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AN INVESTIGATION OF THE REACTION OF BROMOPICRIN WITH LIQUID AMMONIA

A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemistry.

By Seymour L. Meisel

Approved by Frederic C. Schmidt

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INTRODUCTION

The purpose of this research was to study the reaction between bromopicrin, also referred to as nitro-bromoform or tribromomononitromethane, with liquid ammonia. It seems surprising, but very little has been done on the reaction between these halogen nitro derivatives of methane and liquid ammonia.

Franklin and Kraus[1] in 1905 studied the reaction between tetranitromethane and liquid ammonia and came to the conclusion that a nitro group was replaced by a hydrogen on the carbon atom to give nitroform ammonia. The following equation was proposed by them to explain the reaction:

$$6C(NO_2)_4 + 14NH_3 \rightarrow 6C(NO_2)_3NH_4 + 3NH_4NO_3 + 3H_2O + 4N_2$$

Hsing-Han Liu and Peter P.T. Sah[2] attempted to prepare guanadine from bromopicrin and alcoholic NH_3, but reported that the reaction exploded.

In an unpublished paper by Schmidt, Sunderlin and Cole[3] the reaction between dibromodinitromethane and dichlorodinitromethane with liquid ammonia was studied with the investigators coming to the conclusion that the halogen, rather than the nitro group, was replaced by hydrogen. The following formula was proposed for the reaction, which was verified partially by experimental results:

(X = halogen)

$$3X_2C(NO_2)_2 + 8NH_3 \rightarrow 3XC(NO_2)_2NH_4 + NH_4X + N_2$$

A preliminary investigation of the reaction between bromopicrin and liquid ammonia was made by Stone.[4] However, no definite conclusions were reached by him except that a colorless gas was evolved and a mixed salt formed.

In view of the work done previously, the following plan of procedure was adopted in the study of the reaction:

(1) To prepare the bromopicrin in sufficiently pure form.

(2) To react the bromopicrin in liquid ammonia and compute the ratio between moles of reactant and moles of product.

(3) To formulate an equation which would satisfy the experimental evidence.

(4) To prove the identity of the products formed by either isolating them in pure form and taking physical constants on them or by synthesizing from them known common compounds.

(5) To devise a mechanism which satisfactorily explains the reaction taking place.

PREPARATION

The bromopicrin used in the work was prepared according to the method of Bolas and Groves.[5] 30 g. of picric acid and 4 g. of CaO were added to 300 c.c. of water. After thirty minutes of boiling, the substances dissolved, forming calcium picrate. The solution was orange-red in color.

A second solution containing 180 g. of CaO in 900 c.c. of water was heated to dissolve the oxide, continuously stirred and then cooled. 75 c.c. (231 g.) of C.P. bromine were then added in small portions to form calcium hypobromate. The mixture was stirred and cooled during addition.

After both solutions had been sufficiently cooled, the picrate was added in about 5 c.c. portions to the hypobromate solution. The bright yellow color of the brompicrin was immediately observed. The solution was steam distilled directly until the solution became decolorized. The distillate formed two distinct layers, the bottom one containing nearly pure bromopicrin.

The distillate was separated by means of a separatory funnel and dried over sodium sulfate. The impure bromopicrin was then vacuum distilled with the fraction being collected that came over at constant temperature. The bromopicrin collected distilled over at a temperature range of 85°-87° at 19 mm. pressure.

The yields by this method were 75% of theoretical. However, if the reaction mixture were not allowed to stand at least a day before steam distilling, the yields were very poor. Optimum results were produced with about two days of standing.

EXPERIMENTAL

The apparatus used to study the reaction is shown in Figure I. A thin glass bulb (1) was filled with bromopicrin.

The air above it was then evacuated and the bulb sealed. The bulb was then attached to a glass rod (2) to be used as a plunger and put in reaction tube (3). A dewar flask (4) filled with liquid ammonia kept the reaction tube at -33° C. The entire system having been evacuated, ammonia gas was then let into the reaction tube under pressure which, combined with the existing low temperature, was sufficient to liquefy the ammonia. When the entire bulb (5) was covered with liquid ammonia (30 c.c.), the stopcock from the ammonia inlet was closed. The bulb was then broken and the stopcocks leading to the eudiometer tube (6) were opened.

Immediately upon breaking of the bulb, the ammonia became colored with an intense yellow which, upon evaporation of ammonia, was found to be the yellow reaction product.

After about five minutes, gas began to be evolved; evolution of the gas after this point was rapid. The ammonia was removed from the evolved gas by maintaining a flow of water in the container through which the gases passed.

