ACETONECHLOROFORM

FIRST PAPER

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In a series of investigations upon the reactions between acetone and alkyl halids in the presence of alkalies, acetonechloroform was discovered by Willgerodt.¹ By bringing together acetone and chloroform, and adding powdered potassium hydroxid to the cooled mixture in small portions at a time, allowing to stand until the reaction was completed, and fractioning the fluid products, a white solid was obtained from the higher boiling portions, which bore a striking resemblance in smell and general appearance to camphor. It was purified by recrystallization and sublimation and its properties noted. A detailed description of the substance will be given below. Analysis and a vapor-density determination corresponded to a composition indicated by the formula $(\text{CH}_3)_2\text{CO}.\text{CHCl}_3$. Further study of the compound by Willgerodt,² and other investigators working with him, established the constitution of the substance. It is trichlorotrimethyl carbinol, $(\text{CH}_3)_2\text{C}.\text{CCl}_3\text{OH}$, or a derivative of tertiary butyl alcohol. Willgerodt describes it generally as trichlorid of acetic acid or oxyisobutyric acid. It is more commonly known as acetonechloroform.

In the distillation of the products from which acetonechloroform was obtained was a portion which on fractioning boiled approximately constant as 170° , remained fluid on cooling if kept

¹ Ber. chem. Ges. Berlin, **14**, 2456 (1881).

² Ibid. **15**, 2305 (1882); **16**, 1585 (1883); Jour. prakt. Chem. [2] **37**, 361 (1888); [2] **39**, 283 (1889); [2] **41**, 515 (1890).

from moisture, and which had the same composition as acetonechloroform. If poured into water or allowed to come into contact with moist air, it rapidly changed into the solid acetonechloroform, from which it was not possible to obtain it again. It was at first supposed to be a polymer of the solid variety, or an instable physical modification of it. But Willgerodt and Geneiser¹ finally decided it to be an isomer, and by ingenious though inaccurate reasoning, based on its supposed analogy to the acetone-hydrocyanic acid addition-product of Bredt² ascribed to it a formula. The relative orientation of the two compounds was indicated thus :

The reactions of the liquid modification with reagents were in all essential features the same as those of the solid, and Willgerodt and Geneiser assume that under the conditions of these reactions it first undergoes a molecular rearrangement. Wherein the reactions of these two compounds may differ and the probable reasons therefore will be presently noted. With a view to establishing more fully the nature of these two compounds and their interrelations, this investigation was undertaken.

The material was prepared as directed by Willgerodt and Geneiser. A fractional separation by distillation under diminished pressure was found to be impracticable from the choking of the condenser tubes with the solid substance. The liquid variety was refractioned several times. In every case, some solid material came over at the beginning of the distillation. A portion of the liquid variety was distilled into a dried specimen vial, into which a stream of dried carbon dioxide was constantly passing. The fraction boiled at 165–167°. A few crystals formed in the neck of the vial and were washed into it with the liquid and the vial sealed by drawing out the neck to a capil-

¹ Jour. prakt. Chem. [2] 37, 361 (1888).

² Ber. chem. Ges. Berlin, 15, 2306 (1882).

lary tube. This specimen was labelled A, and at room temperature (about 25°C) was a clear nearly colorless liquid, containing a few crystals.

Another portion of the liquid variety distilling at $170^{\circ}\text{--}171^{\circ}$ was distilled into a vial, so arranged that a considerable space about it was filled with carbon dioxide, carefully dried by passage through a column of sulfuric acid. This specimen was labelled B, and was a perfectly clear, colorless liquid, containing at no time, any trace of solid matter. The two specimens, A and B, were now cooled to -4° . In A there was a further deposition of crystals, but the entire mass would not solidify. In B no change appeared. Both vials were then placed in a mixture of solid carbon dioxide and ether. The contents of both solidified, A rapidly, B rather slowly. After staying at this temperature some time, both specimens were brought to room temperature again, melting over a wide range of temperature, and appearing to have undergone no change. They were then submerged in a bath at 55° for 72 hours, the crystals in A entirely dissolving, but reappearing on cooling. When brought to ordinary temperature again, neither specimen appeared to have changed. Assuming the presence of two modifications in either specimen, it seemed impossible to displace the equilibrium through a temperature range of at least 140°C .

