

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE PREPARATION AND PROPERTIES OF SODIUM AMIDE.

BY J. M. MCGEE.

Received October 23, 1920.

A desire to study the blue solutions, reported by Titherly,¹ of the alkali metals in the fused amides of these metals was the incentive for the present investigation. Sodium amide was selected because it is typical of this class of compounds and has the lowest recorded melting point of any of the alkali amides.

The amides of sodium and potassium were first prepared by Gay-Lussac and Thenard² by passing dry ammonia gas over the heated metal. Since that time these amides have been prepared and studied by Beilstein and Geuter,³ by Titherly,¹ by Franklin and Kraus,⁴ by Dennis and Brown,⁵ and by Wöhler and Stanglund.⁶

Franklin and Kraus have prepared the alkali amides by the action of dry liquid ammonia on the dissolved metal, using finely divided platinum as a catalyst. The reaction by which the substance is obtained is as follows: $2\text{NH}_3 + 2\text{Na} = 2\text{NaNH}_2 + \text{H}_2$. The sodium metal dissolves in the liquid ammonia giving a bronze-colored solution, which becomes blue as the concentration of the dissolved metal decreases. Kraus⁷ has shown that the blue color is a very delicate indication of dissolved sodium and that its fading indicates that the last of the metal has disappeared. The reaction besides being catalyzed by finely divided platinum is also catalyzed by the amide itself.

Experimental Procedure.

The amide was in each case prepared in the container in which it was to be investigated and never came in contact with either air or moisture.

The conductivity apparatus consisted of a glass cell (see Fig. 1) fitted with small carefully ground stopcocks. This cell consisted of an inverted U-tube of 3 mm. inside diameter, near the extremities of the arms of which small platinum electrodes were sealed in. From the bend of the inverted U-tube a connecting tube led to the larger tube of one cm. bore, in which was placed a cylinder of freshly platinized platinum gauze, D.

The sodium metal was introduced into the cell at C from an auxiliary apparatus, by the method of Kraus.⁸ The sodium so introduced was filtered from all trace of oxide or other solid impurity and appeared in the cell as a bright metallic globule. The dry liquid ammonia was distilled into a bulb containing a small piece of sodium

¹ Titherly, *J. Chem. Soc.*, 65, 504 (1894).

² Gay-Lussac and Thenard, "Recherches Physico-chimiques," [I] 337.

³ Beilstein and Geuter, *Ann. Chem. Pharm.*, 108, p. 88.

⁴ Franklin and Kraus, *Z. physik. Chem.*, 69, 290 (1909).

⁵ Dennis and Brown, *Z. anorg. Chem.*, 40, 82 (1904).

⁶ Wöhler and Stanglund, *Z. Elektrochem.*, 24, 261 (1918).

⁷ C. A. Kraus, *THIS JOURNAL*, 30, 653 (1908).

⁸ C. A. Kraus, *ibid.*, 30, 1206 (1908).

metal, which was attached to the main apparatus just above the stopcock (see Fig. 2) by surrounding the bulb with a Dewar bath of liquid ammonia through which a stream of air was bubbled. The cell and bulb were next sealed off at A (see Fig. 2) from the ammonia supply and the ammonia bath removed from the bulb and placed about the cell; the liquid ammonia then distilled into the cell and dissolved the sodium metal. When all the ammonia needed was in the cell, the stopcock was closed and the bulb cracked off at B. The tube above the stopcock was then heated and drawn out into a capillary, the tip of which was sealed. The cell was next removed from this bath and

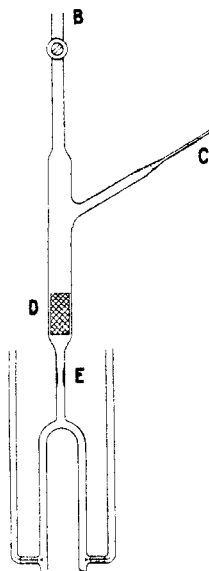


Fig. 1.