After the volume of gas collected in the eudiometer tube was measured, it was drawn up into the P_2O_5 tube (7) and dried for several days. The gas was then drawn into the evacuated density bulb (8) and its density determined.

From the density, the molecular weight of the gas was calculated and results of 28.0 to 28.5 were obtained in several different determinations. This is in excellent agreement with the molecular weight of nitrogen, 28.0. From its inertness,

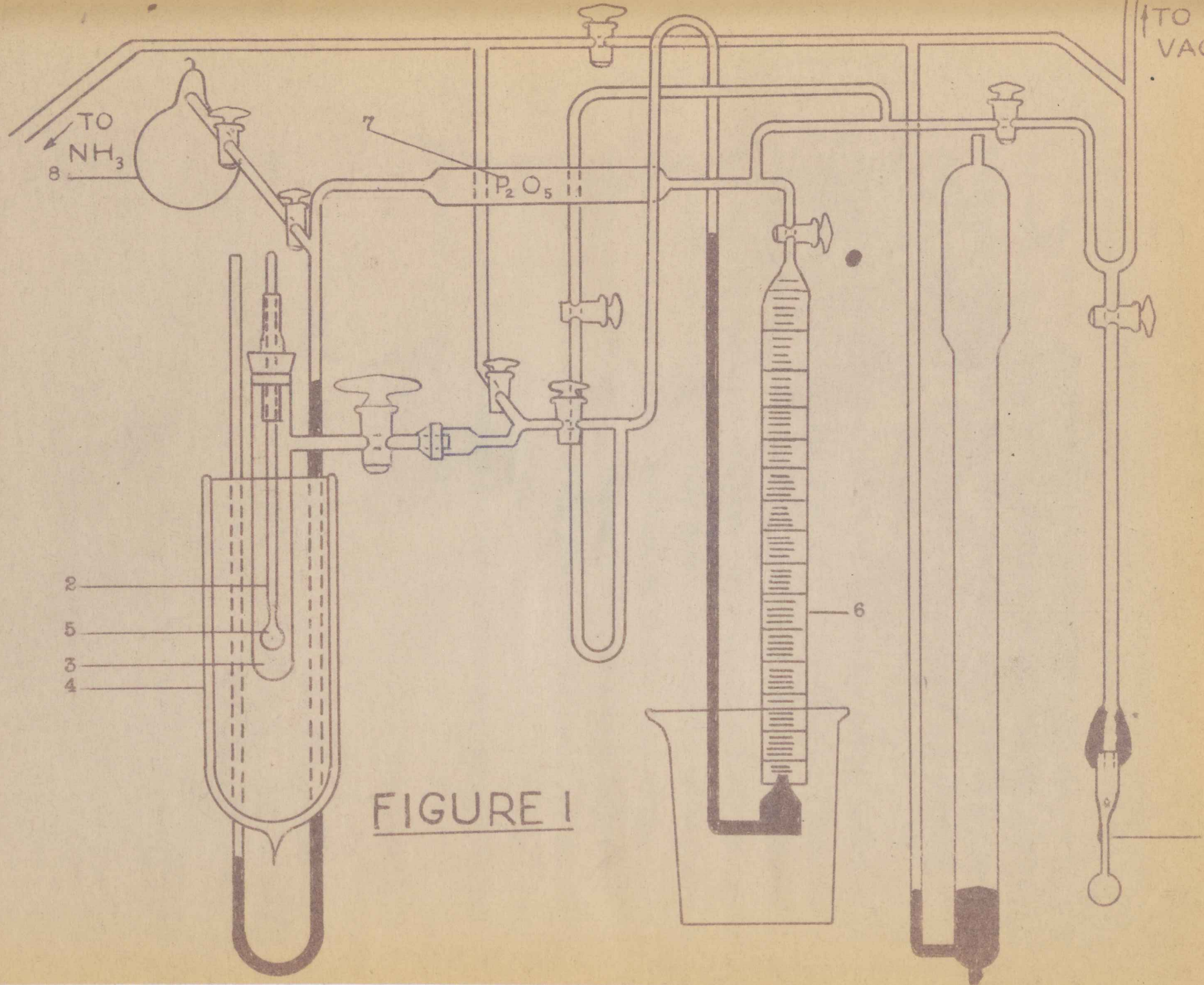


FIGURE 1

its insolubility in water, and its determined molecular weight, it was concluded beyond a doubt that the gas was nitrogen. This confirmed a previous belief that the gas was nitrogen, having come to that conclusion from studying the results obtained by Franklin and Kraus[1] and those obtained by Schmidt, Sunderlin and Cole.[3]

The next problem was to determine the number of moles of nitrogen liberated per gram mole of bromopicrin. This was accomplished by first measuring the volume of water displaced in the eudiometer tube and then correcting to S.T.P. The International Critical Tables give the solubility of nitrogen in water as 1.4 c.c. per 100 c.c. of water. This volume, corrected, was added to the already corrected volume to compensate for the solubility of the nitrogen, the length of the eudiometer tube being 100 c.c.