The two vials were then opened and weighed portions of their contents poured into about equal volumes of water, the whole brought just to boiling, by which a very small portion volatilized. On cooling, the solid formed was filtered, washed with cold water, quickly dried and weighed. For specimen B which was supposed to be very pure, we give the figures: 14.95 g oil yielded 12.90 g of the solid, or 86.3 percent, leaving out of consideration the water known to be present in the crystals. Therefore at least 13 percent of the original material remained in the filtrate. This filtrate was brought into a narrow vessel, and potassium carbonate added; it first became milky, and then separated into two layers, the upper being quite small, a yellowish liquid having the smell and general appearance of acetone. It evaporated over night, leaving a few crystals of the solid

acetonechloroform floating on the surface of the remaining liquid. The amount of acetone separating was too small to make possible a more positive identification.

Anhydrous solid acetonechloroform was then prepared by heating the material in a distilling bulb, with an oil bath at 75° , and under diminished pressure. By this process, water and some crystals of the material sublimed into the condenser tube. When no more water appeared to come off, the bulb was attached to another condenser tube without jacket, and the material distilled. It practically all distilled at 166.4° to a beautiful colorless liquid, which solidified on cooling to a mass bearing a striking resemblance to camphor which has been fused. It melted at 91° – 92° and solidified at the same point.¹ 14.5 g of this anhydrous material was weighed into a distilling bulb and 2.2 g of purified acetone added. The solid completely dissolved at 25° . The solution was then distilled, the temperature rising rapidly to 163° and but a few drops of the material distilling. The temperature then rose slowly to 166.4° , the major portion of the substance distilling as a clear, colorless liquid, which did not solidify even at 4° . The thermometer remained constant at 166.4° , the remainder of the material distilling at that temperature and solidifying at once in the condenser tube. It melted at 91° – 92° . The liquid distilling at 163° – 166° poured into water or exposed to moist air yielded a solid melting at 78° – 79° . It appeared to be liquid acetonechloroform in everything but its boiling-point. About 40 g of solid acetonechloroform was placed in a distilling bulb and moistened with water. On distillation the thermometer rose rapidly to 98° . Water and a portion of the material sublimed at this temperature. The temperature rose slowly to 110° , more and more rapidly to 135° , and then at once to 169° , and the greater portion of the material came over at 170° – 171° , the temperature finally rising to 174° . A repeti-

¹ This melting-point determination was made after the usual manner, in a capillary tube. Subsequent melting-point determinations of the same material taken in larger quantities and in the more accurate manner described in this paper, did not confirm the statement made above. Another illustration of the little value of such determinations when made in the conventional way.

tion of this experiment with very pure materials gave practically all the material distilling at $170-171^{\circ}$. It appeared that acetonechloroform retained readily appreciable quantities of acetone and water at its boiling-point, and with the latter there is probably a mixture with a maximum boiling-point. From these experiments we concluded that *liquid acetonechloroform did not in fact exist*, but that the supposed compound is a mixture of solid acetonechloroform with acetone and water. All the known phenomena observed in connection with the substance confirms this view. In its conduct towards reagents in general, as has been pointed out, it behaves in the same way as the pure solid, but being, as Willgerodt has said "a little less reactive." This statement is purely qualitative, and is undoubtedly justified by the main reactions being more or less disguised by the reactions of the acetone and water present. The only reagent towards which there was a notable difference in the conducts of the two substances was phosphorus pentachlorid,¹ where the same products were obtained, but accompanied in the case of the liquid variety, by a very volatile substance which attacked the mucous membrane. It is well known that some of the chlorin derivatives of acetone possess this property, and its presence in this case is not therefore surprising, granted our premises. The gradual darkening of the liquid on standing in the light can be accounted for by the action of traces of hydrochloric acid on the acetone. That these traces of hydrochloric acid are present is shown by the fact that the liquid acetonechloroform is acid enough to redden litmus, as was noticed by Willgerodt and Geneiser,² and, further, the fact also noticed by them, that whenever the solid acetonechloroform was distilled with water, the water is always slightly acid owing to the formation of oxyisobutyric acid. Its greater activity as a poison is due to the fact of its being in solution in acetone, in which it is marvelously soluble even when considerable quantities of water are present. Any discussion of the

¹ Willgerodt and Geneiser. Jour. prakt. Chem. [2] 37, 361 (1888).

² Jour. prakt. Chem. [2] 37, 364 (1888).

formula proposed is superfluous in view of the facts just presented.

