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THE CHLORINATION OF ACETONE

Marie Borries

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Submitted in partial fulfillment for the  
Degree of Master of Science

1919

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## THE CHLORINATION OF ACETONE.

This problem originated in an attempt to make methyl glyoxal in quantity. Several methods of making methyl glyoxal are mentioned in the literature but in none of them is acetone used as a starting point. Since this seemed a new field it was decided to chlorinate acetone hoping to obtain some product which might be easily converted into methyl glyoxal.

Technical acetone was purified and dry chlorine was passed through this warm acetone in the presence of sunlight. During the process three distinct steps were noticed in the reaction. The first step was completed in the first half hour. During this time the acetone was held at the temperature of a boiling water bath and the chlorine was rapidly absorbed with an evolution of hydrochloric acid. At the end of this time the second step in the process set in, which lasted for two hours. Throughout this period no hydrochloric acid was evolved. The chlorine seemed to be simply absorbed with a marked heat of reaction. During the first half hour of this period the water bath was retained, but after that it was noticed that the heat of reaction was sufficient to keep the temperature up to  $80^{\circ}\text{C}$ . This seemed to be the critical temperature for this step of the reaction, for whenever the temperature exceeded  $80^{\circ}\text{C}$  a violent reaction occurred with a

flame. As the heat of reaction was so intense during this step it was frequently necessary to cool the reaction mixture.

At the end of this period a third step in the chlorination set in, during which the reaction slowed down a little. The heat of reaction was sufficient to maintain a temperature of  $80^{\circ}\text{C}$  but at no time did the temperature rise above  $80^{\circ}\text{C}$ , and since the temperature remained at  $80^{\circ}$  there was no tendency to flaming and no necessity for cooling the mixture. Hydrochloric acid was again evolved during this period though not as abundantly as in the first period, which was to be expected, as it required three and one half hours to complete this step, while only one half hour was required for the first. At this time, just six hours after the operation was begun, chlorine was observed above the acetone and the reaction was believed to be complete. Throughout the chlorination a very volatile gas with an ethereal odor was freed, which it was impossible to condense. During the second step a white crystalline deposit also began to form. This increased slowly in quantity until after cooling the mixture at the end of the reaction, about one gram of the powder was obtained. On analysis this powder proved to be ammonium chloride.

After filtering out the ammonium chloride, the resulting liquid was separated into three fractions by distillation under diminished pressure. Each fraction

was apparently a pure compound as each had a well defined boiling point, and the temperature rose rapidly between the boiling points of the fractions. As the time was limited it was decided to examine only one of the three fractions. The heaviest fraction, which was also the one with the highest boiling point, was selected for study.

This fraction was a heavy greenish liquid with a density of 1.42. It was immiscible with water, not even reacting with it on long boiling, but was miscible in all proportions with alcohol, ether, and chloroform. It had a marked effect on the eyes, most noticeable on slight warming, producing copious tearing and intense pain if freed in any quantity. The vapors were neither acid nor basic, nor was an acid, base, or salt formed on boiling it with dilute acids or bases. It reduced silver nitrate and Fehling's solution and united violently with dry ammonia and phenylhydrazine; but not with sodium bisulphite. On treating the fraction with phenylhydrazine in ethereal solution in the presence of potassium carbonate, white crystals were obtained. The percent of chlorine was determined by heating the fraction in a sealed tube with calcium oxide and precipitating the chlorine from the water solution of the product with silver nitrate. The percent of chlorine obtained was 65.5. The percent of chlorine for the formula  $\text{CH}_3\text{COCCl}_3$  is 65.8. The weights for this determination will be found in the

experimental section.

#### EXPERIMENTAL.

Technical acetone was used. It was dried over anhydrous calcium chloride, and as it contained a large amount of water it was found necessary to repeat the drying. During the drying it lost nearly one third of its volume. After filtering, it was distilled and the fraction boiling between  $56^{\circ}\text{C}$  and  $65^{\circ}\text{C}$  only was used. 325cc of this acetone were placed in a flask connected with a long reflux condenser so arranged that a constant stream of dry chlorine could be passed through the acetone. The flask was placed on a boiling water bath for the first half hour, and was in a position where it would be in direct sunlight for the greater part of the six hour period, during which the chlorine was admitted.

