium.

(5) The above reactions were assumed to proceed in the neighbourhood of the cathode on electrolysis of sodium nitrate in liquid ammonia.

(6) It was concluded that the explosion occurred by the electrolysis of sodium nitrate will be due to the formation of disodium nitrite.

Part I.   The Reaction between Nitrates and Metals

Introduction

Salts to be used for producing alkali metals in liquid ammonia by electrolysis in industrial scale should have large solubility in liquid ammonia and be cheap. Nitrates are suitable for the purpose. Metallic sodium can be electro-deposited on a cathode by electrolysing a concentrated liquid ammonia solution of sodium nitrate. At the time, a severe explosion is sometimes occured under some conditions. A reaction between a nitrate and a metal has been studied for clarifying the mechanism of the explosion. There are some studies[1~4] on these reactions. They are, however, not sufficient for quantitatively explaining the explosive phenomena.

(1) E. Divers, Proc. Roy. Soc. (London), 21 (1872–3), 110.

(2) E. B. Maxted, J. Chem. Soc., 1917, 1016.

(3) E. Zintl u. O. Kohn, Ber., 61 (1928), 189.

(4) W. M. Burgess and F. R. Holden, J. Am. Chem. Soc., 59 (1937), 459.

Experimental Methods

A glass pressure-proof reaction tube was used as a reaction apparatus, shown in Fig. 1. The X-shape tube is the reaction part, and a liquid ammonia container or a vessel necessary for the reaction is connected to it by a metallic joint. About 1 g of a nitrate and a suitable amount of metallic sodium are quickly weighed and put in (A) and (B). The vessel (D) containing about 20 g of liquid ammonia is connected.
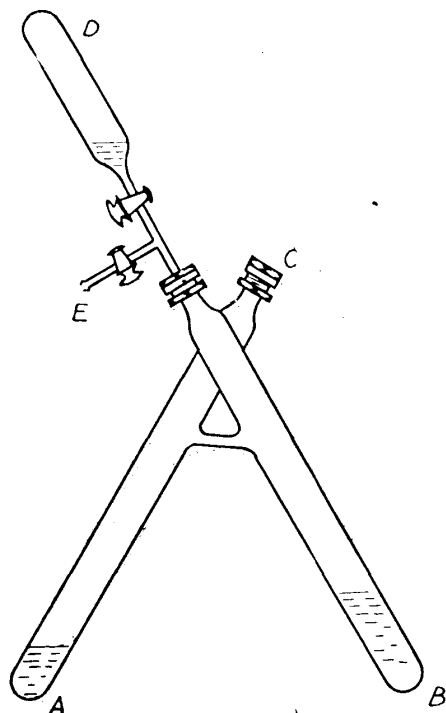
The part (C) is sealed with a metallic plate and the reaction tube is evacuated with a vacuum pump through (E). Remaining impure gases in the tube are removed by repeating operations to introduce a small amount of ammonia and to exhaust it. One third of liquid ammonia is added to a nitrate and two thirds to metallic sodium. The reaction is conducted by gradually introducing the sodium solution into the nitrate solution under ordinary temperature by inclining the whole apparatus. Gas evolved by the reaction is introduced into a gas holder, sealed with dilute sulfuric acid through (E). When the reaction is completed and the gas volume in the holder becomes constant, a rubber tube of (E) is removed. Ammonia in the reaction tube is discharged and the tube is evacuated with a vacuum pump for about 2 hours for completely removing ammonia. Solid residue is washed out with water, diluted and analysed. The solid product contains a nitrate, a nitrite, an amide and a hydroxide. Ammonium nitrate and sodium amide are quantitatively determined by measuring ammonia distilled out from an aqueous alkaline solution of the sample, under the conception that the two compounds can not co-exist at the reaction time. Nitrite was determined by its reducing power for potassium permanganate. There are many analytical methods[5~8] for a mixture of nitrite and hyponitrite. In the present case, they were determined by the difference of the reducing powers before and after boiling.[9] A gravimetric method was also partly applied. For determining nitrogen in the whole acid radicals ($-NO_3$, $-NO_2$, $-N_2O_2$), hyponitrous acid was first oxidised with potassium permanganate in alkaline solution for preventing decomposition and ammonia was

Fig. 1

(5) W. Zorn, Ber., 10 (1877), 1306.

(6) A. Thum, Monatsh. Chem., 14 (1893), 307.

(7) F. Raschig, Schwefel-und Stickstoffstudien, Verlag Chemie, S. 97 (1924).

(8) E. Zintl u. H. H. Baumbach, Z. anorg. Chem., 198 (1931), 98.

