

THE REACTION OF OZONE WITH AN AQUEOUS SOLUTION OF:
I THIOUREA, II SODIUM CHLORIDE

A THESIS

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by

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ANALYSIS OF OZONE WITH THE USE OF A...

FIGURE, II SODIUM...

Approved:

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PART I
THE REACTION OF OZONE
ON THIOUREA

INTRODUCTION

Much work has been done on the reaction of ozone with the ethylenic type of linkage, but the effect of ozone on groups such as the carbon-sulfur double bond is practically an unexplored field.

Weyl¹ passed ozonized air through a water solution of thiourea and found that sulfur was precipitated and that the resulting solution contained sulfuric acid. He made no attempt, however, to determine what happened to the nitrogen in the thiourea, or to make a quantitative study of the reaction.

Later, several experimenters studied the reaction of hydrogen peroxide on thiourea. According to Barnett², a neutral solution of thiourea reacts with hydrogen peroxide to give $\text{NH}=\text{C}(\text{NH}_2)\text{-SO}_2\text{H}$, aminoiminomethanesulfuric acid, which melts at 144°C .

Kitamura³ found that aminoiminomethanesulfuric acid is formed by the oxidation of thiourea with hydrogen peroxide in neutral solution, but that oxidation by the peroxide in basic solution gives urea. After studying a large number of sulfur

¹ Th. Weyl, Chem. Zeitung 25, 292 (1901)

² Edward Barnett, J. Chem. Soc. 97, 63 (1910)

³ R. Kitamura, J. Pharm. Soc. Japan, 55, 300-49 (1935)

C.A. 29, 5210 (1935); 57, 51-4 (1937),

C.A. 32, 3342 (1938); 59, 33-6 (1939),

C.A. 33, 1726 (1939)

compounds, he made the general statement that any compound of the type $-N = C-SH$ or $H-N-C = S$ would be oxidized by a basic solution of hydrogen peroxide to $H-N-C = O$.

Herrera⁴ reviewed and criticised Kitamura's work. He found that while most compounds of the type $H-N-C = S$ are converted to $H-N-C = O$, thiourea is an exception and is instead converted into a light yellow compound "probably an isomer of thiourea".

Thus while the results of the oxidation of thiourea with hydrogen peroxide in acid solution is fairly well established, its reaction in basic solution remains controversial.

The purpose of this work is to complete the investigation begun by Weyl of the reaction of ozone on an aqueous solution of thiourea.

⁴J. Jimenez Herrera, *Anales. Soc. espan. fis. quim.* 33, 877-86 (1935)

APPARATUS AND MATERIALS

The ozone used was produced by means of a simple laboratory ozonizer⁵ the details of which are shown in Figure 1.

"A" represents two U-tubes filled with activated alumina for drying purposes. "B" is a flow meter whose manometer fluid is butyl phthalate. "C" is a large battery jar which contains water. At "D" are two pyrex laboratory condensers joined together, and at "E" are two corks through which a long lead wire serves as an electrode. The lead wires are immersed in a 5 per cent sulfuric acid solution, and are weighted to hold them in a vertical position.

At "F" are ground glass joints which must be used because of the action of ozone on rubber. "G" is the reaction flask and "H" is the ozone destroyer which contains moistened sodium hydroxide pellets.

The potential difference (8,000 V.) between "E" and the water in the jar is furnished by a neon sign transformer.

The condensers are supported by a ring stand.

The thiourea furnished by the Eastman Kodak Company was recrystallized from water giving a product which melted at 177.5-178.5° C. (uncorr.)

All other chemicals and reagents were C.P. grade unless otherwise specified.

