THE VAPOR-PHASE CHLORINATION OF ACETALDEHYDE

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INTRODUCTION

Acetyl chloride has long been recognized as an important acetylating agent. For this reason, its preparation from many different sources has been investigated. Although it had been reported as early as 1857, the action of chlorine on dry, liquid acetaldehyde to produce acetyl chloride had been given little attention. Almost no chlorination of acetaldehyde in the vapor phase had been done.

The purpose of this work was to investigate the vapor-phase chlorination of acetaldehyde to see if this reaction could be an economical source of acetyl chloride. It was also hoped that there could be obtained from an examination of other products of the reaction additional information which would be useful in interpreting the reaction.

This work is an extension of the work of Taylor (24) on the vapor-phase chlorination of ethyl alcohol and of Hamm (7) on the vapor-phase chlorination of paraldehyde.

HISTORY

It had been generally assumed that the chlorination of acetaldehyde
proceeded by the substitution of the hydrogen atoms attached to the alpha-
carbon atom to give mono-, di-, and trichloroacetaldehyde (chloral). It
was in direct contradiction to this view, therefore, that in 1857 Wurtz
(25) reported that the chlorination of dry, liquid acetaldehyde gave acetyl
chloride and a compound (boiling point, 120°) to which he assigned the
formula $C_4H_7ClO_2$. This compound was later suggested by Simpson (21) to
be identical with the α-chloroethyl acetate he had produced by the reaction
of acetyl chloride with acetaldehyde.

The idea of producing chloral from acetaldehyde was not abandoned, how-
ever. In 1870, Kraemer and Pinner began a series of experiments on the
chlorination of acetaldehyde primarily to find a method of producing chloral
by utilizing the low-boiling wastes from the distillation of crude ethyl
alcohol. In the first experiment (10, 11), chlorine was passed into acetal-
dehyde cooled by an ice-salt mixture. The first noticeable change was the
separation of metaldehyde. From the beginning almost all of the chlorine
was absorbed. After a short time hydrogen chloride began to be evolved and
the mixture began to darken. The temperature of the chlorination mixture
was gradually raised to 100° during the course of the reaction. At the end
of twenty-four hours after no further absorption would take place, the reac-
tion mixture was a brown mass consisting of a lighter-colored upper layer
containing mostly hydrochloric acid and a darker lower layer. The two layers

were not separated but were distilled together. A considerable quantity of the material was collected between 90 and 100°, but the main portion distilled between 160 and 180°. No acetyl chloride, acetic acid or α-chloroethyl acetate was detected. The part distilling between 160 and 180° was believed to be "crotonic chloral" formed by the reaction of chlorine with the crotonaldehyde which had been formed by aldol condensation. A later analysis (17) established that this compound was actually α, α, β-trichlorobutyraldehyde.

Kraemer repeated the experiment and got the same results he had observed previously with Pinner. Still no acetyl chloride or α-chloroethyl acetate was detected (12).

In order to prevent the formation of hydrochloric acid, which had catalyzed the formation of crotonaldehyde, Pinner placed marble chips in moist acetaldehyde. The same procedure was followed as before. This time, however, a large amount of acetic acid was produced along with a small amount of chloral (15).

In a more complete analysis of the reaction products, Pinner found ethylidene dichloride, dichloroacetal, and ethyl acetate in addition to chloral, acetic acid, and α, α, β-trichlorobutyraldehyde (14, 16).

Work on this problem was then almost abandoned until 1931. In that year, a French patent stated that the chlorination of paraldehyde below 50°C. in the presence of mineral acids gave chlorinated paraldehydes which could be separated into chlorinated aldehydes upon distillation (22).

For the past seventy-five years, alpha chlorination, as reported by Kraemer and Pinner, has been generally accepted for the chlorination of acetaldehyde. It is common to find in textbooks the preparation of chloral from acetaldehyde by this means.

In 1942 Kato (9) reported in a Japanese patent that acetaldehyde and chlorine form acetyl chloride directly in the vapor phase but that the reaction was explosive at high temperatures and stopped with the formation of α-chloroethyl acetate at low temperatures; however, the specific area of patent coverage was the liquid-phase chlorination in solvents using acetic acid, acetic anhydride, or benzene at "slightly high" temperatures. In acetic acid, the yield was reported to be about 60%.

Shchukina (20), in 1948, reported that the chlorination of acetaldehyde at 16 to 18° gave a substance having the composition indicated by two moles of chloroacetaldehyde, one mole of acetaldehyde, and one of hydrogen chloride. The residue from the distillation of this substance gave "trichloroparaldehyde" (melting point, 83-84°C.). At 70 to 80°, dichloroacetaldehyde was formed; and, at 80 to 90°, trichloroacetaldehyde was formed. Although few details of the experiments were given, the last two temperature ranges--70 to 80° and 80 to 90°--suggest that the reactions were vapor-phase; if they were not, then the reactions must have been carried out with acetaldehyde under pressure or with paraldehyde. Moreover, it is known from the report that the reaction was not a continuous-flow reaction, for a certain quantity of acetaldehyde was chlorinated until no more chlorine was absorbed.

In 1950, Hamm (7) undertook the vapor-phase chlorination of acetaldehyde to see if chloral could be produced by this means. Because of technical difficulties, he was soon forced to use the trimer, paraldehyde, which he introduced into the reaction chamber as liquid paraldehyde. The reaction was carried out at 165 to 180° using an excess of chlorine. The reaction product, which was collected in receivers containing water, was found to consist of acetic acid and chlorinated acetic acids with the possibility of some α-chloroethyl acetate. When attempts were made to collect the product in dry receivers, unexplained explosions occurred.

It was the purpose of this work to see if the vapor-phase chlorination of acetaldehyde could be carried out with safety to give practical yields of acetyl chloride.

EXPERIMENTAL

Apparatus and Procedure

Although several different arrangements were used, these for the most part involved minor variations of the first apparatus constructed; consequently, a detailed description of the first will be given with only the variations pointed out for the others. A description of the run made or attempted will follow each description of apparatus in an effort to show clearly the results obtained. In all, eleven different runs were made.

