

VAPOR-PHASE
CHLORINATION OF PARALDEHYDE

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By

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INTRODUCTION

The purpose of this work was to determine whether the vapor-phase chlorination of acetaldehyde would give a practical yield of trichloroacetaldehyde (chloral).

It seemed possible that direct vapor-phase chlorination of the aldehyde would give fewer by-products, involve fewer steps, and be more adaptable to a continuous process than the present commercial method of production of chloral which involves chlorination of liquid ethyl alcohol and subsequent distillation from sulfuric acid.

This work is an extension of the work of W. E. Taylor, who investigated the vapor-phase chlorination of ethyl alcohol (27).

HISTORY

Chloral and its water-addition product, chloral hydrate, have long been important for their bactericidal, hyponotic, and antipyretic properties. The relatively recent extensive use of chloral as an intermediate for the superior insecticide 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (D.D.T.) has accentuated interest in its production.

Several methods have been suggested and used to some extent for the production of chloral. The oldest and still the most important method is the chlorination of ethyl alcohol in the liquid phase. As early as 1832 Liebig (15) prepared chloral by chlorination of absolute alcohol. Production by this method was of commercial importance by 1873 (6), and its perfection and its adaptation to a continuous process have remained the most fruitful lines of research for manufacturers (12)(7).

Other methods suggested more recently include: (a) treatment of carbon tetrachloride with formaldehyde at high pressures (8), (b) electrolytic reaction of ethyl alcohol and sodium chloride (9), and (c) chlorination of ethylene chlorohydrin (28).

There has been some controversy relative to the products of chlorination of aldehydes. In the earliest work found listed, Wurtz in 1857 claimed that the reaction of chlorine with dry acetaldehyde (liquid-phase) produced acetyl chloride and α -chloroethyl acetate and that the aldehyde group was attacked exclusively unless the aldehyde was allowed to remain in an excess of chlorine, in which case the methyl group reacted (30).

In 1870 Pinner and Kraemer began a series of experiments on the action of chlorine on acetaldehyde undertaken chiefly in the hope of thus obtaining

chloral and being able to utilize the valueless residue from the first runnings obtained in the distillation of crude alcohol. In the first experiment (18)(19) chlorine was passed into aldehyde, which was at first carefully cooled in a freezing mixture and was heated to 100° C. only at the close of the reaction. By this reaction no chloral was produced nor did the experimenters succeed in any case in detecting acetic acid, acetyl chloride or α -chloroethyl acetate. A product boiling at 163-165° was isolated which was at first believed to be "crotonic chloral" formed by aldol condensation followed by chlorination. Later experiments established the fact that the product obtained in this experiment was actually α, α, β -trichlorobutyraldehyde (21).

Kraemer repeated the experiment and could not detect acetyl chloride nor α -chloroethyl acetate among the products of the reaction (13).

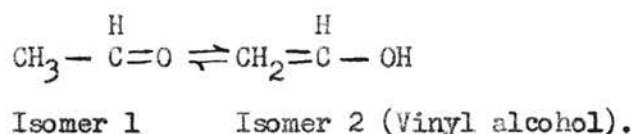
In a later reaction (20) similar to the first, except that moist fragments of marble were added to the acetaldehyde with a view to eliminating the hydrochloric acid (which had catalyzed the aldol condensation) as fast as it was formed, Pinner found that by reason of the presence of water, the greater proportion of the aldehyde was oxidized, but 50 grams of aldehyde yielded 15 to 20 grams of slightly impure chloral.

N. N. Gschukina reported in 1948 that chlorination of acetaldehyde at 16-18° proceeds through a substance composed of two moles of chloroacetaldehyde, one mole of acetaldehyde, and one mole of hydrogen chloride, which on distillation dissociates and gives 60% chloroacetaldehyde. Prolonged chlorination at 70-80° gives mainly dichloroacetaldehyde; while at 80-90° chloral forms mainly, up to 50%, with some α, α, β -trichlorobutyraldehyde (25). The temperature range of 70-90°, which is mentioned for the higher chlorinations, suggests that this may have been a vapor-phase reaction if simple acetaldehyde

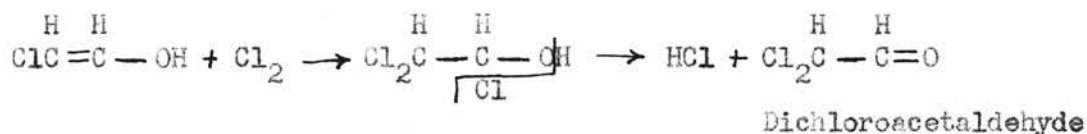
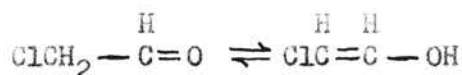
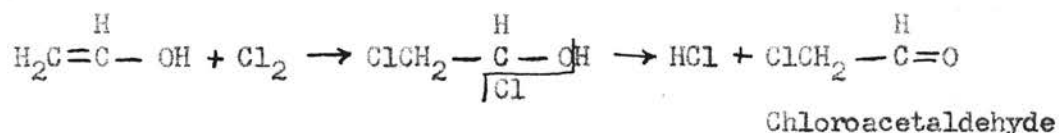
were used. However, since the report mentions that a definite quantity of aldehyde, 44 grams, was chlorinated until no more chlorine was taken up, it must be assumed, either that a solvent was used to hold the acetaldehyde in a liquid state, or that the acetaldehyde was confined in a pressure vessel. In either case the reaction would not be a continuous-flow, vapor-phase reaction such as has been attempted in this work.

