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Heats of solution of halogen methanes in liquid ammonia

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Heats of Solution of Halogen Methanes
in 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

Robert W. Davison

Approved by

Frederic C. Schmidt

May 1942

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Heats of Solution of Halogen Methanes
in Liquid Ammonia

Introductory experiments were carried out to see just which halogen methane derivatives, if any, produce heat changes when dissolved in liquid ammonia. There are indications given in the chemical literature to expect that certain of the halogen methanes should dissolve in liquid ammonia with the evolution or absorption of heat. ⁽¹⁾ This present research work involved investigation of such compounds as chloroform, carbon tetrachloride, bromoform, and also iodoform. Only introductory heat measurements were made. More work must be done to confirm and enlarge upon the results presented here.

Apparatus

The apparatus used for all heat measurements was that in general as described in Sottysiak's thesis.⁽²⁾ The calorimeter itself was a new one made of Nonex glass and described in a paper by Schmidt, Studer, and Sottysiak.⁽³⁾ This calorimeter was found to have a heat constant of 9.16 calories per degree.

It was necessary to prepare a new thermocouple for these heat measurements. This has not yet been calibrated, but it is expected to have a temperature-electromotive force equivalent of .038 millivolts per degree.

Procedure

The method of procedure used in this work was similar to that described by Sottysiak.⁽²⁾ In the one experimental case where ammonia was evolved (during the solution process) and collected in the absorbing flask, the water from the latter was made up to volume in a 250cc. volumetric flask and portions were titrated with standard sulfuric acid. This acid had been standardized with anhydrous sodium carbonate.

Results

A run was made using carbon tetrachloride as the solute. When added to liquid ammonia, this compound produced an endothermic heat of solution. The carbon tetrachloride used for this experiment was obtained from the stock room and purified for "electrical measurements" according to "Organic Solvents"⁽⁴⁾. Results are listed below:-

Weight of sample	2.5563 grams
Moles of sample	0.01661
Temperature change	0.42°C.
Time for the solution process	3.5 minutes
Total heat effect	-14.97 calories
Heat of solution per gram mole	-900. calories

The heat effect was calculated by multiplying the weight of liquid ammonia used as solvent (24.79 grams) by its specific heat of 1.067 and then adding this to the calorimeter constant of 9.16. This gave a total heat constant of 35.61 calories/degree, and by multiplying this factor by the temperature change recorded, the heat change was obtained. Dividing by the moles of sample used gave the heat of solution of one gram mole.

The next experiment involved purified chloroform⁽⁵⁾ as the solute. It was observed beforehand that chloroform would easily dissolve in liquid ammonia, yet when the experiment was carried out in the calorimeter, no heat effect whatsoever was noticed. Although this experiment should be repeated as a matter of course, it was quite apparent to those carrying out the determination that no heat effect capable of being picked up by the thermocouple occurred.

This same result was obtained in the case of iodoform. The sample used was made and purified by the author and the average melting point

of several samples was 118°C . In this case also no heat was either given off or absorbed, although the iodoform was found to go into solution readily enough.

Bromoform was next tried. The compound was prepared by Seldon Knudson, '43, and purified by Dr. F.C. Schmidt with concentrated sulfuric acid, followed by dilute sodium hydroxide washing, and finally vacuum distillation. Unlike chloroform and iodoform, bromoform produced a large negative heat when dissolving in liquid ammonia. Results are shown below:-

Weight of sample	2.2043 grams
Moles of sample	0.00872
Temperature change	1.1°C .
Time for the solution process	3.0 minutes
Total heat effect	-39.17 calories
Heat of solution per gram mole	-4494. calories

In order to measure heats of reduction of silver iodide, the heat of solution of this salt must be accurately known, so one of a series of heat measurements was run on this compound. Results are shown below;