⁵Lee Smith, J. Am. Chem. Soc. 47, 1844 (1925); A. L. Henne, *ibid.* 51, 2676 (1929)

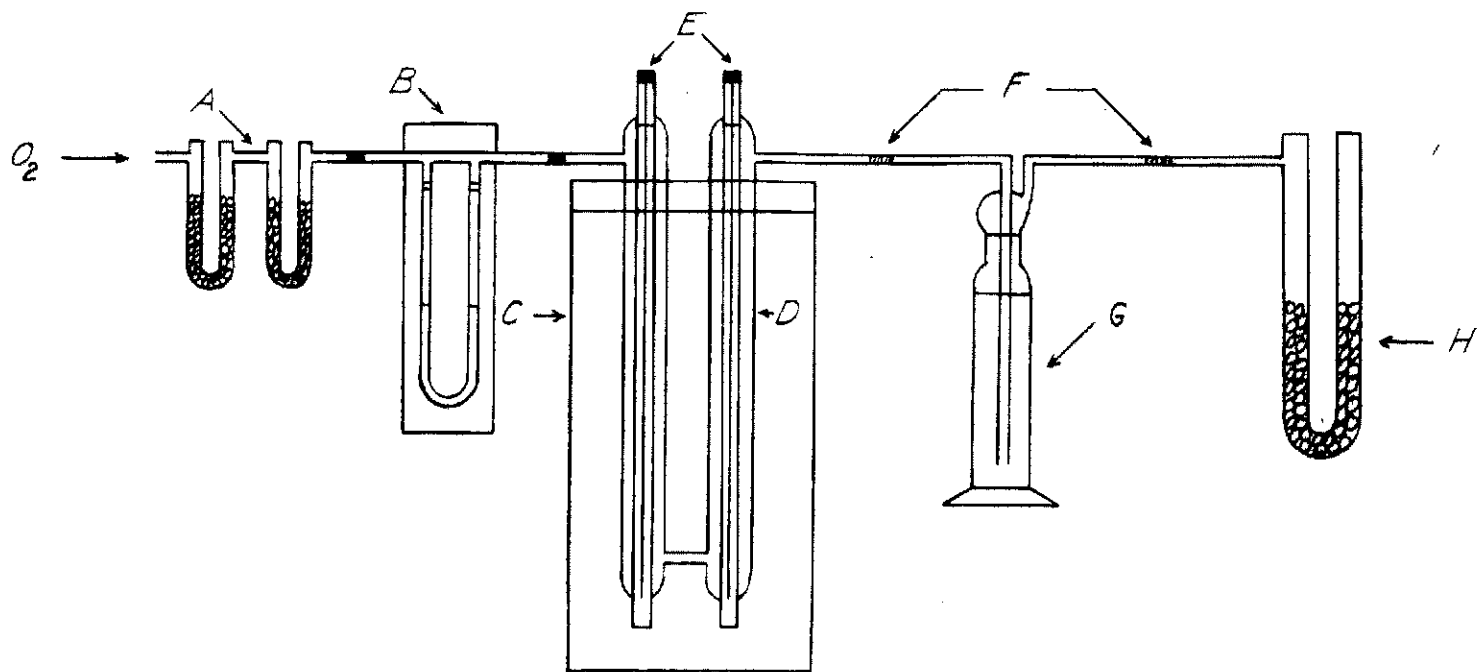


FIGURE - 1

METHODS OF CALIBRATION

1. CALIBRATION OF FLOW METERS.

Since a capillary type flow meter was used in this work and it does not have sufficient latitude for both slow and rapid rates of flow, three different size capillaries were used. The calibration of one of these is described.

The air in a 5-gal. bottle was displaced by a stream of water which flowed at a constant rate. This stream of water was supplied by siphoning water from a constant level bath into the bottle through a 2-hole rubber stopper. The displaced air was made to pass through the flow meter, and the reading of the meter taken. Below is the table of results for the smallest size capillary.

TABLE I

<u>Rate of flow, liters/hr.</u>	<u>"h", flow meter reading</u>
1.9	11.0
3.3	27.5
4.4	47.0
5.0	58.0

The results are shown graphically in Figure 2.