The values obtained for the number of moles of nitrogen liberated as shown in Table I.

TABLE I

	Gms. Br_3CNO_2	Moles Br_3CNO_2	c.c. (N_2) corr.	Moles N_2
(a)	1.4214	4.77×10^{-3}	36.4	1.62×10^{-3}
(b)	2.2549	7.59×10^{-3}	55.8	2.49×10^{-3}

The ratio of moles of bromopicrin used to moles of nitrogen evolved are as follows:

$$(a) \quad \frac{4.77 \times 10^{-3}}{1.62 \times 10^{-3}} = 2.94$$

(b) $\frac{7.59 \times 10^{-3}}{2.49 \times 10^{-3}} = 3.05$

These values showed conclusively, disregarding the slight discrepancies inherent in any experimental procedure, that three moles of bromopicrin were needed to produce one mole of nitrogen.

At this point, cognizance was taken of the similarity between the results thus far obtained and the conclusions arrived at by Schmidt, Sunderlin and Cole.[3] Taking into account the fact that three moles of bromopicrin liberated one mole of nitrogen, and the fact that previous investigators had reported the removal of bromine from the carbon atom, the following equation was proposed:

$$3Br_3CNO_2 + 8NH_3 \rightarrow 3Br_2C(NO_2)NH_4 + 3NH_4Br + N_2$$

Immediately upon setting up this equation, it was decided to see how well the theoretical number of moles of reaction producted expected on the basis of this equation compared with the number of actual moles obtained. In these calculations, the nitrogen was not considered as part of the reaction product since it was given off as a gas.

According to the equation suggested, an equimolar mixture of two salts was formed. Therefore, it was reasoned that the weight of the reaction product divided by the combined molecular weight of the two salts would give the number of moles of reaction product. The results are shown in Table II.

TABLE II

EXPERIMENTAL		THEORETICAL	
Gms. $Br_2C(NO_2)NH_4$	Moles $Br_2C(NO_2)NH_4$	Gms. $Br_2C(NO_2)NH_4$	Moles $Br_2C(NO_2)NH_4$
1.55	4.77×10^{-3}	1.55	4.77×10^{-3}
2.55	7.85×10^{-3}	2.46	7.59×10^{-3}

As can be seen from the table, the agreement between experimental values and theoretical values is quite good. However, after weighing the reaction product the first time, it was noticed that a sharp pungent odor was emanating from the flask. After several days this odor still persisted and the reaction product was weighed again. It was then discovered that the product had lost considerable weight. Therefore, the next time a run was made a careful check was kept on the weight of the product lost per day. The following set of data was obtained:

TABLE III

Time (Days)	Reaction Product (Gms.)
1	2.5554
2	2.4589
3	2.4299
6-1/2	2.4049
7-1/2	2.4039
8	2.4038

The plot of these data is shown in the decomposition curve.

While it was at first supposed that the loss in weight was caused by the evaporation of ammonia attached to the organic salt, this view was dispelled upon the plotting of the curve.

