

This reaction is irreversible, so no carbon disulfide is regenerated after it has once become "fixed."

3. The second stage consists in the reaction of potassium azido-dithiocarbonate with iodine, which results in the precipitation of azido-carbon-disulfide, $(SCSN_3)_2$, as follows: $KSCSN_3 + 2I = (SCSN_3)_2 + 2KI$.

4. The halogenoid substance azido-carbondisulfide liberates triatomic nitrogen from the potassium trinitride, with resultant evolution of ordinary nitrogen gas, as shown by the equations $2KN_3 + (SCSN_3)_2 = 2KSCSN_3 + 2N_3$; $2N_3 = 3N_2$.

5. Combination of these equations with the preceding one leads to the simple expression of the final result obtained when carbon disulfide, potassium azido-dithiocarbonate, or azido-carbondisulfide, in relatively small amount, is brought into contact with a solution containing potassium trinitride and iodine, as confirmed by both iodimetric and nitrometric determinations: $2KN_3 + 2I = 2KI + 3N_2$.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]
**SOME NEW LECTURE EXPERIMENTS WITH HYDRONITRIC
 ACID AND THE TRINITRIDES¹**

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For the purpose of demonstrating certain of the chemical properties of hydronitric acid and the trinitrides a number of experiments suitable for use on the lecture table have been devised. These have been tested repeatedly by actual use in lectures given by one of the authors at this University and elsewhere.

1. Nitridation of Hydriodic Acid by Means of Hydronitric Acid.—This experiment illustrates the similarity between hydronitric acid (hydrogen pernitride) and hydrogen peroxide.

Five cc. of conc. hydriodic acid (sp. gr. 1.5) is poured into a 15cm. test-tube, avoiding stirring to minimize oxidation, and 1 cc. of a 1% solution of hydronitric acid is added, whereupon iodine is liberated and nitrogen is evolved. The presence of the iodine is demonstrated by pouring part or all of the mixture into 2.5 liters of water containing starch solution. The reactions may be represented by the following equations; $2HI + HN_3 = NH_3 + N_2 + 2I$; $HI + NH_3 = NH_4I$; and are analogous to those between hydriodic acid and hydrogen peroxide. Nitrous and nitric acids lie between hydrogen peroxide and hydrogen pernitride in composi-

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tion and character. A blank experiment, in which either water alone or hydrochloric acid is used in place of the hydronitric acid, will prove that the liberation of iodine is really due to the action of the nitridizing agent.

2. Nitridation of Hydrochloric Acid by Means of Hydronitric Acid.—While it is scarcely surprising that so powerful a reducing agent as hydriodic acid should evoke the nitridizing power of hydronitric acid, it is noteworthy that so stable a compound as hydrochloric acid should undergo nitridation with liberation of chlorine. Turrentine² has already shown that hydrochloric acid in presence of hydronitric acid will dissolve platinum.

Five cc. of conc. hydrochloric acid is treated with 1 cc. of a 1% solution of hydronitric acid in a 15cm. test-tube, and is heated to the boiling point and held at this temperature for at least 1 minute. This length of time is usually required to effect appreciable nitridation, but excessive boiling may result in loss of the free chlorine. Evidence of the liberation of chlorine is obtained by pouring the contents of the test-tube, either immediately, or after cooling to room temperature, into 2.5 liters of water containing starch and potassium iodide. When water is used in place of the hydronitric acid, in a blank experiment, the result is negative. The following equations express the reactions involved: $2\text{HCl} + \text{HN}_3 = \text{NH}_3 + \text{N}_2 + 2\text{Cl}_2$; $\text{HCl} + \text{NH}_3 = \text{NH}_4\text{Cl}$.

The formation of ammonia as a reaction product in Expt. 1 or 2 may be demonstrated by mixing either hydriodic or hydrochloric with hydronitric acid, as just described, adding sodium hydroxide in excess and testing for ammonia with litmus paper or, after distillation, with Nessler's solution.

3. Formation of Potassium Manganate by the Action of Potassium Trinitride upon Manganese Dioxide.—The similarity which exists between pernitrides and peroxides of the alkali metals may be illustrated by the conversion of manganese dioxide into potassium manganate which takes place when the dioxide is heated with potassium trinitride (pernitride) in presence of air.

Samples of finely pulverized potassium trinitride and manganese dioxide, weighing 0.5 g. each are mixed very thoroughly on glazed paper, and the mixture is gently heated in a 100cc. porcelain crucible, over a low flame, so adjusted as to cause the reaction to take place in from 30 to 60 seconds. During this process the operator should take care not to stand too near the crucible, as the reaction proceeds with considerable violence, accompanied by a hissing noise and by the emission of numerous sparks.