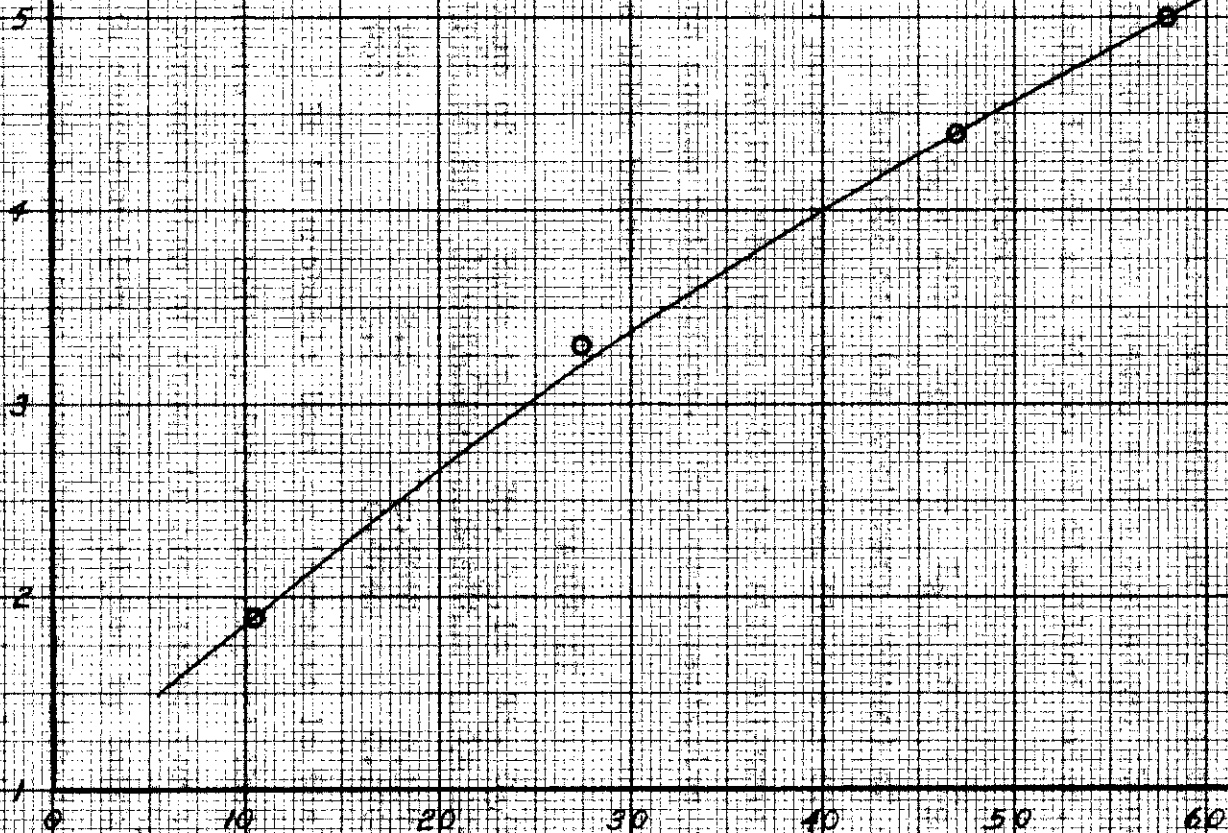
2. DETERMINATION OF THE APPROXIMATE YIELD OF THE OZONIZER.

It is desired to know the approximate yield of the ozonizer so as to get some idea of its efficiency, and for comparison with the ozonizer used by other investigators.

The procedure used in running the analyses was that used by Smith⁶, and a brief description will be given.

⁶ Lee Smith, J. Am. Chem. Soc. 47, 1848 (1925)

RATE OF
FLOW
(Liters Per
Hour)



FLOW METER READING "h"

FIGURE 2

creases and the percentage ozone decreases. The relation between the rate of flow and the percent ozone is of no importance in the present problem, but the relation between the rate and the weight of ozone delivered per hour is of interest. By means of the plot of the flow meter reading versus grams of ozone per hour one can calculate the total grams of ozone used in a reaction.