PRELIMINARY DISCUSSION

The reaction desired and expected in this work was the substitution of chlorine atoms for the hydrogen atoms of the methyl group of acetaldehyde without touching the hydrogen atom on the carbonyl carbon. A good discussion of the proposed mechanism of this reaction is given by Wertheim (29). Wertheim states that in reactions with halogens the hydrogen atom of the alkyl group next to the carbonyl is replaced by halogen atom. This replacement of hydrogen atoms of acetaldehyde by halogen atoms is a rapid reaction even at room temperature. An explanation of this may be found in the tautomeric structures possible to compounds which have a hydrogen atom on the carbon atom joined to the carbonyl group. These two forms for acetaldehyde are shown below:



It seems probable that the enol form of acetaldehyde takes part in the reaction with chlorine as follows:



Another repetition of the above type of reaction would lead to the production of trichloroacetaldehyde or chloral.

Although discovered early in the study of Pinner's work, not much credence was given at first to Wurtz's claim that acetyl chloride and α -chloroethyl acetate were formed by chlorination of acetaldehyde. More credence was given to Pinner's claim that the formation of hydrogen chloride caused aldol condensation to compete with simple chlorination. It was therefore decided to place water and marble chips in the apparatus, as Pinner had done, to oppose this tendency.

The principal products expected from the reaction, were then: Chloroacetaldehyde, dichloroacetaldehyde, chloral, α, α, β -trichlorobutyraldehyde, and some carbon tetrachloride, chloroform, and aldehydes from decomposition of products.

In this work it was first attempted to use acetaldehyde (boiling point, 21°) by allowing it to vaporize at room temperature and pass through a gas flowmeter in the same manner as the chlorine gas. Much difficulty was experienced in finding a flowmeter liquid in which acetaldehyde was insoluble. It was found finally that low-viscosity silicone oil did not dissolve an appreciable amount of acetaldehyde. Two short runs were actually made in which acetaldehyde vapors were metered through a flowmeter containing silicone oil and caused to react with chlorine at $90-100^{\circ}$. However, the hydrogen chloride formed in the reaction eventually backed up in the system and caused the polymerization of the acetaldehyde, probably to paraldehyde (boiling point, 124°), which condensed at room temperature and filled the arms of the flowmeter. Also, it was found difficult to control the flow of acetaldehyde vapors from the bottle, as the liquid aldehyde cooled upon boiling. Since the difficulties experienced in controlling and measuring the flow of acetaldehyde vapors seemed insurmountable, it was then decided to use acetaldehyde

in the form of paraldehyde. The rate of flow was measured using liquid paraldehyde, which was later vaporized in contact with chlorine in the reaction chamber.

It was decided to do the chlorinations with a chlorine-to-acetaldehyde ratio slightly in excess of the theoretical ratio of three to one required for the production of chloral, and at the highest temperatures and flow rates (within the limits of the equipment used) at which the reaction would proceed without explosion of the reaction mixture. It was thought that the higher temperatures might favor complete chlorination in competition with the reversible aldol condensation.

EXPERIMENTAL

Apparatus. The apparatus used in the experiment, which is shown diagrammatically in the accompanying figure, consisted of five functional assemblies:

(a) the chlorine gas supply and flowmeter, (b) the paraldehyde supply and metering device, (c) the mixing venturi and heated reaction chamber, (d) the receiver for the final products, and (e) a wash tower for disposal of gases.

A small tank (5 lb. net weight) of commercial-grade chlorine was used. The flow of the chlorine was regulated by means of the tank valve. The flow rate of chlorine was measured by allowing it to pass through a calibrated flowmeter of the type developed by Benton (2). Concentrated sulfuric acid, which, for better visibility, had been given an orange-red color by the addition of a small amount of solid phenolphthalein, was used for the flowmeter liquid. From the flowmeter the chlorine passed through a small trap, which during the experiment contained a few drops of water and several chips of marble to forestall a back flow of hydrogen chloride gas produced by the reaction. Then the chlorine passed into the chlorine-paraldehyde mixing venturi.

