

In conclusion, the authors wish to express their gratitude to Mr. R. M. McManigal who aided in the performance of many of the experiments herein described.

Summary

1. The voltage at which the luminous discharge in hydrogen disappears in tubes furnished with heated tungsten cathodes, is a function of the pressure for a given tube, passing through a minimum value which is usually a simple multiple of the ionization potential, 30.9 ± 0.4 volts.

2. In mercury vapor the disappearance voltage of the luminous discharge is a simple integral multiple of the ionization potential, 10.7 ± 0.4 volts.

3. A simple hypothesis is advanced to account for these facts.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

REACTION BETWEEN POTASSIUM TRINITRIDE AND IODINE IN THE PRESENCE OF CARBON DISULFIDE¹

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During the course of an investigation of the solubility of iodine in aqueous solutions of potassium trinitride, to be recorded in a later article, the deeply colored solutions obtained were shaken with various non-aqueous liquids in a test-tube for the purpose of ascertaining qualitatively the manner in which partition of the iodine between the two-liquid layers might take place.

When carbon disulfide was brought into contact at room temperature with a solution of iodine in aqueous potassium trinitride, the color of the solution was quickly discharged, as a result of rapid reduction of the iodine, with copious evolution of gas. A similar result was obtained when solutions of potassium trinitride were treated with a solution of iodine in carbon disulfide, or were at first treated with carbon disulfide alone, and then, either in presence or in absence of the excess of carbon disulfide remaining as a second liquid layer, were brought into contact either with a solution of iodine in aqueous potassium iodide, or with crystals of iodine. As each crystal of iodine was introduced, it was vigorously attacked, so long as the solution contained undecomposed potassium trinitride, with the result that reduction of the iodine, accompanied by a brisk evolution of gas, was promptly effected. The gas was subsequently shown by analysis to consist of pure nitrogen.

¹ The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

It has been stated by Hantzsch,² in connection with his work on iodine trinitride, IN_3 , that potassium trinitride and iodine do not react with each other. Raschig³ found that no reaction takes place when a solution of iodine is added to a neutral or acetic acid solution of sodium trinitride. In presence of sodium thiosulfate, in solution or in solid form, complete decomposition of the sodium trinitride was found to occur, with liberation of nitrogen gas. This reaction was suggested as a means of determining hydronitric acid and the trinitrides. It was found possible to use sodium sulfide in place of the thiosulfate, with similar result.

In connection with a comparative study of the foregoing method and a new method for the gas-volumetric determination of hydronitric acid by oxidation with a solution of potassium permanganate in presence of a ceric salt, Sommer⁴ reports that the procedure recommended by Raschig yields excellent results when relatively concentrated solutions of hydronitric acid are used. With very dilute solutions, however, such as 0.02 or 0.01 *N* trinitride solutions, the reaction velocity is greatly retarded toward the end, rendering difficult a satisfactory determination of the end-point. The catalytic acceleration of the reaction between iodine and hydronitric acid was attributed by Sommer to the tetrathionic acid formed by interaction of the iodine and thiosulfate. Experimental evidence was adduced by Raschig⁵ in support of his contention that tetrathionic acid exerts no catalytic action upon iodine and hydronitric acid, but that an unstable intermediate compound, $NaIS_2O_8$, probably formed under certain conditions by interaction of iodine and sodium thiosulfate, is responsible for the acceleration of the reaction, with quantitative decomposition of the hydronitric acid.

Sommer⁶ has succeeded in isolating and analyzing the hydrated sodium and barium salts of azido-dithiocarbonic acid, with the formulas, $NaSCSN_3 \cdot 4H_2O$ and $Ba(SCSN_3)_2 \cdot 5H_2O$. The synthesis of these compounds was effected by allowing equivalent amounts of carbon disulfide to react with an aqueous solution of sodium trinitride or of barium trinitride at 40° to 50°. During an attempt to prepare the potassium salt in similar fashion, a sample of the crystalline product exploded with a "fearful detonation," which led to a discontinuance of the experiments in this direction. Sommer has made a qualitative study of the action of aqueous solutions of sodium azido-dithiocarbonate upon solutions of numerous metallic salts, and upon various oxidizing agents, including potassium permanganate, potassium dichromate, and cerium salts in sulfuric acid solution, as well as iodine in potassium iodide solution. No evolution of gas was noted. Oxidation of the azido-salt resulted in the formation of a white, crystalline precipitate, believed to consist of a disulfide of the formula $N_2:N \cdot CS \cdot S \cdot S \cdot CS \cdot N:N_2$. This product was found to explode with violence even when heated under water, and was not subjected to analysis.