Arrangement No. 1

The first arrangement used is shown in Figure 1 (p. 7). Commercial-grade nitrogen from a large tank was passed through a calcium chloride tube to the flowmeter. The flowmeter was constructed similar to the one designed by Benton (1), in which the gas is forced through a capillary, across which are connected the arms of a U-tube filled with a suitable liquid. The flow of the gas through the capillary causes a pressure difference and, accordingly, a difference in the heights of the flowmeter liquid. The flowmeter liquid used was a light mineral oil. It was necessary to calibrate the flowmeter by allowing nitrogen to flow through it at a constant rate. The nitrogen displaced water in a 500-ml. dispensing burette assembled with another 500-ml. dispensing burette filled with water and open to the air. As nitrogen was passed in, water was allowed to drain from both burettes in a way that maintained the columns of water balanced at the same height in the two burettes. The method was described by Daniels et al. (3). Because there was
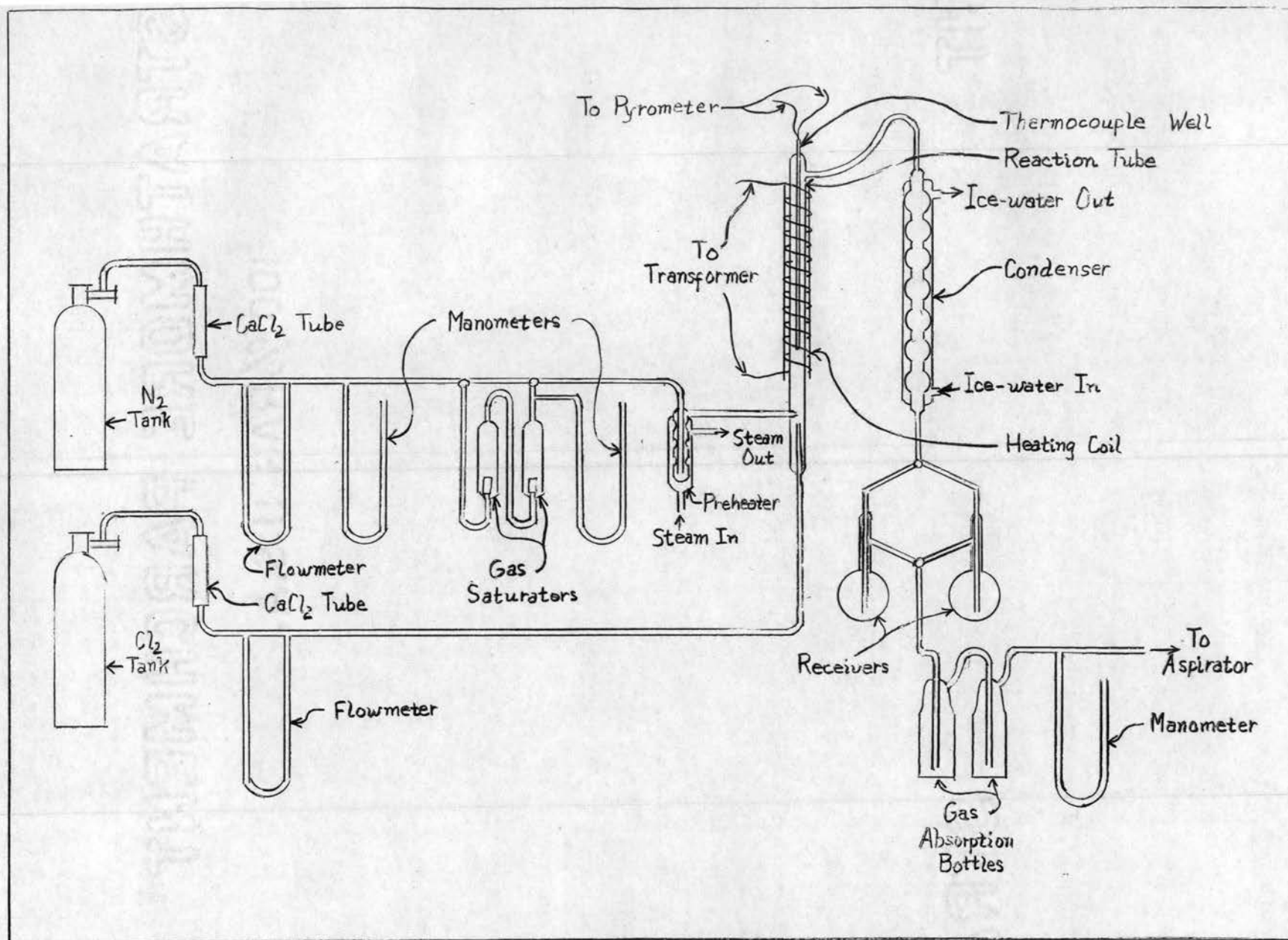
FIGURE 1 - CHLORINATION APPARATUS

appreciable water vapor present in the gas collected, it was necessary to correct for the vapor pressure of water. The time required to displace a certain amount of water was determined by a stopwatch. After the correction for the vapor pressure of water, the resultant rate was converted from milliliters per minute at the reduced pressure to liters per hour at standard pressure (760 mm. of mercury). After values for a large number of different flowrates had been thus obtained, a plot of the square root of the pressure (the change in height of the flowmeter liquid) against rate of flow was made. Nearly the straight line which would be expected theoretically was obtained.

From the flowmeter, the nitrogen passed either through the saturaters or to the preheater directly by means of two three-way stopcocks connecting the saturaters to the main line. This method permitted the system to be swept clear of air before a run was begun. The saturaters consisted of two tubes, each 30 mm. in diameter and 15 cm. in length, with a fritted-cylinder gas-dispersion tube sealed in the bottom. The saturaters contained acetaldehyde which could be kept at $0°$ by being immersed in an ice-water mixture contained in a large Thermos vessel. From the saturaters, the nitrogen-acetaldehyde mixture passed through a steam-heated preheater into the reaction chamber.

In a similar manner, chlorine from a five-pound tank was passed through a calcium chloride tube to the flowmeter and from there to the reaction chamber.

The reaction chamber was a vertical glass tube 20 mm. in diameter and 70 cm. in length. Chlorine was introduced through the bottom by means of a tube tapering to one millimeter in diameter at the jet end 14.5 cm. above the bottom. The nitrogen-acetaldehyde mixture was introduced 15 cm. above the bottom of the reaction tube and about 5 mm. above the chlorine jet.

From 5 cm. above the chlorine inlet extended the main reaction zone, which consisted of a 45-cm. section of the tube filled with 3-mm. glass beads. Enclosing the reaction zone were two concentric tubes, 43 cm. in length and 30 mm. and 40 mm. in diameter respectively. The 30-mm. tube, which was wrapped with nichrome wire, served to heat the reaction tube; the 40-mm. tube served to protect the heating unit from the atmosphere. Glass wool was packed around the top and bottom of each tube to permit the expulsion of air without allowing free circulation. Extending downward through the reaction tube was the thermocouple well with the thermocouple resting 11 cm. above the lower end of the heated zone. This point was chosen arbitrarily; but, once chosen, it was maintained through all the runs.

The thermocouple consisted of two chromel-alumel junctions in the well of the reaction tube connected to two chromel-alumel junctions in a cold well provided by a Thermos vessel containing an ice-water mixture. The leads from the thermocouple went to a calibrated Hoskins pyrometer. A graph had been prepared from which the temperature could be read directly from the pyrometer reading. It was found that a change in temperature of one degree Centigrade caused a change in scale divisions of about 2.8 divisions.