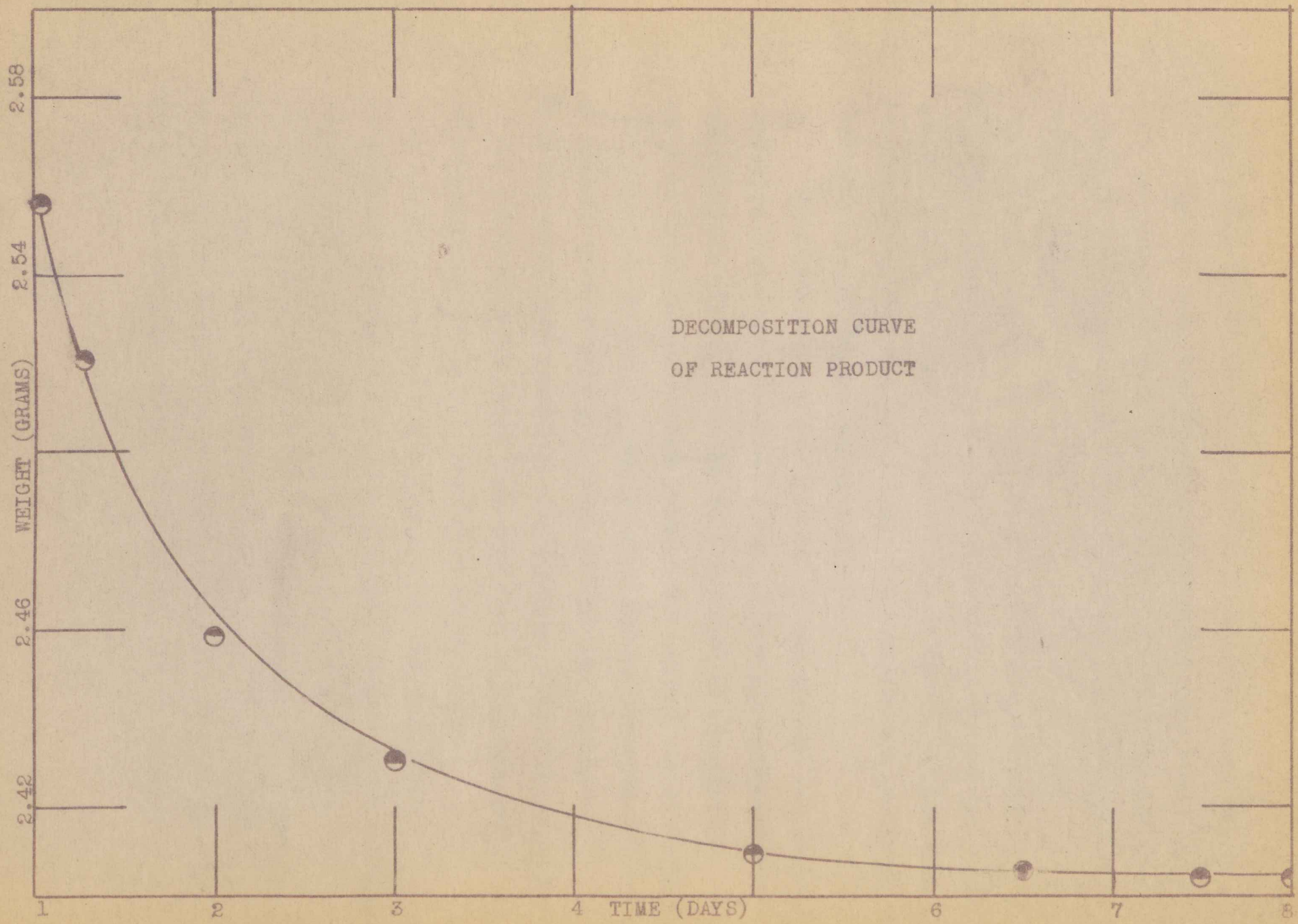
The shape of the curve has the form of a regular rate of reaction curve, rather than a mere evaporation curve. Results obtained later verified this assumption that some reaction was taking place within the product itself. Exactly what the reaction was, was not determined.

In spite of the fact that the weight of the reaction product varied, the results obtained showed conclusively that if the reaction product were weighed within a short time of the reaction, the weight obtained agreed very well with the expected theoretical weight on the basis of the equation proposed.

As a further confirmation for the validity of this equation, the percentage bromine in the reaction product was determined by titrating a 0.1% solution of reaction product with .1N $AgNO_3$. The values obtained for the percentage bromine varied between 69-72%, while the theoretical percentage of bromine is 71.3%.

The next step was to investigate the reaction product thoroughly and see if the structure of the organic salt could be proven. The following procedure was used. A dewar flask was half filled with liquid ammonia and the bromopicrin was added slowly. Immediately upon addition there occurred a violent ebullition of gas and a yellow coloring of the ammonia. In about 24 hours, the ammonia evaporated, leaving behind a yellow residue.

Realizing from the experimental results thus far obtained that the organic part of the residue was probably the


DECOMPOSITION CURVE
OF REACTION PRODUCT
WEIGHT (GRAMS)
2.58
2.54
2.46
2.42
1
2
3
4
TIME (DAYS)
6
7
8

ammonia salt of dibromonitromethane, a thorough search of the literature was made to obtain data on this compound. Only two references were found, one in Beilstein[6] and one by Scholl.[7] The reference in Beilstein merely summarized the work of Scholl.