In the attempt to elucidate the hitherto unstudied reaction which takes place at ordinary temperatures between potassium trinitride and iodine in presence of carbon disulfide, with liberation of nitrogen gas, the authors have performed several series of experiments, which will be recorded under the following headings: (1) reaction between potassium trinitride, or sodium trinitride, and carbon disulfide vapor at ordinary temperatures; (2) reaction between potassium trinitride and iodine in presence of varying amounts of (a) carbon disulfide, (b) potassium azido-

² Hantzsch, *Ber.*, **33**, 522 (1900).

³ Raschig, *Chem.-Ztg.*, **32**, 1203 (1908).

⁴ Sommer, *Ber.*, **48**, 1963 (1915).

⁵ Raschig, *ibid.*, **48**, 2088 (1915).

⁶ Ref. 4, p. 1833.

dithiocarbonate, $KSCSN_3$, and (c) azido-carbondisulfide, $(SCSN_3)_2$. Under the second heading both iodimetric and nitrometric determinations have been made when each of the three substances was employed as catalyst.

1. **Reaction between Potassium Trinitride or Sodium Trinitride, in Aqueous Solutions, and Carbon Disulfide Vapor at Ordinary Temperatures.**—Accurately weighed amounts of pure potassium or sodium trinitride, dissolved in such amounts of water as to yield, for a given series, solutions of identical concentration, and contained in glass-stoppered U-tubes connected by ground-glass joints, were subjected at about 20° to the action of a slow current of air partly saturated with carbon disulfide vapor, and containing moisture just sufficient to prevent either condensation or evaporation of water in the U-tubes. At frequent intervals the U-tubes were detached and weighed, in order to ascertain the velocity and extent of absorption of the carbon disulfide by the salt under these conditions.

Five series of experiments were performed with potassium trinitride, and three with sodium trinitride⁷ as absorbent. Closely concordant results were obtained in every case, leading to the conclusion that each of these substances absorbs carbon disulfide in equimolecular proportions.

For example, 1.4920 g. of potassium trinitride, dissolved in 4.0337 g. of water, absorbed in 17 hours 1.3963 g. of carbon disulfide, corresponding to 0.9975 molecule of the disulfide to one of the salt, while 1.2000 g. of sodium trinitride, dissolved in 4.0253 g. of water, absorbed in 35 hours 1.4052 g., or 1.0000 molecule of carbon disulfide per molecule of the salt.

The data obtained in these two typical experiments are submitted in the form of curves in Fig. 1.

Toward the end of every experiment, the solution in the absorption tubes began to assume a yellowish, opalescent color, undoubtedly the result of a slow decomposition of the azido-dithiocarbonate, with liberation of sulfur, and probably also with loss of nitrogen gas, which accounts for the gradual decrease in weight of the tube after the theoretical amount of carbon disulfide has been absorbed.

It is possible that solutions of the trinitrides may be of use as absorbents for carbon disulfide in the field of gas analysis. Experiments in this direction are now in progress in this Laboratory.

Further evidence that a chemical reaction takes place between potassium trinitride and carbon disulfide in aqueous solution is afforded by certain preliminary experiments in which the electrical conductance of certain solutions of potassium trinitride was determined at 30° , before and after treatment with liquid carbon disulfide. In one experiment, for example, the specific conductance of 0.02 *N* potassium trinitride was found to be

⁷ The experiments with sodium trinitride were carried out by Miss Sara J. Joffe, to whom the authors take this opportunity to express their gratitude.

