

VAPOR-PHASE
CHLORINATION OF ETHYL ALCOHOL

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CHLORINATION OF ETHYL ALCOHOL

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INTRODUCTION

Much work has been done in the study of the direct chlorination of ethyl alcohol in the liquid phase. This process leads to the production of chloral, a compound valuable as a drug and as an intermediate in the preparation of many compounds, particularly 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (D.D.T.). The chlorination process must be controlled at a low rate and low temperatures to prevent decomposition and volatilization of intermediate products.

It seemed possible that chlorination of ethyl alcohol in the vapor phase would lead to faster, more easily controlled reactions. Very little study has been made of the vapor-phase chlorination of ethyl alcohol.

The purpose of this work is to study the effects of changes in reaction temperatures and ratio of reactants in the vapor-phase chlorination of ethyl alcohol.

HISTORY

The chlorination of ethyl alcohol in the liquid phase has been studied rather extensively by many workers. As early as 1832 Liebig (20) prepared trichloroacetaldehyde (chloral) by continuous chlorination of liquid alcohol. Most of the succeeding work on the chlorination of alcohol had as its main purpose the production of trichloroacetaldehyde. Though numerous methods for production of chloral have been developed, the continuous chlorination of liquid alcohol still remains the commercially important method (9).

The process for production of chloral by action of chlorine on liquid alcohol (25) is divided into two stages: (a) the preparation of chloral alcoholate (b) its conversion into chloral. The chlorine is passed into dehydrated alcohol with crystalline ferric chloride as a catalyst, with the reaction mixture cooled at first, then heated to 60° C., and further to 100° C. The reaction is vigorous at first and then slows down. On cooling, a white mass of chloral alcoholate is obtained. This alcoholate, when distilled with sulfuric acid, gives chloral. Various by-products are formed in the reaction of chlorine with liquid alcohol. A few that have been detected are 1,1-dichloroethane, 1,2-dichloroethane, 1,1,2-trichloroethane, β,β,β -trichloroethanol, ethyl dichloroacetate, and chloroform (2) (18).

Other methods for the production of chloral have been suggested: (a) direct chlorination of acetaldehyde (26), (b) treatment of ethyl formate with thionyl chloride (13), (c) distilla-

tion of starch or sucrose with manganese dioxide and hydrogen chloride (27), and (d) high-pressure catalytic treatment of carbon tetrachloride with formaldehyde and thionyl chloride (12).

The importance of chloral and its derivatives is twofold: (a) they show definite physiological properties, and (b) display a wide range of chemical reactivity. Chloral has been found to be a hypnotic and an antipyretic (14). Various other derivatives of chloral have been found to be useful physiologically.

With respect to its chemical reactivity chloral is almost universally reactive. It reacts with hydrocarbons, phenols, alcohols, acids, bases, and other reagents such as hydrogen sulfide, halogens, phosphorus halides, acid chlorides, cyanides and cyanates, and oxidizing agents (15).

Since the reaction of chlorine with liquid alcohol is conducted at a low rate in order to obtain practical yields of chloral, it was suspected that the reaction could be accelerated by allowing it to take place in the vapor phase. Such a process was patented by Besson in 1902 (5). No further work on vapor-phase chlorination was reported until 1933, at which time Akashi (1) reported work on the vapor-phase chlorination of various organic compounds, including ethyl alcohol. He studied the vapor-phase reaction of ethyl alcohol with chlorine in the presence of a catalyst, nickel chloride, at a temperature of 100° C. In this reaction the products formed were dichlorodiethylacetal, dichloroacetaldehyde ethyl alcoholate, and chloroacetaldehyde ethyl alcoholate. No further work on the vapor-phase chlorination of ethyl alcohol has been reported.

PRELIMINARY DISCUSSION

This work consisted of chlorinating vaporized ethyl alcohol at atmospheric pressure. In the consideration of the problem, it was observed that the variables in the reaction conditions could be classified as follows: (a) catalyst, (b) temperature, (c) flow rate of chlorine, and (d) volume ratio of chlorine to alcohol.

In order to simplify the problem and to concentrate on the determination of the effects of the other variables on the reaction, no catalyst was used in this study.

