[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY.]

TETRAMETHYLAMMONIUM TRINITRIDE.[1]

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In connection with an extended investigation that has been in progress in this laboratory for a number of years it was found desirable to prepare certain of the alkylammonium salts of hydronitric acid. Preliminary experiments in this direction were carried out some years ago by G. E. F. Lundell, who readily obtained several of these substances in crystalline form by passing dry hydrogen trinitride vapor into alcoholic solutions of the amines.

Tetramethylammonium trinitride may be prepared by double decomposition of tetramethylammonium iodide and silver trinitride, as expressed by the equation

$$N(CH_3)_4I + AgN_3 = N(CH_3)_4N_3 + AgI.$$

The silver trinitride used in the present investigation was prepared by slowly adding a one % solution of silver nitrate, in excess, to 50 cc. of a 1.5% solution of hydronitric acid, obtained by distillation from a solution of (Raschig) sodium trinitride acidified with sulfuric acid. The filtered precipitate was washed with cold distilled water until free from silver ions, and was then suspended in 100 cc. of cold water. To this suspension of silver trinitride successive portions of a one % solution of (Kahlbaum) tetramethylammonium iodide were added, until the total amount was somewhat less than that sufficient to react with all of the silver trinitride, which therefore remained in excess. The reaction was carried out in a liter flask, which was enclosed in a wooden box provided with a long handle. During the process of mixing the reacting substances, and for about 5 minutes after the introduction of the last portion of the iodide, the apparatus was thoroughly but cautiously shaken, in order to insure satisfactory contact between the reagents. After the resulting silver iodide had been removed by filtration, the solution of tetramethylammonium trinitride was concentrated over the water bath to the point of crystallization, and was then allowed to cool, with the result that a considerable amount of the solid was obtained in crystalline form. This solid was found to contain neither silver nor iodine in appreciable amount.

The composition of the crystals was established by determining the percentage of nitrogen present in the form of the N_3 group. This was accomplished by precipitating and weighing the nitrogen as AgN_3 in the usual manner. The results of 5 determinations are given in the following table:

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[1] The present article is based upon an investigation carried out by the author during his senior year in the Course in Chemistry, in fulfillment of the requirement for "senior research." The experimental work was completed in May, 1918.

No. of expts.	Wt. of $N(CH_3)_4N_3$. G.	Wt. of AgN_3. G.	Calc. % of N_3. (Theory, 36.18%.)
1	0.3020	0.3903	36.24
2	0.3031	0.3921	36.27
3	0.2671	0.3446	36.17
4	0.2399	0.3105	36.28
5	0.2669	0.3450	36.24

Tetramethylammonium trinitride is a fairly stable substance that does not explode when struck with a hammer, when ground in a mortar, or when dropped upon a hot plate. When heated in the air bath, however, the dry salt begins to decompose at about 125°. At higher temperatures the decomposition is more rapid, and results in the liberation of vapors possessing the fishy odor of the methyl amines. It is readily soluble in water, showing a marked increase in solubility with rise of temperature, and is slightly soluble in certain other liquids. At 20° one cc. of the saturated aqueous solution was found to contain about 0.5 g. of the salt, while in the case of other solutions the amount of solid contained in one cc. at this temperature was found to be approximately as follows: ethyl alcohol, 0.05 g.; methyl alcohol, 0.02 g.; benzene, 0.004 g.; chloroform, 0.001 g.; ether, 0.0005 g. With carbon tetrachloride the salt forms a two liquid layer system, the lower layer of which was found to contain, at 20°, in the presence of an excess of the solid phase suspended in the upper layer, about 0.005 g. of the salt per cc. Under ordinary conditions of temperature and pressure the salt seems to show no tendency to form either hydrates or ammonates when treated, respectively, with water or ammonia.

The crystals of tetramethylammonium trinitride show the characteristics of the tetragonal system[1] [a : c = 1 : 0.7245]. The individuals that gave good reflection on the goniometer were crystallized from water. Their habitus is prismatic, due to the predominance in development of the {100} faces, terminated by the bipyramid {111}. Very small faces were observed in the positions {110} and {101}, but neither of these forms had faces large enough to permit accurate measurement.

The angle {110} to {111} was determined as 59° 36′ from 11 good measurements ranging from 59° 32′ to 59° 43′. The close approximation of this shape to that of tetramethylammonium iodide (C = 0 7223) and the resemblance in both cases to the angles of a rhombic dodecahedron of the regular system are worthy of note. There is a strong tendency toward thin, tabular habitus, in case the crystals have grown on the bottom of the container. Under the polarizing microscope the substance shows parallel extinction, very strong double refraction, and negative optical character.

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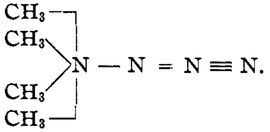
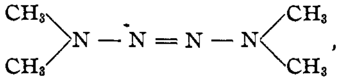
[1] The crystallographic study of tetramethylammonium trinitride was very kindly undertaken by Professor A. C. Gill of the Department of Geology at Cornell University, to whom the author wishes to express herewith his sincere appreciation.

Tetramethylammonium trinitride is empirically isomeric with tetramethyltetrazone, $(CH_3)_2N.N : N.N(CH_3)_2$, which has been prepared and studied by Renouf.[1]

If the correctness of the structural formula for hydronitric acid independently suggested by Angeli,[2] Thiele,[3] and Turrentine[4] be assumed, the formula for tetramethylammonium trinitride would be as follows:



From a comparison of this formula with that of the isomer, tetramethyltetrazone,



it would seem reasonable to suppose that under suitable conditions the unsymmetrical compound might be caused to undergo transformation into the symmetrical. It has been suggested, in fact, by D. Mendeléeff,[5] that ammonium trinitride might by certain treatment, such as heating its solution, be caused to change into a symmetrical amide, $N\ NH_2\ NH_2N$ (tetrazone?).

Preliminary experiments on the thermal treatment of tetramethylammonium trinitride were performed, with a view to discovering if possible the conditions under which this transformation might be effected. No positive indication of the formation of any isomer was obtained. Similar experiments performed by other investigators in this laboratory with ammonium trinitride were also unsuccessful. Neither by heating the substance in crystalline form or in aqueous solution in sealed tubes, nor by fractional sublimation of the crystals, could any evidence of a tendency toward molecular rearrangement be obtained. Further work along this line, both with ammonium trinitride itself and with various substitution products, will be undertaken in this laboratory as soon as circumstances permit.

The present investigation was undertaken at the suggestion of Professor A. W. Browne, and was carried out with his coöperation.

ITHACA, N. Y.

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[1] *Ber.*, 13, 2169–74 (1880).

[2] *Atti accad. Lincei*, [V] 20, I, 625–7(1911).

[3] *Ber.*, 44, 2522–5, 3336 (1911).

[4] THIS JOURNAL, 34, 385–7 (1912).

[5] *Ber.*, 23, 3464–3472 (1890).