As stated before, the reaction occurred in three distinct steps. During the first period chlorine was rapidly absorbed, and a large amount of hydrochloric acid was evolved. This was the only part of the chlorination in which it was found necessary to heat the acetone, and the steam of a boiling water bath was sufficient here. During the second period the action was very vigorous, a flame starting up in the tube through which the chlorine entered whenever the temper-

ature rose above  $80^{\circ}\text{C}$ . As the heat of reaction was so great it was frequently necessary to cool the flask with a stream of cold water to prevent this flaming, and in one instance it was necessary to shut off the chlorine and admit air before the action could be controlled. Whenever this burning occurred it was noticed that carbon and hydrochloric acid were formed as if some volatile hydrocarbon were completely decomposed by chlorine in a reaction resembling that of turpentine and chlorine. During the third period the action was not quite so intense. The temperature did not rise above  $80^{\circ}\text{C}$ , there was no burning and hydrochloric acid was again evolved.

It was noticed during the second period of chlorination that small white crystals were beginning to form, and after cooling the reaction mixture about one gram of these was filtered out. On examination these crystals were found to be insoluble in alcohol, ether, acetone, or toluene, but soluble in water. They readily sublimed and on analysis proved to be ammonium chloride.

After filtering out the crystals an attempt was made to separate the reaction mixture into fractions by distillation, but it was found impossible to obtain fractions with definite boiling points and distillation in vacuo was then resorted to. The vacuum was obtained with an ordinary filter pump, and while the pressure was diminished between the limits of 30.5 cm. and 40.5 cm



it remained fairly constant at 34.3 cm. The following fractions were obtained after boiling off and discarding a few cc. of unchanged acetone.

|              | cc  | Pressure  | Collected at  |
|--------------|-----|-----------|---------------|
| 1st Fraction | 53  | 40.54 cm. | 55°C - 65°C   |
| 2nd Fraction | 113 | 40.54 cm. | 70°C - 80°C   |
| 3rd Fraction | 55  | 40.54 cm. | 145°C - 155°C |

The greater part of the first fraction came over at 63°C, of the second at 73°C, and of the third at 153°C. All three fractions were clear liquids, the first two colorless, the third, green and all three affected the eyes.

The 153°C fraction was selected for examination. It seemed to be a stable compound, heavy and oily, not hydrolyzing with water, dilute acids or bases, although dilute ammonium hydroxide split out some of the chlorine as ammonium chloride. On oxidation with fuming nitric acid it was found impossible to split out more than a small part of the chlorine even when this was carried out in a pressure bottle for a period of several days. The percent of chlorine was determined by heating a .5 gram sample of the fraction with calcium oxide in a sealed glass tube. The tube was placed in an iron pipe sealed at both ends and heated intensely for several hours. After cooling, the powder was washed with about 100cc of warm water, acidulated with nitric acid and the solution was filtered off. The chlorine was precipitated from this solution with silver nitrate and fil-

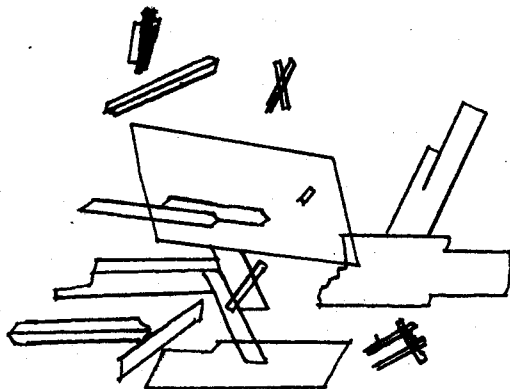
tered, washed and weighed as silver chloride.

|                                |             |
|--------------------------------|-------------|
| weight of sample               | .5904 gms.  |
| weight of silver chloride      | 1.5628 gms. |
| percent of chlorine determined | 65.5        |
| percent of chlorine calculated | 65.8        |

By this method the percent of chlorine was determined as 65.5, the percent of chlorine calculated for  $\text{CH}_3\text{COCCl}_3$  was 65.8.