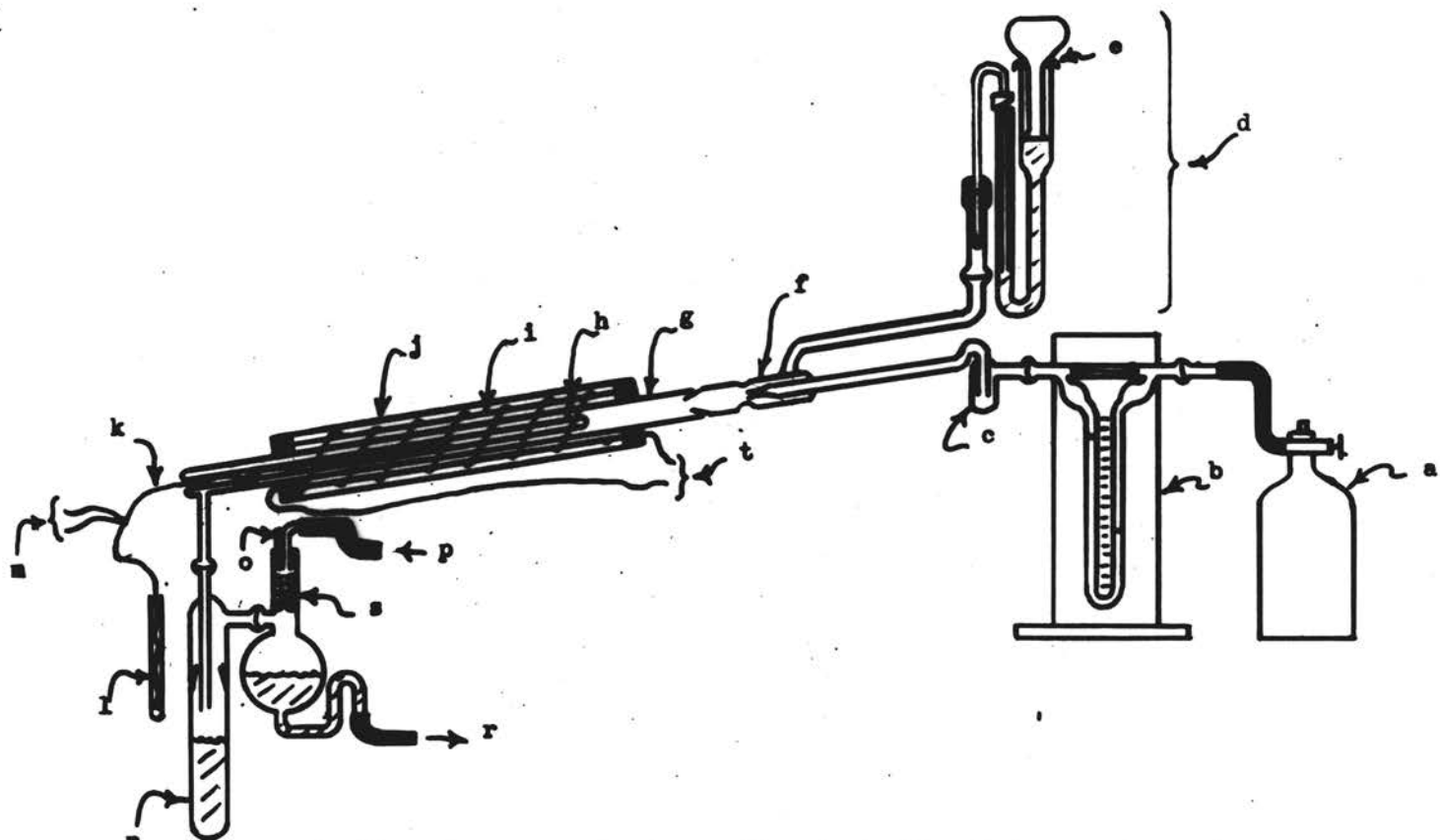
U.S.P.-grade paraldehyde was used. The supply of paraldehyde was drawn from a 100-ml. volumetric flask inverted and suspended in the enlarged open end of a U-tube containing paraldehyde so that a constant level of paraldehyde was maintained at the level of the mouth of the flask. The unjointed arm of a smaller U-tube was supported in the other arm of the large U-tube by a section of cork, which held the smaller tube and rested on the edge of the larger one but left the latter open to atmospheric pressure. The smaller U-tube consisted of a bent length of one-millimeter-inside-diameter capillary tube, with a

95-mm. length of fine capillary tube (from a broken 360° thermometer) butted up to the end of its shorter arm and held by Tygon tubing.

The thermometer section of the capillary U-tube was centered and held by Tygon tubing in one half of a ground-glass spherical joint which connected into the main apparatus. The paraldehyde was syphoned through the thermometer capillary and flowed through a short length of tubing into the mixing venturi.

In the mixing venturi (11) the chlorine inlet tube was drawn to a capillary, the end of which was located in the throat of the venturi. The paraldehyde was introduced through an opening in the mixing unit behind the venturi. The purpose of the venturi was to insure thorough mixing of the chlorine and aldehyde vapors before they were introduced into the reaction chamber, but its effectiveness was no doubt lost when liquid paraldehyde was substituted for low-boiling acetaldehyde in the experiment.

The reaction chamber consisted of three concentric glass tubes, each forty centimeters in length and with internal diameters of twenty-five, thirty-five, and forty millimeters, respectively. The paraldehyde and chlorine mixture passed through the innermost tube. The second tube was wound with a nichrome heating coil and was separated from the inner tube by a dead air space. The third tube was separated from the second by a dead air space and served to insulate it from the atmosphere. The ends of the tubes were sealed with a paste made by soaking asbestos paper in water. A thermocouple well was located in the center of the innermost tube. It housed a doubled chromel-alumel junction thermocouple. The hot junction of the thermocouple was kept at the midway point of the reaction chamber. The cold junction of the thermocouple was kept at a constant temperature of 0° C. in a Dewar flask containing a water-ice mixture. The thermocouple was connected to a calibrated Hoskins pyrometer.



a. chlorine tank, b. flowmeter, c. trap, d. paraldehyde feeding device, e. bent glass rod supports, f. mixing venturi, g. reaction tube, h. thermocouple well, i. wire wound heating tube, j. air jacket, k. hot junction of the thermocouple, l. cold junction, m. to the pyrometer, n. receiver, o. air vent, p. water inlet, r. water outlet, s. wash tower, t. to the powerstat.