In attacking the problem, it was observed that the vapor-phase reaction of ethyl alcohol with chlorine would probably be highly exothermic with the possibility of explosion occurring under certain conditions of temperature and rate of flow of chlorine. It was necessary to avoid explosion of the reaction mixture since this caused carbonization of the alcohol. It was desirable to have the flow rate of chlorine as high as possible without explosion in order to obtain maximum yield of products. The upper limit for the flow rate was found to depend on the temperature and the ratio of chlorine to alcohol. Preliminary reaction runs were made to determine these limits.

In these runs it was found that a chlorine-to-alcohol ratio of four to one with a flow rate of chlorine of three liters per hour could be employed below 200° C. without explosion of the reaction mixture. If this flow rate and ratio were increased somewhat, it was found that explosions would occur at

at a temperature as low as 125° C. After these observations were made, it was decided that the upper limits for the reaction should be: (a) chlorine flow of three liters per hour, (b) chlorine to alcohol ratio of four to one, and (c) a temperature of 150° C.

It was also observed that the reacting gases should be thoroughly mixed before being passed through the heated tube. In an effort to prevent condensation of alcohol vapor, a small heating coil was wound around the alcohol delivery tube and the mixing unit. This coil was regulated to a temperature of 90° C. It was found that with this coil in operation explosions would occur at a temperature as low as 100° C. with a chlorine-to-alcohol ratio of three liters to three-fourths of a liter per hour. These explosions originated at the point of mixing, and when the heater was not operating such explosions did not occur.

The flow ratios of chlorine to alcohol selected for study were four to one, two to one, and one to one. These runs were made at a temperature of 125° C. indicated at a reference point selected in the reaction tube. Thus, it was supposed that the effect of varying the flow rate of alcohol on the reaction could be determined. With a chlorine flow of three liters per hour, the following reaction periods were required to give workable quantities of products: (a) four to one ratio--twenty-four hours, (b) two to one ratio--eighteen hours, (c) one to one ratio--twelve hours. The volumes of alcohol chlorinated in these periods were forty-two, sixty-three, and eighty-four milliliters, respectively.

In order to determine the effect of temperature on the reaction, the one to one ratio run was repeated at 100° C. and 150° C. indicated at the reference point.

EXPERIMENTAL

Apparatus. The apparatus for the chlorination is shown diagrammatically in Figure 1. The chlorine was commercial grade and was drawn from the original tank at the time of use. The flow of chlorine was regulated by means of the tank valve. Since it was found that the chlorine flow from the tank fluctuated, it was necessary to place a large flask between the tank and the chlorination system to act as a cushion bottle to remove the fluctuations. This cushion bottle was equipped with a three-way stopcock with one arm connecting to a vacuum pump. By means of this pump the cushion bottle was evacuated before the chlorine flow was begun.

From the cushion bottle the chlorine was allowed to flow through a calcium-chloride drying tube which was equipped with a stopcock. The purpose of the stopcock was to shut off the cushion bottle and drying tube from the atmosphere at the end of a run. The flow rate of chlorine was measured by allowing it to pass through a calibrated flowmeter of the type developed by Benton (4). The flowmeter liquid first used was pentachloroethane. After the liquid had been in use for some time, crystals of hexachloroethane were formed in it, requiring replacement of the pentachloroethane. Concentrated sulfuric acid was then tried as the flowmeter liquid and served very well. From the flowmeter the chlorine flowed through a small dry trap, the purpose of which was to prevent alcohol from running back into the flowmeter. The dry trap was directly connected to the chlorine-