Weight of sample	1.1810 grams
Moles of sample	0.00503
Temperature change	0.0933°C .
Time for the solution process	15 seconds
Weight of ammonia evolved	0.0821 grams
Heat effect due to evolved ammonia	27.192
Heat effect due to temperature change in calorimeter and contents	3.008 calories
Total heat effect	30.20 calories
Heat of solution per gram mole	6004. calories

(Kraus and Ridderhof previously determined this heat to be 6700 cal.) (6)

The amount of ammonia evolved was determined by titrating water from the absorbing flask with sulfuric acid whose normality was found, using anhydrous sodium carbonate as standard, to be .1248 normal. The weight of ammonia was then multiplied by 327.1, the number of calories necessary to vaporize one gram of ammonia. This produced the heat effect due to the evolved ammonia. The total heat effect was positive, and the heat of solution is therefore exothermic in the case of silver iodide. The heat of solution value of 6004 calories per mole is almost 700 calories less than Kraus and Ridderhof's value, but the latter obtained their value under more difficult experimental conditions.

Summary

The heats of solution of carbon tetrachloride, chloroform, bromoform, and iodoform, as well as that of silver iodide, were investigated. The results are summarized below:-

<u>Compound</u>	<u>Heat of Solution</u>
Carbon tetrachloride	-900. calories/mole
Chloroform	no heat observed
Bromoform	-4494. calories/mole
Iodoform	no heat observed
Silver iodide	6004. calories/mole

The author wishes to thank Dr. F.C. Schmidt and J.J. Naughton of the Union College Chemistry Department for their help in making these heat measurements.

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A Study of the Properties and Reaction with
Liquid Ammonia of Phenylnitromethane
and Derivatives

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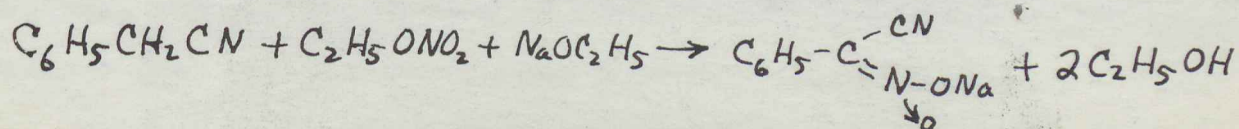
The purpose of this research work was to investigate more fully the properties of three aromatic nitromethane compounds --- phenyl-nitromethane, phenylbromnitromethane, and phenylbromcyanonitromethane. The available chemical literature does not contain much definite data concerning these compounds. Further, reactions of the above-mentioned compounds with liquid ammonia might prove of value in understanding the type of mechanism operating for chemical reactions in the nitrogen system. This thesis therefore deals with the preparation, properties, and liquid ammonia reaction of these three aromatic nitromethane compounds.

Phenylnitromethane

Preparation

Earlier methods for the preparation of phenylnitromethane include nitration of toluene with dilute nitric acid in a sealed tube,⁽¹⁾ the interaction of benzenediazonium chloride and nitromethane in alkaline solution,⁽²⁾ and the action of silver nitrite on benzyl chloride or iodide.⁽³⁾ In 1902 Wislicenus and Endres successfully made phenylnitromethane by the condensation of ethyl nitrate with benzyl cyanide and consequent hydrolysis.⁽⁴⁾ This method, as described by Gatterman and Wieland,⁽⁵⁾ was used to prepare most of the phenylnitromethane used in this research work. A modification of this process, using methyl nitrate instead of the ethyl compound, was also used since it is a safer procedure.⁽⁶⁾

The first step in making phenylnitromethane is the preparation of benzyl cyanide.⁽⁷⁾ This compound was made by refluxing for four hours an ethyl alcohol solution of purified benzyl chloride and an aqueous sodium cyanide solution. The resulting impure benzyl cyanide was distilled under reduced pressure. Ethyl nitrate was made by carefully refluxing concentrated nitric acid with ethyl alcohol on a sand bath.⁽⁸⁾ It was found advisable to dissolve some urea in the nitric acid before reacting it, in order to prevent resultant dangerous oxidation of the ethyl nitrate formed. The ethyl nitrate was washed and distilled as directed. It was used as soon as possible. After making an alcoholic solution of sodium ethoxide and cooling this solution, an ice-cold mixture of benzyl cyanide and ethyl nitrate was added in small portions. The reaction evolved much heat and the mixture turned from orange to a deep red finally. The sodium salt of phenylcyanonitromethane occurs in the following way:-