(9) E. Divers, J. Chem. Soc., 1899, 104.

exoelled by boiling; then the nitrogen was determined as ammonia by reducing with Devarda's alloy. The free alkali was titrated with sulfuric acid. (The sample contains sodium hydroxide and ammonia from the amide in case of the reaction between ammonium nitrate and sodium, but in case of the reaction between sodium nitrate and sodium, ammonia is not contained, because the titration was conducted after boiling.) The evolved gas was composed of nitrogen, nitrous oxide and hydrogen, and analysed by the ordinary method. When an exploxive yellow precipitate was produced in a reaction, in which larger amount of sodium to ammonium nitrate being used, the tube was cooled, by expelling a portion of liquid ammonia in the reaction vessel and the upper part of the vessel was taken off, and the content was taken out after exposing to air for about one day. For confirming the presence of hyponitrite, 5 g of ammonium nitrate were reacted with about 3 g of sodium and 0.4385 g of bright yellow silver compound was obtained by the ordinary method.[5][9] The analysis of the product gave 77.8 per cent silver (theoretical value, 78.17 per cent) and 10.1 per cent nitrogen (theory, 10.16 per cent), proving the presence of silver hyponitrite.

Experimental Results

(1) *Reaction between ammonium nitrate and sodium.* The reaction proceeds by stages. When a sodium solution is added into a solution of ammonium nitrate, in the range of 0~0.9 molar ratio (Na/NH_4NO_3), the blue color of sodium quickly disappears and the solution becomes colorless and transparent without producing any precipitate. When the molar ratio becomes larger than about 0.9, white substance begins to precipitate. In the part where sodium solution is added, bright yellow precipitate is produced, which becomes white one by shaking. At about 2.6 molar ratio, the yellow precipitate does not disappear, but increases and a mixture of the yellow and the white precipitates is formed. The intensity of the yellow color is most strong at 3~4 molar ratio. Passing the range,

Fig. 2

the color becomes somewhat lighter. The precipitate violently explodes by contacting with air or moisture. At the range of 4.2~4.3 molar ratio, the blue color of sodium begins to remain in the reacting solution, which is decolorised by evolving hydrogen, when let alone. It is assumed that the dissolved sodium is changed into sodium amide. The measured results are shown in Fig. 2.

As seen from the figure, when the amount of sodium increases, ammonium
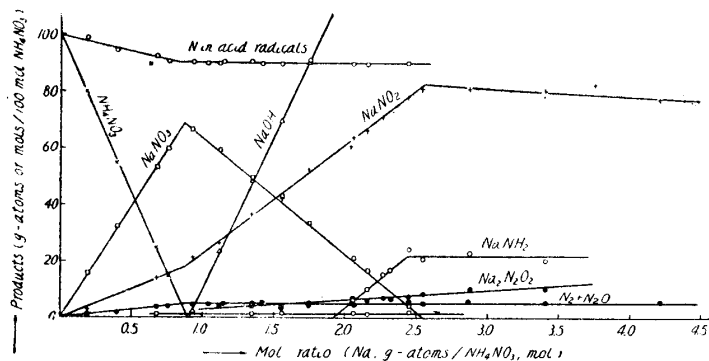
nitrate decreases while sodium nitrate and nitrite increase almost in straight line until 0.9 molar ratio. At above 0.9 molar ratio, ammonium nitrate disappears, and sodium hydroxide and sodium hyponitrite, the primary reduction product of sodium nitrite, begin to appear, and the reducing power of the solution quickly increases. On the other side, nitrogen in the acid radicals and evolved gas becomes constant.

At above 1.9 molar ratio, ammonia, which is assumed to be derived from the amide, begins to appear in the reaction product and increases in straight line until 2.6 molar ratio. Sodium nitrate is in the maximum amount at 0.9 molar ratio and gradually decreases to zero at about 2.6 molar ratio. The product formed at above 2.6 molar ratio contains yellow precipitate and violently explodes.