The experimental results are shown in the table below and the graph in Figure III.

TABLE III

<u>"l", Flow Meter Reading</u>	<u>Grams O₃ per Hour x 100</u>
2.0	8.1
2.2	9.2
3.5	14.7
3.6	13.5
4.4	18.0
5.0	20.5
5.1	19.6
5.7	22.8
7.5	28.2
8.1	29.5
8.8	32.8
10.3	36.8

From the graph it is noted that the function is practically linear.

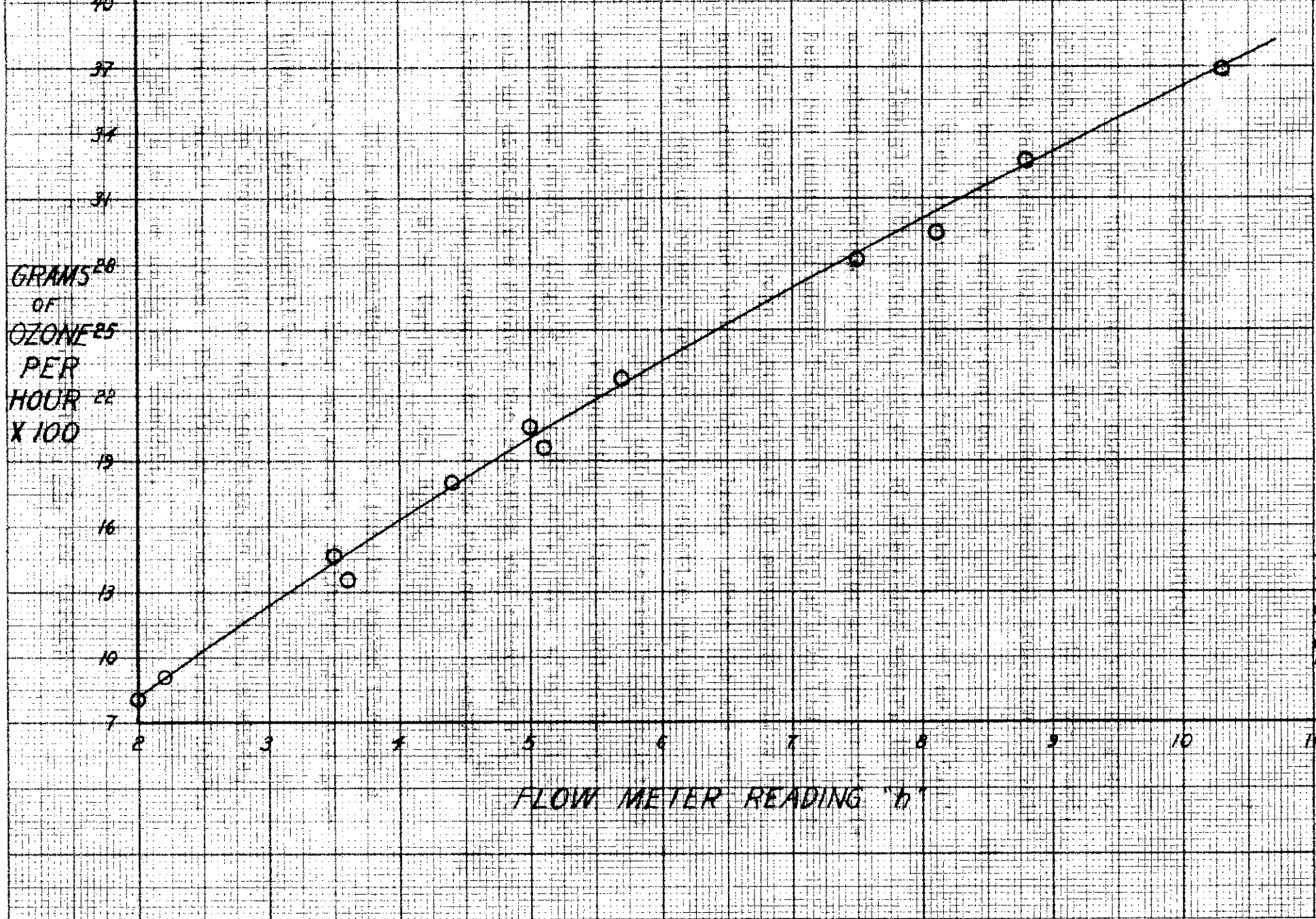


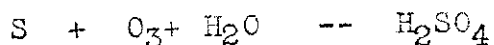
FIGURE 3

PROCEDURE AND DISCUSSION OF RESULTS

Before the reaction of ozone on thiourea was started, it was decided to test the effect of oxygen on this compound. Oxygen was passed through an aqueous neutral solution of thiourea, but there was no reaction.

When ozone was passed into a neutral solution of 0.13 mol (10 g) of thiourea in 400 cc. of distilled water, it was absorbed completely, even with rates of flow as high as 30 liters per hour. In about ten minutes milky sulfur had appeared and in about two hours a precipitate of amorphous sulfur had accumulated on the bottom of the flask. After the absorption of 0.36 mol of ozone (twenty hours) reaction ceased.

The sulfur was filtered off and the resulting solution evaporated. During the evaporation of the solution large amounts of sulfur dioxide were given off. Even after all the sulfur dioxide was evolved the solution was strongly acid to litmus. This was probably due to the following reaction⁸



This reaction was checked by passing ozone through a mixture of powdered sulfur and water. Sulfuric acid was produced in small quantities.

On evaporation of the solution to dryness, a white, greasy solid resulted. The mixture decomposed around 300°C. to give a yellow solid and ammonia.

⁸ Th. Weyl, Chem. Zeitung 25, 292 (1901)

