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著者	ABE Suekichi, KAWAKAMI Tadao, OKABE Taijiro
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The Preparation of Sodium Azide in Liquid Ammonia. II

The Yield of Sodium Azide

Suekichi ABE, Tadao KAWAKAMI and Taijirô OKABE

The Chemical Research Institute of Non-Aqueous Solutions

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Synopsis

When excess of nitrous oxide was reacted with a liquid ammonia solution of sodium the azide formation was large, and when sodium amide is reacted with excess of nitrous oxide, the azide formation was slower, but the sodium utility was greater than that in the former case.

Introduction

Many manufacturing methods of sodium azide have been studied and the authors have studied the method to manufacture the compound using liquid ammonia at room temperature. The former methods may be classified as follows:

- (1) The reaction between hydrazine and sodium nitrite.⁽¹⁾
- (2) The reaction between fused sodamide and nitrous oxide.⁽²⁾⁽³⁾
- (3) The reaction between fused sodamide and sodium nitrate.⁽⁴⁾
- (4) The reaction between sodamide and sodium nitrate in liquid ammonia.⁽⁵⁾
- (5) The reaction between sodium and nitrous oxide in liquid ammonia.⁽⁶⁾

At present, the dry high temperature method (2) is generally adopted. The method gives the product of low purity in poor yield and is dangerous in the manipulation. The other methods are moreover lacking of their fundamental studies. The method (4) was fairly thoroughly studied by Franklin and his co-workers. At room temperature, the yield of sodium azide was poor and the separation of the produced azide was difficult.

At the method (5) an alkali azide was formed by passing excess of nitrous oxide into a liquid ammonia solution of an alkali metal at -35°C . Recently an American patent⁽⁷⁾ was granted to a method manufacturing sodium azide by adding excess of nitrous oxide to sodium amide, which was previously prepared from a liquid ammonia solution of sodium using an iron catalyst. The authors have independently studied the manufacturing method of sodium azide by reacting nitrous oxide upon a liquid ammonia solution of metallic sodium or sodium amide at room temperature as an application of liquid ammonia to manufacturing chemistry. The yield and

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- (1) Thielé, Ber., **41** (1908), 2680.
 - (2) W. Wislicenus, *ibid.*, **25** (1892), 2085.
 - (3) L. M. Dennis and A. W. Brown, J. Am. Chem. Soc., **26** (1904), 577.
 - (4) A. W. Brown and F. Wilcoxon, *ibid.*, **48** (1926), 682.
 - (5) E. C. Franklin, *ibid.*, **56** (1934), 568.
 - (6) A. Joannis, Compt. rend., **118** (1894) 714.
 - (7) U. S. P., 2,373,800.

manufacturing conditions of sodium azide obtained by using a pressure vessel made of stainless steel will be reported.

(A) Experimental methods.

(1) Apparatus.

The experiment was conducted using an 18-8 stainless steel pressure vessel having 60 cc capacity, which is shown in Fig. 1.