（2） *Reaction between sodium nitrate and sodium.* For confirming the part of the high molar ratio which is most important in the former reaction, the present reaction was conducted. At 0~2.0 molar ratio (Na/NaNO₃), white precipitate is produced in the reacting solution and at above 2.0 molar ratio, the yellow precipitate is produced as in the case of ammonium nitrate; the intensity of the yellow color is the strongest at about 3.0 molar ratio. At above 4.0 molar ratio, the blue color of sodium begins to remain. The time necessary for decolorisation of the blue color is a few minutes at 4.3 molar ratio; a few ten minutes at 4.5; about 1 day at 5.0; and 3 days at 5.5. The results are shown in Fig. 3.
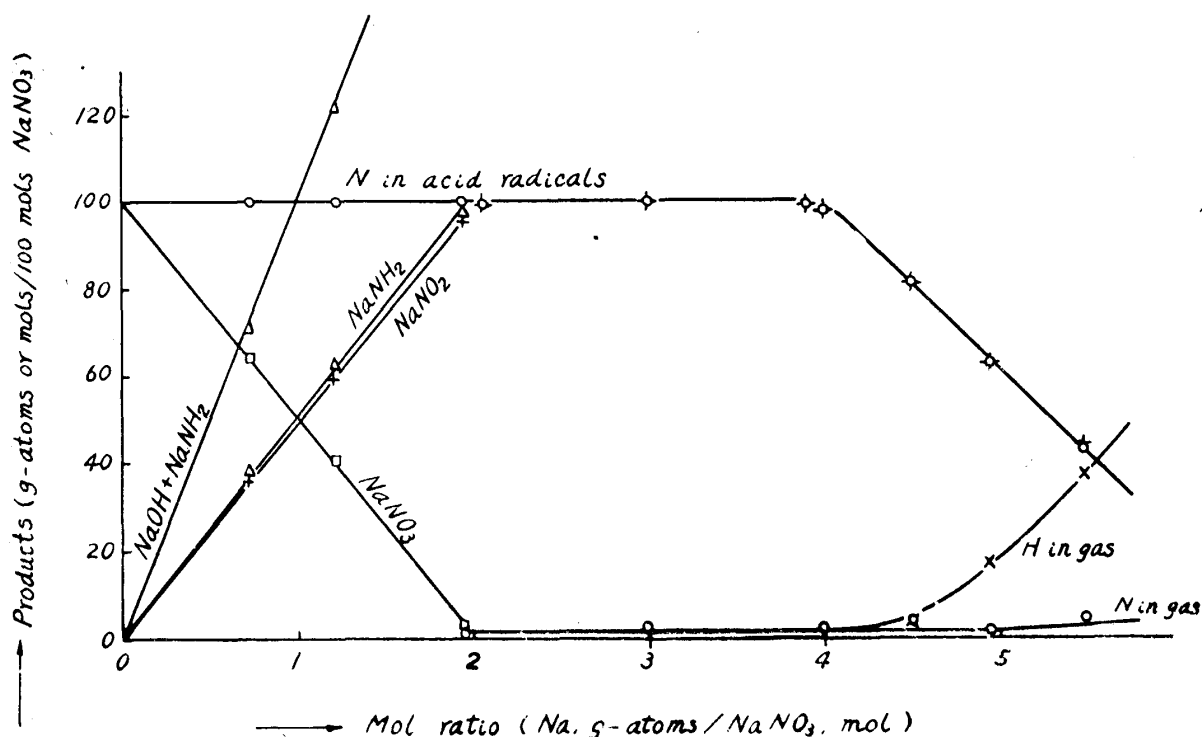

Fig. 3

As seen from the figure, the same amounts of nitrous acid and ammonia, and

the double amount of sodium hydroxide exist in an aqueous solution of the solid products until 2.0 molar ratio. And they increase in the straight line with the increase of the molar ratio. At above 4.0 molar ratio, sodium hyponitrite is produced and a very small amount of gas is evolved, which contains nitrogen and hydrogen and the latter quickly increases as the ratio increases.

(3) *The treatment of the reaction products with alcohol.* According to Zintl, et al., the yellow precipitate produced at the part of the large molar ratio explodes by treating with alcohol. On treating the reaction product of sodium nitrate and sodium with an equivalent mixture of alcohol and liquid ammonia, no explosion occured but it reacted with the mixture and changed into white substance producing a large amount of gas. The gas is mainly composed of nitrogen and nitrous oxide, and a comparatively large amount of sodium hyponitrite is contained in the solid product. The hyponitrous acid was gravimetrically determined as a silver salt. The results are shown in Fig. 4.
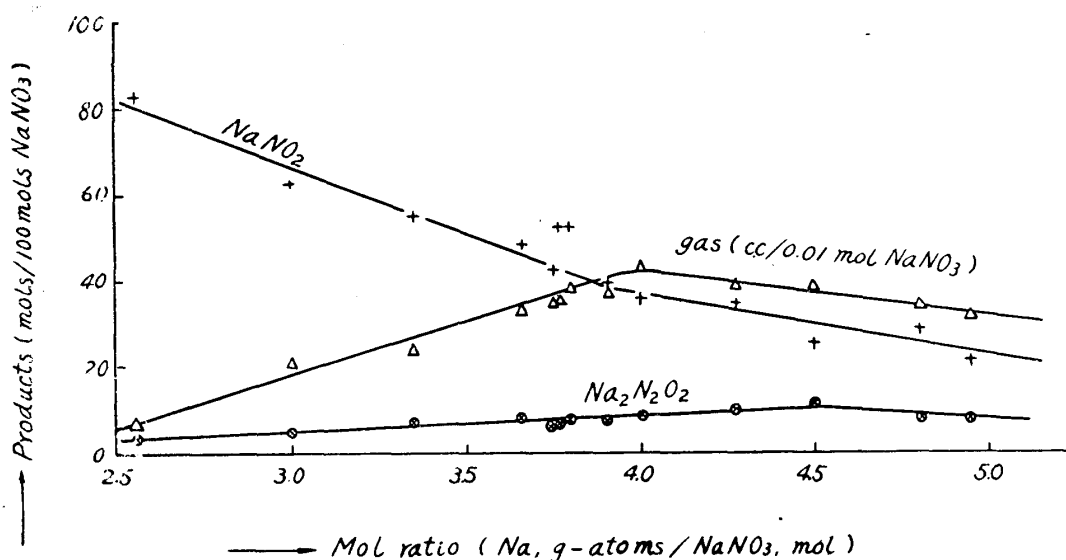