In an effort to purify the solid, it was dissolved in water and recrystallized four times. The final product consisted of pure white crystals which were easily dried to a white powder. This substance decomposed from 300-310°C giving off ammonia. The reaction of sodium hydroxide upon the substance to give ammonia indicates either an ammonium salt or an amide. A water solution of the substance conducted a current, so probably an ammonium salt was present. A positive test for the sulfate ion was found and the conductivity of different concentrations of the salt in water approximated that of ammonium sulfate so it was thought that the unknown compound itself was ammonium sulfate.

Analyses were run on the first and final recrystallization products to determine the percentage of NH_4^+ and $\text{SO}_4^{=}$.

The Kjeldahl method for nitrogen was run to determine the amount of NH_4^+ present, and the gravimetric sulfate method was used to calculate the per cent $\text{SO}_4^{=}$. The standard Kjeldahl procedure was followed with the exception that the material did not have to be digested before distillation.

The results are shown in Table IV.

TABLE IV

THEORETICAL COMPOSITION OF $(\text{NH}_4)_2\text{SO}_4$		BLANK DETERMINATION ON $(\text{NH}_4)_2\text{SO}_4$ (U.S.P.)	
27.3%	- NH_4^+	-	27.4%
<u>72.7%</u>	- $\text{SO}_4^{=}$	-	<u>73.0%</u>
100.0			100.4

TABLE IV (Continued)

ANALYSIS OF 1ST RECRYSTALLIZATION PRODUCT				ANALYSIS OF 4TH RECRYSTALLIZATION PRODUCT	
21.7%	-	NH_4^+	-	27.4%	
55.2%	-	$\text{SO}_4^{=}$	-	72.3%	

Under the microscope the crystals of pure ammonium sulfate and the recrystallized product appeared identical, and the solubility of the product in water was approximately the same as ammonium sulfate.

The above evidence indicates that the reaction product is ammonium sulfate which could probably be isolated as the pure salt after continued recrystallization.