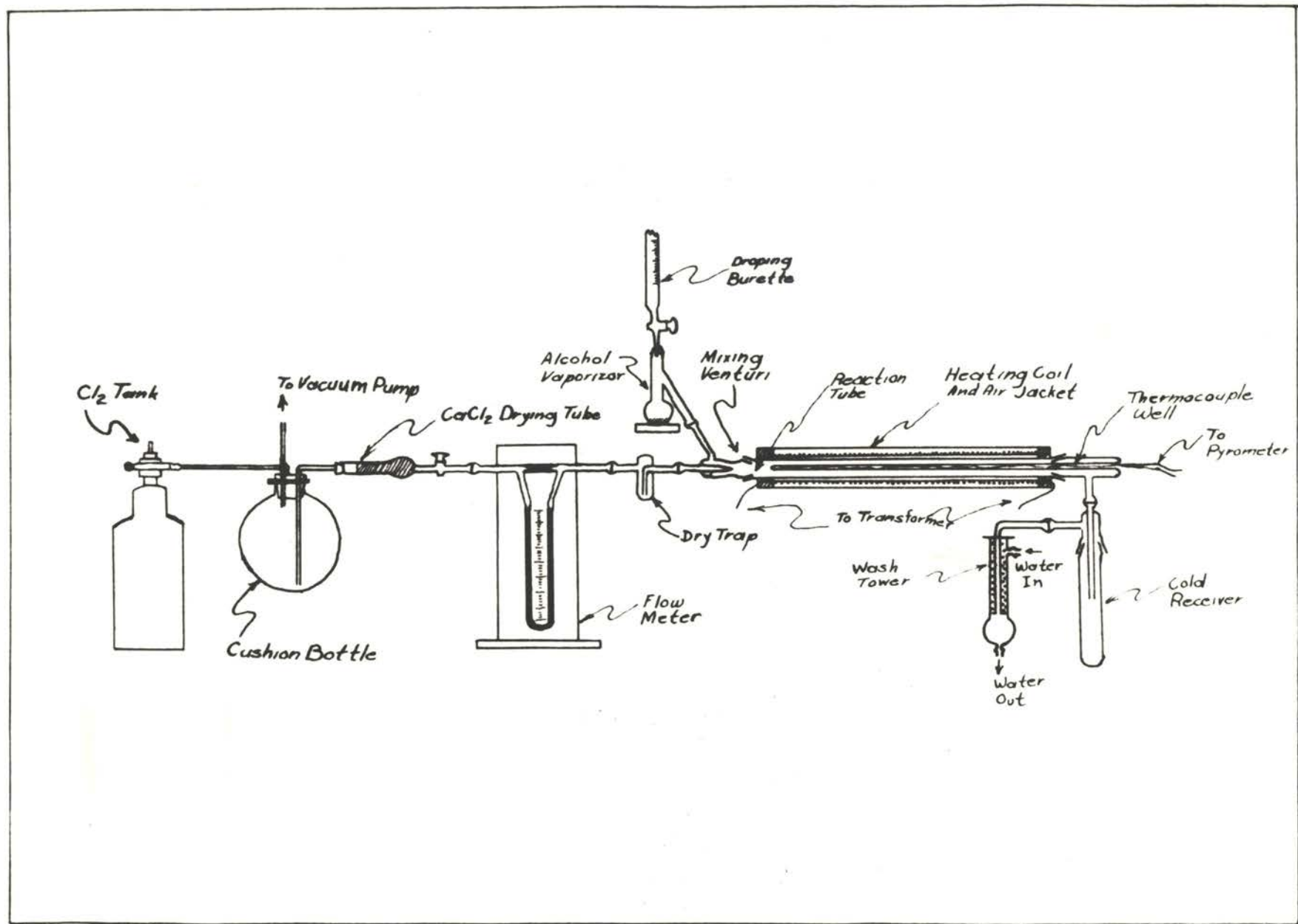


FIGURE 1-CHLORINATION APPARATUS

alcohol mixing unit.

The alcohol was introduced into the system by means of a burette which also served as a measuring device for the alcohol flow. The alcohol dropped from the burette into a flask heated by means of an oil bath at a temperature of 90° C. The bottom of the inside of the flask was covered with fibrous asbestos, which served to allow the alcohol to evaporate more uniformly than if it were to fall directly on the surface of the flask. The vaporizing flask was connected to the mixing unit.

This mixing unit (17) was in effect a mixing venturi. The chlorine inlet tube was drawn to a capillary, the end of which was located in the throat of the venturi. The alcohol vapor 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 the alcohol vapor before it was introduced into the reaction tube.

The reaction tube consisted of three concentric glass tubes, each forty centimeters in length. The reaction mixture passed through the innermost tube. The second tube was wound with a nichrome wire heating coil, and was separated from the inner tube by a dead air space. The third tube served to insulate the second tube from the atmosphere. The diameters of the three tubes were twenty-five, thirty-five, and forty millimeters, respectively. A thermocouple well was located in the center of the innermost tube. It housed a chromel-alumel junction thermocouple which could be moved to various positions along the length of the reaction tube. The thermocouple was connected to a cali-

brated Hoskins pyrometer.

The temperature of the reaction tube was not uniform over the entire length of the tube. Hence a reference point in the tube was selected and the various reaction temperatures chosen were those indicated at this reference point. In addition a temperature contour line was drawn for each reference temperature and flow ratio with the tube empty and with the gases flowing through the tube. These contours are shown in Figure 2.