Fig. 4

A reaction product from sodium nitrite and sodium in equimolecular ratio was treated with a mixture of alcohol and liquid ammonia. Namely, on gradually adding a liquid ammonia solution of sodium into the same solution of sodium nitrite, the blue color of sodium disappears and bright yellow precipitate is immediately produced. Reacting with a mixture of alcohol and liquid ammonia, the yellow precipitate changes into white substance, producing a large amount of gas. The ratio of nitrogen in the products formed by the action of alcohol to that in sodium nitrite is as follows:

	Molar ratio	Solid products (%)		Gaseous products (%)		
		$NaNO_2$	$Na_2N_2O_2$	N_2	N_2O	NO
No. 1	1.00	57.8	15.1	6.3	7.7	0.2
No. 2	1.01	58.6	12.4	6.4	8.)	0.9

The residual nitrogen, which was not recovered, was missing. An alcoholic

solution obtained by expelling only ammonia after treating with a mixture of alcohol and liquid ammonia is cloudy due to a small amount of white precipitate, differing from the case of sodium nitrate.

(4) *Reaction between ammonium nitrate and calcium.* For comparing with the action of metallic sodium, reaction between ammonium nitrate and calcium was studied. The reaction state differs from the case of sodium. The first stage of the reaction is almost same with the former case, but after the second stage, no different phenomena from the first stage is observed. The blue color of calcium remains without decolorisation and the reaction corresponds to the third stage of sodium, in which amide is formed. No yellow nor explosive compound is formed. The results are shown in Fig. 5.
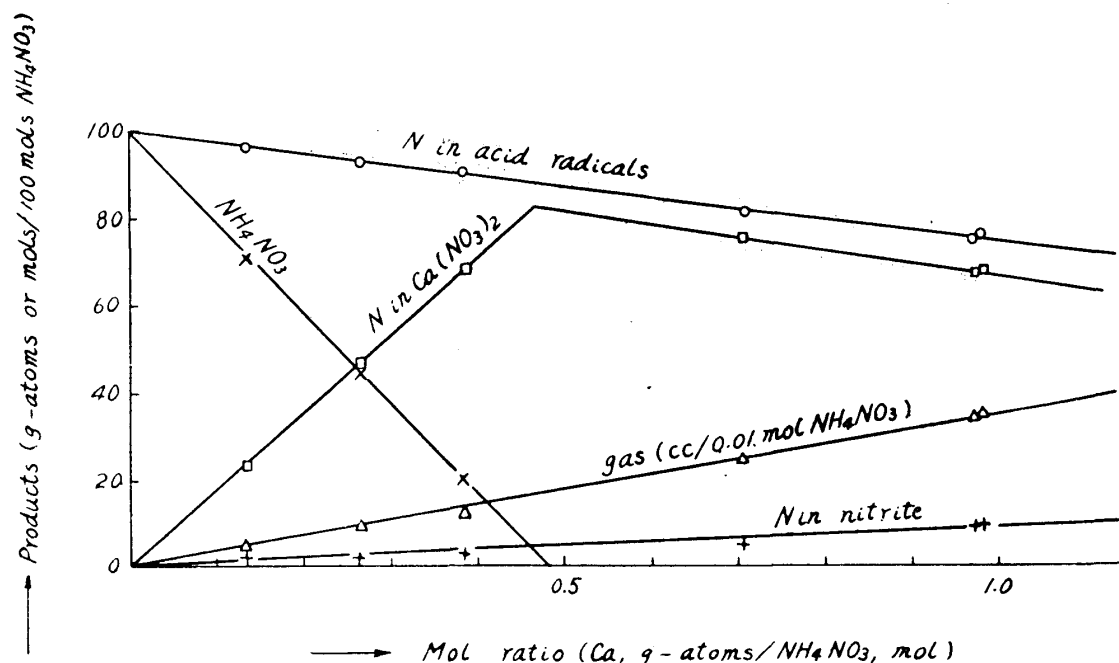

Fig. 5

Comparing with the case of sodium, the amount of produced nitrous acid is about one half, but the decreasing amount of nitrogen in the acid radicals and the amount of the evolved gas increased. Nitrogen, nitrous oxide and hydrogen was detected in the gas, but no hyponitrous acid.