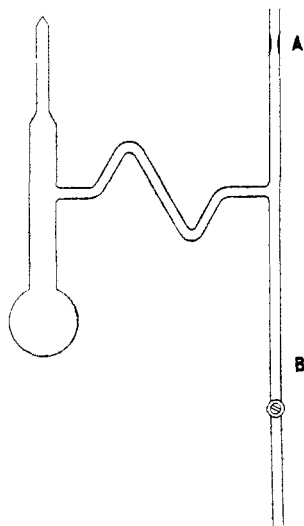


Fig. 2.

allowed to come to room temperature, at which temperature, the reaction proceeded at a fairly rapid rate. Every half hour the cell was cooled in the liquid ammonia bath, the sealed tip of the capillary broken off, the stopcock cautiously opened and the hydrogen gas generated by the reaction allowed to escape. The tip of the capillary was then resealed and the cell allowed to come to room temperature again. When all of the sodium metal had been converted to the amide as was indicated by the complete fading out of the blue color, the excess liquid ammonia was allowed to escape slowly and the pure crystalline amide was left behind. The first cell so filled was then sealed off at E, but it was found unnecessary to do this and the other cells were not sealed off.

Melting points were determined by placing a standard mercury thermometer reading to 0.05° , beside the cell containing the amide and raising the temperature of the oil-bath slowly, when in the neighborhood of the melting point of the amide. The thermometer was immersed in the oil-bath nearly to the 200° mark so that no stem correction would be necessary.

The solid product obtained by the method described above was a white crystalline substance melting sharply at 208° , with no preliminary softening as described by Titherly. The melting points as determined on 10 different preparations, none of which was removed from the tube in which it was prepared, are as follows: 208.0° , 208.05° , 208.0° , 208.0° ,

207.95°, 208.0°, 208.10°, 208.0°, 208.0°, 208.0°. Sodium amide is but slightly soluble in liquid ammonia and most of the amide crystallized out of the solvent as fast as formed. The fused amide was water-clear and at 210° was quite mobile. An attempt was made to determine the specific conductivity of the fused amide over a range of temperature, but the decomposition in the presence of platinum and the consequent decrease in conductivity became so rapid with increased temperature that no reliable results could be obtained except at 210°. At this temperature the decomposition was slow and the resistance of the cells remained constant for about an hour after the amide had first melted.

The cell was slowly heated up in an oil-bath and as soon as the contents had melted, the cell was placed in an oil thermostat regulated at $210 \pm 0.2^\circ$ and the resistance of the cell contents was determined. These determinations were made every 10 minutes until the resistance had increased materially. The cell constant was determined in a water thermostat maintained at $25 \pm 0.01^\circ$, using normal aqueous solution of potassium chloride as the conducting solution.

Analyses of the material, which had been fused but a few minutes in order to check the melting point, were made with 2 different samples. The method used was that of Dennis and Brown¹ modified in that absolute alcohol was first introduced, and then the water, a few cc. at a time, until the amide was completely decomposed, thus eliminating the danger of loss of ammonia due to the gas being generated too rapidly.

Experimental Data.

The specific conductivity of the fused amide at 210° as determined in 3 different cells was found to be 1.661, 1.671 and 1.665 mhos, respectively.

The specific conductivity is thus shown to be 1.665 ± 0.005 mho when platinum electrodes are used. This value is considerably higher than that obtained by Wöhler and Stanglund, who found it to be 0.593 mho at 210°, when nickel electrodes are used.

A series of determinations of the resistance of a cell with the calculated specific conductivities of the amide at 10° intervals from 210° to 240° gave the specific conductivities 1.665, 1.684, 1.718 and 1.732 mhos, respectively.

After these determinations had been made, the temperature of the bath was allowed to fall to 210° and the resistance of the cell contents was again determined. The specific conductivity was found to be 1.375 mhos.