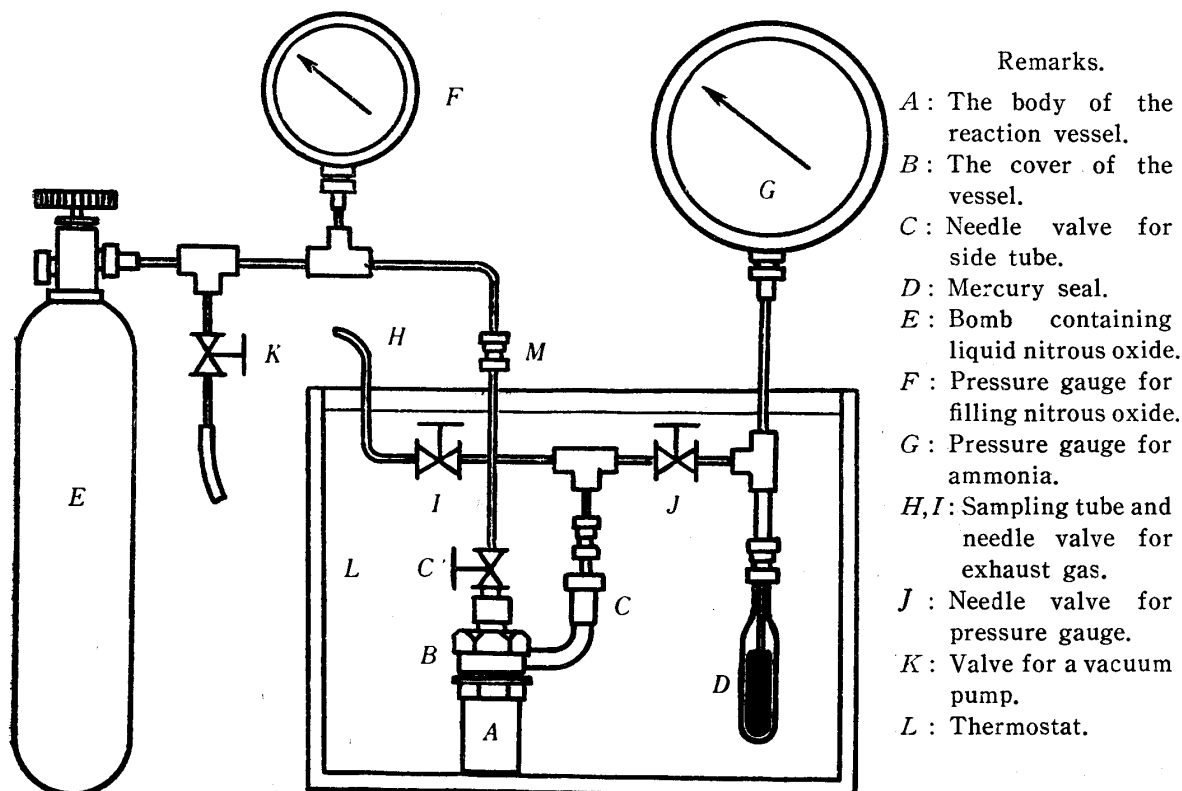


Fig. 1

For conducting the experiment, the lower part of the apparatus including *I* and *J* parts are immersed in the thermostat as shown in the figure. The mercury seal (*D*) was inserted for preventing the condensation of liquid ammonia in the pressure gauge. The lower tube from the three way junction below the gauge *G* is made of double wall. The outer tube connects *A* and upper part of *D* through *J* and *C*, while the inner tube is a steel one connecting *G* and *D*. It is filled with machine oil and opens its lower part in the mercury, by which the tube is disconnected with upper space of *D* by mercury.

(2) The material and sampling.

Sodium: Commercial product was used after taking off the surface part. At the latter half of the experiment, it was purified and filled into a glass ampoule.

Liquid ammonia: It was filled into a glass vessel from a commercial bomb by distillation or introduced into a reaction vessel previously evacuated and cooled with ice through the side tube after dehydrated with sodium.

Nitrous oxide: It was prepared by cautiously decomposing purified ammonium

nitrate at about 250°C* and purified through solution of ferrous sulfate, pyrogallol and caustic alkali, and solid caustic potash.

It was then dried through concentrated sulfuric acid and phosphorus pentoxide and compressed in a small bomb. The purity was determined by the combustion method: 95% N₂O, 0.6% NO, trace O₂ and the rest N₂. As the vapor pressure of liquid nitrous oxide at room temperature was 50~60 atmospheric pressures, it was sufficient for charging the oxide into the reaction vessel containing liquid ammonia. Nitrous oxide of high pressure was filled into an introducing tube including the pressure gauge and then it was charged into the reaction vessel at a stretch and the charged amount was calculated from the difference of before and after readings of the gauge *F* and condition of the vessel, volume of the part and temperature.

(3) End point of the reaction.

The progressive state of the reaction was observed by the relation between the change of the pressure and time after adding nitrous oxide. As the vessel was not agitated nor shaken, when the decrease of the pressure stopped at a definite temperature, the reaction vessel was taken out from the thermostat and the reaction product was analysed as follows.

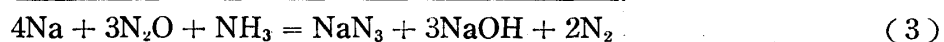
(4) Analysis of the products.

The solid product was washed out with distilled water and diluted to a definite amount. The free alkali and the total alkali were determined as stated in the Part I. From the difference of the amounts, the quantity of sodium azide was calculated. Small amounts of sodium and sodium amide remaining in the product were calculated as free alkali, as they were changed into sodium hydroxide.

(B) Experimental results.

(I) The case in which excess of nitrous oxide was directly reacted with a liquid ammonia solution of sodium.

As stated in the Part I, the reaction was assumed to be as follows:



Using excess of nitrous oxide for sodium, the yield of sodium azide to the equation (3) was obtained as shown in Table 1.