Chlorinating Apparatus

From the reaction chamber the gases passed into the receiver, which was kept at a constant temperature of 0° C. in a water-ice mixture. The reaction products were condensed in the receiver.

The excess chlorine and the hydrogen chloride formed passed uncondensed to a wash tower filled with Raschig rings. Water was allowed to trickle into the top of the tower and was drawn off at the base. Since the tower was vented to the atmosphere, the pressure inside the system was atmospheric.

All joints in the system were ground-glass spherical or standard-taper connections, with the exceptions of: the connections between the chlorine tank and the flowmeter, the connections for the capillary tube placed in the flowmeter, and the connection for the thermometer tube and spherical joint placed in the paraldehyde-feeding device. Gum rubber or Tygon tubing was used for these connections.

The chlorine flowmeter was calibrated (Table 1) by use of a gas buret assembled from two 500-ml. burets and patterned after one described by Daniels et al (5).

Table 1
Calibration Data for the Chlorine Flowmeter

Height of Flowmeter Head (inches)	Rate of Flow of Chlorine (liters/hour)
2.0	1.75
3.7	2.90
5.7	4.35
8.5*	6.26
11.0	7.60
11.7	7.32

* This point was read from the graph prepared, not actually measured.

The paraldehyde-feeding device was calibrated by counting the drops contained in one milliliter and then adjusting the height of head between the bottom of the thermometer capillary and the surface of the liquid at the mouth of the volumetric flask (by sliding the cork along the syphon tube) to give the required drop time. It was calculated, by use of the perfect gas law, that 3.6 ml. of paraldehyde were equivalent to two liters of acetaldehyde vapors at room temperature and pressure. One drop of paraldehyde falling every 24.4 seconds delivered this amount of paraldehyde per hour.

The Hoskins pyrometer was connected to the thermocouple and calibrated by heating the hot junction of the thermocouple in an oil bath while the cold junction was kept at a constant temperature of 0°C . by immersion in an ice-water bath. It was found that each one-degree rise in the temperature of the oil bath gave a three-degree rise in the pyrometer reading.

Chlorination Procedure. Three different runs, each under different conditions, were made. The first run is described in detail, while only the changes in conditions are pointed out for the other two.

For the first run the apparatus was assembled as shown in the diagram. A few chips of marble and several drops of water were placed in the small trap between the chlorine flowmeter and the mixing venturi. The tap was opened so that a small stream of water trickled through the wash tower. The terminal of the hot junction of the thermocouple was inserted in the well to the mid-point of the reaction chamber; the cold junction was placed in an ice-water mixture in a Dewar flask. A substitute cold-trap receiver containing chips of marble and 10 ml. of water was set in place. The receiver also was immersed in an ice-water mixture. The paraldehyde was syphoned over, and the head was adjusted to deliver one drop of paraldehyde every thirty-three

seconds, equivalent to one and one-half liters of acetaldehyde vapors per hour. The chlorine tank was opened and adjusted to give a flowmeter head of 11 inches equivalent to 7.5 liters of chlorine gas per hour. This constituted a chlorine-to-aldehyde ratio of five to one. It was not intended that such a large excess should be used but an error in calibration of the chlorine flowmeter, which was later corrected, led to use of the ratio in this one run.

The paraldehyde and chlorine were allowed to flow through the system without heating for about fifteen minutes to displace air from the system. After fifteen minutes the Powerstat used to heat the wire coil was turned up gradually so that the reaction chamber was heated to 110° within a period of forty-five minutes. After the temperature reached 110° the substitute receiver was replaced with a clean receiver containing chips of marble and 10 ml. of water. The reaction chamber was then heated to 175° during the course of an hour. During the remainder of the run the rate of flow of the reactants was held constant, and the temperature was kept between 165 - 180° . The receiver was replaced once more during the run with a clean receiver containing marble chips and 10 ml. of water. The run was closed down after 53.25 hours of continuous operation. The reaction went smoothly the entire time, with no explosions or incidents of any kind.

The run yielded approximately 100 ml. of bright yellow liquid, including water. Only one liquid phase was observed. More marble and an additional 10 ml. of water were added to the combined portions, which were kept in an open test tube in an ice-water mixture for several days, and finally in an open test tube at room temperature. Dissolved hydrogen chloride, and possibly other constituents, reacted vigorously with the marble at first and never ceased entirely to react. The liquid product became almost

colorless upon standing and then gradually assumed a pale orange-brown tint and syrupy consistency.