Thus far sulfur, sulfur dioxide, sulfuric acid, and ammonium sulfate have been found, yet no compound containing carbon has been isolated.

To see if carbon dioxide has escaped as a gas from the reaction chamber, the exit gas was passed through barium hydroxide solution. Toward the end of reaction much gas (mostly carbon dioxide) was liberated.

It is possible that some compound, probably of organic nature, is in the residue obtained by evaporating the ozonized solution.

Since ammonium sulfate is insoluble in organic solvents an attempt was made to extract the solution after ozonization with various organic solvents. Several runs were made with

ozone and thiourea and the sulfur filtered off, and evaporation continued until all sulfur dioxide was removed. An attempt was made to extract the solution with ether, but on evaporation of the ether layer no residue was found. Extractions were also tried with chloroform and benzene with no better results.

On failure to extract the solution, it was evaporated to dryness and the white residue dried in a desiccator. Extraction of these crystals with chloroform, ether, and benzene failed, so finally absolute alcohol⁹ was tried. This extraction yielded grey white crystals and left crude ammonium sulfate as a residue. An analysis of the residue gave 25.50 per cent NH_4^+ and 71.01 per cent SO_4^- .

The crystals resulting from the extraction were mushy and could not be dried in a desiccator. The melting point, 98-106°C showed a large amount of impurity. When the crystals were left on a porous clay plate for several days they gradually became dry. The dry crystals melted from 118-123°C.

The presence of thiourea was tested for by fusing the solid and adding a solution of ferric chloride to the residue. Absence of a blood red color proved no unreacted thiourea was present.

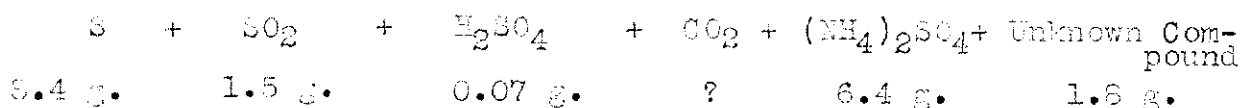
The crystals were found to be soluble in water and alcohol, and insoluble in chloroform, ether and benzene. They undergo vigorous oxidation with cold concentrated nitric acid with the evo-

⁹The alcohol was tested with anhydrous copper sulfate to make certain no water was present.

lution of considerable heat. The water solution will reduce mercurous nitrate to free mercury, and insoluble complexes are formed with heavy metals such as copper, mercury, and silver.

A sodium fusion revealed the presence of nitrogen and sulfur. A qualitative test showed that carbon was present.

Several other runs were made in order to get a quantitative estimation of the reaction. The diagram below shows the products resulting from 10.0 g. of thicurea.



The sulfur was filtered and weighed directly, while the sulfur dioxide and the sulfuric acid were determined by titration with sodium hydroxide using methyl red indicator. An aliquot portion of the solution after removal of the sulfur, was titrated with standard base and an equal aliquot was boiled to remove sulfur dioxide and then titrated with base. Thus the acidity in terms of sulfur dioxide and sulfuric acid was calculated. The resulting values are approximate and serve only to show the relative amounts of sulfur dioxide and sulfuric acid present. The amount of ammonium sulfate was found in another run by extracting the solid obtained by evaporation with absolute alcohol and weighing the residue.

An effort was made to isolate the unknown compound by the addition of barium hydroxide to the solution after ozonization. On addition of excess barium hydroxide the following

reaction took place:



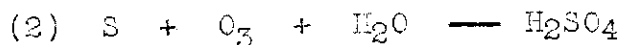
The solution was heated to drive off excess ammonia and filtered to remove barium sulfate. Carbon dioxide was passed into the filtrate to precipitate excess barium hydroxide and the solution filtered to remove the resulting barium carbonate. The filtrate was then evaporated to dryness in the hope that a pure organic compound would be left. Only a small residue was left from which no pure compound could be isolated.