Acetonechloroform is a white crystalline solid, readily soluble in most organic solvents to a very remarkable extent. It is not appreciably soluble in cold water, but fairly so in hot water. Its melting-point when free from water lies above 97° and probably near this figure, but when obtained from solutions containing water or standing exposed to the air for a time it shows melting-points from 76° to 82° . By crystallizing from solvents insoluble in water, by distillation or sublimation, the melting-point is raised. It burns with a greenish flame. Small particles thrown on water rotate violently as does camphor under the same conditions. In general appearance the substance, especially when cooled from a molten magma, very strongly resembles camphor. It has the same characteristic odor, and apparently in as intense a degree. This smell to a faint extent is said to be characteristic of the mother substance trimethylcarbinol. Acetonebromoform, prepared by Willgerodt¹ in an analogous way, has as intense an odor but more like pepper. It is readily volatile with steam. It volatilizes very readily with volatile solvents, when left in open vessels, and the dried material evaporates fairly rapidly at ordinary temperature, so that weighing must be made in closed vessels. It dissolves in and is decomposed by strong nitric or sulfuric acid, and with the latter gives off hydrochloric acid. According to Willgerodt² it materially increases the deposition of metallic silver, from a solution of silver nitrate and aniline in water. On standing in contact with an ammoniacal silver nitrate solution, a gray powder is deposited. A vapor-density determination by Willgerodt, according to the method of Hofmann, indicated the formula $(\text{CH}_3)_2\text{CO} \cdot \text{CHCl}_3$; calculated, 88.5; found, 88.7. Determinations of the molecular weight in benzene were made by the freezing-point and boiling-point methods and in acetone by the boiling-point method. By freezing-point method, apparatus of Beckmann:

¹ Willgerodt. Ber. chem. Ges. Berlin, **14**, 2458 (1881).

² Willgerodt. Ibid. **14**, 2455 (1881).

Solvent: Benzene

[K = 49.0]

g solvent	g solute	Δ	mol. wt.
18.075	0.1094	0.174	171
	0.2646	0.414	173
	0.4107	0.635	175
	0.5591	0.829	183
	At infinite dilution		169
	Theoretical		176

By boiling-point method, apparatus of Orndorff and Cameron:¹

Solvent: Benzene

[K = 26.6]

g solvent	g solute	Δ	mol. wt.
122.75	1.0584	0.127	182
	2.0765	0.240	190
	3.0351	0.352	189
	4.1014	0.465	194
	5.0029	0.551	198
	At infinite dilution		179
	Theoretical		176

Solvent: Acetone

[K = 16.7]

g solvent	g solute	Δ	mol. wt.
114.55	1.9910	0.157	190
	3.9297	0.307	192
	5.4232	0.427	190
	6.6791	0.536	189
	7.9054	0.633	187
	At infinite dilution		190
	Theoretical		176

¹ Orndorff and Cameron. Am. Chem. Jour. 17, 517 (1895).

Experiments were made to determine the proportions in which the reagents would give the best yields of acetonechloroform, and to try and obtain an insight into the reaction by which it is formed.

To a mixture of 200 g acetone and 400 g chloroform were added little by little 400 g of pulverized caustic potash, in such a way as to require about 48 hours to complete the operation. The reacting materials were in a balloon flask of about 3 liters capacity, which was kept in a cooling bath of snow and water and frequently shaken. The contents gradually assumed a yellow pulpy appearance, and towards the end of the reaction they became quite dark. The flask which was closed by a rubber stopper bearing a tube with capillary opening was then allowed to stand for two days longer in a bath of cold water. The contents were then poured on a filter, the liquid portion drawn off with the aid of the pump, and the solid washed several times with acetone and chloroform. It was found in previous experiments that some alkali was always to be expected in the filtrate, which would decompose the acetonechloroform on distilling. The liquid and washings were therefore brought into a large separating funnel and washed several times with water, whereby probably but a small amount of the desired material was lost, and then transferred to a distilling flask. On distilling, the temperature rose gradually to 110° acetone, chloroform, and water coming over. From 110° on the temperature rose rapidly, the operation was then interrupted, the contents of the flask poured into a relatively large amount of cold water, and the flask washed out with a small quantity of acetone, which was added to the water. The acetonechloroform at once separated as a crystalline mass, but slightly colored. After standing over night it was filtered, pressed dry and weighed; yield 21.4 g. The distillate below 110° gave no appreciable addition to this amount on refractioning.