From the reactor, the reaction products passed upward through an inverted U-shaped tube and then down to a vertical Allihn condenser through which ice water was circulated by means of a centrifugal pump. From the condenser, by means of three-way stopcocks, the product could be collected in alternate 250-ml. receivers immersed in an ice-salt mixture. From the receivers, the waste gases were passed first through an empty gas-absorption bottle and then through a gas-absorption bottle containing a suspension of calcium carbonate. The unabsorbed gases were then drawn through an aspirator through which water was running just fast enough to produce a slightly reduced pressure. To

measure the pressure in the system there were manometers before and after the gas saturaters and before the aspirator.

The connections used throughout the apparatus were glass--ground-glass joints or glass seals--with four exceptions: (1) the rubber tubing used to connect the tanks to the calcium chloride tubes, (2) the Tygon tubing used to connect the manometers to the system, (3) the Tygon tubing used to hold the thermocouple well in place in the reaction tube, and (4) the rubber tubing used to carry the unabsorbed gases from the gas-absorption bottles to the aspirator.

In the system, each unit was constructed so that it could be easily removed for cleaning or replacement.

The apparatus, although consisting of many parts, was relatively simple in principle. It had been anticipated that the introduction of acetaldehyde into the reaction tube would be a problem. From the high vapor pressure, 337 mm. at 0° (4, 6), it appeared preferable to introduce an inert gas saturated with acetaldehyde at that temperature. An additional advantage of using an inert gas would be the dilution of the reacting gases to give a less vigorous reaction. A preheater was used so that the nitrogen-acetaldehyde mixture would not have an adverse cooling effect on the reaction tube. The decision to pack the reaction tube with beads came from the belief that this would promote a more uniform reaction. In order to prevent harmful channeling effects, it was necessary to use a vertical tube. The volume of the heated part of the reaction tube was 85 ml. with the thermocouple well in place. It was found that the beads had a free space of 40%. The actual volume of the packed column, therefore, was 34 ml.--the value used in calculating contact time.

Run No. 1

In the first run, the reaction tube was heated to 112° before the flow of nitrogen was started. The aspirator was adjusted so that the nitrogen passed through the flowmeter at nearly the same pressure under which the flowmeter was calibrated. Chlorine was also permitted to pass through the reaction tube. After the system had been swept nearly free of air, and after the flow of chlorine had been stopped, the stopcocks on the saturaters were turned to allow the passage of nitrogen through the acetaldehyde. The flow of chlorine was again begun. When the chlorine and nitrogen flow-rates had been carefully adjusted, the alternate receiver was switched in and the time for the beginning of the run was recorded. At the end of 2.7 hours at 112° and with a flow-rate of 3.3 liters/hr. for chlorine and for nitrogen, only five grams of product had been collected.

The product was a colorless liquid which fumed strongly. It was allowed to stand in a corked test tube where it separated into two layers--an almost clear upper layer and a brown lower layer--in about two days. In three days the entire mixture was black; and after several weeks the mixture had set to a gel. No tests were run on this mixture.

The acetaldehyde in the saturaters was left in the ice-water mixture although the saturaters had been removed from the rest of the apparatus in the process of cleaning it. It was noticed that white crystals of metaldehyde, the tetramer, were separating out. This would probably indicate that hydrogen chloride was backing up into the saturaters, for it is known that the formation of metaldehyde from acetaldehyde is catalyzed by acids (13). The formation of both paraldehyde and metaldehyde could account for the small yield.

Run No. 2

A run similar to the first but at 150° was attempted using a new bottle of acetaldehyde. Greater precaution was taken to prevent the backing-up of hydrogen chloride by increasing the flow-rate of nitrogen. The chlorine flow-rate had to be increased accordingly. At the end of one hour, no product (more than a few drops) was collected so the run was shut down.

Arrangement No. 2

Apparently there was no way to prevent the polymerization of acetaldehyde; consequently, there appeared the possibility of starting with paraldehyde at a temperature at which its vapor-pressure was appreciable. Because there were no vapor-pressure data on paraldehyde available, the boiling points of paraldehyde at two reduced pressures, 225 and 235 mm., were obtained and found to be 84.5 and 87.5° respectively. The boiling point at 760 mm. was known to be 124°; hence, with these data the Miles vapor-pressure rule can be used, assuming paraldehyde to be similar to ethers. The value obtained for 100° was 375 mm.; therefore, it seemed logical to try the same thing as before but with paraldehyde at 100°.

The only changes made in apparatus were in substituting boiling water for the ice-water and in covering the tube from the saturater to the preheater with asbestos around which a heating coil was wound to prevent condensation.

Run No. 3

The procedure used for the third run was similar to that used in the first run. When nitrogen was passed through the paraldehyde, the paraldehyde depolymerized so rapidly that the run could not be continued. It is known that paraldehyde is depolymerized almost quantitatively in the presence of mineral acids in the temperature range 45 to 85° and in the pressure range 5 to 80 mm. (2).

Arrangement No. 3

If paraldehyde would depolymerize quantitatively at higher pressures, its depolymerization would afford a method of introducing acetaldehyde into the reaction chamber. In a preliminary test, a few milliliters of paraldehyde heated in a small distilling flask began to distill at 90°. After the paraldehyde in the flask had cooled, a drop of 80% phosphoric acid was added. When heating was begun again, the paraldehyde began to depolymerize rapidly at 40° leaving a small amount of brown tar. In order to determine the amount of tars produced, a known weight of paraldehyde from a burette was allowed to run onto glass beads and a few drops of phosphoric acid contained in a small Erlenmeyer flask heated by water to 100°. By weighing the flask before the addition of the paraldehyde and after its subsequent depolymerization, the weight of the tars produced could be determined. It was found that the yield of tars amounted to 2.6 to 3.0%, increasing for decreasing rates of addition of the paraldehyde. Although the vapor pressure of phosphoric acid at 100° is about 160 mm. (23), the few drops used should interfere very little. It was thus seen feasible to obtain the acetaldehyde through the depolymerization of paraldehyde.

The next step was the designing of a depolymerizer which would deliver a known, constant rate of flow of acetaldehyde vapors. The depolymerizer itself was a large test tube 40 mm. in diameter and 20 cm. in length around which an asbestos jacket containing a nichrome heating coil was placed. The tube itself contained a few drops of phosphoric acid and about 100 ml. of glass beads. In the mouth of the test tube was placed a rubber stopper with holes for the tube admitting the paraldehyde, the tube carrying off the acetaldehyde, and the thermometer. The paraldehyde was introduced by means of a capillary tube in the shape of a horizontal "S" attached to a 50-ml. burette

by means of rubber tubing. The rubber tubing was employed so that a pinch-cock could be used to start or stop the flow of paraldehyde into the depoly-merizer. The purpose of the S-shaped tube was to permit the level of the paraldehyde in the burette to reach the level of the paraldehyde in the tip, thus providing a head of zero. The paraldehyde was dispensed from a 200-ml. gas burette, which was like a calibrated test tube, to which a 10-mm. tube was attached by means of a rubber stopper. This tube permitted setting the head at any desired level in the burette either by raising or lowering the gas burette or by replacing the 10-mm. tube with others of various lengths. It was planned originally to calibrate the dispensing system by determining the rates of flow for various levels, but it was decided that a more precise method would be to set the level to give about the rate of flow desired and to obtain the actual rate of flow from the difference in the paraldehyde level in the gas burette before and after the run.