From the reaction tube the gases passed into a cold trap receiver, which was kept at a constant temperature of 0° C. in a Dewar flask containing a water-ice mixture. The cold junction of the thermocouple was also immersed in this flask. The reaction vapors were condensed in the cold trap.

The hydrogen chloride formed and the excess chlorine passed uncondensed from the cold trap to a wash tower filled with glass beads. 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 exception of the connections between the chlorine tank, cushion bottle, and the drying tube. For these connections gum rubber tubing was employed. This rubber tubing showed only slight deterioration after considerable time in use.

The flowmeter was calibrated in the system by the displacement of water which had been saturated with chlorine (4). Caution was taken to make sure that all joints in the system were

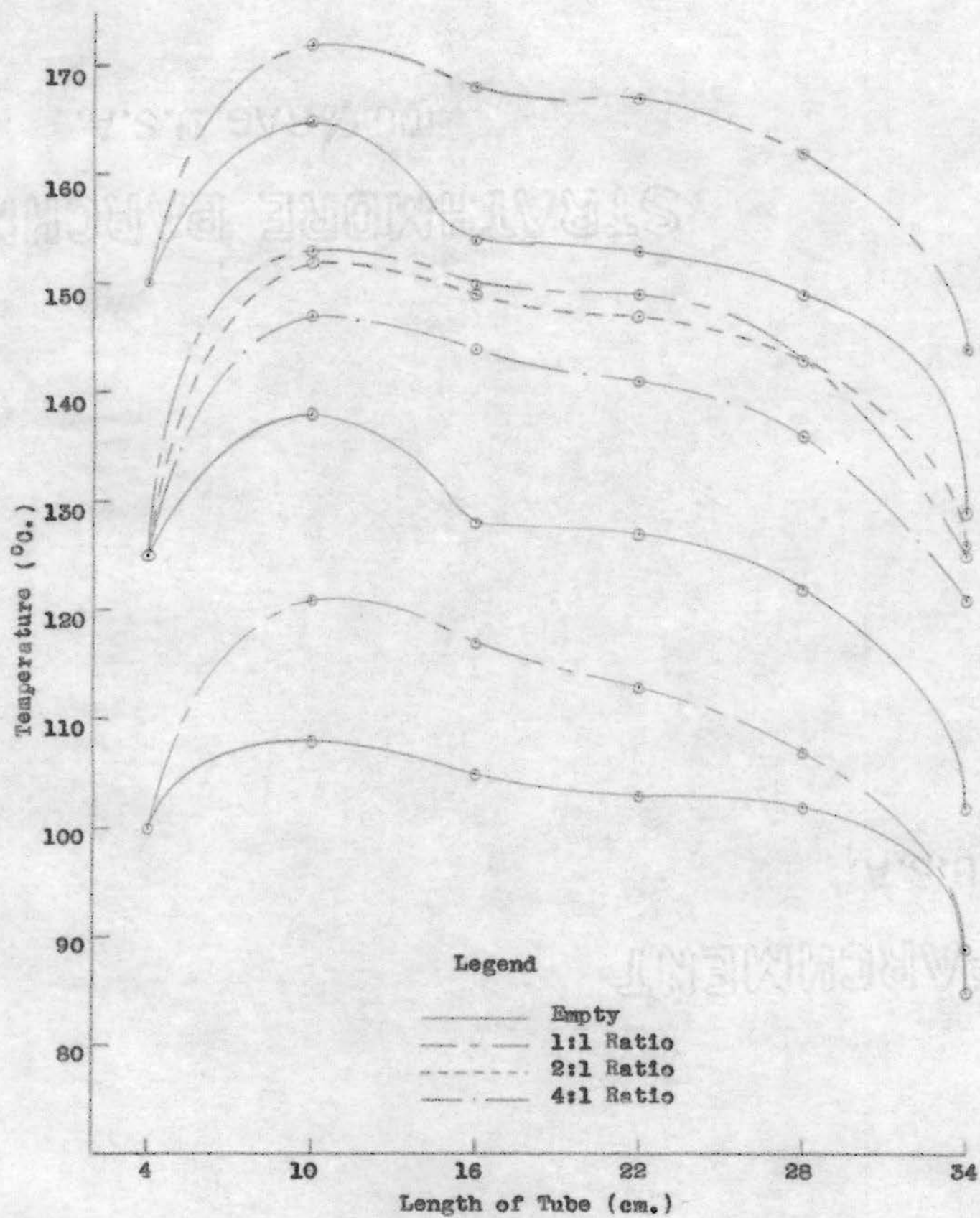


Figure 2. Temperature Contours

secure by passing ammonia gas around the outside of the connections. The chlorine flow was set for various rates and the amount of liquid displaced per unit time was measured. A graph was made in which flow rate was plotted against the square root of head which was read on the flowmeter. This plot resulted in a straight line which would theoretically be expected (28).