Scholl claimed to have prepared dibromonitromethane from bromonitromethane, and merely listed one physical property, boiling point. However, in his article he mentioned that when he treated the dibromonitromethane with concentrated potassium hydroxide, he obtained a red precipitate.

Upon treating a water solution of the product with concentrated potassium hydroxide, a red, flocculent precipitate was obtained. Hydrolyzing the salt produced no discernible oil. In fact, no matter what reagent the product was titrated with (bromine, HCl, H_2SO_4, etc.), with the exception of KOH, no visible results were produced. It was then remembered that the reaction product had been standing quite a while, and it was previously expounded that some type of reaction might be taking place within the reaction product itself.

A new quantity of reaction product was prepared and immediately treated with various reagents. Both HCl and bromine water produced oils with the fresh product, but had no effect on it after it had been standing for several days. However, in treating the product with KOH, the most peculiar anomaly occurred: On the freshly prepared product the KOH had no effect, while with the product that was allowed to stand for

several days it produced a red precipitate. This irregularity was extremely puzzling and still remains unsolved.

The oils obtained from treating the reaction product with HCl and bromine were separated from the mass of solid particles occurring with the oils in each case, and attempts were made to purify them so that physical constants might be obtained on them. In the case of the oil obtained with HCl this was nearly impossible since about 60 grams of reaction product produced about 1 c.c. of oil. However, the oil was washed and dried and a refractive index taken on it:

$$n = 1.5430$$

It is possible that the product when treated with HCl oxidized the HCl giving chlorine, which reacted with the product to produce dibromochloronitromethane (Br_2ClCNO_2) in small amounts. Later treatment of the organic product suggests this to be the case.

Approximately 7 c.c. of impure oil were obtained from treating 60 g. of reaction product with bromine water. The oil was then washed and dried over anhydrous sodium sulfate. The resulting oil was slightly yellow and its odor seemed identical with that of bromopicrin. The oil was then vacuum distilled, coming over between 80°-81° at 17 mm.

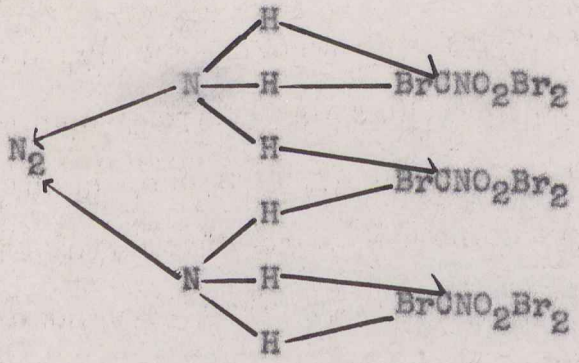
From the curve plotted by Stone[4] of vapor pressure of bromopicrin against temperature, it was determined that at a pressure of 17 mm., the boiling point of bromopicrin was approximately 78°.

For further proof that the oil was actually bromopicrin, an index of refraction was taken of the oil after vacuum distillation, with a value of n = 1.5760 being obtained. When purifying the bromopicrin for the first time an index of refraction was taken on it after vacuum distillation and the value obtained then agreed exactly with this latter value, being 1.5760 in each case. This value is slightly lower than that given in the literature; probably repeated distillations in an inert atmosphere being necessary to give a better value.

By means of this synthesis, it has been definitely established that the bromine was removed in the reaction, which, with the evidence already presented, proved that the organic salt must be the salt of dibromonitromethane.

DISCUSSION

It is often beneficial, especially when dealing with reactions of a similar nature, to have a pictorial view as to how the reaction takes place. The following mechanism, although merely in the hypothesis stage, seems to satisfactorily explain the manner in which the reaction takes place:



Three hydrogens from the two ammonia molecules combine with the bromine of the bromopicrin to form HBr, which is

ammonolyzed. The other three hydrogens then take the place of the liberated bromines and molecular nitrogen is formed. The dibromonitromethane then formed has a hydrogen attached to the carbon atom. The excess ammonia then attaches itself to the hydrogen to form the organic salt.

SUMMARY

(1) The products of the reaction between bromopicrin and liquid ammonia were identified.

(2) An equation which satisfied the experimental evidence was formulated.

(3) A secondary reaction within the reaction product itself was discovered, but not explained.

(4) A mechanism for the primary reaction was proposed.

REFERENCES

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(5) Bolas and Groves; J. Chem. Soc., 23, 153 (1870).

(6) Beilstein - I, 77.

(7) Scholl; Ber. 29, 1825 (1896).