It was desirable to secure a rapid mixing of nitrogen with the acetal-dehyde vapor after its formation and to inject the mixture into the reaction chamber before polymerization could cause any condensation. To accomplish this, there was constructed a mixing venturi in which nitrogen from a jet was mixed with the acetaldehyde as it passed through a constricted tube.

No other changes were made in the apparatus.

Run No. 4

In this run, it was desired to have a flow-rate of three liters per hour for each of acetaldehyde, chlorine, and nitrogen; however, difficulties in adjusting the tank valves on the chlorine and nitrogen tanks gave flow-rates a little different from those desired.

In preparing for the run, after the system had already been swept clear by nitrogen and chlorine, the heating coils for the reaction tube and the

depolymerizer were turned on. Nitrogen was then allowed to begin flowing while the paraldehyde level was adjusted to give the desired rate of flow. The paraldehyde was also allowed to begin flowing. The aspirator was turned on to give a slightly reduced pressure, the temperatures of the reaction tube and depolymerizer were adjusted to 140° and 100° respectively, and chlorine was started flowing. After the temperature of the reaction tube was adjusted to 150°, the gas flow-rates were regulated to give as nearly as possible the desired rates. After minor adjustments had been made from time to time over a period of an hour, the conditions remained nearly constant. The alternate receiver was switched in, and the run was begun.

The run was shut down after twelve hours of continuous operation with no difficulties. Adjustments in flow-rates and temperature were made only twice during the run. One unexpected discovery was that the carbonaceous matter and tars in the depolymerizer appeared to be much less than 3% as indicated by the clean appearance of the glass beads. The chlorination of 47 g. of acetaldehyde had yielded 39 g. of yellow product which gradually became colorless as it evolved chlorine upon approaching room temperature.

The flow-rate of acetaldehyde from the perfect gas law was calculated to be 3.1 liters/hr. at 150° and 740 mm.; the flow-rate of chlorine was 4.6 liters/hr.; and the flow-rate of nitrogen was 3.5 liters/hr.

The contact time is the average length of time the reactants are in the reaction tube. It is seen, therefore, that the contact time in seconds will be obtained by dividing the volume of the reaction tube, in milliliters, by the rate of flow of the reactants, in milliliters per second. For this reaction the contact time was found to be 11 seconds.

The ratio of chlorine to acetaldehyde was 4.5 to 3.1, or 1.5 to 1.0.

A description of the further treatment of the product obtained is given under the section on analysis.

Arrangement No. 4

The receivers in the previous runs had been cooled by an ice-salt mixture contained in a large crock. This had necessitated the frequent renewal of ice and salt. To eliminate this, the 250-ml. receivers were replaced by 100-ml. long-necked receivers which were placed in Thermos vessels. Otherwise the apparatus was not changed.

Run No. 5

It was intended that this run would be under almost the same conditions as the previous one in order that more data on the reaction products could be obtained. In this run, the chlorination was allowed to continue for forty-seven hours during which 141 g. of paraldehyde was used giving 146 g. of product, which, as before, became colorless upon standing. An additional 20 ml. of yellow viscous liquid were collected in the well below the reaction tube. The rates of flow at 150° and 740 mm. were the following: acetaldehyde, 2.8 liters/hr.; chlorine, 4.3 liters/hr.; and nitrogen, 3.5 liters/hr. The contact time was 12 seconds. The ratio of chlorine to acetaldehyde was 4.3 to 2.8, or 1.5 to 1.0.

Arrangement No. 5

For this run the apparatus was simplified by the substitution of a Friedrich condenser cooled by tap water for the Allihn condenser cooled by ice-water. The effluent gases from the gas absorption bottles were passed on to a gas absorption tower, as shown in Figure 2, p. 17. This arrangement was used for all the rest of the runs.
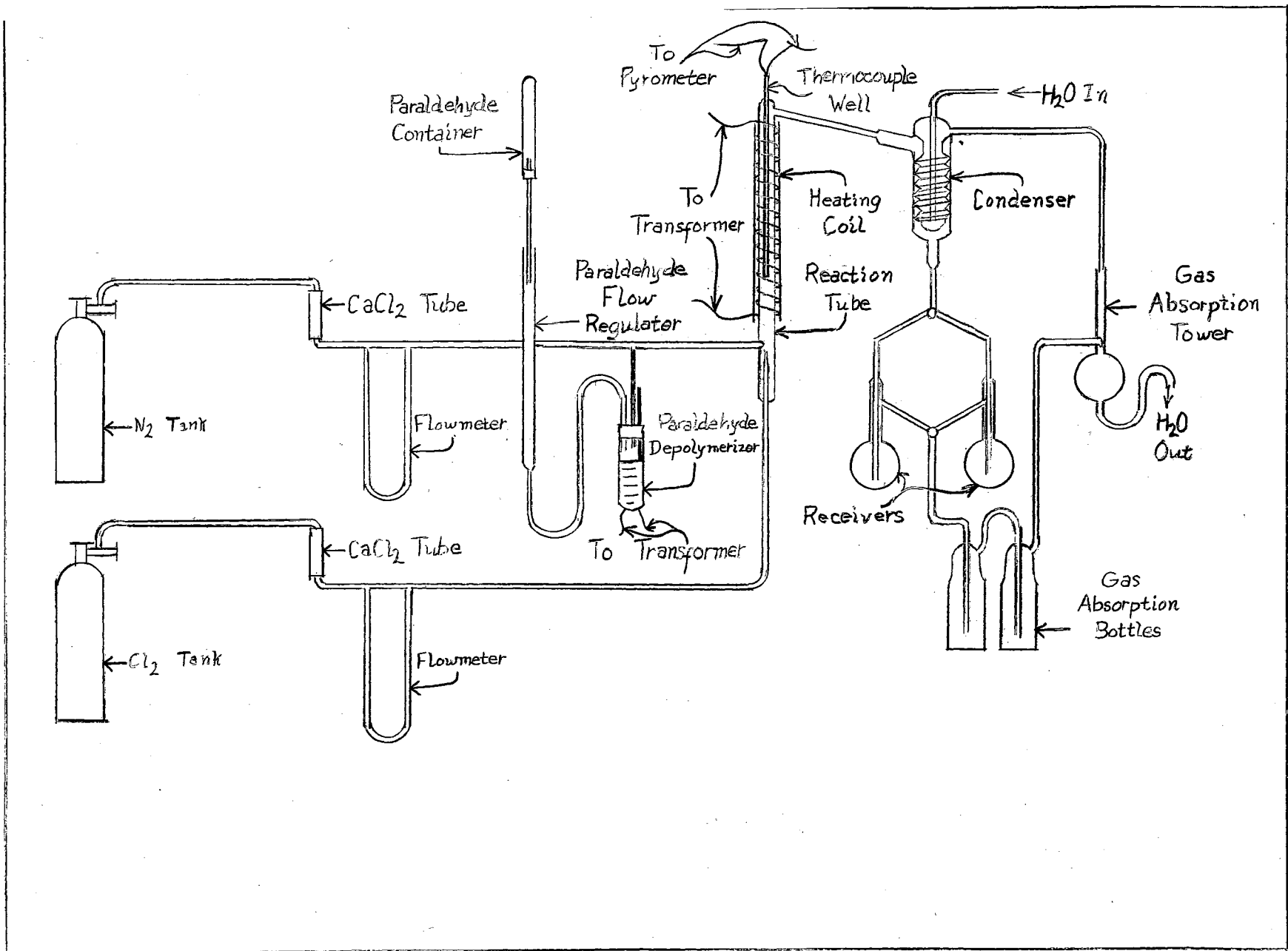
FIGURE 2 — CHLORINATION APPARATUS

