

A STUDY OF AN INDUSTRIAL RESIDUE FORMED  
BY THE  
HALOGENATION OF GAS OIL

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## HISTORICAL DISCUSSION

In the past some studies have been made on the composition of organic residues formed by the rectification of bromine manufactured from sea weed. The first work of this kind was done by M. Hermann (1) who, by fractional distillation and crystallization, separated bromoform and a fraction he was unable to purify. Hamilton (2) found bromoform and carbon tetrabromide to be present in another residue and postulated their formation to be due to the action of bromine on the organic matter derived from the sea weed from which the bromine was obtained. Shortly afterward, Dyson (3), working with the same residue, substantiated Hamilton's work and in addition found chlorodibromomethane to be present.

Recently, a residue formed by the rectification of bromine manufactured from oil-well brine was obtained from the plant of the now non-existent Texaco Salt Products Company, a subsidiary of the Texas Company. The composition of this residue has been the object of this study.

## FORMATION OF RESIDUE

The purpose of this plant (4), located in Tulsa, Oklahoma, was that of recovering salts naturally occurring in the brine of oil wells by alternately circulating the brine through the condenser boxes of the adjacent petroleum refinery and allowing it to cool, thus crystallizing the salts present. After removal of magnesium salts by precipitation with lime and of sodium and potassium chlorides by crystallization, a mother

liquor was left which contained about fifty percent of calcium chloride and all of the bromides which were originally present. The liquor was then transferred to the storage tanks and from there charged to the bromine plant. In the storage tanks, it was always possible to find a layer of oil on top of the brine. An analysis of this oil showed it to be of a gas oil fraction (5). In the bromine plant free bromine was liberated by treatment with chlorine.

It seems reasonable to assume that any of this oil which might be carried in with the brine would be subject to various reactions: substitution of hydrogen by bromine or chlorine, or cracking on the part of the hydrocarbons to give a lighter product which would in turn be brominated or chlorinated, or other reactions which might take place at high temperature and pressure.

The crude bromine was collected by condensing the vapors from the top of the bromine tank, separated from the water by decanting, and then distilled through a fractionating column heated by the introduction of live steam into the lower portion. The heavier fractions were allowed to reflux in the fractionating column and eventually to drop out the bottom through a trap. It is on these heavier fractions that this study has been made. The plant at Tulsa made no tests on the material except to run a distillation (5). The boiling point was found to range from "quite low" to above 500°F., and a solid residue was left. No mention was made of decomposition with heat.

Since there was a lapse of several years from the time this residue was collected to the beginning of this study, it is quite probable that there had been some polymerization in the interim.

#### PRELIMINARY EXAMINATION

The material was a dark brown, oily liquid having a perceptible odor of free bromine along with the characteristic sweetish odors of brominated hydrocarbons. A small amount of water was present. This water contained bromine, hydrobromic acid and inorganic salts, of which bromides and chlorides were found to be the only halides. The specific gravity of the original liquid was 2.37.

An analysis for additional elements showed bromine to be present; although chlorine was later found to be present, it was not detected at this stage. The liquid was insoluble in water, hydrochloric acid, sodium hydroxide, and concentrated sulfuric acid, and soluble in acetone, ether and similar organic solvents.

Repeated washing with water, hydrochloric acid, and sodium hydroxide caused no change in volume or color; however, when allowed to stand for some time with concentrated sulfuric acid, the material cleared up somewhat and was a dull red color. When the acid layer was diluted and extracted with ether, there was found to have been removed only a small amount of a black, gummy substance. This probably represented aromatics and oxygenated compounds.



Upon distillation, the original liquid began to boil at about  $100^{\circ}\text{C}.$ , and the temperature rose steadily to  $126^{\circ}$  at which point it remained for some time before decomposition took place. A distillation at 35 mm was then made on 120 cc of the original liquid. Distillation began at  $46^{\circ}\text{C}.$ , and the temperature rose steadily to  $88^{\circ}$ , at which point decomposition occurred. As the distillate -- approximately 50 cc -- was found not to decompose appreciably upon boiling, a fractional distillation was made at atmospheric pressure. Two fractions were separated: one containing 25 cc which boiled at  $145-150^{\circ}$  and the other containing 10 cc which boiled at  $120-25^{\circ}$ . There was a small amount which boiled above  $150^{\circ}$ .

Since the halogenated hydrocarbons were found to be volatile with steam, it was thought that steam distillation would be the most effective method of separating these compounds from the polymerized substances present. This would practically eliminate decomposition which was the principal difficulty encountered.