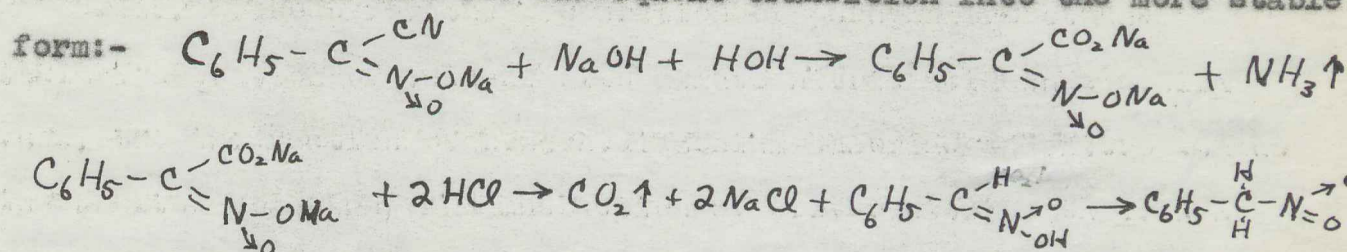
This sodium salt separated as almost colorless crystals and was washed first with an ether-alcohol solution and then with ether alone. The usual yield is 69-78%. Yields 60-70% were obtained.

The sodium salt appears in the needle form and decomposes above 277 degrees C. The salt is soluble in water and to a slight extent in ether; it is more soluble in alcohol.

According to the other method used to prepare this sodium salt, of phenylcyanonitromethane, methyl nitrate was made by first mixing concentrated nitric and sulfuric acids (cooled well in an ice bath) and also preparing a mixture of sulfuric acid and methyl alcohol under the same conditions. ⁽⁹⁾ These two separate solutions were then cautiously mixed together while controlling the temperature as directed. Purification of the resulting methyl nitrate involved only washing with salt solution, dilute sodium hydroxide, and water. The dried compound was reacted with sodium ethoxide and benzyl cyanide in a manner similar to the ethyl nitrate method. It was found that better yields of the sodium salt were obtained when using ethyl nitrate than when the less dangerous methyl nitrate was used.

To prepare crude phenylnitromethane, the cyanide group of the sodium salt was hydrolyzed by lengthy gentle boiling of the salt with two normal sodium hydroxide solution. Much ammonia was given off during this hydrolysis, and the completion of this evolution of gas indicated the extent of hydrolysis. The resulting solution was cooled with the aid of dry ice, and the temperature was kept below -4 degrees C. while acidification with six normal hydrochloric acid took place. During this very vigorous reaction, large volumes of carbon dioxide were evolved. The product first appeared as a white precipitate, later as a grey scum lighter than the solution liquid, and after standing at room temperature overnight, it changed into a dark red oil possessing a rather pleasing odor.

This oil was crude phenylnitromethane. The intermediate product is identified as the aci-compound. The equations below demonstrate both the reactions and the subsequent transition into the more stable form:-



The crude phenylnitromethane was extracted with ether, the ether then distilled off, and the residue was steam distilled. The ratio of phenylnitromethane to water was very small, thus prolonging the distillation. The product came over as a light yellow oil which darkened appreciably if not cooled and kept in the dark. Several attempts were made to vacuum distill this compound in order to further purify it, but the nature of phenylnitromethane causes it to decompose with ease at temperatures somewhat above 100 degrees C. This, plus the fact that pressure could not be reduced enough to permit efficient distillation below 100 degrees C., forced the author to use largely phenylnitromethane purified by steam distillation only. Densities taken of the compound purified to this extent proved to be satisfactorily close to the Handbook value of 1.160²⁰ gm/cc. so that the chemical was deemed pure enough without vacuum distillation.