This final determination of the conductivity of the amide was made 12 hours after the initial one. If the amide did not decompose, the conductivity would increase even more rapidly with increased temperature than is indicated above.

¹ Dennis and Brown. *Z. anorg. Chem.*, **40**, 93 (1904).

The results of the analyses of 2 samples of amide are as follows:

Weight of amide taken: Amides, 0.09397 g., 1.9070 g.; 23.54 cc., 48.56 cc. of *N* HCl used to neutralize NH_3 ; 23.70 cc., 48.78 cc. of *N* HCl used to neutralize NaOH.

From the above data the ratio of sodium to amine in the 2 analyses is found to be 1 to 0.6923 and 1 to 0.6936, respectively, while theoretically it would be 1 to 0.6967 for sodium amide.

Hence the results of these analyses clearly show that the substance obtained by this method is sodium amide, NaNH_2 , and also that the substance so prepared contains no ammonia of crystallization.

Decomposition of Sodium Amide by Platinum.

Fused sodium amide was not found to have as great a solvent action upon flint glass as has been reported by Titherly and others whose preparations must have contained considerable amounts of sodium hydroxide, as is indicated by the low and inconsistent melting points reported by them. The amide prepared as described above showed no tendency to attack the glass vessel when kept fused for 14 hours at a temperature not over 240° . It was found, however, when sodium amide was kept fused for 2 or 3 days at a temperature of 270° to 300° , that the walls of the cells were slightly etched.

It was thought by the author when this investigation was planned that the solvent action of the amides upon platinum would be found to be due to the sodium hydroxide contained in the amide and that pure sodium amide would have no such action. However, quite the contrary is shown to be the case; the platinum black of the gauze catalyzer and the platinum electrodes of the conductivity cells not only were slowly dissolved but the platinum at the same time catalyzed the decomposition of the amide. The rate of decomposition was slow at 210° but increased rapidly with increased temperature. The gas evolved was collected in an evacuated bulb of 500-cc. capacity, which was fitted with 2 well-ground stopcocks so that the gas could be replaced by dry mercury and samples of it could be drawn off and analyzed. Upon investigation the gas was found to have the characteristic odor of ammonia and was completely absorbed by conc. sulfuric acid. Therefore the gas evolved could have contained appreciable amounts of neither nitrogen nor hydrogen.

The residue left in the cell after heating for 14 hours at a temperature of 300° was examined and analyzed. The contents of a cell so heated when decomposed with absolute alcohol and distilled water gave ammonia gas only but no hydrogen, as would have been the case if sodium metal had been left as a residue. This fact, together with the absence of nitrogen in the gas evolved during the decomposition of the amide, clearly indicates that the residue was either sodium imide or nitride and not sodium metal, along with any undecomposed amide. Neither of these

compounds has ever been prepared in the pure state, although Titherly tried repeatedly to prepare them by heating the amides with excess of the same metal. A second sample of sodium amide was decomposed in this same manner and the gas evolved analyzed with the same result as before. In each case, the material during the heating slowly dissolved all platinum in contact with the fused amide; the contents of the tube gradually becoming red, then brown, and finally black, with apparently increased viscosity.

The residue left in a cell when the decomposition of the amide at 270° to 300° had practically ceased, solidified at about 260° and had a smaller conductivity than the undecomposed amide. When decomposed with absolute alcohol and distilled water as described above, 2.5505 g. of residue required 47.65 cc. of *N* hydrochloric acid to neutralize the ammonia and 79.04 cc. to neutralize the sodium hydroxide formed.