#### SEPARATION

Accordingly, three liters of the material was washed with water, placed in a twelve-liter, round bottom flask, and connected with a laboratory steam line. Distillation was quite rapid at the beginning, 720 cc of product distilling over with 660 cc of water. The yield dropped quite rapidly, however, and at the end of approximately ten hours

only 24 cc of product distilled with 1092 cc of water. In all 1636 cc of product was obtained. The first portion was colored by the unremoved bromine; however, treatment with sodium bisulfite solution rendered it colorless. The latter portion had a clear yellow color which was not removed by the above treatment. The residue consisted of a fairly large amount of a light semi-solid and a dark, almost black, viscous liquid. An analysis on this dark material obtained from a smaller run showed it still to contain 51.87% bromine and no chlorine.

The product was washed with sodium bisulfite solution to remove the dissolved bromine, dried with calcium chloride, and distilled until it began to decompose, at a little above 150°C. The residue was then distilled until vacuum (approximately 10 mm). The first portion had a constant boiling point at 51°, and all which distilled up to this temperature was placed with the lower fraction. The remainder distilled at a constant rate with increase in temperature; this was divided into two fractions: (A) that distilling from 51-100°, and (B) that distilling from 100-145°. Owing to lack of time and the difficulties encountered in vacuum fractional distillation, no attempt was made to purify these higher boiling fractions; however, from the nature of the distillation curve, there appeared to be only one component which boiled above 150° at atmospheric pressure. An investigation of fraction (B) showed it to contain 87.30% bromine and to have a specific gravity of

2,057.

The fraction not decomposed by heat, which totalled 1270 cc, was refractionated. A Snyder column was used and care was taken to maintain a five to one reflux ratio. After repeated fractionation, two fractions were obtained: (I) one boiling at 115-120°, containing approximately one-third of the total that was collected below 150°, and (II) another at 145-50°, making up the remainder of this fraction which was not decomposed by heat.

Both fractions decomposed somewhat at room temperature owing to the action of air and light but were easily restored to their original appearance by washing with sodium bisulfite solution.

#### ANALYSIS OF FRACTIONS

##### Fraction I

Repeated fractionation of the first fraction yielded a compound which boiled at 117.5-18° at 740 mm. This compound was shown to be chlorodibromomethane.

For the determination of chlorine and bromine a combination of gravimetric and indirect volumetric methods was used. The quantitative method for the determination of bromoform of treatment with cold alcoholic potassium hydroxide, which was first proposed by Hermann (1) was used to decompose the compound. After reaction the solution was acidified with dilute nitric acid, and an excess of standard silver nitrate was added. The precipitate was collected in

a weighed Gooch crucible, dried and weighed. The filtrate was titrated with standard potassium thiocyanate by the Volhard method. From the titration, the weight of the halides could be calculated as 100% silver chloride; and the weight of the mixed silver halides being known, the percentages of chlorine and bromine could be calculated. It was found that the Stepanow method of analysis for organic halogen by the reaction of the compound with sodium ethylate (6) gave essentially the same results.

Analyses for halogen:		Theoretical values for
I	II	chlorodibromomethane:
Br - - 74.99%	75.18%	Br - - 76.33%

The freezing point method employing benzene as the solvent was used to determine the molecular weight.

Molecular weight determination:		Theoretical value for
I	II	chlorodibromomethane:
196	192	208

The specific gravity was taken in a Sprengel type pyknometer at 20° with reference to water at 20°.

Specific gravity:	Values given in literature
2.4119	2.4450 at 15° (9)
$\frac{20^\circ}{20^\circ}$	2.477 (3)

To determine the freezing point the compound was placed in a freezing mixture of acetone and solid carbon dioxide. A hexane thermometer was used. Supercooling was avoided by

first freezing the liquid and then allowing it to melt while it was thoroughly agitated. After melting had begun, the temperature remained constant until all had melted; this point was taken as the freezing point.

Freezing Point:

- 28°C.

Values given in literature:

- 22°C.

- 32°

The refractive index was taken by means of an Abbe refractometer, and the specific refractivity was calculated by the formula of Lorentz and Lorenz:

$$r = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$$

where

r is the specific refractivity

n is the refractive index

d is the density

The molecular refractivity was then found by multiplying the specific refractivity by the molecular weight. The atomic refractivities of Eisenlohr (7) were used to determine the calculated value.

Refractive Index:

n = 1.5468 at 20°

Observed molecular refractivity - - 27.38

Calculated molecular refractivity - 27.49

The surface tension was determined at 20° by means of a stalagmometer. From this value the parachor was determined

by substitution in the equation:

$$P = \frac{\gamma^{\frac{1}{2}} \cdot M}{d}$$

in which

P is the parachor

M is the molecular weight

$\gamma$  is the surface tension

d is the density

The values for atomic parachors used to determine the calculated value were those of Mumford and Phillips (8).

Surface Tension:

$$\gamma = 30.615 \text{ at } 20^{\circ}$$

Observed parachor - - 203.2

Calculated parachor - 217.6

Treatment with benzene in the presence of aluminum chloride resulted in the formation of a derivative, which after distillation and crystallization from alcohol proved to be a white solid with a melting point of  $90^{\circ}$ . Triphenyl methane has a melting point of  $92.5^{\circ}$ .