Run No. 6

In this run it was to be determined whether or not a reaction temperature of 250° could be attained without a flash occurring. Instead of following the procedure used formerly, this time the reaction was started at 150° and increased gradually to 250° over a two-hour period.

The reaction was allowed to continue at this temperature for 6.9 hours, during which 14 g. of chlorinated product were collected from 17 g. of paraldehyde. The product after cooling to room temperature was colorless.

The flow rates at 250° and 740 mm. were these: acetaldehyde, 2.5 liters/hr.; chlorine, 4.8 liters/hr.; and nitrogen, 4.3 liters/hr. The contact time was 10 seconds. The ratio of chlorine to acetaldehyde was 4.8 to 2.5, or 1.9 to 1.0.

Run No. 7

Immediately after Run No. 6, another receiver was switched in and Run No. 7 was begun primarily to determine the upper temperature—or flash point—limit for the reaction. The rates of flow of paraldehydehyde, nitrogen, and chlorine were the same initially; but, during the run, the chlorine flow-rate began decreasing. An attempt to remedy this caused the chlorine flow-rate to rise rapidly to about 9 liters/hr. at a time when the temperature was above 300°. At this point there occurred a small amount of charring at the top of the beads used as packing in the reaction tube and extending downward about 10 cm. into the beads. As the flow-rate of the chlorine was brought back to 4.8 liters/hr., it was observed that about 10 cm. from the top of the beads a liquid had begun refluxing with decomposition. This was not actually a "flash" point, so the temperature was allowed to increase further to about 325°. After an hour when the charring from the refluxing liquid

had become excessive, the run was shut down. During the last hour, the conditions had remained nearly constant.

The conditions for the run as a whole varied too much to allow accurate calculations to be made. Assuming that the rates of flow for this run were the same as for the previous run, the contact time was estimated to be approximately 9 seconds.

Run No. 8

Over a period of 25 hours, 45 g. of paraldehyde gave 38 g. of chlorinated products. The rates of flow at 250° and 740 mm. were these: acetaldehyde, 1.8 liters/hr.; chlorine, 5.7 liters/hr.; and nitrogen, 4.3 liters/hr. The contact time was 10 seconds. The chlorine to acetaldehyde ratio was 5.7 to 1.8, or 3.2 to 1.0.

Run No. 9

It was decided to attempt a run at 350°. As before, after the desired rates of flow were obtained at a lower temperature, the temperature was slowly increased. At 290°, smoke appeared in the condenser. At 300°, the acetaldehyde began to burn brightly in the chlorine about 3 cm. above the entering gases. No product was collected.

The rates of flow at 300° and 740 mm. were the following: acetaldehyde, 4.3 liters/hr.; chlorine, 8.7 liters/hr.; and nitrogen, 4.6 liters/hr. The contact time was 7 seconds. The ratio of chlorine to acetaldehyde was 8.7 to 4.3, or 2.0 to 1.0.

Run No. 10

Over a period of 16.5 hours, 31 g. of acetaldehyde was chlorinated giving 21 g. of products. At 250° and 740 mm., the flow-rates were as follows:

acetaldehyde, 2.0 liters/hr.; chlorine, 4.7 liters/hr.; and nitrogen, 4.4 liters/hr. The contact time was 11 seconds. The ratio of chlorine to acetaldehyde was 4.7 to 2.0, or 2.4 to 1.0.

Run No. 11

In this run an excess of acetaldehyde was used. After four hours, the chlorination of 43 g. of acetaldehyde had given 27 g. of reaction products in the receiver and about 5 g. in the well below the reaction tube. The rates of flow at 250° and 740 mm. were these: acetaldehyde, 11 liters/hr.; chlorine, 4.7 liters/hr.; and nitrogen, 4.4 liters/hr. The contact time was 6 seconds. The ratio of chlorine to acetaldehyde was 4.7 to 11, or 0.43 to 1.0.

A summary of the runs made is given in Table I.

TABLE I

SUMMARY OF RUNS

Run	Temperature (°C.)	Contact Time (sec.)	Cl_2/CH_3CHO	Duration (hours)	CH_3CHO (g.)	Product (g.)
1[a]	112	-	-	2.7	-	5
2[a]	150	-	-	1.0	-	0
3[b]	150	-	-	-	-	-
4	150	11	1.5	12	47	39
5	150	12	1.5	47	141	146
6	250	10	1.9	6.9	17	14
7	325	9	1.9	1.0	-	-
8	250	10	3.2	25	45	38
9[c]	300	7	2.0	-	-	-
10	250	11	2.4	16.5	31	21
11	250	6	.43	4	43	27

a. Polymerization of acetaldehyde took place.
b. Paraldehyde was carried over into the reaction tube.
c. Combustion occurred.

Analysis

A few milliliters from Run No. 4 were distilled to see whether it would be worthwhile to attempt a fractionation of the product. Fuming occurred early in the distillation but decreased as the distillation progressed.

In another preliminary investigation, to 13 ml. of the crude product dissolved in 50 ml. of ether was added a strong potassium carbonate solution until the mixture was basic. After agitation in a separatory funnel, the water layer was drawn off and retained. The ether layer was poured off into a flask which was then heated to drive off the ether. There remained 6.5 ml. of black liquid which was distilled from a small distilling flask. The fractions obtained and the refractive indices are listed below in Table II.

TABLE II

DISTILLATION OF A PORTION OF RUN NO. 4
AFTER PRELIMINARY TREATMENT

Boiling Range (°C.)	Volume (ml.)	n_D^{39}
41-42	1.0	1.35
42-75	0	
75-88	0.2	1.38-1.39
88-90	0.5	1.408
90-93 (dec.)	0.5	(discolored)

All the refractive indices were taken by a Fisher refractometer.

It is probable that most of the material obtained from the ether extraction of the basic solution had undergone aldol condensations to give the large amount of non-distillable residue.

One-half of the basic water solution was made acidic with dilute hydrochloric acid and extracted with ether, after which the ether was evaporated.

There was left behind about 0.5 ml. of a viscous liquid with a sharp odor.

