

A Study of the Physical Properties  
of Dibromodinitromethane and its  
Reaction in Liquid Ammonia

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## The Physical Properties of Dibrom- dinitromethane and its Reaction with Liquid Ammonia

Although there are at least half a dozen methods of preparing dibromdinitromethane given in the literature(1), the only physical properties mentioned are the freezing and boiling points(2). Hence, after making the compound in order to study its reaction in liquid ammonia, data was obtained on other physical characteristics.

### Preparation

The method of preparation chosen was that of Downing and Orr(3) since it required only common, inexpensive reagents. First symmetrical tribromaniline was made by passing bromine vapor through a solution of aniline hydrochloride in water and then filtering and drying the precipitate. This was reacted with concentrated nitric acid in the ratio 5cc of acid per gram of tribromaniline.

The reaction was exothermic so the flask was cooled to maintain control. Bromine vapor and oxides of nitrogen were evolved during the reaction. At its completion the reaction mixture was steam distilled, the dibromdinitromethane coming over easily as a greenish-black, heavy, insoluble oil.

The water layer of the distillate was decanted and the dark liquid shaken with dilute caustic solution.



After several such treatments it became a light opaque yellow and was then washed with water. The dibromdinitromethane was extracted with chloroform and dried over calcium chloride. Separation from the chloroform and final purification was accomplished by repeated fractional vacuum distillations.

A molecular weight determination by the freezing point depression of benzene gave a value of 260 gm per gm mol while the sum of the atomic weights is 264, the variance being within the limits of experimental error.

#### General Characteristics

The dibromdinitromethane was a clear light yellow liquid freezing at 4-5C. It was a strong lachrymator and extremely corrosive, resembling nitric acid in its oxidizing action.

The instability of the compound (it explodes at about 150 degrees C.)(4) necessitated its distillation in vacuum. At temperatures above 80 degrees C. decomposition proceeded at an appreciable rate, the liquid becoming dark brown. This reaction was also observed to proceed photochemically at room temperature for the liquid darkened more rapidly when kept in a clear bottle exposed to sunlight than when kept in the dark.

Dibromdinitromethane was found to be completely miscible with organic liquids such as ether, benzene

and chloroform and completely insoluble in water.

### Physical Properties at 20° C.

#### Density

The density of the liquid was determined with 10cc pycnometers, thermostated with a large beaker of water. The temperature was constant to two tenths of a degree. The samples are from separate preparations.

Sample	Determinations of Density	
	1st	2nd
I	2.4400	2.4401
II	2.4379	2.4380
III	2.4407	2.4412

Average value of density 2.440 gm/cc

#### Surface Tension

A Du Nouy Tensimeter was calibrated with weights and the surface tension of water determined to check the calibration.

Experimental value for S.T. of water 72.4 dynes/cm

Accepted value for S.T. of water 72.1 dynes/cm

The surface tension of dibromodinitromethane was then found to be 47.7 dynes/cm.

The chief source of error was in the temperature control. An error of as much as one degree Centigrade may be involved.



Sugden's Parachor calculated from the experimental values of the surface tension and density of dibromdinitromethane was found to be given by  $P = 284.3$  where

$$P = \frac{M}{D-d} \gamma^{\frac{1}{4}}$$

$$M = 263.9$$

$$D = 2.440$$

$$d = 0$$

$$= 47.7$$

Taking the sum of the atomic and group parachors gives the following result.

2 NO <sub>2</sub>	⊙ 73.0	146.0
2 Br	⊙ 68.0	136.0
1 C	⊙ 4.8	<u>4.8</u>
		286.8

This value closely checks the one above, the variance being about nine tenths percent.

### Boiling Point

Recording the temperature with a thermometer calibrated to one tenth of a degree Centigrade, the dibromdinitromethane was vacuum distilled at 72.4° C. under 16mm pressure.

### Index of Refraction

The index of refraction was determined with an Abbe Refractometer using a sodium vapor lamp as the light source. The value obtained was 1.5280.

$$\text{Specific refraction} = \frac{1}{d} \frac{n^2 - 1}{n^2 + 2} = 0.1262$$

$$\begin{aligned} \text{where } d &= 2.440 \\ n &= 1.528 \end{aligned}$$

$$\begin{aligned} \text{Molecular refraction} &= 263.8 \text{ times } 0.1262 \\ &= 33.30 \end{aligned}$$

Taking the sum of the atomic refractions gives the following value for the molecular refraction.

C	⊙ 2.37	2.37
2Br	⊙ 8.86	17.72
2NO <sub>2</sub>	⊙ 6.65	<u>13.30</u>

$$\text{Molecular refraction} = 33.39$$

### Viscosity

An Ostwald viscometer standardized with water was used in making the viscosity determination. The apparatus was thermostated with a large beaker of water, the temperature remaining constant to one tenth degree Centigrade. The maximum variance from the mean in a series of determinations was one tenth percent.