The second run was similar to the first except that the flow rate of paraldehyde was adjusted to one drop every 24.4 seconds equivalent to two liters of acetaldehyde vapors per hour, while the flow rate of chlorine was adjusted to give a head of 8.5 inches, equivalent to 6.26 liters of chlorine gas per hour. This constituted a chlorine-to-aldehyde ratio of 3.13 to one. Receivers were exchanged several times and each new receiver contained marble chips and 10 ml. of water. The run was closed down after 34.25 hours without incident.

The run yielded 200 ml. of bright yellow liquid, including water, which was treated like the batch from the first run. This liquid likewise reacted with marble and became almost colorless and finally darkened and became syrupy upon standing. However, this batch, resulting from a run using a lower chlorine-to-aldehyde ratio, darkened more than the first and after a week assumed a dark-brown color.

The third run was intended to be precisely like the second except that, for the purposes of effecting easier separation and analysis of the products, water and marble were to be eliminated both from the small trap preceding the mixing venturi and from the cold-trap receiver.

However, it was found that without the water and marble, explosions occurred in the reaction chamber at any temperature above 125°. The equipment was dismantled and cleaned, reassembled and checked for leaking joints. Then, the run was tried again with the same results. A compromise was then tried in which a few chips of marble and several drops of water were placed only in the small trap preceding the mixing venturi. The explosions still occurred at 125°. Finally the temperature was lowered to 110-120°, and a run

was made. After about 40 ml. of product was collected in the cold trap receiver, explosions occurred even at temperatures as low as 105° . The run was closed down after 13.25 hours of operation.

The run yielded 46 ml. of bright yellow liquid with black particles of free carbon suspended in the upper portion. This batch was stored in the receiver and kept in an ice-water bath for half a day and then distilled.

Separation. The reaction products were expected to include principally chloral with some unreacted aldehyde, chloroacetaldehyde, dichloroacetaldehyde, α, α, β -trichlorobutyraldehyde, and carbon tetrachloride. Therefore, the first separation attempted was a variation of a method recommended by Beachell and Sveda (1) for the purification of chloral. By this method five per cent by weight of concentrated sulfuric acid is added to the reaction mixture and the whole is distilled to yield chloral in a state of purity sufficient for use in the manufacture of D.D.T. For the purposes of this experiment, in order to remove some of the water that had been added, a large excess of sulfuric acid was added. When two milliliters of reaction mixture from run number one combined with eight milliliters of sulfuric acid were distilled, almost all of the two milliliters distilled over within the narrow range $110-120^{\circ}$. However, when a larger quantity, five milliliters, of the same batch of reaction mixture plus 20 ml. of sulfuric acid was distilled over, almost all of the five milliliters was again recovered; but the boiling temperature varied from $115-157^{\circ}$. Approximately the same results were obtained when the mixture of product and sulfuric acid was distilled immediately as when the product was allowed to stand overnight in sulfuric acid before distillation. When 20 ml. of product from run number one was added to 20 ml. of concentrated sulfuric acid, allowed to stand overnight and then distilled through a

three-ball Snyder column, 15 ml. of distillate boiling within the range 104-126° was recovered. However, when this 15 ml. of distillate was added to 15 ml. of sulfuric acid and redistilled, the boiling behavior was erratic. About 13 ml. of distillate was recovered; 7.5 ml. distilled over within the range 102-110°; after this the temperature went rapidly up to 144°, then dropped to 110°, then ascended again to 150° and higher.

No separation was effected by this method. In fact, the large percentage of recovery in each case above indicated that even the water was not being effectively removed; and the erratic results indicated that decomposition and/or polymerization were taking place. It was therefore decided to try phosphoric acid as a milder agent during distillation.

Twenty-five milliliters of reaction mixture from run number one was added to 20 ml. of 85 per cent phosphoric acid, allowed to stand 16 hours and then distilled through a three-ball Snyder column. Fifteen milliliters of distillate boiled over within the range 104-110° and eight milliliters within the range 110-112°. The total amount of distillate was 23 ml. The first fraction of 15 ml. was added to 15 ml. of phosphoric acid and redistilled. Fourteen milliliters of distillate, boiling within the range 104-106°, was recovered. As a check, 40 ml. of reaction mixture from run number two was submitted to like treatment except that the mixture of product and phosphoric acid was allowed to stand only one hour. In this case the results shown in Table 2 were obtained.

Table 2

Results of Distillation of 40 ml. of Run No. 2 Reaction
Mixture from 85 per cent Phosphoric Acid

Cut No.	Boiling-Point Range (° C.)	Volume of Distillate (ml.)
1	95-100	2
2	101-105	5
3	105-110	8
4	110-115	8
5	115-120	4
6	120-125	5
7	125-127	2
		<u>34</u> Total

Again, no separation was obtained. However, the results in these last three distillations, particularly the first and second in which the total boiling range was 104-112°, seemed significant in indicating that a major portion of the product might be a single low-boiling compound which distilled from phosphoric acid in combination with water. It was thought that the shorter time during which the reaction mixture stood in combination with phosphoric acid prior to distillation might account for the presence of slightly higher-boiling fractions in the final distillation.