The flow rate of alcohol was determined by controlled volatilization of the liquid. It was found that if one drop of alcohol fell into the vaporizing flask every seven seconds, then seven milliliters of alcohol were vaporized each hour. This volume of alcohol represents three liters of alcohol vapor, considering ethyl alcohol as an ideal gas. The other flow rates for alcohol were determined in a similar manner.

Chlorination Procedure. Since all the chlorinations followed the same pattern, the run with the flow ratio of chlorine to alcohol of one to one and a temperature of 125° C. is described as typical.

The thermocouple junction was inserted in the well at the reference point. The temperature of the reaction tube was set at a constant temperature of 125° C. by adjusting the heating coil transformer. The alcohol vaporizer heater which had been previously set to heat the bath to 90° C. was turned on. A substitute cold trap receiver was set in place in the Dewar flask. After the temperatures of the heater and vaporizer were constant at the desired points, the alcohol flow was begun. The alcohol drop rate was controlled by means of the burette stopcock and was adjusted to a rate of one drop every seven seconds. The al-

cohol alone was allowed to pass through the system for about fifteen minutes in order to sweep oxygen from the system. Up to this point the stopcock of the calcium chloride tube was closed. The cushion bottle was then evacuated to remove all oxygen. The chlorine tank valve was then opened slightly to fill the cushion bottle with chlorine. The drying tube stopcock was opened and the chlorine valve adjusted so that the flowmeter reading indicated a chlorine flow of three liters per hour. A small stream of water was allowed to pass through the wash tower.

The temperature of the reaction tube was observed to change with the reaction mixture passing through the tube so the temperature was readjusted to 125° C. The drop time of alcohol was checked again and if not correct was adjusted to the proper rate. The chlorine flow was also checked and adjusted if necessary. With these factors properly adjusted, the burette reading was made. Immediately after the burette reading was taken, the substitute cold trap receiver was removed and was replaced by a clean dry one.

The temperature, flow rate, and drop time were checked periodically at intervals of not more than fifteen minutes. After the reaction had been allowed to run for exactly twelve hours, the chlorine flow was shut off, and the stopcocks on the drying tube and on the burette were closed. The wash tower water was shut off and the final burette reading was made. The receiver was removed and the reaction mixture was poured into a storage bottle. The storage bottle was loosely plugged with glass wool to allow the excess hydrogen chloride in solution to escape.

Separation. The reaction mixtures were expected to contain acetaldehyde, chlorinated acetaldehydes, acetal, chlorinated acetals, and other compounds.

Separation of the reaction mixture into its components was first attempted by fractional distillation. This method proved undesirable, probably because of further reaction of the hydrogen chloride in solution with the other components.

The reaction mixture was next treated according to the method of Chattaway and Backeberg (7) to achieve separation. First, solid potassium carbonate was added to the mixture in order to neutralize the hydrogen chloride in solution. Next, the reaction mixture was refluxed for eight hours in the presence of solid calcium carbonate and excess ethyl alcohol in order to convert the aldehydes to acetals. This treatment was followed by fractional distillation of the products. This method proved unsatisfactory, however, for two reasons: (a) the potassium carbonate tended to make the reaction mixture basic enough to allow aldol condensation to take place rather extensively; and (b) the aldehydes present were only partially converted to acetals.

In another attempt to prepare the reaction mixture for separation, calcium carbonate was added to neutralize the hydrogen chloride; concentrated sulfuric acid was added; and the mixture was distilled. This treatment resulted in decomposition of the products with the formation of a polymerized mass in the still-pot.

The next method attempted (11) was to reflux the products with excess ethyl alcohol in the presence of calcium chloride.