0.00286 prior to treatment, and 0.00241 after 100 cc. of the solution had stood in contact with 0.3768 g. of carbon disulfide, at constant temperature and with shaking at regular intervals, for a period of 53 hours. On the assumption that the effect of a possible change in viscosity of the solution is negligible, this lowering of the conductance indicates either that the potassium azido-dithiocarbonate is relatively less dissociated than is

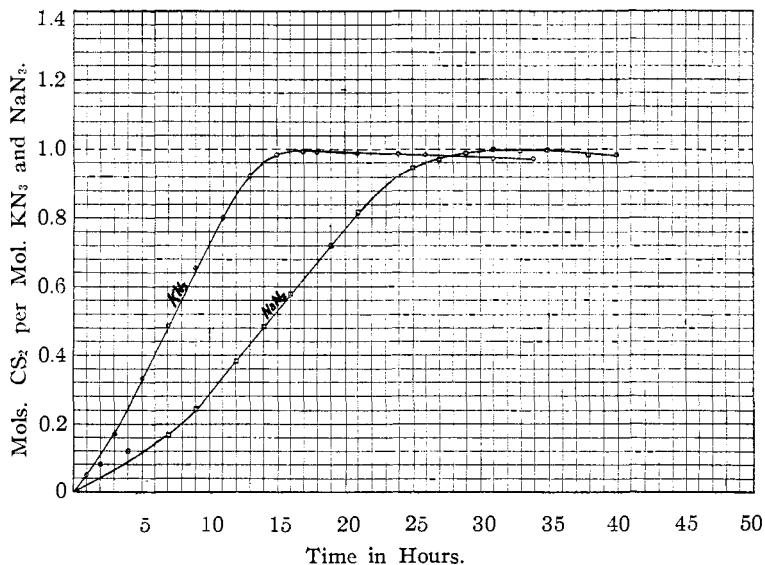


Fig. 1.

potassium trinitride, or that the anion, SCSN_3^- , possesses a migration velocity slower than that of N_3^- .

2. Reaction between Aqueous Solutions of Potassium Trinitride and Iodine in Presence of Varying Amounts of (a) Carbon Disulfide.—It was quite apparent from the start that carbon disulfide acts either directly or indirectly as a catalyst capable of initiating or accelerating the decomposition of potassium trinitride by means of iodine. It has been definitely proved that the first reaction taking place when carbon disulfide is brought into contact with a solution of potassium trinitride, even at ordinary temperatures, results in the formation of potassium azido-dithiocarbonate, in accordance with the following equation.



Until this reaction, which is by no means instantaneous, has proceeded to at least a slight extent, the color of an iodine solution added to the solution of potassium trinitride containing carbon disulfide is not discharged. This has been shown by the following experiments.

To 20 cc. of 0.1 *N* potassium trinitride was added 0.304 g. of carbon disulfide, or double the amount required by theory on the basis of Equation 1. The mixture was shaken thoroughly, and was allowed to stand until a total of 30 seconds had elapsed after the time of bringing the substances together. Successive 2cc. portions of this mixture were now taken from the flask, at intervals of 0, 5, 20 and 30 minutes, and of 4, 6, 27 and 76 hours, and were poured into test-tubes, each of which contained 1 cc. of 0.1 *N* iodine solution diluted with 5 cc. of water. The color of the iodine was completely discharged only after 27 minutes in the first experiment, and after 10 minutes in the second. In the third, and in all subsequent experiments, however, the color disappeared in less than 1 second. A slow evolution of nitrogen gas was noted in Expt. 1, and a more rapid evolution in Expt. 2. In Expts. 3 and 4 a copious evolution occurred from the start, and a slight opalescence soon appeared in the solution. In Expt. 5 only a very small amount of gas was liberated, and a white precipitate was formed immediately after mixing with the iodine. This was also the case in the last three experiments, in which no gas whatever was liberated.