Experiments with ether extractions of small amounts of reaction mixture now revealed the surprising fact that while ether would extract about 75 per cent of untreated reaction mixture it would extract only a minute portion of reaction mixture which had been completely neutralized with sodium hydroxide or sodium bicarbonate. It had been evident from the beginning that the

reaction mixture was acid, but this acidity was attributed to the presence of hydrogen chloride formed during the reaction. However, it was now evident that a considerable part of the products of the reaction was organic acid.

Separation was now attempted by ether extraction of 40 ml. of reaction mixture from run number one. This mixture was expected to contain, besides the chlorinated products, water, calcium chloride, calcium carbonate and hydrogen chloride. Twelve milliliters of aqueous residue left from this extraction was discarded. The ether extract was then neutralized with sodium hydroxide and the ether layer was separated and dried over Drierite. The water layer was acidified with hydrochloric acid and again extracted with ether. However, since the volume of water was now about 200 ml., and since the organic products seemed quite water-soluble, this second extraction was not complete, even though several extractions were made. The ether layer was now separated and dried over Drierite, and the water layer was discarded.

After drying overnight the two ether extracts were decanted, and each was distilled. The ether layer which had been separated from the basic solution and should have contained the neutral products of the reaction yielded only one milliliter of dark-brown liquid. This confirmed our conclusion that most of the reaction products were organic acids. However, the ether layer which had been separated from the acidic solution and which should have contained all the organic acids from the reaction yielded only 12 ml. of dark red-brown liquid. About 15 ml., or half the organic portion of the reaction mixture, was thus not extracted.

Like results were obtained by a similar extraction of 40 ml. of reaction mixture from run number two.

Since so much of the organic portion of the mixture was lost in the excess of water added in attempting separation in the above extractions,

the remainder of the reaction mixture from run number two (run number one was now exhausted) was subjected to a simple ether extraction without attempt at separation. One hundred and fifteen milliliters of the mixture was extracted by 275 ml. of ether in portions varying from 15 to 100 ml. each. An aqueous residue of about 30 ml. was discarded. The ether extract was dried with Drierite overnight, and the ether was distilled to leave 98 ml. of dark-brown liquid which still contained 10-15 ml. of ether. This residue was stored over Drierite pending its analysis.

Analysis. Solubilities were first checked. The reaction mixture proved to be soluble in all organic solvents, except for turbidity caused by the water present, and in water. A white precipitate of calcium salt was obtained in both sulfuric acid and phosphoric acid. When completely neutralized with sodium bicarbonate or sodium hydroxide the reaction mixture had a sweet, fruity odor indicative of the presence of an ester.

Extracts of the reaction mixtures did not decolorize a five per cent bromine solution nor a two per cent potassium permanganate solution. This indicated that all products of the reaction were saturated, as was expected.

Since it was thought that the principal products would be chlorinated aldehydes, classification tests were attempted to see whether this was true. Tests with both Fehling solution and Benedict solution gave copious red precipitates indicating the presence of aldehydes in the reaction mixture. However, no solid was precipitated when sodium bisulfite was added to a water solution of the reaction mixture. Also, the results of the Schiff test were unsatisfactory; in the presence of the fuchsin-aldehyde reagent the reaction mixture gave a faint purple only after ten minutes.

Confirmation of the presence of chlorinated compounds was sought through various color tests. Heating a few drops of reaction mixture in three milliliters of 20 per cent sodium hydroxide covered by a two-millimeter layer of pyridine gave a clear pink to deep-red color in the pyridine layer indicating the presence of a trichloromethyl compound (23). Similarly, heating a few drops of the reaction mixture with phloroglucinol, cooling, and adding potassium hydroxide gave a deep red-brown color indicative of the presence of a trichloromethyl compound (14). However, the results were only partially successful for a color reaction of chloral suggested by Pesetz (17) in which the colors yellow-pink, violet, blue, orange-red, violet and red are successively noticed when chloral is slowly heated in a solution of sulfuric acid, potassium bromide and resorcinol and then treated with water and finally sodium hydroxide. The only two colors of the series that were definitely distinguished were the initial yellow-pink, and a faint blue ring at stage three. It could therefore be assumed from this test only that some of the groups present in chloral might be present in the reaction mixture.

Both the tests for aldehydes and the tests for trichloromethyl compounds thus gave mixed results, some being positive and some negative or doubtful. It was then attempted to confirm the presence and identity of any aldehydes present by the making of derivatives (3) (26).

Preparations of the oxime, semicarbazone, and 2,4-dinitrophenylhydrazone were attempted. No derivatives were obtained in any case. A reaction was obtained with the 2,4-dinitrophenylhydrazine, but the product did not melt although it was heated above 300° .

Also, chloral hydrate from the storeroom was distilled with the findings that: the hydrate distilled alone at $98-99^{\circ}$, and immediately recrystallized in the condenser and receiver; the hydrate distilled from an equal amount of

water at a constant temperature of 97° and immediately recrystallized; and the hydrate distilled from phosphoric acid at a constant temperature of $96-97^{\circ}$. These observations cast doubt that the products of this reaction which distilled from phosphoric acid over the range $95-127^{\circ}$ (see Table 2) contained any considerable amount of chloral or the lower-boiling aldehydes containing less chlorine.