Tendency to Decompose

As stated above, phenylnitromethane changes in color if allowed to stand at room temperature or exposed to sunlight, turning from a light yellow transparent oil to a less transparent red liquid. Phenylbromnitromethane, and especially phenylbromcyanonitromethane, also exhibited this tendency to darken when left at room temperature or exposed to sunlight. This photochemical reaction appears to be a

characteristic of several of the nitromethanes at any rate, because Cole mentions the same phenomenon in the case of dibromdinitromethane.⁽⁶⁾

When heated above 100 degrees C. at ordinary pressure, phenylnitromethane decomposed very violently, forming first a needle-like straw-colored crystal. Further decomposition produced a tarry substance. A slight odor of benzaldehyde could sometimes be noticed during the decomposition. It was also present in the partially decomposed compound. The needle compound was recrystallized from hot alcohol. Repeated recrystallization still left the substance with a yellow-brown straw color. Melting point 239° to 241° C. The resulting liquid was brown. The crystal contained nitrogen, was insoluble in hot and cold water, cold alcohol, ether, dilute HCl, and dilute NaOH.

Physical Properties of Phenylnitromethane

Using a weight pipette constructed by David Blake, '42, and having a volume of 1.0854cc., approximate densities were taken of two different preparations of this organic compound. The mean value was 1.156 gm/cc. at 24 degrees C. and checks with the Handbook value of 1.160²⁰ gm/cc. The densities were taken only to identify the compound.

The index of refraction was determined with an Abbe Refractometer calibrated to read indices for sodium vapor light (the sodium D line). The average value obtained was 1.5353. Taking the molecular weight of the compound as 137.06, the following molecular refraction was found:-

$$\text{Molecular Refraction} = \frac{M \cdot n^2 - 1}{d \cdot n^2 + 2}, \text{ where } M = 137.06$$

$$d = 1.160^{20} \text{ gm/cc.}$$

$$n_D = 1.5353 \text{ (20 C.)}$$

$$\text{Molecular Refraction} = \underline{36.75}$$

The molecular refraction can be found in a theoretical manner by

taking the sum of the atomic and group refractions, whose values are given in Getman and Daniels.⁽¹⁾ The following molecular refraction results

7 C @ 2.501	17.507
7 H @ 1.051	7.357
3 double bonds @ 1.707	5.121
one nitro group	<u>6.65</u>

Molecular Refraction = 35.635

The surface tension of phenylnitromethane was determined with a Du Nuoy Tensimeter which had been calibrated with weights and checked with distilled water. The surface tension for phenylnitromethane was found to be 46.48 dynes/cm. at 20 degrees C. Sugden's Parachor was then calculated from the values of the density and surface tension according to the equation:-

$$P = \frac{M}{D-d} \gamma^{\frac{2}{3}}, \quad \text{where } M = 137.06$$

$$D = 1.160^{\circ} \text{ gm/cc (liq.)}$$

$$d \approx 0.00 \text{ gm/cc (vapour)}$$

In this way the parachor was found to be 308. By taking the sum of the atomic and group parachors the following result was obtained:-

7 C @ 4.8	33.6
7 H @ 17.1	119.7
one nitro group	73.0
3 double bonds @ 23.2	69.6
one six-membered ring	<u>6.1</u>

$$P = 302.0 \quad (\text{Values given by Glasstone})^{(2)}$$

The theoretical and calculated molecular refractions vary by .25%, while the theoretical and calculated parachors vary by 2%.