The other half of the basic solution was acidified with phosphoric acid, and the mixture was distilled. Only one milliliter of distillate was obtained between 65 and 99°. Almost all of the remaining liquid was distilled over at 99°, leaving behind crystals of potassium phosphate.

All fractions collected gave positive tests with 2,4-dinitrophenylhydrazine. The derivatives prepared, even after two or three recrystallizations, still gave wide melting ranges indicating mixtures.

It was at this point that 146 g. of product from Run No. 5 was obtained. When it was discovered that the conditions for Runs No. 4 and 5 were almost identical, analysis of the former was abandoned in favor of thoroughly investigating the latter.

The analysis of the products from Run No. 5 was begun with the determination of the amount of acetyl chloride as the primary objective. Three methods were tried: the first was the reaction of the products with ethyl alcohol, followed by the fractional distillation of the resultant mixture; the second was the reaction of the products with ethylmagnesium bromide, followed by hydrolysis and fractional distillation; and the third was the fractional distillation of the crude product.

In the first method, to 50 g. of absolute alcohol was added 25 g. of product, slowly at first with shaking and frequent immersing in ice water, for the reaction was quite vigorous. The mixture was allowed to stand for 52 hours. Potassium carbonate and water were added to neutralize the acids present. The oily upper layer and the aqueous lower layer were separated in a separatory funnel.

The oily layer after being dried over magnesium sulfate weighed 10.5 g. A simple distillation gave the data in Table III.

TABLE III

DISTILLATION OF THE MIXTURE RESULTING FROM TREATING A PORTION OF THE PRODUCT FROM RUN NO. 5 WITH ALCOHOL

Fraction	Boiling Range (°C.)	Volume (ml.)	n_D^{25}
1.	71-76	2.0	1.365
2.	76-80	3.0	1.368
3.	80-120	0.6	1.375
4.	120-140	0.2	1.401
5.	140-146	0.4	1.416
6.	146-153	1.6	1.420

Fraction 1 should consist mostly of ethyl acetate (boiling point of the ethyl alcohol-ethyl acetate azeotrope, 71.8°; boiling point of ethyl acetate, 77.1°; ethyl acetate, n_D^{19} 1.3728). Fraction 3 could contain acetal (boiling point, 104°; n_D^{20} 1.3819). Fraction 5 was probably ethyl chloroacetate (boiling point, 144°; n_D^{20} 1.4216). From the relatively low recovery, it was decided that this method would be unsatisfactory for quantitative estimations.

In the second method, an excess of the Grignard reagent, ethylmagnesium bromide, was added to 25 g. of the product slowly and with vigorous stirring. It was necessary to cool the mixture in ice during the addition. The mixture was then allowed to come slowly to room temperature and was afterwards warmed to complete the reaction. Hydrolysis was accomplished by pouring the liquid into a mixture of ice and dilute sulfuric acid. More ether was added, and the aqueous layer was extracted repeatedly with small portions of ether. After evaporating off the ether and drying the oily layer over magnesium sulfate, the volume of the dry solution obtained was 16.5 ml. (15.7 g.). A fractional distillation of the solution gave the results in Table IV.

TABLE IV

DISTILLATION OF THE MIXTURE RESULTING FROM TREATING A
PORTION OF THE PRODUCT FROM RUN NO. 5 WITH ETHYLMAGNESIUM BROMIDE

Fraction	Boiling Range (°C.)	Volume (ml.)	n_D^{25}
1.	35-50	2.6	
2.	50-70	0.6	
3.	70-82	0.4	
4.	82-94	2.0	1.396
5.	94-110	0.6	
6.	110-130	3.0	1.416
7.	130-184	5.0	

The product from the reaction of ethylmagnesium bromide with acetyl chloride is 3-methylpentanol-3 (boiling point, 122.5°; n_D^{20} 1.4196). With acetaldehyde the reaction product is butanol-2 (boiling point, 99.5°; n_D^{22} 1.3924). It is probable that fraction 6 was composed largely of 3-methylpentanol-3. The small amount of fraction 5 does not necessarily indicate that a small amount of butanol-2 was formed, for solubility in water may have interfered in its recovery by ether extraction. It was concluded that this method would be good enough for the determination of acetyl chloride and esters of acetic acid even though it was not necessarily the most desirable from the operational viewpoint. Moreover, the accuracy of this method for determining other components of the mixture was questionable.

The third method used in separating the products was the fractional distillation of the crude product. This method had not been tried first because it was hoped that a satisfactory method of stabilizing the mixture against decomposition could be found. A fractionation of 25 ml. gave the data in

Table V. A charred residue remained. Fuming occurred at the receivers
throughout the distillation.

TABLE V

DISTILLATION OF A PORTION OF THE PRODUCT FROM RUN NO. 5

Fraction	Boiling Range (°C.)	Volume (ml.)	n_D^{28}
1.	35-47	0.2	1.372
2.	47-55	0.2	1.383
3.	55-60	0.6	1.385
4.	60-70	0.4	1.385
5.	70-77	0.9	1.398
6.	77-80	1.0	1.400
7.	80-83	1.0	1.405
8.	83-85	2.3	1.413
9.	85-90	1.4	1.422
10.	90-93	3.7	1.440
11.	93-98	1.6	1.440
12.	98-102	2.0	1.435

Fraction 2 was probably acetyl chloride (boiling point, 51-52°; n_D^{20} 1.3898).
Fraction 12 could contain chloroacetyl chloride (boiling point, 105°; n_D^{20}
1.4541).

There was still sufficient product from Run No. 5 left to attempt other
methods of separation, but it was considered inadvisable to use more until the
procedure for quantitative estimation had been developed. Runs No. 6 and No. 7,
which were made about this time, provided product for the next method.

Since the compounds formed in the treatment of the product with ethyl al-
cohol are appreciably soluble in water, and since the potassium carbonate solu-
tion used in neutralizing the mixture may have caused aldol condensations, the
next method which was tried was to fractionate the alcoholic mixture directly
with no previous separation attempted. In a trial distillation, when a mixture
of 4 ml. of product and 10 ml. of absolute alcohol were distilled, the data in
Table VI were obtained.

TABLE VI

DISTILLATION OF THE MIXTURE RESULTING FROM TREATING A
PORTION OF THE PRODUCT FROM RUN NO. 6 WITH ALCOHOL

Fraction	Boiling Range (°C.)	Volume (ml.)	n_D^{22}
1.	50-70	0.2	1.355-1.385
2.	70-80	4.2	
3.	80-85	4.0	1.385
4.	85-86	2.0	
5.	86-141	0	
6.	141-146	2.0	1.413
7.	146-153	0.6	1.420

Fraction 2 should consist of a mixture of ethyl alcohol and ethyl acetate;
hence, the refractive index was not taken. Fractions 6 and 7 probably contained
ethyl chloroacetate (boiling point, 144°; n_D^{20} 1.4216) and ethyl dichloroacetate
(boiling point, 158°; n_D^{20} 1.4386).

A similar treatment of Run No. 7 gave the data in Table VII.