Finally preparation of an intermediate of isatin, melting at 175° , as reported in Organic Syntheses (16) was twice attempted. The reference stated that chloral by this procedure gave 80-91 per cent yield of the solid intermediate; whereas two attempts using a portion of the reaction mixture as a reactant gave no yields whatsoever of any solid organic compound.

It was therefore concluded that chloral or other aldehydes were present only in trace amounts and formed no considerable body of the products of this reaction. It was concluded, also, that the trichloromethyl compounds indicated by the color tests were compounds other than chloral and probably consisted principally of simple chloroform and/or carbon tetrachloride formed by decomposition of reagents and products.

It was at this point that experiments with ether extraction revealed that a considerable portion of the reaction products were organic acids. Identification based on this knowledge immediately proved more fruitful.

First, some of the data already obtained were more readily explained. The fruity, ester-like odor obtained on neutralization of the reaction mixture with base is indicative of the presence of the α -chloroethyl acetate reported by Wurtz. Also, the boiling points of $113-116^{\circ}$ and $119-121^{\circ}$ reported for this ester and the report that the ester readily decomposes in water to yield acetic acid, acetaldehyde and hydrogen chloride (10) are in line with accumulated data.

In addition, a degree of correlation could be traced between the boiling-temperature data contained in Table 2, and boiling-temperature data found (22) for acetic acid-water mixtures (Table 3).

Table 3
Boiling Temperatures at Atmospheric Pressure
of Acetic Acid-Water Mixtures

Acetic acid (mole per cent)	Boiling Point ($^{\circ}$ C.)
0.0	100.0
5.0	100.3
10.0	100.6
20.0	101.3
30.0	102.1
40.0	103.2
50.0	104.4
60.0	105.8
70.0	107.5
80.0	110.1
90.0	113.8
95.0	115.4
100.0	118.1

Investigation of the acid products was begun by determining neutralization equivalents. The equivalent weights were run on portions of reaction mixtures on which no separation, except the removal of some of the water, had

been attempted. The results were as follows: an indicated weight of 127.5 for a portion of run number one distilled from sulfuric acid; 127.5 and 128.8 for portions of run number one distilled and redistilled from phosphoric acid; 124 and 125 for portions extracted with ether, after neutralization and subsequent acidification, from run number two. These equivalents confirmed that a high proportion of the reaction mixture was acid. The weights obtained are high for simple acetic acid (60) but are near an average of the weights of chloroacetic acid (95), dichloroacetic acid (130), and trichloroacetic acid (165). Also, it was noted that α -chloroethyl acetate (123) would yield two acids, acetic acid and hydrochloric acid, upon hydrolysis so that the indicated equivalent weight would be only half of the actual equivalent weight. The presence of any neutral compounds such as aldehydes, carbon tetrachloride, chloroform, or even water would add to the observed equivalent weights. Any dissolved hydrochloric acid would lower the observed equivalent weights.

Preparation of derivatives of the acids was now begun. The first derivatives were prepared from portions of reaction products extracted with ether, after neutralization and subsequent acidification, from run number two. An anilide was obtained which melted at 129-130° after the second recrystallization. The melting point of the anilide of chloroacetic acid is listed as 134°. A benzylisothiuronium derivative melted at 146-148° after the first recrystallization. A mixture of this derivative with the original reagent (melting point, 150-151°) melted at 124-141°. The corresponding derivative of trichloroacetic acid melts at 149°. A *p*-phenylphenacyl bromide derivative melted at 103-104° after the second recrystallization. A mixture of this derivative with the original reagent (melting point, 125.5°) melted at 87-101°. No definite indications were received

from this derivative. The melting point of the corresponding derivative of acetic acid (111°) is closest to the observed melting point; but the melting point of the derivative of chloroacetic acid is 116° . Preparations of the amide and phenylhydrazide were attempted without success.

At this time preparation of the methyl esters was attempted using 50 ml. of the ether extract taken from run number two, 60 ml. of methyl alcohol, and 3 ml. of concentrated sulfuric acid. After esterification was considered complete, distillation of the reaction mixture was begun. Distillation began at 45° . The temperature went rapidly up to 57° , and several milliliters came over at $57-59^{\circ}$. The distillate collected within this range was considered to be the methyl ester of acetic acid (boiling point, 57.1°).

Afterwards, the temperature went gradually up to 70° , and distillation was stopped for fear the hot sulfuric acid would decompose the esters. The distillate was recombined with the residue from the distilling flask and the whole was neutralized with water and solid sodium carbonate. The water-insoluble layer which separated at this point was removed and the water layer was discarded. Only about ten milliliters of ester was recovered. This amount was distilled and the boiling points recorded at every 0.2 ml. were plotted. Distillation began at 65° and the temperature went quickly up to 125° . At 125° the temperature curve began to flatten out and about a third of the distillate was collected within the range $125-132^{\circ}$. This was considered to be the methyl ester of chloroacetic acid (boiling point, 131.5°). From 132° the temperature curve swung up gradually to 142° then at once dropped slightly to 140° . It is possible that this portion of the curve indicated the presence of the methyl ester of dichloroacetic acid (boiling point, 143.0°), but insufficient distillate was collected to show a definite plateau in the temperature curve. Beyond 142° the temperature curve went sharply up

to 200°, but only decomposition products were obtained. Not all the information desired was obtained from this esterification. It was intended that esterification should lower and spread the boiling points of the several chlorinated acids so that they could be separated and identified by distillation. However, a poor choice of esters was made in that only the methyl ester of chloroacetic acid is relatively water-insoluble. The methyl esters of both formic acid (possible decomposition product) and acetic acid are quite water-soluble. These two esters were then lost in the neutralization process before the final distillation above was carried out. This explains why the temperature curve plateau at 57-59° noticed in the preliminary partial distillation was not noticed in the final distillation.