Part II.   The Electrolysis of Sodium Nitrate

In the Part I the condition, in which a violently explosive yellow precipitate is produced in the reaction between liquid ammonia solutions of a nitrate and metallic sodium, was confirmed. In the present part it was examined that what compounds will be contained in the catholyte according to the formation of metallic sodium in the electrolysis of sodium nitrate.

There are some studies on the electrolysis of alkali nitrates or nitrites in liquid ammonia,[1~4] but the electrodeposition of the metal is not recorded. The present authors, however, perceived the electrodeposition of metallic alkali on the cathode in the electrolysis of a concentrated liquid ammonia solution of an alkali nitrate.[5]

Experimental Method

A glass-pressure-proof electrolytic apparatus, composed of a liquid ammonia vessel, a manometer and an electrolytic cell, was used for the experiment, as shown in Fig. 1. The electrolytic cell is a reservoir of 3 mm thick, 40 mm in inner diameter and 150 mm in height, having a delivery cock (A) at the lower part. (B) is a metallic joint. And (C) is a large air-tight and electrically insulated box nut containing a pair of metallic plates and a rubber sheet packing piled alternately, and is connected to an electric terminal. A cylindrical aluminum plate was used as the cathode and a graphite rod as the anode, and filter paper as the diaphragm. About 20 g sodium nitrate dissolved in 50 g liquid ammonia were used as the electrolyte. The initial electrolytic voltage
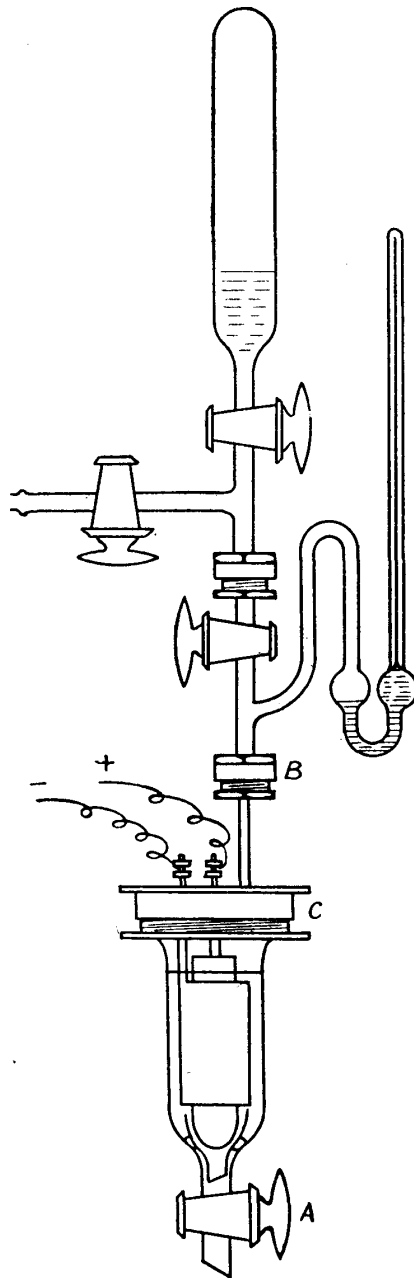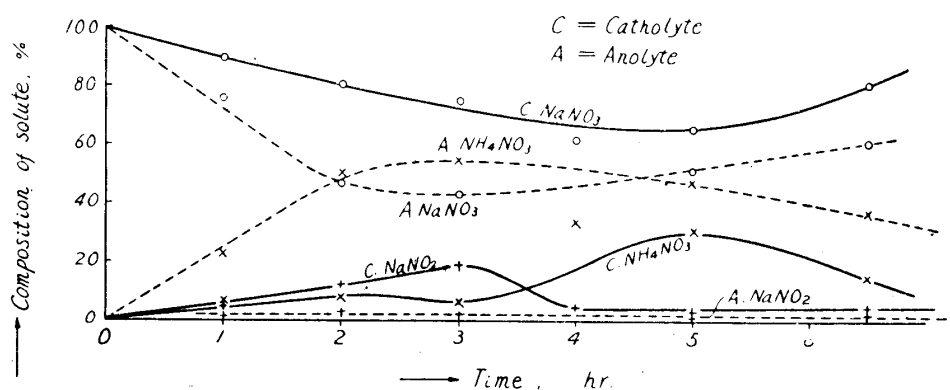

Fig. 1

(1) Kameyama and Mori, J. Soc. Chem. Ind. Japan, **37** (1934), 361.