The compound reduced Fehling's solution and silver nitrate readily, and reacted violently with dry ammonia gas and phenylhydrazine base, but not with a saturated solution of sodium bisulphite, even when warmed, or with phenylhydrazine hydrochloride. When dry ammonia was passed into 5cc of the fraction surrounded by a freezing mixture a white crystalline salt was obtained, but this salt decomposed so rapidly on exposure to room temperature it was impossible to obtain its melting point or even to examine its crystalline form under the microscope. When dry ammonia was passed into a solution of the compound in ether a reaction also occurred, but very slowly, with the formation of a very small amount of the white crystals. The study of these crystals was then dropped, and the reaction with phenyl hydrazine was more closely examined. As the reaction with phenylhydrazine was so violent, solutions of the compound and phenylhydrazine in alcohol, chloroform and ether were tried. It was found by using solutions of the compound and phenylhydrazine in ether

in a ratio of five of ether to one of compound or phenylhydrazine and by mixing the two solutions in the presence of potassium carbonate that the reaction could be controlled so that the crystals formed only after two or three minutes, and it took two or three hours for the reaction to run to completion. By filtering and washing these crystals immediately with ether, a mass of very light stable white crystals was obtained. Under the microscope they seemed to be very thin and transparent with the following shapes.



In the formation of these crystals water was evolved.

The melting point of the unpurified crystals was  $237^{\circ}\text{C}$ . On attempting to recrystallize from water slight decomposition took place and the resulting crystals had a melting point of  $239^{\circ}\text{C}$ . These crystals sublimed readily and dissolved easily in water, but were insoluble in ether and chloroform. The water solution of the crystals gave a test for chlorine ions. On treating the water solution with a strong solution of sodium hydroxide no ammonia was freed, but on heating the crystals directly with calcium oxide, ammonia was

freed. On boiling the crystals with dilute acids or even with concentrated hydrochloric acid no decomposition took place. After cooling, the crystals simply settled out of solution again. Finally a Kjeldahl determination of the nitrogen in the crystals was made with the following results.

1cc NH<sub>4</sub>OH = .003470666 gms. of N.

|           | wt. of sample | No. of cc. of NH <sub>4</sub> OH used to neutralize acid | No. of cc. of NH <sub>4</sub> OH equi to N. in sample | Wt. of N. represented by cc of NH <sub>4</sub> OH | % of N. |
|-----------|---------------|--|---|---|---------|
| Blank I   |               | 53.9   |   |   |         |
| Sample I  | .1256         | 50.9   | 3.  | .01411998   | 8.29    |
| Blank II  |               | 54.74  |   |   |         |
| Sample II | 1.0376        | 29.8   | 24.94   | .08655841004                                      | 8.34    |

The percent of nitrogen calculated for the formula CH<sub>3</sub>C(NHC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CCl<sub>3</sub> is 8.49.

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### SUMMARY

Three distinct products were obtained by this method of chlorinating acetone. It was not determined why the chlorination took this form. However, some nitrogen compound, possibly pyridine, must have been present as an impurity in the acetone, which on treatment with chlorine yielded ammonium chloride. Either the compound itself or the ammonium chloride acted as

a catalyzer and caused the formation of the three products. The volatile by-product was also probably a decomposition product of this impurity.

The percent of chlorine determined in the product examined points to the empirical formula  $C_3H_3Cl_3O$  for this product. Since the determination of the percent of nitrogen in the crystalline product obtained from the reaction of this substance with phenylhydrazine agrees with the percent of nitrogen calculated for the formula  $CH_3C(NHC_6H_5)_2CCl_3$  it is highly probable that the formula for the compound is  $CH_3COCCL_3$ . For if the point attacked by the phenylhydrazine is the oxygen, and if the product formed is not a hydrazone, but one with two  $NHC_6H_5$  groups substituted for the oxygen, and with no unsaturated valence it would indicate that each end of the chain is saturated, the one with hydrogen, the other with chlorine. The fact that the crystalline product is stable and does not revert to the ketone on boiling with acids, is also explained by the formula  $CH_3C(NHC_6H_5)_2CCl_3$ . That a carbonyl group is present in the product examined is indicated by the reactions with silver nitrate, Fehling's solution, dry ammonia and phenylhydrazine. These reactions would then lead to the belief that the substance  $CH_3COCCL_3$  was one of the products of this method of chlorinating acetone.

June 26, 1919