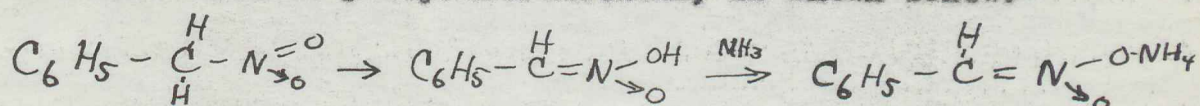
Below is a list of boiling points observed for various low pressures

when vacuum distilling phenylnitromethane:-

135°-136° C.	at 35mm. p.
118°-119° C.	at 16mm. p.
95°-96° C.	at 8mm. p.
90° C.	at 6mm. p.

Reaction with Liquid Ammonia

Phenylnitromethane was added to liquid ammonia, with the production of a deep red-brown color during a short, rather vigorous reaction. After the ammonia had evaporated, a yellow salt containing an adherent oil remained. The salt, which was soluble in water, was assumed to be the ammonium salt of phenylnitromethane, as shown below:-

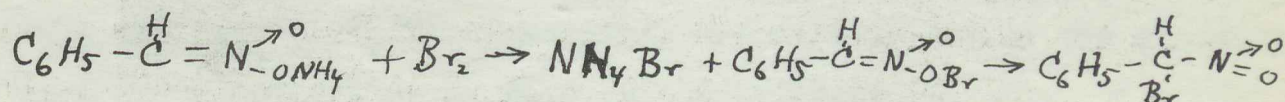


The oil was taken up with ether and probably consisted of impure phenylnitromethane. In one case, reacting 20 grams of the pure compound and 15 grams of impure phenylnitromethane with liquid ammonia produced 20 grams of the ammonium salt and also about 15 grams of the residual oil mentioned above. This would point to an almost quantitative formation of the ammonium salt from the pure phenylnitromethane, whereas the impure compound in several cases would scarcely react at all. This salt-formation reaction with liquid ammonia was utilized in preparing phenylbromnitromethane, the second compound studied.

Phenylbromnitromethane

Preparation

This compound was made from the ammonium or sodium salt of phenylnitromethane. In one case, the ammonium salt described on the preceding page was dissolved in water and an equivalent amount of bromine added to form the monobrom derivative. This was calculated by assuming that a molecule of bromine would react with a molecule of the salt to form one molecule of the corresponding bromide and one of the phenylbromnitromethane, according to the equation:-



After addition of the bromine the mixture was stirred vigorously to bring the heavy bromine into contact with the aqueous salt solution. A reddish colored oil which gradually turned light yellow formed in the bottom of the beaker. This oil was washed with bicarbonate solution and with water, to remove excess bromine, and was then steam distilled. A light yellow oil came over which was dried over anhydrous sodium sulfate. The reaction of 20 grams of the ammonium salt of phenylnitromethane with an equivalent amount of bromine produced 11 grams of the monobrom derivative. The % yield was 39.3%.

Another method used to prepare this compound was to react phenylnitromethane with NaOH solution, to form the sodium salt. This reaction produced a reddish water layer and a few drops of a yellow oil at the surface. The latter was extracted with ether and the water layer was reacted with bromine in a manner similar to the treatment of the ammonium salt solution. A similar yellow oil was formed and it was also steam distilled and dried over ~~sodium~~ sodium sulfate. The yellow oil drops previously mentioned as extracted with ether had the odor of benzaldehyde. The compound obtained from the sodium salt was slightly darker than that obtained from the corresponding

ammonium salt but possessed the same physical properties and was therefore assumed to be identical with this.

Physical Properties of Phenylbromnitromethane

This derivative of phenylnitromethane was found to have a considerably greater density than the starting chemical. The average density of phenylbromnitromethane was determined with the weight pipette to be $1.54\frac{20}{4}$ gm/cc. The compound was found to be more stable than phenylnitromethane but would darken very slowly if left at room temperature in the sunlight. Its index of refraction at 20°C. was found to be 1.5696, and its molecular refraction, computed by use of the equation of page 5, turned out to be 45.9 :- $M = 215.97$

$$M.R. = \frac{M}{d} \cdot \frac{n^2 - 1}{n^2 + 2} = 45.9$$

$$d = 1.54\frac{20}{4} \text{ gm/cc.}$$

$$n_D = 1.5696$$

By taking the sum of the atomic refractions, the following molecular refraction was obtained:-

7 C @ 2.501	17.507
6 H @ 1.051	6.306
3 double bonds @ 1.707	5.121
one nitro group	6.65
one bromine	<u>8.927</u>

$$\text{Molecular Refraction} = 44.511$$

This involves a 3% variance.