It is clear from these experiments that until appreciable amounts of the azido-salt are formed, no reaction between iodine and the trinitride takes place. During the interval between the first formation of the azido-salt and the complete transformation of the potassium trinitride into azido-salt, nitrogen is invariably evolved when iodine is added.

This statement has been confirmed by a second series of experiments, in which 20 cc. of 0.1 *N* potassium trinitride was shaken with 0.0161 g. of carbon disulfide dissolved in 8 cc. of water at 20°. This corresponds to about $\frac{1}{10}$ of the amount of carbon disulfide required by calculation on the basis of Equation 1. Potassium trinitride was therefore always present in considerable excess. After the mixture had remained standing for 30 seconds, successive 3cc. portions, withdrawn at intervals of 0, 5, 10, 20 and 40 minutes, and of 18, 48, 96 and 120 hours, were poured into test-tubes each of which contained 1 cc. of 0.1 *N* iodine diluted with 5 cc. of water. The time required for the discharge of the iodine color in the first 3 tests was 29, 27 and 6 minutes. In the fourth the same result was obtained in 30 seconds, and in the fifth, within 1 second. In the four remaining tests this same velocity was observed. Gas was evolved slowly in the first two, and rapidly in all subsequent tests.

Under the conditions prevailing in this second series of experiments, the excess of potassium trinitride prevents the permanent formation of the white precipitate obtained in the first series, by reacting with this substance as soon as formed, with liberation of nitrogen.

In the first series complete conversion of the potassium trinitride into azido-salt was accomplished in about 4 hours. Thereafter, addition of iodine had the effect of precipitating azido-carbondisulfide, $(SCSN_3)_2$, as expressed by the following equation.



The reaction between potassium trinitride and iodine in presence of varying amounts of carbon disulfide has been investigated quantitatively by both iodimetric and nitrometric methods. The procedure followed in the iodimetric work⁸ consisted in weighing out in each case 0.1990 g.

⁸ Certain of these experiments were performed by Miss Hazel E. Braman, of whose work the authors wish to express herewith their appreciation.

of potassium trinitride, and dissolving the sample in 20 cc. of water. The specified amount of pure, redistilled carbon disulfide, in the form of an aqueous solution containing 0.00201 g. per cc., was added and the result-

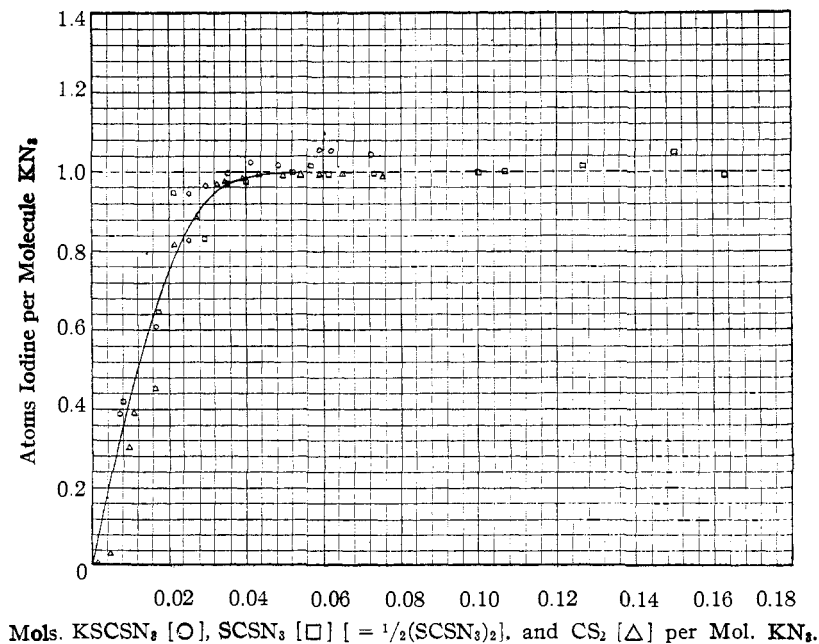


Fig. 2.