This same process was repeated starting with 100 g acetone, 400 g chloroform and 100 g pulverized caustic potash. It required about a day to introduce all of the potash. The contents of the flask were not appreciably colored at the end. They

were allowed to stand for three days before being filtered, distilled, etc.; yield 21.4 g acetonechloroform. A third experiment starting with 200 g acetone, 400 g chloroform and 100 g potash was carried on at the same time and in the same manner as the one last described. The contents of the flask at the end were very slightly colored yellow; yield 60.8 g of acetonechloroform, perfectly white and in quite pure condition. The solid filtrate, after being washed with acetone and ether, was dried and weighed 110 g. It contained a small amount of potassium carbonate and some organic material, probably salts of organic acids. Analysis¹ of the material showed about 98.5 percent of potassium chlorid. In comparison with the other experiments, the yield in this last case was most noteworthy, being nearly three times as much. The product also was much cleaner and contained relatively much less organic matter. The proportions suggested by Willgerodt and Geneiser are in near agreement with the results of this experiment, but the use of somewhat less potash and longer standing than they advise, is indicated.

The formation of acetonechloroform was attempted by heating the constituents in sealed tubes at various temperatures from 150° to 250°, but unsuccessfully, as had already been found by Willgerodt. The introduction of potassium bisulfite did not produce an apparent modification of the results. In every case there was considerable charring. Chloroform, water and a volatile constituent containing chlorin were the products. By suspending the material in a sealed vial in an oil bath at 150° the charring was avoided but no formation of acetonechloroform was detected. Heating acetonechloroform in sealed tubes resulted in charring of the contents, dependent on the temperature and time of heating. On cooling, the contents of the tubes were found to be under diminished pressure as was also noted by Willgerodt. In one case the tube was heated to 400° and the charring was found to be quite complete, but a very small amount of crystalline substance presenting an entirely different

¹ Kindly made for us by Mr. C. A. Soch.

appearance from acetonechloroform was obtained. It could not be examined farther however. Acetonechloroform in a sealed vial was suspended in an oil bath at 170° for some hours without change. On being kept at 205° for three hours, it darkened somewhat, but entirely solidified on cooling, and showed no change which could be studied. The mechanism of the reaction by which acetonechloroform is obtained is not obvious. It is not, in view of these experiments, an addition-product in the ordinary acceptance of that terminology and its usual name therefore is ill-advised.

The simplest reaction and the one which seems to have the greatest probability may be expressed in two stages, thus:

The potash seems to be reacting here as a catalytic agent. In favor of this view is the fact that a better yield is obtained when a relatively small amount of potash is used. This potash is gradually removed by action on the chloroform, giving potassium chlorid, formate and water, but under the conditions given this decomposition is relatively slow. A proof of this view is not now possible, but will be the subject of a future investigation.

One, two or all the chlorin atoms can be substituted by aromatic radicles¹ by the Friedel-Craft's reaction. With caustic alkali it is readily converted into oxyisobutyric acid and the barium salt² of the acid has been prepared and analyzed. With phosphorus pentachlorid³ it forms chlorisobutyric acid chlorid, as well as other substances needing further investigation. It has

¹ Willgerodt and Geneiser. Jour. prakt. Chem. [2] 37, 365 (1888).

² Willgerodt. Ber. chem. Ges. Berlin, 15, 2305 (1882).

³ Jour. prakt. Chem. [2] 37, 365 (1888).

been reduced to trimethylcarbinol by nascent hydrogen.¹ From these reactions its constitution is undoubted; it is indicated by the formula $(\text{CH}_3)_2\text{C.OH.CCl}_3$. When crystallized from water or solvents containing water, or even if allowed to stand exposed to the moisture of the air, the crystals contain water. Willgerodt² finally obtained crystals by distilling with steam, and recrystallizing from aqueous alcohol and ether which melted at $81^\circ\text{--}82^\circ$ and gave on analysis the following figures:

	Found	Calculated
C	25.54	25.0
H	4.59	4.29
Cl	$\left\{ \begin{array}{l} 56.8 \\ 57.17 \\ 57.3 \end{array} \right.$	57.1

which indicate the formula $2[(\text{CH}_3)_2\text{C.CCl}_3.\text{OH}] + \text{H}_2\text{O}$. This formula had presumptive evidence in its favor from the fact that trimethylcarbinol itself is said to form a hydrate³ of the composition $2(\text{CH}_3)_3\text{C.OH} + \text{H}_2\text{O}$. Analysis for chlorine by the method of Carius gave us figures indicating a composition varying from one to two molecules of water to one of acetonechloroform. Therefore the following method was used to determine this point.

A round bottom flask was fitted with a cork containing a slit in the side. The cork was bored to fit a test-tube, and the test-tube was in turn fitted with a stopper containing a thermometer. The test-tube was partially filled with a weighed amount (about 10 g) of the anhydrous compound, the thermometer put in place with its bulb well down in the tube so as to be covered when the material melted, and the whole tube fitted into the bulbed flask, which was partially filled with water to a convenient amount. Four such pieces of apparatus were arranged

¹ Willgerodt and Dürr. Jour. prakt. Chem. [2] 39, 283 (1889).