The surface tension was found to be 48.66 dynes/cm. at 20°C. Sugden's Parachor was then computed to be 370. By the addition of atomic and group parachor equivalents:-

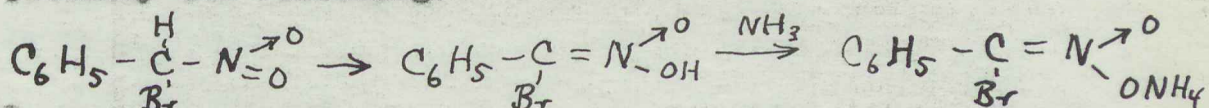
7 C @ 4.8	33.6
6 H @ 17.1	102.6
one nitro group	73.0
one bromine	68.0
3 double bonds @	69.6
one six-membered ring	<u>6.1</u>

The difference involved in these two values for the parachor is 4.6%. Since an error of 3% was found in comparing the two molecular refraction values, it seems quite possible that both of these differences might be attributed to an error in the density value. If the density were found to be one or two percent larger than reported, the values for molecular refraction and Sugden's parachor would be much closer the theoretical values. More work on the density determination of phenylbromnitromethane seems to be necessary.

In order to see if phenylbromnitromethane possessed optical activity, a dilute solution of the compound in ethyl alcohol was made up and examined in a polarimeter. The result was negative. This might indicate either no optical activity or a racemic mixture of dextro and levo phenylbromnitromethane. Or it might conceivably be that the hydrogen atom supposedly attached to the asymmetric carbon atom might shift to one of the oxygens of the nitro group, thus forming a pseudo acid even in alcoholic solution. This pseudo acid is known to be present in a basic solution, since the sodium salt is formed in this way.

Reaction with Liquid Ammonia

Phenylbromnitromethane reacted with liquid ammonia in much the same way as did phenylnitromethane. A short vigorous reaction caused the liquid ammonia solvent to turn a deep red color. Evaporation of the solvent left behind a yellow solid which would be the ammonium salt of phenylbromnitromethane, if an analogy with the phenylnitromethane reaction in liquid ammonia be made. The reaction equation is probably the following:-



More work must be done in identifying this reaction product as the ammonium salt.

Phenylbromocyanonitromethane (PBCN)

This very unstable compound was produced from the sodium salt of phenylcyanonitromethane which was an intermediate product in the preparation of phenylnitromethane. It was found that an aqueous solution of this sodium salt would react with bromine, upon vigorous stirring, to form a cloudy yellow oil. This cleared up on being dried over calcium chloride. An attempt to form PBCN, as it is called, by direct bromination of the sodium salt resulted in a violent reaction which culminated with the combustion of the organic sodium salt.

Physical Properties

The PBCN turned from light yellow to brown within a day or two, even though it was kept cool and in the dark. A rough density taken on the compound gave its density as 1.58_{4}^{20} gm/cc. at 20°C . Its surface tension at the same temperature was determined to be 47.85 dynes/cm. From this value, Sugden's Parachor was computed:-

$$P = \frac{M}{D-d} \gamma^{\frac{2}{3}}, \text{ where } M = 240.97, D = 1.58_{4}^{20} \text{ gm/cc.}, d \cong 0.00$$

$$P = \underline{401.}$$

In summing up the atomic and group parachor equivalents, the following result was obtained:-