(2) E. I. Akumov, N. A. Goncharov, E. A. Ezenova, J. Gen. Chem. (U.S.S.R.), 5(1935), 1744 ; Chem. Abst., **30** (1936), 2500.

(3) E. I. Akumov, N. V. Deryabina, J. Gen. Chem. (U.S.S.R.), **6** (1936), 1157 ; Chem. Abst., **31** (1937), 613.

(4) Kumao, Rept. Chem. Res. Inst. Non-Aq. Solns., Tohoku Univ., 1 (1951), 37.

(5) Japanese patent, 141722 (1941).

was 6~7 volts, which was so regulated that 2 amperes of the current was maintained and the current density about 50 A per dm². As heat was evolved during the electrolysis, the apparatus was cooled with ice or a refrigerant of ice and sodium chloride. After a definite hour, the cathodic solution and then the anodic solution were separately taken out from the lower cock. After evaporating the ammonia to dryness the residue was analysed. The cathode was taken off by detaching from the part (C). The analytical method was almost same with that adopted in the Part I. The evolved gases were not analysed and the current efficiency was not measured.

Electrolytical Results

As fast as the electrolysis begins, metallic sodium is produced in the form of indigo color solution on the cathode. When the solution is sufficiently cooled, the appearance of the surface of the cathode remains unchanged for about 2 hours, after that it is gradually whitened. But when the cooling is insufficient, the whole surface of the cathode becomes almost white, resulting no passing of the current after 0.5~1 hour. The longest duration of electrolysis continued for 6.5 hours. The cathode was not taken out as it was, but it became white during the process to take out from the cell. When the current was stopped in the early stage of the electrolysis, yellow substance is seen mixed in the substance deposited on the cathode. As the electrolysis proceeds, the electrolyte is colored with yellowish brown and the residue obtained by evaporation of ammonia to dryness from the solution is also colored. The change of the compositions of the solutes in both the anolyte and the catholyte according to the electrolytic duration is shown in Fig. 2.

Note = Points on the 4 hrs. show the composition of mixture.

Fig. 2

As seen from the figure, main part of the electrolysis for the first 2~3 hours is that of sodium nitrate. After that, secondary electrolytic reaction occurs and the result is inexplicable, i. e., the raw material, sodium nitrate, predominates again in the composition of the electrolyzed products and the rate of ammonium nitrate, the product, decreases. As the hour needed for the theoretical electrolysis is 3 hours and 9 minutes, the electrolysis is supposed to proceed

in fairly good current efficiency for first about 2 hours. The reaction which is supposed to become active after the first reaction is the electrolysis of ammonium nitrate produced in the anode and the reduction of nitric acid radical by hydrogen produced in the cathode. The residue obtained by evaporation of ammonia from the electrolytic solution after long hours' electrolysis contains water which is supposed to be due to the reduction of a nitric acid radical and to the decomposition of ammonium nitrite and hyponitrite. Under the presence of such water, it is thought that the rate of ammonium nitrate decreases as shown by the experimental result. By adding a silver nitrate solution to an aqueous solution of the residue obtained by evaporating off ammonia from the electrolyte, a large amount of white precipitate is produced, which is supposed to be silver nitrite, because it is soluble in water. When the electrolysis is conducted more than 3 hours, the product contains a small amount of water-insoluble yellowish brown compound in addition to the above product. The colored compound contains nitrogen besides silver, reduces potassium permanganate and makes free iodine from potassium iodide. One gram of the compound reduces 158, 175 and 181 cc of a tenth normal potassium permanganate solution, while 1 gram of silver nitrite reduces 131.5 cc of the permanganate solution. A similar compound obtained by 6.5 hours' electrolysis burns instantaneously by igniting with flame. From these facts, the compound is supposed to be a silver salt of a lower oxy-acid of nitrogen compound than silver nitrite. A substance deposited on the cathode is almost white and very hygroscopic. On analysis, it is composed of 70~78 per cent free alkali (as sodium hydroxide), about 15 per cent of a compound supposed to be sodium hyponitrite and a small amount of sodium nitrite. On washing with 99 per cent alcohol, the substance gives a small amount of a white substance. On washing with ether and dried in vacuo, the white substance is insoluble in liquid ammonia, but easily soluble in water, giving alkaline reaction. By neutralising with dilute sulfuric acid, the aqueous solution gives bright yellow silver compound, the color of which changes to brown and then black at room temperature. When mixed with an acid, the compound decomposes, evolving gas having an odor of nitrogen peroxide. As it has also a fairly strong reducing power, it is supposed to be sodium hyponitrite, but not confirmed.