What some of the yields were more than 100% would due to reactions differing from the reacton (3). The velocity of amide formation from sodium and liquid ammonia in the vessel is fairly large. After introducing nitrous oxide, the amide formation by this oxide is more easily occurred than before introducing it.

* The decomposition of ammonium nitrate begins at below 200°C, but the decomposition was conducted at about 240~260°C, as its decomposition velocity was slow at low temperature. When only the nitrate was used at above 260°C, the reaction was too vigorous and higher oxides of nitrogen were produced largely as the evolved heat could not be regulated by air cooling.

Table 1.

Liquid ammonia (g)	Metallic sodium (g)	Nitrous oxide (N. T. P.)		Azide formation		Produced amount of azide (g)	Yield of azide (%)
		Filled amount (cc)	Ratio to theory	Temp. (°C)	Time (hr)		
16.14	0.5384	730	1.86	30.0	21	0.3760	98.8
14.79	0.6420	780	1.66	"	7.5	0.4665	103.0
16.37	0.5057	390	1.05	"	22	0.3757	105.0
16.35	0.494 ₃	1530	4.24	"	26	0.3670	105.0
15.91	0.943 ₃ *	1220	1.77	"	16	0.4980	74.8
16.14	0.532 ₅	560	1.44	"	25	0.4180	111.0
16.22	0.549 ₃ *	1210	3.04	"	23	0.3325	85.6
16.00	0.428 ₅	800	2.56	"	22	0.2935	96.7
9.00	0.450.	1000	3.05	-40.0	—	0.267 ₃	84.0 ⁸⁾
15.90	0.3395	excess	>1	14.3	—	0.238 ₃	99.2 ⁹⁾

Note: * ... Unreacted sodium remained.

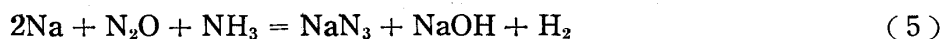
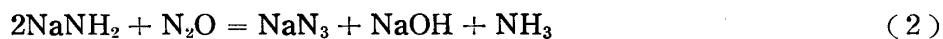
By the analysis of the produced gas, it was found that the amount of hydrogen produced in the presence of nitrous oxide was less than that by the amide formation from sodium and ammonia only. When the yield of the azide was more than 100%, a small amount of sodium was thought to have gone into the reaction:



Moreover, sodium amide thus formed was thought to become sodium azide, and the hydrogen corresponding to the equation (4) should be produced. This will be more probable for explaining the formation of more than 100% sodium azide. When the yield of the azide was less than 100%, the gas was proved to be composed of only nitrous oxide and nitrogen by the analysis. The reaction was therefore thought to have occurred according to the equation (3). When the azide was formed according to this equation (3), only 25% of sodium was utilized to the formation of sodium azide.

(II) The case in which nitrous oxide is reacted with a sodium amide solution.

The reaction under these conditions would be as follows (compare Part I):



The amide formation from a liquid ammonia solution of sodium in the vessel at room temperature was described in Part I. The amide formation according to the equation (4) was conducted at different conditions, and then nitrous oxide was added to the resulted solution at the unchanged state or taking off the evolved hydrogen and supplying liquid ammonia. The yield of azide formation was not almost different. The result was shown in Table 2. When sufficient time was given to the reaction, also in this case, the yield of sodium azide to the equation (5)

(8) Kikuchi and Yama'ai, Unpublished results.

(9) B. Shima, A graduation thesis, Chem. Tech. Dept., Fac. Eng., Tôhoku Univ. (1949).

was nearly 100%. To the reaction was quantitative, and 50% of sodium being utilized for the azide formation.