The hydrogen chloride in solution acted as a condensing agent for the formation of acetals. Water, which had been cooled to approximately 0° C., was circulated through the condenser by means of a centrifugal pump. This measure was taken to insure condensation of the acetaldehyde present in the mixture. The mixture was refluxed for a period of eight hours, then treated with calcium carbonate to neutralize the excess hydrogen chloride, filtered, and then fractionally distilled at atmospheric pressure.

On refluxing, the reaction mixtures were observed to become badly discolored. It was found that, if the reaction mixtures of the one-to-one and two-to-one ratios were allowed to stand for at least twenty-four hours before refluxing, the discoloration on refluxing was greatly decreased. This waiting period seemed to have little effect on the four-to-one ratio mixture as it was found to discolor considerably on standing. The reaction mixtures were observed to decompose on distillation. This decomposition was evident in the fact that the temperature would gradually decrease as higher-boiling fractions were being removed. This decomposition was minimized by vacuum distillation. Since the major portion of the material was low-boiling, it was necessary to begin the distillations at relatively high pressures, then decrease the pressure periodically as the boiling point of the distillate increased.

The separation procedure finally used was as follows: (a) the reaction mixtures were allowed to stand for at least twenty-four hours after formation before further treatment; (b) an a-

amount of ethyl alcohol equal to the weight of the reaction mixture and one-third of this weight of calcium chloride were added to the reaction mixture and this mixture was then refluxed for eight hours; (c) the reaction mixtures were then treated with calcium carbonate to neutralize the hydrogen chloride present, and filtered; and (d) these filtrates were then fractionally distilled under reduced pressure.

At one point in each of the distillations it was observed that the distillate consisted of two immiscible layers. The upper layer was found to contain water, while the lower layer consisted of organic liquid. Distillation was continued until only one phase was being received. At this point the two phases were separated and the organic layer was returned to the still-pot. The water layer was discarded.

The data compiled from the distillations are shown in Tables 1, 2, 3, 4, and 5.

Analysis. The refractive index was determined for each cut of each distillation. For each plateau cut the density was also determined. The values for these properties are shown in the tables.

It has been reported that acetal forms an azeotrope with ethyl alcohol which boils at 78.3° C.(3). For this reason, the cuts which had a boiling point in this range were combined for each distillation and analyzed for acetaldehyde, to which the acetal was hydrolyzed, by the following method (16). A saturated aqueous solution of 2,4-dinitrophenylhydrazine which was also 2 N with hydrochloric acid was prepared. A few drops of acetalde-

Table 1

Chlorine:alcohol-1:1
Temperature-150°

Cut No.	Pressure (mm.)	Boiling Point (°C.)	Weight (g.)	Refractive Index $n_D^{33^\circ}$	Remarks
1a	165	44	7.96	1.3641	
2a	165	44	7.92	1.3594	
3a	165	44	7.83	1.3598	
4a	111	47-49	2.53	1.3788	
5a	111	49-53	7.89	1.4189	----Water removed.
6a	111	53-94	2.57	1.4271	
7a	111	94	1.89	1.4165	
8a	111	94-95	7.41	1.4170	Density-(33°)-1.0276g/ml.
9a	111	95-96	6.80	1.4168	

Table 2
 Chlorine:Alcohol-1:1
 Temperature-125°

Cut No.	Pressure (mm.)	Boiling Point (°C.)	Weight (g.)	Refractive Index $n_D^{33^\circ}$	Remarks
1b	165	45	6.82	1.3593	
2b	165	45	6.59	1.3588	
3b	165	45-46	6.74	1.3581	
4b	165	46-49	7.24	1.3593	
5b	37	47 $\frac{1}{2}$	3.23	1.3923	--Water removed.
6b	37	46-47 $\frac{1}{2}$	2.41	1.3898	
7b	36	44-69	2.81	1.4201	
8b	36	69-71	8.37	1.4149	Density-(33°)-1.0198g/ml.
9b	36	71-72	8.47	1.4154	

Table 3

Chlorine:Alcohol-1:1
Temperature-100°

Cut No.	Pressure (mm.)	Boiling Point (°C.)	Weight (g.)	Refractive Index n_D^{23}	Remarks
1c	165	44-45	11.08	1.3600	
2c	165	45-45 $\frac{1}{2}$	9.81	1.3580	
3c	165	45 $\frac{1}{2}$	10.03	1.3580	
4c	165	45 $\frac{1}{2}$	5.53	1.3588	
5c	165	45 $\frac{1}{2}$	1.88	1.3590	
6c	113	40-48	1.81	1.3716	
7c	113	48-49	1.90	1.3903	
8c	111	52	1.96	1.4201	-----Water removed.
9c	111	52-92	4.28	1.4275	
10c	111	92-94	5.65	1.4159	
11c	111	94-96	7.71	1.4169	Density-(53°)-1.0211g/ml.
12c	111	96	3.68	1.4168	