Part III.   The Consideration

Discussion

(On the results of the first and the second parts)

The reaction between ammonium nitrate and metallic sodium, reported in the first part, is assumed to be composed of the following three stages from the experimental results:

The first stage (molar ratio: 0~0.9). — In this stage, *as the molar ratio of sodium* (Na/NH_4NO_3) *increases, ammonium nitrate decreases and the formation of sodium nitrate and nitrite increases, but no precipitate is yet produced in the reacting liquor.* — In the reaction, ammonium radical of ammonium nitrate is replaced with sodium producing sodium nitrate and hydrogen according to the formula (1):

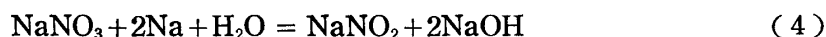$$2NH_4NO_3 + 2Na = 2NaNO_3 + 2NH_3 + H_2 \qquad (1)$$

Main part of hydrogen thus produced is consumed to reduce nitric acid radical to nitrous acid. In this stage, however, the reaction expressed with the formula (1) predominates, while that of the formula (2) is small:
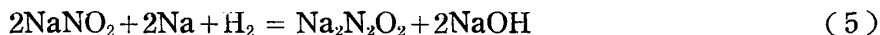
$$NaNO_3 + H_2 = NaNO_2 + H_2O \qquad (2)$$

Namely, in the first stage, sodium nitrate and hydrogen are produced by the action of metallic sodium and then sodium nitrite and water by the action of hydrogen. This fact is confirmed, as the total sum of ammonium nitrate (not reacted), sodium nitrate and nitrite and decomposed part of the acid radical is almost 100 per cent. But the determined amount of hydrogen corresponding to the difference between (1) and (2) was too small to express in the figure. The decomposition of the acid radical will be due to the formation of nitrogen, nitrous oxide and water by the decomposition of ammonium nitrite or hyponitrite produced in a small amount by the side reaction.

The second stage (molar ratio: 0.9~2.6) — In this stage, *ammonium nitrate disappears and the reducing power of the solution suddenly increases and sodium hydroxide and hyponitrite are newly produced. The amount of nitrogen in the acid radical and the gas becomes constant and white precipitates are produced in the solution.* — As clear from the experimental result, in the former part of this stage until 1.9 molar ratio, hydrogen produced by the reaction (3) between water, produced in the first stage following the formula (2), and metallic sodium gives again sodium nitrite and water by the formula (2). Repeating the reaction by addition of sodium, the whole reaction is assumed to proceed as the formula (4).
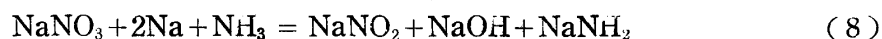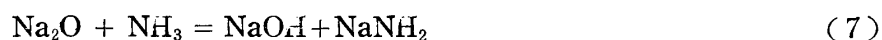
$$2H_2O + 2Na = 2NaOH + H_2 \qquad (3)$$

$$NaNO_3 + 2Na + H_2O = NaNO_2 + 2NaOH \qquad (4)$$

In this case, the decreasing rate of sodium nitrate is equall to the producing

rate of sodium nitrite and about double rate of sodium hydroxide [exactly, the producing rate of sodium hydroxide is slightly larger than twice, which being the effect of the reaction (5) , which is shown in Fig. 2 of the Part I from which the above assumption is assumed to be correct. On the other side, sodium hyponitrite is produced a little by the reduction of sodium nitrite:

$$2NaNO_2 + 2Na + H_2 = Na_2N_2O_2 + 2NaOH \qquad (5)$$

The constancy of production of nitrogen and nitrous oxide due to the absence of ammonium radical and also the constancy of amount of nitrogen in the whole acid radicals show that ammonium nitrite and hyponitrite to be decomposed are unable to be produced. On the variation of amount of sodium in the first stage it will be consumed according to the formula (1). After that it will be consumed mainly according to the formula (3) or (4), therefore, the inclination of the line of sodium nitrite should change at a point near 0.9 molar ratio. At the latter half of the stage, in which the molar ratio being above 1.9, the reaction product, from which liquid ammonia has been expelled, seems apparently to contain no water, but its aqueous solution becomes again to contain ammonia, which is supposed to be due to the formation of sodium amide. Namely, owing to the completion of the reaction (2), the reactions (3) and (4) become difficult to occur and sodium amide is formed by the following reaction, as suggested by E. F. Whyte [6] and E. Zintl [7]:

$$NaNO_3 + 2Na = NaNO_2 + Na_2O \qquad (6)$$

$$\underline{Na_2O + NH_3 = NaOH + NaNH_2} \qquad (7)$$

$$NaNO_3 + 2Na + NH_3 = NaNO_2 + NaOH + NaNH_2 \qquad (8)$$

In this case, the decreasing rate of sodium nitrate should be equivalent to the increasing rate of sodium nitrite and amide, which was clearly shown in Fig. 2 of the report Part I, described by the experimental data. Also that the lines showing sodium nitrate and nitrite have no point of intersection is easily understood by comparing the formula (4) with (8). And the reaction between sodium amide and sodium nitrate or nitrite, suggested by F. W. Bergstrom,[8] has no need to consider as its velocity is very small.

The third stage (molar ratio: 2.6~4.3) — The stage in which *yellow explosive substance is produced from sodium nitrite and metallic sodium.* — According to E. B. Maxted[9] and E. Zintl, sodium nitrite produces disodium nitrite reacting with metallic sodium according to formula (9), which explodes by contacting with air, moisture or alcohol, etc.:

$$NaNO_2 + Na = Na_2NO_2 \qquad (9)$$

The reaction of the present stage is the case of absence of hydrogen in the formula (5) and producing disodium nitrite according to formula (9). In the

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(6) E. F. Whyte, J. Am. Chem. Soc., 45 (1923), 1781, foot note.
(7) Loc. cit.
(8) F. W. Bergstrom, J. Am. Chem. Soc., 62 (1940), 2381.
(9) Loc. cit.

present experiment, explosion frequently occured, breaking the reaction appa-
ratus on all such occasions. The result obtained by treating the yellow pre-
cipitate produced from sodium nitrite and metallic sodium is almost same with
that obtained by Zintl[7] on carefully acting water vapor on disodium nitrite.
An alcoholic solution of the product obtained by the above treatment with
alcohol contains a small amount of white precipitate suspended in the solution,
which is assumed to be sodium hyponitrite, insoluble in alcohol, because the
reaction product does not contain sodium amide, differing from the case using
sodium nitrate. According to the formula (9), sodium nitrite and metallic
sodium should react each other in equimolecular proportion. But the formation
of many other additional products of sodium is assumed from the remains of
unreacted metallic sodium and the amount of produced substances by the
alcoholic treatment. Such compound was not, however, confirmed as the ex-
perimental value was not definitely reproducible.

If ammonium nitrate and metallic sodium react in liquid ammonia by such a
mechanism, the experiment on the reaction between sodium nitrate and sodium
in the Part I is to manage the reaction mechanism after the second stage in
the presence of sodium nitrite and the measuring result is almost explained by
this mechanism. That the explosive yellow precipitate produced at high molar
ratio of sodium is disodium nitrite, is deduced from the experiment treating
the reaction product of sodium nitrate and sodium in the Part I with alcohol.
The reaction between calcium and ammonium nitrate (Fig. 5, Part I) is more
gentle than the case with sodium, and although the molar ratio of calcium
becomes larger, the reaction stage does not proceed.

By increasing the current density of the cathode in the electrolytic experiment
in the Part II, an attempt to promote the reaction between sodium nitrate and
sodium in comparatively short time by the above reaction mechanism was tried
with failure, perhaps owing to too small experimental scale. In the former
electrolytic experiments (conducted by Abe in the Asahi Glass Co.), explosion
was frequently experienced and the yellow substance described in the present
report was perceived in the deposit on the cathode. From these results the
reaction was assumed as follows: According to the progress of the electrolysis,
the produced metallic sodium reacts with the remaining sodium nitrate near
the cathode producing sodium nitrite which is then changed into disodium
nitrite and then explosion occurs.

Conclusion

The reaction between ammonium nitrate and metallic sodium in liquid am-
monia proceeds in the following three stages according to the increase of the
molar ratio of sodium.

The first stage. — Mainly ammonium nitrate is changed to sodium nitrate by
the action of sodium and one part of which is reduced to sodium nitrite.

The second stage. — In the former part, by the action of water produced in

the first stage and sodium, sodium hyponitrite and hydroxide are produced and the amount of sodium nitrite increases. In the latter part, the remaining sodium nitrate is reduced by metallic sodium into sodium nitrite, hydroxide and amide.

The third stage. — By the reaction between sodium nitrite and metallic sodium, a yellow explosive substance is produced, which being assumed to be disodium nitrite.

By the electrolysis of sodium nitrate, metallic sodium is deposited and the products by the electrolysis are almost same with those produced in the above reaction. The explosion during the electrolysis is assumed to be due to the formation of disodium nitrite. The action of metallic calcium for ammonium nitrate is slow and mild, comparing with that of sodium.