TABLE VII

DISTILLATION OF THE MIXTURE RESULTING FROM TREATING A
PORTION OF THE PRODUCT FROM RUN NO. 7 WITH ALCOHOL

Fraction	Boiling Range (°C.)	Volume (ml.)	n_D^{22}
1.	70-85	6.7	
2.	85-90	2.7	1.385
3.	90-140	0.6	
4.	140-146	1.1	1.407
5.	146-154	1.2	1.420
6.	154-160	0.5	1.422

It now appeared that the best procedure for the analysis of the product would be the reaction of the product with ethyl alcohol followed by a good fractional distillation. Low-boiling fractions known to contain both ethyl alcohol and ethyl acetate could be analyzed by running saponification equivalents, a standard procedure in the analysis of alcoholic beverages (18). Before carrying out this procedure, four more runs were made so that the same analyses could be made on all the products at about the same time.

In preparing the mixtures for fractionation, it was desired to use 25 ml. of the product and 75 ml. of alcohol. For Runs Nos. 5, 8, and 11, there was enough product left; but there was not enough for Runs Nos. 6 and 10. Owing to an error in calculating the acetaldehyde flow-rate in Run No. 6, these two runs appeared to be almost identical insofar as the ratio of chlorine to acetaldehyde and the contact time were concerned; therefore, they were combined for the purpose of analysis.

In carrying out the esterifications, absolute ethyl alcohol was allowed to drop from a dropping funnel into the product contained in a three-neck

flask fitted with a reflux condenser and a mechanical stirrer. The flask was at first cooled by an ice-salt mixture and afterwards allowed to come to room temperature slowly. The mixture was poured into glass-stoppered flasks where it remained for use. As a security measure, only half of the mixture--50 ml.-- was used for the fractional distillation through the Todd column. In the fractional distillation, the fractions were collected in weighed, glass-stoppered Erlenmeyer flasks. The data obtained appear in the following tables.

TABLE VIII

FRACTIONAL DISTILLATION OF 46.2 g. OF THE ALCOHOLIC MIXTURE
CONTAINING 14.6 g. OF CHLORINATED PRODUCT FROM RUN NO. 5

Fraction	Boiling Range (°C.)	Weight (g.)
1	65-70	2.54
2	70-73	4.33
3	73-75	4.91
4	75-78	1.72
5	78-80	1.44
6	80-85	12.70
7	85-90	3.00
8	90-92	3.47
	Residue	3.22
	Total recovery	37.33

TABLE IX

FRACTIONAL DISTILLATION OF 45.7 g. OF THE ALCOHOLIC MIXTURE
CONTAINING 14.8 g. OF CHLORINATED PRODUCT FROM RUN NO. 8

Fraction	Boiling Range (°C.)	Weight (g.)
1	to 65	1.25
2	65-70	2.00
3	70-73	9.22
4	73-75	3.58
5	75-78	6.84
6	78-80	.98
7	80-83	6.94
8	83-86	.08
9	86-90	2.52
10	90-92	1.31
11	92-96	2.84
12	96-100	1.04
13	Residue	6.17
	Total Recovery	44.77

TABLE X

FRACTIONAL DISTILLATION OF 44.7 g. OF ALCOHOLIC MIXTURE
CONTAINING 13.9 g. OF CHLORINATED PRODUCT FROM RUN NOS. 6 AND 10

Fraction	Boiling Range (°C.)	Weight (g.)
1	45-65	.32
2	65-70	1.97
3	70-73	17.48
4	73-75	1.22
5	75-78	5.70
6	78-80	.51
7	80-83	4.41
8	83-88	.56
9	88-90	.88
10	90-92	4.96
11	Residue	4.77
	Total Recovery	42.78

TABLE XI

FRACTIONAL DISTILLATION OF 44.6 g. OF ALCOHOLIC MIXTURE
CONTAINING 13.8 g. OF CHLORINATED PRODUCT FROM RUN NO. 11

Fraction	Boiling Range (°C.)	Weight (g.)
1	45-65	1.32
2	65-70	7.23
3	70-73	6.78
4	73-75	2.06
5	75-78	4.56
6	78-80	6.94
7	80-85	2.61
8	85-90	4.62
9	Residue	2.60
	Total Recovery	38.72

Saponification equivalents were determined on the combined fractions 1 to 5 for Run No. 5 and 2 to 6 for the others. Before saponification equivalents could be run, however, it was necessary to determine first the amount of free acid in the mixture by titrating weighed samples with sodium hydroxide.

The saponifications were carried out in 100-ml. round-bottom standard-taper flasks connected with short condensers. Three samples and one blank were heated simultaneously for six hours in a water bath heated to 85°. To carry out the saponification, 25 ml. of about one normal alcoholic potassium hydroxide was pipetted into each flask. A 2-ml. pipette was used to transfer samples to the three flasks. The amount of liquid delivered by the pipette had been previously determined by weighing three 2-ml. deliveries. At the

end of the saponification, the material was titrated with 0.140 N hydrochloric acid. The titration of the blank gave the milliequivalents of potassium hydroxide added to each flask. The hydrochloric acid used along with the hydrochloric acid known to be present originally and determined previously gave the amount of excess base. The difference in the number of milliequivalents added and the number found represents the milliequivalents of ester present. The weight of the ester was found by multiplying the number of milliequivalents by 0.088, the grams of ethyl acetate per milliequivalent. From the weight of the sample, the per cent of ester could be calculated. From this and the total weight of the combined fractions used in the saponification, the total amount of ethyl acetate in the combined fractions could be calculated. This was used to determine the grams of ethyl acetate in the mixture obtained initially by mixing the product with ethyl alcohol. By converting this to grams of acetyl chloride, the per cent of acetyl chloride in the original product and the percentage yield could be determined. A summary of this is given in Table XII.

TABLE XII

RESULTS OF ANALYSES

Run	Acetyl chloride in product (%)	Total yield of acetyl chloride (g.)	Acetaldehyde Chlorinated (g.)	Yield (%)
5	34	54	141	21
8	47	19	45	24
6 and 10	65	24	48	27
11	61	19	43	25

It is interesting to note that in every case the reaction at 250° produced a little more acetyl chloride than the one at 150°. Increasing the ratio of chlorine to acetaldehyde from 0.43 to 2.2 increased the amount of acetyl chloride but decreased it from 2.2 to 3.2. It was assumed that the decrease was due to the formation of chloroacetyl chlorides. To confirm this, the 6.17 g. of residue from the fractionation of the alcoholic mixture from Run No. 8 (see Table IX, p. 30) was fractionated to give 2.91 g. of distillate between 138 and 150° (n_D^{24} 1.4227). This was probably mostly ethyl chloroacetate (boiling point, 144°; n_D^{20} 1.4216). On that assumption, the product consisted of about 18% by weight of chloroacetyl chloride—a yield of about 7%.

For a comparison, residues from Run No. 5, Run Nos. 6 and 10, and Run No. 11 were also fractionated, but no distillate could be collected above 92, 100 and 92°, respectively because of excessive decomposition.