However, since the supply of reaction products was running low, it was decided to do a direct distillation of the last 48 ml. of extract from run number two rather than attempt a different esterification. It was expected that the chlorinated acids present would decompose below their boiling points, which proved to be the case, but valuable information was received concerning the remainder of the reaction (Table 4).

Table 4

Information from Direct Distillation of a 48-ml. Extract
of Reaction Products

Cut No.	Boiling Range (° C.)	Volume (ml.)	n_D^{25}	d_4^{25} (g./ml.)	Probable Compound
1	38- 64	6	1.3540	--	Ether; n_D 1.3497
2	90-103	3	1.3960	--	--
3	105-112	9	1.3930	1.1169)	Acetic acid;
4	112-115	10	1.3800	1.0748)	n_D 1.3718
5	115-164	3	1.4025	1.1704)	d 1.049
6	165-175	5	1.4416	1.4134)	Chlorinated acids and decomposition products.

As shown in the above table, 20 ml. of this extract, or half of the total quantity, excluding the first nine milliliters which was mostly ether left from extraction use, boiled over within the range 103-115° and had a refractive index and density approaching that of acetic acid. Since acetic acid is expected from hydrolysis of both acetyl chloride and α -chloroethyl acetate, it was not surprising that it should form the principal part of the reaction mixture after it was accepted that the reaction proceeded as claimed by Wurtz.

Cut number four from the above distillation, containing the portion considered likely to be most nearly pure acetic acid, was used to prepare derivatives. Three derivatives were obtained confirming the presence of acetic acid (Table 5).

Table 5

Derivatives of Acetic Acid from Run Number Two

Derivative	Melting Point Observed ($^{\circ}$ C.)	Melting Point in the Literature ($^{\circ}$ C.)
Anilide	108 -112	114
<u>p</u> -Toluidide	143.5-146	147
<u>p</u> -Bromophenacyl ester	81.5- 83.5	85

This concluded the major part of this work. But, since it was obvious that the acetyl chlorides must have been the first products formed in both runs one and two, and since the acetyl chlorides are lower-boiling than their corresponding acids and might therefore be capable of separation by simple distillation, a third run, described on page 14, was made in which water and marble were not present in the system. It was found impossible to make this run at temperatures above 120° , as compared to the $165-180^{\circ}$ for the other two runs, so that this run was not strictly under vapor-phase conditions, and precisely the same products could not be expected.

The only effort made at separation or identification of the 46 ml. of products from this last run was a direct distillation of the reaction mixture, after it had stood for eight hours, through an eight-ball Snyder column. The boiling-temperature curve was erratic, having a rounded peak with its climax at 86° (13 ml.) and then a valley at 72° (20 ml.). No plateau was found in the temperature curve at 55° , the boiling point of acetyl chloride. However, there was a definite but short plateau at 119° which may have indicated the presence of some α -chloroethyl acetate (boiling point, $119-121^{\circ}$).

Combination and redistillation of the cuts from the first distillation gave an even more erratic curve with four peaks and as many well-defined valleys. Since no definite stable products were distinguishable, the reaction mixture from this run was discarded.

DISCUSSION OF RESULTS

This work has disclosed the significant fact that at temperatures of 165-180° chlorine and paraldehyde react to give acetyl chloride, chlorinated acetyl chlorides, and probably α -chl methyl acetate rather than chlorinated aldehydes. All of the primary products were subsequently hydrolyzed to the corresponding acetic acids by the water which had been placed in the cold-trap receiver.

Including the methyl esters four derivatives were secured to confirm the production of acetic acid; two derivatives confirmed that of chloroacetic acid; an ester of dichloroacetic acid was possibly obtained; and one derivative was obtained for trichloroacetic acid.

One plausible explanation of the course taken by this reaction is that at the high temperatures used direct substitution of a chlorine atom for the hydrogen atom on the carbonyl group proceeds more rapidly than the tautomerism to the enol form which is required before substitution of the hydrogen atoms of the methyl group can take place. If this is the case, use of barium hydroxide as a catalyst to promote enolization as suggested by Conant and Thompson (4) and confirmed by Schreck (24) may yet permit production of chloral by a vapor-phase chlorination of acetaldehyde.

However, production of the acetyl chlorides by this process might be profitable if the chlorides could be recovered as such and not hydrolyzed to the acids. This would require the elimination of water from the system and the experience of this work indicates that under these conditions changes must be made to avoid explosions. One such change might be the mere reduction of the flow rates of the chlorine, or paraldehyde, or both.

Other possibilities are the introduction of an inert gas such as carbon dioxide or nitrogen into the system or the use of catalysts such as cuprous chloride.

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