Table 4

Chlorine:alcohol-2:1
Temperature-125°

Cut No.	Pressure (mm.)	Boiling Point (°C.)	Weight (g.)	Refractive Index $n_D^{33^\circ}$	Remarks
1d	166	45 $\frac{1}{2}$	13.65	1.3590	
2d	166	45 $\frac{1}{2}$ -46	5.78	1.3590	
3d	166	46-54	1.34	1.3600	
4d	113	47-50	4.71	1.3888	
5d	113	50-52	3.77	1.3913	----Water removed.
6d	37	46-65	3.52	1.4318	
7d	37	65	4.11	1.4190	Density-(33°)-1.0271g/ml.
8d	37	65-71	2.92	1.4181	
9d	37	71	6.71	1.4131	Density-(33°)-1.0263g/ml.
10d	37	71-64	2.17	1.4198	

Table 5

Chlorine:Alcohol-4:1
Temperature-125°

Cut No.	Pressure (mm.)	Boiling Point (°C.)	Weight (g.)	Refractive Index $n_D^{33^\circ}$	Remarks
1e	165	44	1.59	1.3588	
2e	165	44-45	13.83	1.3594	
3e	165	45-51	1.88	1.3590	
4e	43	50-52	2.81	1.4330	----Water removed.
5e	37	52-61	1.59	1.4296	
6e	37	61-72	1.01	1.4211	
7e	37	72-75	1.75	1.4202	
8e	37	75-95	0.79	1.4222	
9e	37	95-96	6.32	1.4301	Density-(33°)-1.1275g/ml.

hyde were added to the solution to make it saturated with 2,4-dinitrophenylhydrazine and the solution was filtered. The cuts previously mentioned were then added to 200 ml. of this solution and the mixture was allowed to stand. The mixture was then filtered through a tared crucible with a fritted disc. The filtrate was tested by addition of fresh 2,4-dinitrophenylhydrazine solution to determine if all of the acetaldehyde had reacted. This was repeated until further addition of the solution caused no precipitation. The crucible and precipitate were then dried in a vacuum desiccator until the weight was constant. From the weights of 2,4-dinitrophenylhydrazine formed the amount of acetaldehyde produced in each reaction was calculated. These figures are shown in Table 6. The melting point of each of the 2,4-dinitrophenylhydrazones formed is also shown in this table.

Each plateau cut was tested with ammoniacal silver nitrate solution. In each case the silver was oxidized, indicating that aldehydes were present. Derivatives were formed for each of the plateau cuts with the exception of cuts 5b, 8c, 5d, 7d, and 4e. These derivatives and their melting points are shown in Table 6. The semicarbazones were formed by reaction of the test liquid with semicarbazide and sodium acetate (6). The phenylosazone was formed by the method used by Chattaway and Farinholt (8).

Unsuccessful attempts were made to form aldehyde derivatives such as phenylhydrazones and semicarbazones of cuts 5b, 8c, 5d, and 4e. These cuts were found to contain dissolved water and thus were assumed to be azeotropic mixtures. When more water was added to each of these cuts and the refractive index of the or-

Table 6

Derivatives

Out No.	Weight 2,4-Dinitro- phenylhydrazones (g.)	Melting Point 2,4-Dinitro- phenylhydrazones (°C.)	Calculated Weight Acetaldehyde (g.)	% Conversion of Alcohol to Acetaldehyde	Melting Point of other Derivatives (°C.)
1a } 2a } 3a }	1.0468	148-148	0.2068	0.33	
1b } 2b } 3b }	0.7863	147-149	0.1652	0.28	
1c } 2c } 3c } 4c } 5c }	0.7484	142-144	0.1474	0.24	
1d } 2d }	0.5686	142-146	0.1122	0.27	
1e } 2e }	0.3323	145-148	0.0656	0.21	
8a					Semicarbazide 144-146
8b					Semicarbazide 145-146
11c					Semicarbazide 145-147
9d					Semicarbazide 144-146
9e					Phenylosazone 164-170

ganic layer which separated was taken, it was observed to be lower than that of the original cut.