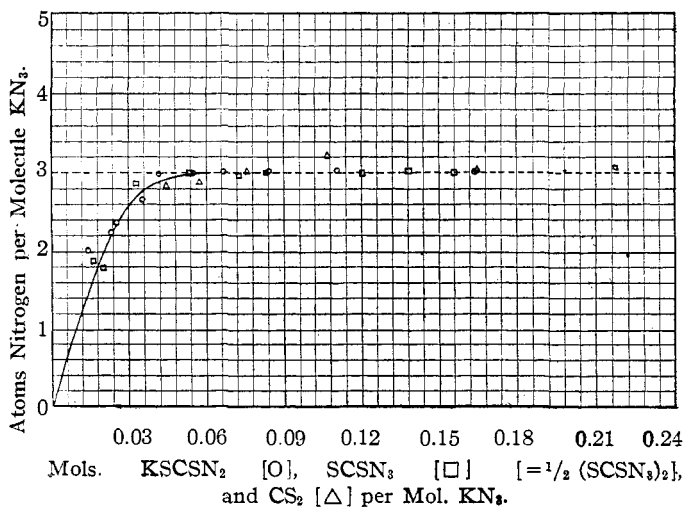


Fig. 3.

ing mixture was titrated with 0.1 *N* iodine. The data obtained are plotted in Fig. 2.

In the nitrometric work weighed amounts of potassium trinitride were caused to react in the presence of the specified amounts of carbon disulfide with an excess of iodine in the form of a solution with potassium iodide. A water-jacketed Lunge nitrometer was employed. The results are shown in Fig. 3.

From these results, it is evident that potassium trinitride reacts in aqueous solutions with iodine in presence of relatively small amounts of carbon disulfide, varying from about 0.04 to 0.08 mols. per mol. of potassium trinitride, in the ratio expressed by the following equation.



(b) **Potassium Azido-dithiocarbonate.**—In order to ascertain whether or not the carbon disulfide that combines with potassium trinitride in accordance with Equation 1, is subsequently regenerated, during other stages of the reaction, several experiments were performed, of which the following is typical. A sample of pure, dry, solid potassium azido-dithiocarbonate weighing 0.1974 g. was dissolved in 20 cc. of a 20% solution of potassium trinitride.

A concentrated solution of iodine in potassium iodide was introduced, drop by drop, below the surface of the solution, while a slow current of air was continuously bubbled through the reacting mixture and then through an alcoholic solution of potassium hydroxide. The azido-salt used would correspond to a total weight of carbon disulfide amounting to 0.0955 g. No indication whatever of the presence of carbon disulfide in the gases from the flask was obtained when the alcoholic solution was tested in the usual way with acetic acid and copper sulfate, although the operation of bubbling air through the flask was continued for 20 minutes. When 0.001 g. of carbon disulfide, dissolved in 0.5 cc. of water, was introduced with the iodine, however, a characteristic yellow precipitate of cupric xanthate was obtained in the final test.

Experiments similar to that just described were performed, in which azido-carbondisulfide was employed in place of the potassium azido-dithiocarbonate.

In one typical case, a sample of the pure, dry, solid weighing 0.1982 g. was employed. This corresponds to 0.1277 g. of free carbon disulfide. The results of the test for carbon disulfide were entirely negative although, as before, positive results were readily obtained after the introduction of 0.001 g. of carbon disulfide into the reacting mixture.

These experiments show conclusively that no detectable amount of carbon disulfide is regenerated during the interaction of iodine and potassium trinitride in presence of carbon disulfide, when once the disulfide has become fixed by combination with the potassium trinitride.

The potassium azido-dithiocarbonate and the azido-carbondisulfide used in the experiments noted in the current article have been isolated, analyzed, and studied in detail, and will be described in a later communication.

When a sample of potassium azido-dithiocarbonate weighing 0.1573

g. was dissolved in 10 cc. of water and mixed with 20 cc. of 0.1 *N* iodine, immediate precipitation of azido-carbondisulfide occurred in accordance with Equation 2. When 1cc. portions of this mixture were successively added, after various time intervals, to 5cc. portions of 0.1 *N* potassium trinitride, discharge of the color due to the excess of iodine took place within 1 second, with vigorous evolution of nitrogen. No appreciable change in the rate of this discharge took place until after the mixture had been allowed to stand for several days, when it became apparent that some reaction between the excess of iodine and the precipitated azido-carbondisulfide was slowly taking place, with resultant retardation of the subsequent reaction with potassium trinitride.