² Willgerodt. Ber. chem. Ges. Berlin, 16, 1585 (1883).

³ Butlerow. Liebig's Ann. 162, 229 (1885).

and into the test-tubes were run from a burette, amounts of water calculated to correspond to $1/2$, 1, $1\ 1/2$, and 2 molecules per molecule of acetonechloroform. In each case the same phenomena were observed. The apparatus was heated until the substance had entirely melted. *Two liquid layers were formed.* On cooling the thermometer would fall until a little below 75° . Crystals having started to form it would rise to 75.2° and remain constant until the second liquid phase had disappeared. We thus obtained the quadruple point for solid, two solutions, and vapor, which we had already obtained by a previous experiment for that purpose. But we were forced to the conclusion that our supposed anhydrous material really contained water, or the substance contained less than $1/2$ molecule of water of crystallization. The existence of a hydrate then became questionable and was answered by the following experiment:

A convenient quantity of dehydrated substance was placed in such an apparatus as the one just described, with the addition of wire stirrers run through slits in the sides of the corks. The apparatus was heated until the substance melted and then allowed to cool. As soon as crystals began to form, they were churned into a slush by the stirrer, and then a few drops of water would be added from a pipette with long capillary stem. The freezing-point was lowered; the crystals immediately dissolved. This process was repeated until a mixture was obtained which both melted and froze sharply at 75.2° . This was the lowest point reached. On the addition of more water, *the freezing-point did not rise*, but a second liquid layer separated. The fall of the freezing-point was regular, and the existence of a quadruple point between 75.2° and 92° was answered negatively. Consequently, *no hydrate exists*. Attempts to remove the water and raise the melting-point by subjecting it to great pressure between folds of filter paper were unavailing. By sufficiently strong pressure the substance was so driven into the films of fine Swedish filter paper as to make it almost impossible to separate it mechanically, but specimens so treated showed no elevation of the melting-point.

An attempt to accurately determine the melting-point of

the substance was made in the following way: A test-tube with side arm, such as is used in the Beckmann freezing-point apparatus, was fitted with a thermometer, and by means of the side arm attached to a Chapman filter-pump, with the usual intervention of a Bunsen flask. The tube was partially filled with the substance, sufficient when melted to cover well the bulb of the thermometer. It was then surrounded by a hot water-bath. The temperature of the bath was raised, the melting-point and freezing-point of the substance noted, and then the aspirator would be put in operation for awhile, the bath being kept a little below the melting-point of the substance. In the early part of the operation a fairly large amount of water and substance sublimed into the upper portions of the tube. By repeating the operation, we finally obtained a substance which melted a little above 97° and all solidified before reaching 96° , apparently an approximately pure product. It absorbed moisture so rapidly however, that it was considered inexpedient to attempt an analysis.

It would appear from these facts that the substance does contain water, and in varying amounts. That the water cannot be detected or eliminated by mechanical means. That it is not present to form a hydrate. Therefore it is probably present to form a solid solution. Similar cases have recently been reported by Tammann,¹ who investigated certain of the zeolites. He found that heulandite, desmin, and chabazite, when fully hydrated, contained more water than could be accounted for by the accepted formula, that they lost water regularly over a very wide range, and no inversion point could be detected. The crystals remained throughout clear and transparent. Acetone-chloroform presents additional features in forming two liquid solutions with water and this subject we will investigate at once.

From the work here recorded we conclude:

- I. The existence of but one acetonechloroform, a white crystalline solid, a derivative of trimethylcarbinol.
- II. The substance is not a simple addition-product, and can-

¹ Wied. Ann. **63**, 16 (1897); Zeit. anorg. Chem. **15**, 318 (1897).

not be resolved into its original constituents by direct means.

III. The substance forms no definite hydrate.

IV. The temperature of the quadruple point for solid, two solutions and vapor in the system acetonechloroform-water, is 75.2.

V. The melting-point is near, but above 97°, and in all probability perfectly anhydrous material has not yet been obtained.

VI. The system acetonechloroform and water seems to present the remarkable case of a solid solution and two liquid solutions.

Further investigation of conclusions V and VI will be described in a subsequent communication.

We would here record our acknowledgment of the courtesy of Professor W. D. Bancroft, to whose suggestions the success of the investigation is largely due.

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