#### Fraction II

The second fraction was crystallized by placing it in an ice bath, and the small amount of liquid which did not crystallize was poured off. Upon redistillation, this fraction was then found to have a boiling range of  $147-9^{\circ}$  and a melting point of  $7-9^{\circ}$ . The reaction product with benzene in the presence of aluminum chloride was used as a

derivative. These data proved the second fraction to be bromoform.

Bromoform - M. P.  $9^{\circ}$  B. P.  $148^{\circ}$

Triphenyl methane - - M. P.  $92.5^{\circ}$

#### DISCUSSION

The work of early investigators has been partially substantiated on essentially the same type of residue from an entirely different source. It seems quite probable that, in addition to bromoform, Hermann (1) obtained some chlorodibromomethane, as his analysis was based on the decomposition of this lower fraction with cold alcoholic potassium hydroxide, the value for bromine being obtained by difference. Comparison of his analysis with the theoretical on this basis gives:

Unknown	Theoretical for chlorodibromomethane
H - - 0.44%	H - 0.47%
C - - 5.44	C - 5.76
Br - 94.12	Halogen - (76.33 Br + 17.04 Cl) - 93.37

He found the compound did not freeze at  $-20^{\circ}\text{C}.$ , which is above the values for the freezing point obtained by all investigators.

At no time during this study was there any indication of the presence of carbon tetrabromide as found by Hamilton (2) and Dyson (3).

It seems quite logical that despite discrepancies in theoretical and actual results of halogen analysis and molecu-

lar weight determinations, the chlorodibromomethane obtained in this work is purer than any obtained by previous investigators, since there is such close agreement of observed and calculated molecular refractivities and to a lesser degree between the parachors, and since the boiling range is within one-half of one degree. The boiling range originally reported by Jacobsen and Neumeister (9) was 123-5°; this was improved by Levy and Jedlicka (10) to 118-20°, and later by Besson (11) to 117-9°.

The low values obtained in the molecular weight determination may be explained by the fact that the determination was made on a sample having a two degree boiling range. Later, when the sample had been further purified, the importance of the determination did not seem to warrant another run.

The value obtained for the specific gravity is quite probable, since the samples from which the earlier values were determined were undoubtedly contaminated somewhat with heavier components.

The purity of the sample used would seem to indicate the value obtained for the freezing point to be preferable to that of Levy and Jedlicka (10) as -22° and that of Besson (11) as -32°.

For the purpose of comparison, molecular refractivities were determined for several polyhalogenated hydrocarbons from constants given in the literature. These are as follows:



	Observed	Calculated
$\text{CHCl}_3$	21.26	21.63
$\text{CHBr}_3$	29.84	30.42
$\text{CCl}_4$	26.56	26.58
$\text{CBr}_4$	33.17	38.30

Thus it is seen that the agreement of observed and calculated values for chlorodibromomethane is well within the limits observed for other similar compounds.

For the purpose of comparison, the parachors for several polyhalogenated hydrocarbons were calculated from constants given in the literature:

	Observed	Calculated
$\text{CHCl}_3$	161.5	188.3
$\text{CHBr}_3$	230.0	222.0
$\text{CCl}_4$	219.1	227.5

It may be seen that there is considerable discrepancy in the observed and calculated parachors of several similar halogenated hydrocarbons.

## SUMMARY

An organic residue formed by the rectification of bromine was obtained for analysis from the now non-existent Texaco Salt Products Company.

By means of steam distillation and fractional distillation, two components were obtained in a state sufficiently pure for analysis. These were found to be bromoform and chlorodibromomethane.

Corrections have been made in the reported values of the physical constants of the latter compound. These are: B.P. -  $117.5-8^{\circ}\text{C}$ . at 740 mm, F.P. -  $28^{\circ}\text{C}$ ., and Sp.Gr.  $2.4119_{20^{\circ}}$ . The refractive index was found to be 1.5468 at  $20^{\circ}$  and the surface tension to be 30.62 at  $20^{\circ}$ ; these values have not been previously reported.

A higher boiling fraction which decomposed upon heating was obtained in a state insufficiently pure for identification. A bromine analysis and a specific gravity determination were made on this material.

A bromine analysis was made on the residue from the steam distillation.

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## AUTOBIOGRAPHICAL SKETCH

I, Robert G. Boatright, was born in Cushing, Oklahoma, July 15, 1914. After completing the elementary grades, I entered high school, and in May, 1931, I was graduated from Cushing High School.

My undergraduate work was done at Oklahoma Agricultural and Mechanical College. I received the degree of Bachelor of Science in Chemistry from that institution in May, 1935. For the following two years I remained at Oklahoma Agricultural and Mechanical College taking work leading toward the degree of Master of Science in Chemistry. This work will be completed in May, 1937.

Typist

Maurine Chilton