To ascertain whether or not any reaction takes place between potassium azido-dithiocarbonate and potassium trinitride, 20cc. portions of the 0.1 *N* solutions of each of these substances were mixed, and 2cc. samples were at intervals added to 1 cc. of 0.1 *N* iodine diluted with 5 cc. of water. The results obtained were always the same, even after the solution had stood, before using, for 15 days. Very rapid discharge of the color took place, accompanied by the transitory formation of a white precipitate of azido-carbondisulfide, the disappearance of which was attended by a copious evolution of nitrogen.

Quantitative experiments similar to those described in a preceding paragraph, except that potassium azido-dithiocarbonate was used as the catalyst in place of carbon disulfide, have been performed, and the data recorded in Figs. 2 and 3.

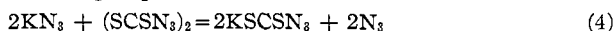
It may be concluded from these data that about 0.04 mol. of potassium azido-dithiocarbonate per mol. of potassium trinitride is required to catalyze completely the decomposition of the latter substance in accordance with Equation 3. With greater amounts of the azido-salt, the amounts of iodine used become distinctly greater than required according to the equation, owing to the reaction between the excess of iodine and the azido-salt, as expressed by Equation 2. The amounts of nitrogen evolved under comparable conditions are not subject to the error resulting from this secondary reaction, and are seen in Fig. 3 to be more closely concordant with those calculated.

(c) **Azido-carbondisulfide.**—A sample of this substance weighing 0.1182 g. was suspended in 10 cc. of water, and mixed with 40 cc. of 0.1 *N* iodine solution. Successive 1cc. portions, withdrawn after thorough shaking, were added after different time intervals, to 5 cc. of 0.1 *N* potassium trinitride. Discharge of the color resulted almost immediately in the earlier tests, but after the original mixture had remained standing for 48 hours, the process required 2 minutes, and finally after 15 days the color persisted for 4 minutes, indicating that a reaction had been slowly taking place between the iodine and the azido-carbondisulfide, as suggested in

an earlier paragraph. This suggestion is supported by the fact that when an iodine solution is added drop by drop to an aqueous suspension of azido-carbondisulfide, the color is for a time discharged, and a slight evolution of gas takes place.

Two 20cc. samples of 0.1 *N* potassium trinitride, diluted in each case with 10 cc. of water, were treated with azido-carbondisulfide. In the first experiment 0.3244 g. of the solid disulfide was employed. This amount represents an excess of the disulfide above the weight required by the ratio $(\text{SCSN}_3)_2:2\text{KN}_3$, or more than sufficient for the quantitative formation of potassium azido-dithiocarbonate. Two-cc. samples of the mixture were withdrawn at intervals, and were brought into contact in each case with 1 cc. of 0.1 *N* iodine solution and 5 cc. of water. In the first test, made after the original mixture had been standing for 30 seconds, discharge of the color required 5 minutes. In the 7 subsequent tests, made at intervals varying from 2 minutes to 8 days, the color disappeared in from 1 to 5 seconds. The evolution of gas, slow in the first, rapid in the second, and gradually decreasing in later tests, ceased entirely in the sixth test, made after the original mixture had been allowed to stand for 45 hours.

The relative slowness of the reaction at the start indicates that appreciable time is required for the solution of the catalyst. The gradual diminution in the amount of gas evolved indicates that the azido-carbondisulfide has reacted with the potassium trinitride, forming potassium azido-dithiocarbonate, which reacts with the iodine added later, in accordance with Equation 2, thus regenerating the azido-carbondisulfide, the reappearance of which was clearly noted in the experiments. The reaction between azido-carbondisulfide and potassium trinitride yields nitrogen gas even before iodine is added, and probably takes place as expressed by the following equations.