At the end of the analysis, the products collected from Run Nos. 5 and 8—the only two remaining—were still colorless.

There still remained one fraction which existed in sufficient quantity to deserve some attention. This was fraction 6 from the fractionation of the alcoholic mixture from Run No. 5 (see Table VIII, p. 29). Between 80 and 85°, 12.7 g. of the liquid (d_4^{24} = .882; n_D^{24} 1.384) had been collected with most of it distilling at 84°. The fraction gave a yellow precipitate with 2,4-dinitrophenylhydrazine, was oxidized by cold basic potassium permanganate solution, and did not decolorize a dilute solution of bromine in carbon tetrachloride. It was soluble in water and ether. Heating with sodium hydroxide gave a white precipitate. From these tests it was believed that the compound was a saturated aldehyde. By reacting it with dimethyldihydroresorcinol, the "dimethone" derivative (melting point, 146-148°) was prepared.

An attempt to prepare the 2,4-dinitrophenylhydrazone gave a substance having a wide melting range. Two recrystallizations gave a substance softening at 134-137° and melting at 165-170°. From a preparation of the p-nitrophenyl-hydrazone using glacial acetic acid as the solvent, a compound was obtained melting at 180-185°.

It had been seen originally that the three principal possibilities were chloroacetaldehyde (boiling point, 85°), aldol (dec. point, 84-85°), and crotonaldehyde (boiling point, 102°), which is a dehydration product of aldol. A comparison of these and fraction 6 are given in Table XIII.
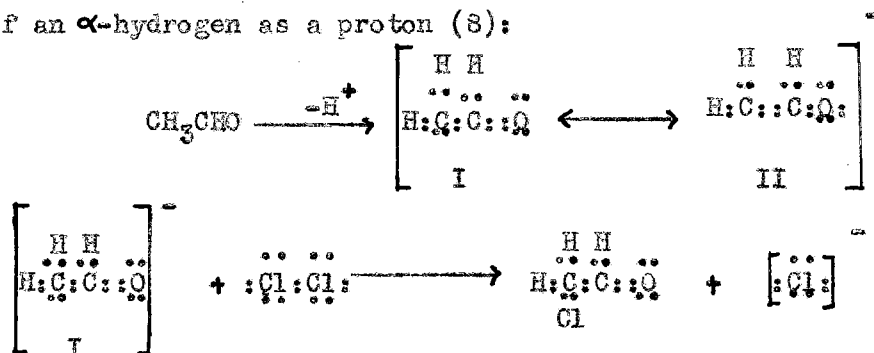
TABLE XIII

COMPARISON OF PROPERTIES OF FRACTION 6 WITH THOSE OF SIMILAR COMPOUNDS

	b.p. (°C.)	d_4^t (g./ml.)	n_D^t	Dimethone m.p. (°C.)	2,4-Dini-trophenyl-hydrazone m.p. (°C.)	p-Nitro-phenylhy-drazone m.p. (°C.)
Fraction 6	80-85	0.882^{24}	1.384^{24}	146-148	134-137 165-170	180-185
Aldol	d.84-85			146-148		109-111
Crotonaldehyde	102	$0.852^{20.5}$	$1.4362^{20.5}$	186	190	185
Chloroacetaldehyde	84				158	

From these data it was concluded that fraction 6 consisted of aldol and cro-tonaldehyde.

DISCUSSION

The chlorination of acetaldehyde may involve either an ionic or a free-radical mechanism. A proposed mechanism is the formation of a carbanion by the removal of an α-hydrogen as a proton (8):

$$CH_3CHO \xrightarrow{-H^+} \left[\overset{H}{\underset{I}{H{:}\overset{H}{C}{:}C{:}\overset{..}{\underset{..}{O}}}} \longleftrightarrow \overset{H\ H}{H{:}C{:}{:}C{:}\overset{..}{\underset{..}{O}}{:}} \right]^{-}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad I \qquad\qquad\qquad\qquad\qquad\qquad II$$

$$\left[\overset{H\ H}{\underset{I}{H{:}\overset{..}{C}{:}\overset{..}{C}{:}{:}\overset{..}{O}}} \right]^{-} + {:}\overset{..}{\underset{..}{Cl}}{:}\overset{..}{\underset{..}{Cl}}{:} \longrightarrow \overset{H\ H}{\underset{Cl}{H{:}\overset{..}{C}{:}\overset{..}{C}{:}{:}\overset{..}{\underset{..}{O}}}} + \left[{:}\overset{..}{\underset{..}{Cl}}{:} \right]^{-}$$

The process could be continued to give chloral.

The uncatalyzed thermal decomposition of acetaldehyde between 300 and 500° gives as the main products methane and carbon monoxide (19). Catalyzed by diethyl ether, the thermal decomposition is interpreted as follows (5):

$$CH_3CHO \xrightarrow{R^{\cdot}} CH_3CO^{\cdot}$$
$$\downarrow$$
$$CH_3^{\cdot} + CO$$
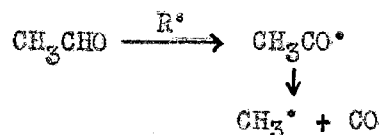
The chlorination of acetaldehyde to give acetyl chloride may then be explained by the following:

$$CH_3CHO \xrightarrow{Cl^{\cdot}} CH_3CO^{\cdot} + HCl$$

$$CH_3CO^{\cdot} + Cl_2 \longrightarrow CH_3COCl + Cl^{\cdot}$$
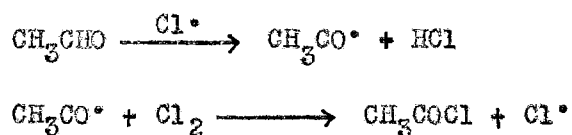
It is reasonable to assume that the reason for the old controversy over the products from the chlorination of acetaldehyde has been due to the fact

that two different mechanisms have been involved. Under ionic conditions, chlorinated aldehydes predominate; under free-radical conditions, acetyl chloride and chlorinated acetyl chlorides predominate.

SUMMARY

The chlorination of acetaldehyde was carried out safely and smoothly at the temperatures of 150 and 250° and with several ratios of chlorine to acetaldehyde to give yields of acetyl chloride varying from 21 to 27%. It was found that, while acetyl chloride was formed in every case, the yields were highest at 250°. Increasing the ratio of chlorine to acetaldehyde increased the yield up to a ratio of about 2 to 1 but then decreased it as the higher ratios increased the formation of chlorinated acid chlorides.

A free-radical mechanism is proposed, in which the acetyl radical reacts with chlorine.

Suggestions for further work include (1) the complete analysis of the reaction products, (2) the use of catalysts to increase yields of acetyl chloride, (3) the use of higher ratios of chlorine to acetaldehyde to attempt the production of mixtures of chlorinated acid chlorides, and (4) the vapor-phase chlorination of propionaldehyde to see how specifically the -CHO group is attacked.

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