It is found by calculation from the above data that the ratio of the number of gram atoms of sodium to the number of gram atoms of nitrogen in the residue is 1.658 : 1, while the theoretical ratio in sodium amide, NaNH_2 , is 1 : 1; in sodium imide, Na_2NH , it would be 2 : 1, and in sodium nitride, Na_3N , it would be 3 : 1. From the above experimental results it is impossible to state whether the residue is a mixture of sodium imide and undecomposed amide, or of sodium nitride and amide, or of all 3 of these compounds; but as has already been stated, there can be no sodium metal present in the residue as one of the products of the decomposition of sodium amide. The equation for the decomposition must be either $2\text{NaNH}_2 = \text{Na}_2\text{NH} + \text{NH}_3$, or $3\text{NaNH}_2 = \text{Na}_3\text{N} + 2\text{NH}_3$.

A sample of the amide was prepared in a glass bulb, but the reaction was stopped before all of the sodium metal had been converted to amide by allowing the liquid ammonia to escape and the mixture of sodium amide and sodium metal was heated to 300° . The metal melted and collected in a globule which floated on the fused amide but did not appear to dissolve to any noticeable extent. No blue solution was formed, although the mixture was kept at 300° for 4 hours and was frequently shaken vigorously. The amide melted at 200° , thus indicating that a small amount of the metal had dissolved in it, but otherwise acted as it did when heated with no sodium metal present. The sodium metal did not dissolve in fused sodium amide to give the deep blue solution reported by Titherly. Kraus¹ has observed that mixtures of sodium and potassium metals dis-

¹ From unpublished observations of Professor C. A. Kraus, which he has kindly permitted the author to use. Dr. Kraus suggests that the non-formation of a blue color in the above case is due to the fact that platinum was present, which catalyzes the decomposition of the amide into an imide or nitride and ammonia; this ammonia in turn would tend to react with any free metal present to form the amide again. The metals are only slightly soluble in the fused amides and it would require but a slight decomposition of the amide to account for the failure of the blue color of the metal to make its appearance.

solved in a mixture of the fused amides at temperatures as low as 100° exhibit the characteristic blue color of the solutions of these metals in liquid ammonia, which resembles in every way the blue color which appears when metallic sodium is treated with ammonia gas slightly above the melting point of the amide.

Summary.

Sodium amide was prepared from pure sodium metal and water-free liquid ammonia, using a platinized platinum gauze as a catalyst.

The amide was found to be a white crystalline solid melting at 208° and having a specific conductivity of 1.665 ± 0.005 mho at 210°, when platinum electrodes were used. The specific conductivity found by Wöhler and Stanglund, using nickel electrodes, is 0.593 mho at 210°. The conductivity was found to increase with increasing temperature, but qualitative results only could be obtained, due to the decomposition of the substance.

Platinum metal was found to catalyze the decomposition of sodium amide into either sodium imide or nitride, with the evolution of ammonia gas, the platinum at the same time being dissolved.

No blue solutions of sodium metal in fused sodium amide, as reported by Titherly, could be obtained.

This investigation was begun under the direction of the late Dr. William L. Argo, who died during the war while in military service in France. The author wishes to acknowledge his indebtedness to Professor William C. Bray for his encouragement and many helpful suggestions.

TUCSON, ARIZONA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

PERCHLORO-METHYL-MERCAPTAN.¹

By O. B. HELFRICH AND E. EMMET REID.

Received November 1, 1920.

Introduction.

Perchloro-methyl-mercaptan, or perchloro-mercaptan, has the composition CSCl_4 and is commonly assumed to have the structure $\text{Cl}_3\text{C.S.Cl}$ analogous to methyl mercaptan. Although one of the simplest organic compounds, it has been studied only superficially, partly because of the lack of a good method of preparation and partly because of its unattractive properties. It is the purpose of this paper to present a rapid and efficient method of preparation, together with a few notes on some of its reactions. This work was undertaken originally with the Bureau of Mines on account of the possible use of perchloro-methyl-mercaptan as a "war gas," and also because it is a source of thiophosgene.

¹ This work was done in the Johns Hopkins Branch Laboratory of the Chemical Warfare Service and is published with the consent of the Chief of the Chemical Warfare Service, U. S. Army.