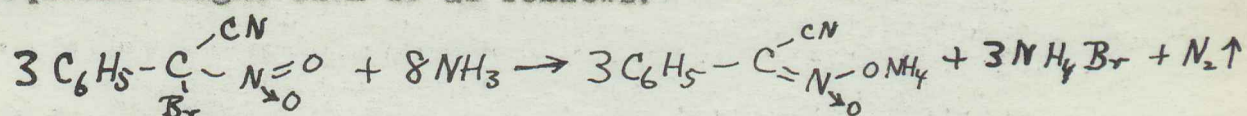
8 C @ 4.8	38.4
5 H @ 17.1	85.5
one nitro group	73.0
one bromine	68.0
one nitrogen	12.5
3 double bonds @ 23.2	69.6
one triple bond	46.6
one sixmembered ring	<u>6.1</u>

$$P = 399.7$$

Thus, the two computed parachors differ by .25%.

Reaction with Liquid Ammonia

16 grams of the PBCN prepared was reacted with liquid ammonia. In this case the reaction was much more violent than in previous trials with phenylnitromethane and its bromine derivative. A gas and also bluish smoke were evolved, and the liquid ammonia turned deep red. After the ammonia had evaporated, a tan colored solid was found to be the residue. This solid was soluble in water and caused a silver nitrate solution to form a yellow precipitate which was assumed to be silver bromide, although it might possibly have been a complex organic silver salt. Since ammonia will react with dibromdinitromethane to form the ammonium salt of the monobrom compound and ammonium bromide, ⁽¹⁰⁾ it was expected that the liquid ammonia might also displace the bromine of PBCN in a similar manner, thus forming ammonium bromide which would produce the reaction witnessed with silver nitrate. The tan solid would then be composed of ammonium bromide plus the ammonium salt of phenyleyanonitromethane. The reaction equation might then be as follows:-



The solid was soluble in ether and alcohol, as well as in water, and formed a red solution with hot alcohol. From the 16 grams of PBCN, 18.4 grams of solid material were formed, and this seemed to be losing weight all the time. The odor of ammonia and bromine were noticeable as coming from this solid. If ammonium bromide and the organic ammonium salt are assumed to be formed in equivalent amounts, as is the case with dibromdinitromethane, then the percent yield of the ammonium salt of phenyleyanonitromethane would be close to 100%. Time was not available for the analysis of this salt. Further study of this reaction should be made.

Summary

The properties of three aromatic nitromethane compounds--- phenylnitromethane, phenylbromnitromethane, and phenylbromcyano-nitromethane --- have been studied and the results reported. Reactions of these compounds with liquid ammonia are also described. Below is a summary of the physical data collected on these three compounds:-

<u>Phenylnitromethane</u>	<u>Phenylbromnitromethane</u>	<u>PBCN</u>
Density -- 1.160 ²⁰ gm/cc.	1.54 ²⁰ _γ	1.58 ²⁰ _γ
Surface -- 46.48 dynes/cm. (20° C.) tension	48.66	47.85
Index of -- 1.5353 (n _D at 20° C.) refraction	1.5696	-----
Sugden's -- 302.0 (theoretical) parachor	352.9	399.7
308. (calculated)	370.	401.
Molecular -- 36.635 (theoretical) refraction	44.511	-----
36.75 (calculated)	45.9	-----
Molecular -- 137.06 weight	215.97	240.97

Future Possibilities for Investigation

This research work was planned with the idea of studying various aromatic methane compounds by attaching many different combinations of groups such as nitro, cyano, halogen, and phenyl to a single carbon atom. Since these compounds have not yet been investigated to any great extent, the goal was the determination of the physical properties of these compounds, following their synthesis and purification. Then, the reactions of these compounds with liquid ammonia was to be considered, especially from the point of view of the reaction mechanisms involved, as well as replacement priority.

Much work remains to be done with such compounds as phenyldibromnitromethane, PBCN, and chemicals such as phenylchlorbromnitromethane. In the latter case, it should be interesting to see just which group is replaced in the liquid ammonia reaction. In the case of PBCN it has been pointed out that probably the bromine was removed, although a complete proof of this assumption is lacking.

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