The physical constants of cut 7d are in good agreement with those found in the literature for α,β -dichlorodiethyl ether. The value for the boiling point at a pressure of 37 mm. calculated from literature values (24) is 63° C. compared to 65° C. which was the boiling point of this fraction. The literature value given for the density of α,β -dichlorodiethyl ether is 1.174g./ml. at 23° C. (22) compared to the value found of 1.0971 g./ml. at 33° C. No solid derivative is listed in the literature for this compound.

It was concluded that cuts 7a, 8a, 9a, 8b, 9b, 10c, 11c, 12c, 9d, and 10d were chloroacetaldehyde diethyl acetal. The literature value for the refractive index at 20° C. is 1.4171 (10); the reported density at 20° C. is 1.017g./ml. (10); and the calculated boiling points at pressures of 111 and 37 mm. are 99° C. and 72° C., respectively (10) (19). The reported melting point of chloroacetaldehyde semicarbazone is 148° C. (6).

It was concluded that cut 9e was dichloroacetaldehyde diethylacetal. The literature value for the density of this compound is 1.1383g./ml. at 14° C. (21). The calculated boiling point at a pressure of 35 mm. is 94° C. (23). The melting point of glyoxal phenylosazone, which is formed when dichloroacetaldehyde reacts with phenylhydrazine (8), is $169-171^{\circ}$ C.

DISCUSSION OF RESULTS

From the information obtained from the vapor-phase chlorinations performed in this work it is indicated that chloral is not obtained in appreciable quantities under these conditions. Under the conditions of the experiment it was necessary to allow the reaction to proceed with rather small rates of flow of chlorine and alcohol vapor to prevent explosion of the reaction mixtures. This resulted in rather small quantities of products considering the length of time of reaction.

The main products of the reaction after treatment with ethyl alcohol were found to be acetal, chloroacetal, α,β -dichlorodiethyl ether, and dichloroacetal. The proportion of free aldehydes in the original reaction mixture was not determined.

The effect of temperature on the course of the reaction was evident since it was observed that for the reactions effected at the one-to-one ratio, the yields of acetal and chloroacetal increased with increase in temperature.

When the ratio of chlorine to alcohol vapor was increased, the percent yield of acetal was seen to decrease. While the yield of chloroacetal increased for the two-to-one ratio, it decreased for the four-to-one ratio. It is interesting to note that no detectable amounts of dichloroacetal were formed in the runs with chlorine-to-alcohol ratios of less than four to one, while this compound was the main product for the reaction in which the ratio is four to one.

It was observed that there was a large amount of distillate

collected between the boiling points of the alcohol-acetal cuts and the chloroacetal cuts. It was shown that the fractions distilled in this range contained considerable water. It is obvious that these cuts also contained compounds other than the ones actually shown to be present. This was pointed out by the fact that the refractive index was higher for these cuts than for any of their known components. It is possible that these cuts may contain chloral, dichloroacetaldehyde ethyl alcoholate, or chloral alcoholate, since each of these compounds boils in the range covered by these fractions.

This investigation has indicated several ideas for future workers in the field. In order to investigate the individual compounds formed in the vapor-phase chlorination of ethyl alcohol more fully, it would be necessary to have larger amounts of reaction products formed under reproducible conditions. It might be possible to depress the formation of acetals and to chlorinate at higher temperatures by using a large amount of water vapor in the reaction. Re-circulation of the lower-boiling reaction products might lead to the formation of greater proportions of more highly chlorinated products and a more efficient use of the chlorine.

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BIOGRAPHY

Wallace Edmondson Taylor was born in Little Rock, Arkansas on September 1, 1923.

He attended grade and high schools in that city and was graduated from Little Rock High School in January, 1941. He entered Hendrix College in Conway, Arkansas, in the fall of 1941 and attended there until the spring of 1943.

In July, 1943, he began active service with the United States Navy as a member of the Naval Reserve Air Corps, receiving his commission as Ensign in January, 1945. He was separated from active service in January, 1946, and returned to Hendrix College to receive the Bachelor of Science degree in Chemistry in May, 1947.

Entering Oklahoma Agricultural and Mechanical College in September, 1947, he served as a teaching assistant in the Chemistry Department on a fellowship from the College.

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