Table 2

Exp. No.	Liquid ammonia (g)	Metallic Sodium (g)	Amide formation		Nitrous oxide		Azide formation		NaN ₃ (g)	Yield (%)
			Temp. (°C)	Time (hr)	Filled amount (cc)	Ratio to theory	Temp. (°C)	Time (hr)		
1	15.95	1.174 ₃	30.0	16	1250	2.18	30.0	32.5	1.385	83.5
2	(15.93)	0.529 ₇	"	23	620	2.40	"	20	0.661	88.2
3	(16.10)	0.502 ₁	"	15	590	2.41	"	27	0.604	85.2
4	16.88	0.531 ₃	"	12	550	2.12	"	44.5	0.577	76.8
5	(16.38)	1.066 ₄	"	17.5	690	1.33	"	2	0.700	46.6
6	16.55	0.526 ₉	"	24	530	2.07	"	48	0.570	76.6
7	(16.42)	1.199 ₂	"	58	690	1.29	"	29	1.518	89.6
8	(15.77)	1.042 ₃	"	63	810	1.59	"	51.5	1.428	97.7
9	(16.55)	0.550 ₅	"	43.5	540	2.02	ca. 10	69	0.741	95.2
10	(16.04)	0.572 ₇	20.0	52	580	2.08	20.0	3 ^(d)	0.715	88.2
12*	(15.92)	0.854 ₆	Room temp.	180	760	1.83	ca. 8	0.5	0.461	37.4
13	(16.20)	0.729 ₆	10, 20, 30	55	920	2.59	ca. 10	96	0.979	96.3
14	(16.17)	0.580 ₈	10.0	23	500	1.77	10.0	26	0.693	84.3
15	(16.13)	0.607 ₁	"	28.5	900	3.03	6.5	2	0.457	67.6
16	(16.30)	1.064 ₄	"	10	1310	2.54	5.4	2	1.070	71.8
17*	(15.35)	0.504 ₃	Room temp.	9.75	1500	6.05	7.0	2	0.594	88.7

Note: () Azide formation was conducted after amide formation without changing the state.

* Reacted in the glass vessel.

Exp. No. 11 was erased because of wanting in the datum of yield.

(C) Discussion on the experimental results.

From the experimental results of (I), the following may be pointed out. (1) although more of nitrous oxide than calculated amount from the equation (3) was used, any special relation between the ratio to the theoretical amount and the yield of sodium azide was not observed. But more than 4 times of nitrous oxide were not used. (2) The concentration of sodium in liquid ammonia was about 3.4~5.9 g per 100 g NH₃, and the inner pressure of the reaction vessel just after charging nitrous oxide was 19.2~28.8 atm. The change of the pressure during the azide formation was irregular and it was difficult to know the velocity of the azide formation unless under a definite agitation.

The shortest time needed for getting a constant pressure was 7.5 hours, which may be however shortened by agitation as seen from the reaction conducted in a glass vessel. The formation velocity of the azide will gradually become smaller when the solution was not agitated. As Kikuchi and Yama'ai studied the reaction at about -40°C, the present work was done at 30°C. But the reaction temperature has almost no effect on the yield of sodium azide.

From the experimental results of (II), the following may be pointed out. Catalysts were used for the amide formation as follows: Platinum wire in No. 12, nichrome wire in No. 14, two drops of water in No. 15, iron rust in No. 16 and platinum black in No. 17 and the contents were brought to the azide formation at the unchanged states. In the cases of Nos. 12, 15, 16, and 17, the reaction vessel

was shaken with a shaking machine after detaching from the pressure gauge. Comparing these results with those in Nos. 15, 16 and 17 conducted at the same temperature, there was a tendency that the azide formation was easily progressive when the amide was formed at shorter time. The reaction temperature of the azide formation had almost no effect on the yield of the azide. In liquid ammonia, sodium amide reacts with nitrous oxide which dissolves in ammonia and diffuses, producing easily soluble sodium azide (practically the azide forms fairly difficultly soluble double salt with the produced sodium hydroxide) and insoluble sodium hydroxide and the azide formation proceeds until all unreacted amide is exhausted. By making nitrous oxide soluble and diffusible in liquid ammonia and keeping difficultly soluble sodium amide in active state, sodium azide should be produced completely and quickly. Experiments under agitation are now progressing. When the reaction conditions were almost equal, the time needed for completion of the reaction (I) was shorter than that of (II), which means that sodium amide produced from nitrous oxide and sodium solution was more profitable than that produced in absence of nitrous oxide. But the amount of the raw material for manufacturing the same amount of sodium azide will be needed 2 times sodium and 3 times nitrous oxide in case of (I) than the case of (II). The produced sodium azide contained a very minute amount of ferric (not contained when a glass vessel was used) and nitrous compounds, the latter would be due to nitric oxide or oxygen contained in nitrous oxide.

Summary

(1) When excess of nitrous oxide was reacted with a liquid ammonia solution of sodium in a stainless steel vessel, the velocity of sodium azide formation was large and the yield of the azide to the equation (3) was about 100%.

(2) When sodium amide, previously produced from sodium in liquid ammonia, is reacted with excess of nitrous oxide, the time for the azide formation was longer than that in the former case (1) and the yield of sodium azide to the equation (5) was more than 95% at 30~10°C.