Table of Viscosity Measurements (time of flow through viscometer in seconds)

Dibromdinitromethane	Water
179.4	94.6
179.6	94.2
179.4	94.2
179.2	94.4
179.6	94.6
179.2	94.4
Ave. <u>179.4</u>	Ave. <u>94.4</u>

Relative viscosity of dibromdinitromethane =

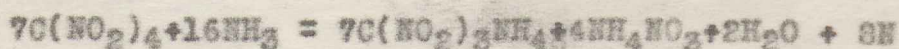
$$\frac{2.438}{.998} \times \frac{179.4}{94.4} = 4.642$$

Viscosity of water at 20° C. = 10.09 millipoises

Absolute viscosity of dibromdinitromethane  
at 20° C. = 46.84 millipoises.

## The Reaction of Dibromodinitromethane with Liquid Ammonia

The reaction of tetranitromethane with liquid ammonia was studied by Kraus (5). His conclusion was that a nitro group was replaced by a hydrogen on the carbon atom to give nitroform which then became nitroform ammonia or the ammonium salt of nitroform. The reaction was then represented by some equation such as the following:



The reaction of dibromodinitromethane with liquid ammonia presents the possibility of different products from the above in that the reduction can occur by removal of either bromine atoms or nitro groups.

When a glass bulb filled with dibromodinitromethane was broken beneath the surface of liquid ammonia contained in a Dewar a violent reaction took place with the evolution of a colorless gas and the formation of a clear yellow solution. The gas was collected over water to remove the ammonia. On the assumption that it was nitrogen calculations showed that one mole of the gas was formed by 3.8 moles of dibromodinitromethane. The determination was very approximate due to poor temperature control, and the presence of water and ammonia vapor in the gas burette.



The yellow liquid ammonia solution on evaporation yielded a bright yellow solid which decomposed readily when heated leaving a white solid residue. The latter was found to be ammonium bromide. The presence of two substances in the reaction product was also indicated by the formation of two types of crystals when a water solution was evaporated.

The percentage of ammonium bromide in the reaction product was found to vary considerably, ranging from 36% to 43%. Old samples as well as those which had been heated even slightly showed high percentages indicating the volatilization or decomposition of the organic substance.

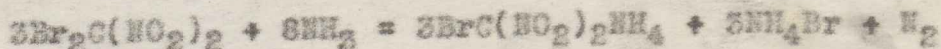
Caustic soda was added to a water solution of the reaction product and the ammonia distilled over. Although the sample contained only 40.0% ammonium bromide corresponding to 6.95% ammonia the total amount of ammonia released by the base was found to be 12.0%. The excess must then have come from the organic compound which was apparently the ammonium salt of an organic acid.

The salt-like character of this organic substance was also evidenced by its ability to dissolve in water and the lower alcohols and its insolubility in ether, benzene, and chloroform.

The addition of a strong acid to an aqueous solution of the reaction product changed it from yellow to

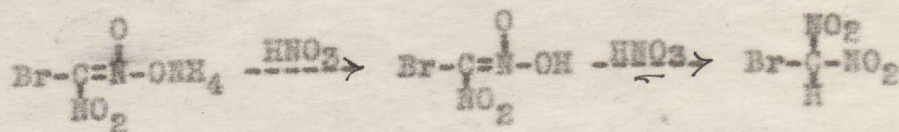
colorless, while neutralization of this colorless solution brought back the yellow color. A tautomeric shift in the organic salt with a change in the pH of the solution was thus indicated.

The evidence is satisfied by the equation



The ratio of the number of moles of dibromodinitromethane per mole of nitrogen would be 3:1 as compared with the rough experimental determination of 3.8:1. The percentage of ammonium bromide would be 32.7 while the higher and inconsistent percentages found are explained by the ready decomposition of the organic product. A mixture of these two substances containing 40% ammonium bromide would contain 12% ammonia checking the observed value.

The change in color may be explained by the following reactions.



Thus in acid solution the bromodinitromethane would be almost completely prevented from going into the aci-form in which it is colored.



The general conclusion formed is that ammonia, in reducing dibromodinitromethane, attacks the bromine atoms in preference to the nitro groups and that the reduction ceases when one bromine has been replaced by a hydrogen. The bromodinitromethane thus formed rearranges into the aciform and then combines with a molecule of ammonia to form the ammonium salt.

#### Summary

Data on the physical properties of dibromodinitromethane and its reaction with liquid ammonia are given. An equation and a mechanism for the reaction are suggested.

### References

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|--------------------------|------------------------|
| (1) Scholl and Schmidt   | Ber. 35,4291           |
| Loganitch                | Ber. 15,472            |
|                          | Ber. 16,2731           |
|                          | Ber. 17,848            |
| Willstatter & Hottenroth | Ber. 37,1779           |
| Wolff                    | Ber. 26,2219           |
| (2) Scholl               | Ber. 31,651            |
| (3) Downing and Orr      | J.C.S. 1671(1934)      |
| (4) Same as (2)          |                        |
| (5) Kraus                | J.A.C.S. 27,211,(1905) |