In the second experiment 0.1182 g. of the solid disulfide, or $1/2$ of the amount required by the ratio $(\text{SCSN}_3)_2:2\text{KN}_3$, was mixed with potassium trinitride in exactly the manner adopted for the first experiment. Successive 2cc. samples were mixed with 0.5cc. portions of 0.1 *N* iodine and 5 cc. of water. The iodine was in general decolorized within 2 or 3 seconds, throughout the entire series of tests, extending finally through an interval of 15 days. Abundant gas was evolved at first, but distinctly less in the later tests. Small amounts of solid azido-carbondisulfide were regenerated, in the form of a white precipitate, in the last four experiments of the series. The continued evolution of nitrogen is attributable to the constant presence of an excess of potassium trinitride.

To test the reasonableness of the conclusion that the azido-carbondisulfide actually liberates triatomic nitrogen, N_3 , from solutions of potassium trinitride, in accordance with Equation 4, and that this unstable substance is quickly transformed into diatomic nitrogen as expressed in Equation 5, small amounts of the solid disulfide were shaken up with solutions of potassium iodide containing starch. The immediate formation of the characteristic blue color indicated that iodine was liberated in the sense of the following equation.



The reaction indicated by this equation is exactly the reverse of that expressed by Equation 2, which is, therefore, to be regarded as a reversible reaction. Under ordinary circumstances, however, the reaction proceeds almost quantitatively with precipitation of azido-carbondisulfide, because of the relative insolubility of this substance.

Quantitative iodimetric and nitrometric experiments, in which various amounts of pure, solid azido-carbondisulfide were used as the catalyst in the reaction between potassium trinitride and iodine, have been performed. The data are presented in Figs. 2 and 3.

From these results it is evident that about 0.05 mol. of SCSN_3 ($= \frac{1}{2} (\text{SCSN}_3)_2$) per mol. of potassium trinitride is the minimum amount of this catalyst necessary for the complete decomposition of the trinitride in accordance with Equation 3. As a rule, no marked tendency toward the consumption of appreciably more iodine than required by the equation was noted in experiments in which relatively large amounts of the catalyst were employed, for the reason, no doubt, that the excess of iodine reacts but very slowly with the catalyst.

Inspection of the curves shown in Figs. 2 and 3 leads to the conclusion that the employment in comparative experiments of carbon disulfide, potassium azido-dithiocarbonate, and azido-carbondisulfide in equivalent proportions, as catalysts in the reaction between potassium trinitride and iodine is productive of substantially identical results.

In view of the fact that the carbon disulfide used in the reaction is not itself regenerated, this substance is not to be regarded as the true catalyst, but merely as the material from which the catalyst is prepared, at the expense of a part of the potassium trinitride, as expressed in Equation 1. Either the readily soluble azido salt or the slightly soluble azido-carbondisulfide plays the role of a true catalyst, however, as each of these, after having been converted to the other, is regenerated in the manner shown in Equations 2 and 4. Thus potassium azido-dithiocarbonate reacts at once with iodine, forming azido-carbondisulfide, while this substance, probably in the nascent state, as the radical SCSN_3 , reacts with potassium trinitride regenerating the azido salt and setting free nitrogen. By adding together Equations 2, 4, and 5 and canceling out the terms common to both members, Equation 3 is obtained, which represents in simple form the decomposition of potassium trinitride by iodine in the presence of either of these catalysts.

Summary

1. Potassium trinitride reacts with iodine in presence of carbon disulfide, with formation of potassium iodide and liberation of nitrogen.
2. The first stage in this reaction consists in the formation of potassium azido-dithiocarbonate, KSCSN_3 , by interaction of potassium trinitride and carbon disulfide, as expressed by the equation $\text{KN}_3 + \text{CS}_2 = \text{KSCSN}_3$.

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: $2KN_3 + 2I = 2KI + 3N_2$.

ITHACA, NEW YORK

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

BY A. W. BROWNE AND A. B. HOEL

Received May 18, 1922

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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