The mechanism of the reaction of ozone and thiourea may be formulated in several different ways, the one given below being the most probable.

It may be assumed that the first step is that of desulfurization of the thiourea to form urea.



Then:

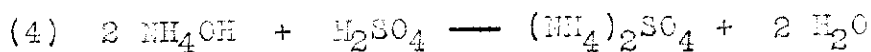


Also, the following reaction is known to take place slowly in the presence of sulfuric acid as a catalyst.

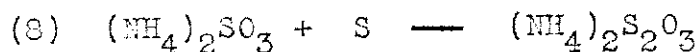
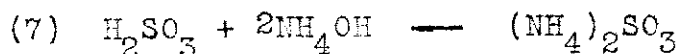
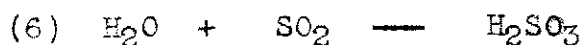


To verify this, ozone was passed through a water solution of urea acidified with sulfuric acid. Carbon dioxide was found to be given off, the residue being ammonium sulfate.

The ammonia formed in reaction (3) will then react with sulfuric acid to form ammonium sulfate.



The following reactions may also take place.



That ammonium thiosulfate is actually formed is indicated by the action of sulfuric acid on the solution of thiourea after ozonization. Upon acidification of this solution, milky sulfur was precipitated with the evolution of sulfur dioxide.

It may be concluded that the products of the reaction of thiourea with ozone are sulfur, sulfur dioxide, sulfuric acid, ammonium sulfate, carbon dioxide and probably ammonium sulfite and ammonium thiosulfate and a small amount of organic compound or compounds which have not yet been identified. This small fraction was finally purified to a substance which melted at 120-123°C containign carbon, sulfur and nitrogen. It is thought to be impure urea (m.p. 132°C) whose presence can easily be explained by the above mechanism. At this writing, work is being done to purify and identify it.

It will be noticed that an excess of ozone was used in the reaction. If 10 g. of thiourea was completely converted into ammonium sulfate, approximately 13 g. of ozone would be needed. Actually 17 g. of ozone was passed into the reaction flask. This may be explained partially by the fact that during the last few hours of the ozonization the ozone was only

partially absorbed by the solution and consequently the 17 g includes all the excess ozone that was not used up.

It will also be noticed that ozone seems to be far more destructive in its action on thiourea than hydrogen peroxide. It was found that aminoiminomethanesulfuric acid was the main product in the reaction of hydrogen peroxide on thiourea, but ozone has the effect of splitting up the molecule completely, forming mostly inorganic compounds and only a small part of organic products. It seems quite unusual that so many inorganic compounds should be formed from an organic compound.

In continuing the study of this reaction, it would be interesting to investigate the action of substituted thiourea such as phenyl thiourea, diphenyl thiourea, methyl thiourea, etc. Also, the ozonization of basic and acidic solutions of thioureas would prove an interesting and valuable contribution.

SUMMARY

1. A laboratory ozonizer, which gave a 4 per cent by volume concentration of ozone, was constructed.
2. The reaction of ozone on an aqueous neutral solution of thiourea was studied.
3. While ammonium sulfate was the main product, free sulfur, sulfur dioxide, and carbon dioxide were also formed.
4. A mechanism for the reaction was formulated.
5. Although it was not definitely proved, the reaction mechanism indicates the formation of urea, ammonium sulfite, and ammonium thiosulfate as intermediate or final products of the reaction.
6. A small fraction of the products consisted of a mixture of unidentified organic compounds.

PART II
THE REACTION OF OZONE ON
SODIUM CHLORIDE

INTRODUCTION

A survey of the literature revealed that little work has been done on the action of ozone on inorganic compounds.

The purpose of this study is to see if the following reaction takes place:



Since this reaction has a negative free energy value it is possible. The following experiments have been tried to see if any chlorate is formed.

There is a possibility that free chlorine or sodium hypochlorite could be formed along with the chlorate.

The apparatus was the same as that used in Part I.