To minimize loss of the reacting material, a 200cc. crucible may be inverted over the 100cc. crucible before heat is applied, but the smaller crucible should be heated for a few minutes after the reaction has occurred and the

² Turrentine, *THIS JOURNAL*, **34**, 385-387 (1912).

larger crucible has been removed, in order to permit the second stage of the process, which results in formation of the manganate, to take place.

In either event, the crucible containing the dark green product is allowed to cool to room temperature, and the contents are treated with about 25 cc. of water. After solution has taken place, the resulting liquid is poured into 2.5 liters of water. The deep green color soon changes, on standing, to that of a permanganate solution, especially if a small amount of dil. sulphuric acid be added.

The main reaction involved in this experiment takes place in three stages: first, decomposition of the potassium trinitride into its elements; second, reduction of the manganese dioxide by the action of metallic potassium, with formation of manganous oxide and potassium oxide, or possibly of potassium hypomanganite; third, oxidation of the hypomanganite to potassium manganate by means of atmospheric oxygen. These three stages may be expressed by the equations: $2\text{KN}_3 = 2\text{K} + 3\text{N}_2$; $\text{MnO}_2 + 2\text{K} = \text{K}_2\text{O} \cdot \text{MnO}$; $\text{K}_2\text{O} \cdot \text{MnO} + \text{O}_2 = \text{K}_2\text{MnO}_4$.

In the early work on the subject conducted in this Laboratory³ traces, only, of ammonia were detected in the product obtained. Later experiments have shown that considerable quantities of ammonia are formed under certain conditions. Immediately after the addition of a small quantity of water to the residual green product a strong odor of ammonia may be perceived, and the presence of this substance may be confirmed by the usual tests.

The presence of ammonia as a reaction product indicates that the process does not take place entirely in accordance with the equations given above, but that a part of the nitrogen of the potassium trinitride is fixed, probably as a product of nitridation, in the form of a potassium ammonomanganite or manganate, or of a compound that is essentially a mixed ammono-aquo-manganite or manganate.

4. Detonation of Silver Trinitride with the Aid of a Fuse Composed of Paper Impregnated with Potassium Trinitride.—A strip from 0.5 to 1.0 cm. wide and from 0.25 to 0.5 m. long is painted on a large filter paper or paper towel with the aid of a small brush dipped in a 5% aqueous solution of potassium trinitride. While this is drying, a sample of silver trinitride is prepared by adding, in slight excess, drop by drop, a dilute solution of silver nitrate to 25 cc. of a 1% solution of hydronitric acid, diluted with an equal volume of water. The flocculent precipitate is collected upon a small filter, and is washed with successive small portions of cold water until the excess of the precipitant has been removed. While still moist, a quantity of the silver trinitride, about sufficient to cover an 18 mm. disk to a depth of 1 mm., is carefully pressed upon the filter paper or paper towel, on one end of the painted strip. If any difficulty

³ Goldberg, *THIS JOURNAL*, 34, 886 (1912).

is experienced in causing the explosive to stick to the paper, a small amount of adhesive may be used, or the solid may be held in place by covering it with a thin piece of filter or tissue paper, glued around the edge. It is important that the paper beneath and around the explosive be treated with a liberal amount of the potassium trinitride solution. After both fuse and explosive have been thoroughly dried, the sheet is suspended from a suitable frame or molding so that the air has free access to both sides of the paper. When the end of the fuse farthest from the silver trinitride is touched with a glowing splint or with a small flame, the combustion gradually progresses toward the explosive, which finally detonates with a sharp report. Interest in the experiment is considerably enhanced if an appropriate crayon sketch is made upon the paper. For example, the explosive cap may be concealed in the figure of an airplane, while the lower end of the fuse is located at the muzzle of an anti-aircraft gun.

This experiment serves to illustrate (a) the highly explosive character of the heavy-metal trinitrides, which may in general be detonated either by heat or by mechanical impact, and (b) the similarity between potassium trinitride and potassium nitrate when employed in the manner suggested.

When potassium nitrate of corresponding concentration is used for the fuse, the combustion progresses with a velocity about double that noted when the trinitride is used. The paper evidently burns at the expense of the oxygen of the potassium nitrate. With the trinitride, the initial reaction is undoubtedly the exothermal decomposition of the substance into potassium and nitrogen, with subsequent combustion of the free metal, and incidentally of the paper, in the oxygen of the air. While these are the main reactions, it is probable that nitridation accompanies oxidation, at least to a limited extent, as is attested by the presence of ammonia in the products of the reaction.

Summary

The present article contains a brief description of several new lecture experiments designed to illustrate

- (1) nitridation of hydriodic acid by means of hydronitric acid (hydrogen pernitride);
- (2) nitridation of hydrochloric acid by means of hydronitric acid;
- (3) formation of potassium manganate by action of potassium trinitride (potassium pernitride) upon manganese dioxide;
- (4) detonation of silver trinitride with the aid of a fuse composed of paper impregnated with potassium trinitride.