METHOD OF ANALYSIS

The reaction mixture was analyzed for sodium chlorate by the method used by Kolthoff and Furman.¹⁰ The solution of sodium chloride after ozonization was diluted to the mark in a 250 ml volumetric flask and 25 ml aliquots were taken for analysis. About 1 cc. of concentrated hydrochloric acid was added and about 0.2 g of sodium bicarbonate was added three times in succession to remove air from the flask. Immediately afterward the solution was treated with 2 g of potassium iodide and about 15 cc of concentrated hydrochloric acid, and after five minutes the solution was titrated with standard thio-sulfate.

If hypochlorites or chlorites are present they will show up in this analysis. If the above analysis indicates the absence of chlorates, it is positive proof also that no hypochlorites or chlorites are formed.

A blank determination was run on the reagents to establish their purity.

¹⁰Kolthoff and Furman, Volumetric Analysis, John Wiley and Sons, Vol. II, p. 388.

PROCEDURE AND DISCUSSION OF RESULTS

Ozone was passed through a neutral solution of 5.0 g of sodium chloride in 75 cc of water at a slow rate for a period of twenty hours. At the slowest rate attainable, unreacted ozone was detected in the exit gases, thus showing that the reaction, if any, is a slow one.

After ozonization the solution was allowed to stand to make sure all the ozone was decomposed, and then an analysis was run. (See Method of Analysis). The results showed no chlorate or available chlorine present.

An attempt to ozonize a basic solution of sodium chloride was then tried. Five grams of sodium chloride was dissolved in 75 cc of water and about 0.4 g of sodium hydroxide was added. This solution absorbed ozone no better than the previous one and the analysis showed chlorate to be absent.

Five grams of sodium chloride was then added to 75 cc of water and the solution made acid with 5 cc of dilute sulfuric acid. After twenty hours of ozonization no chlorate was found in this solution.

It was thought that hydrogen peroxide added to a neutral solution of sodium chloride would catalyze the reaction, so 5 cc of 30 per cent hydrogen peroxide was added to 5.0 g of sodium chloride in 75 cc of water. A twenty hour run with ozone still gave no evidence of chlorate.

The use of platinum as a catalyst was then tried. In this

experiment an electrode freshly plated with platinum black¹¹ was placed in the reaction flask so that the ozone was in continuous contact with it. The solution was ozonized for twenty hours and the analysis showed no trace of chlorates.

In conclusion, it is thought that although the reaction is thermodynamically possible, a slow reaction rate prevented the formation of sufficient chlorate in the short time of ozonization.

It is suggested that in the event of any future work on this reaction that it be run at different temperatures and that other possible catalysts be tried.

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Clark, W. M., The Determination of Hydrogen Ions, The Williams and Wilkins Company, p. 286-290 (1928)

SUMMARY

Ozone was passed through:

- (1) A neutral aqueous solution of sodium chloride.
- (2) A basic solution of sodium chloride.
- (3) An acid solution of sodium chloride.
- (4) A solution containing hydrogen peroxide and sodium chloride.
- (5) A solution containing sodium chloride and a platinum catalyst.

Negative results were obtained in each case.

BIBLIOGRAPHY

- Henne, A. L., "A Laboratory Ozonizer", Journal of the American Chemical Society, 51, 2676 (1929)
- Hunt, J. K., "The Formation of Ozone in the Electrical Discharge at Pressures Below Three Millimeters", Journal of the American Chemical Society, 51, 30-38 (1929)
- Long, Louis, "The Ozonization Reaction", Chemical Reviews, Vol. 27, No. 3, p. 437-489 (1940)
- Smith, L. J., "A Laboratory Ozonizer Yielding High Concentrations of Ozone", Journal of the American Chemical Society, 47, 1844-1850 (1925)
- Taube, H., "Chain Reactions of Ozone in Aqueous Solutions", Journal of the American Chemical Society, 63, 2453 (1941)