Chlorination of Acetaldehyde

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THE demand for the insecticide DDT (dichlorodiphenyltrichloroethane) has provided the main reason for an increased interest in the production of chloral (α,α,α-trichloroacetaldehyde). The long-established method of manufacturing chloral consists of the chlorination of ethyl alcohol, and because this compound has so many other vital uses, the search for an alternative raw material is of practical concern. For reasons of both economy and chemical constitution acetaldehyde was selected for investigation.

In 1832 Wöhler and Liebig (*7*) had demonstrated the production of acid chlorides through the chlorination of aromatic aldehydes. Würtz (*8*) confirmed these data by his trials in 1857 with aliphatic aldehydes, when he introduced the aldehyde into large flasks filled with chlorine gas in direct sunlight. The object of his experiments, however, had been the preparation of chloral—α,α,α-trichloroacetaldehyde. Further trials in 1872 (*9*) were directed toward blocking the reactive —CHO group, so that chlorination could proceed at the methyl group. To obtain the reaction as he conceived it, alcohol, water, and hydrochloric acid were added to the aldehyde prior to chlorination. Twenty to 30% conversion of aldehyde to a mixture of di- and trichloroaldehydes indicated the partial success of his methods.

Concurrently, in 1875, Pinner (*6*) was also concerned with the same problem. His procedures, which differed from those of Würtz, involved the use of aldehyde or paraldehyde and low initial temperature for chlorination. The removal of hydrochloric acid was felt imperative to prevent aldolization and the production of "croton chloral," now called butyl chloral and known to be α,α,β-trichlorobutyraldehyde. In spite of claims to a "main product," the conversion of aldehyde to chloral could have been only 15% by the best calculations from his data. The work herein described was essentially directed to the chlorination of acetaldehyde at the α-carbon position.

Experimental Work

Preliminary trials using apparatus and methods described by Würtz and Pinner confirmed the results as given above. Analyses for the reaction products were developed along the following lines.

Compound	Basis of Test
CCl_3CHO	Caustic breakdown to chloroform
$CH_3CHClCCl_2CHO$	Caustic breakdown to 1,1-dichloropropene
$CHCl_2CHO$	Caustic breakdown and estimation of chloride
CH_3COOH	Titration of total acids and estimation of HCl as chloride
$CHCl_2COOH$	Monoethanolamine breakdown and estimation of chloride by Fajan's method
H_2O	Karl Fischer method

The data given in the tables are for conversion of aldehyde, as these were the values of practical concern. The weight percentage figures obtained by analysis (the sums of which were found = 100 ± 1.5%) were converted into corresponding aldehyde weights and then to per cent conversion. This method accounts for the fact that the total for each table is exactly 100%.

The course of this investigation and its results were dependent essentially upon modifications of apparatus and procedure, the chemical reactants remaining little changed. Results are therefore grouped in terms of the equipment and method of its use, the table and figure captions indicating the systems involved.

Using apparatus such as the first stage shown in Figure 3, two major changes were made in technique: (1) Dispersion of chlorine was greatly improved and (2) the rate of introduction of the gas was increased.

In general, the interdependent rates of addition of chlorine and increase of kettle temperature were maintained at as high a level as was consistent with just providing for an excess of chlorine in the solution. Specifically, in the initial portion of the run, where absorption appeared instantaneous, the chlorine was introduced as fast as the heat of reaction could be removed. Experience imposed an upper limit of 10° C. for this portion of the reaction. The accuracy of control was ±2° C.

The most successful of these runs was one in which 310 grams of acetaldehyde mixed with 200 grams of water were chlorinated (excess chlorine at all stages) at temperatures from 4° to 92° C. in 43 hours; 675 grams of product boiling at 95–97° C. were obtained, which represented a 65% conversion of aldehyde to chloral. The main by-product was butyl chloral. Record of chlorine absorbed, temperature, and time are given in Figure 1.

Examination of per cent conversion results from a series of such runs indicated that between the limits 1 to 3 moles of water per mole of aldehyde the reaction was not sensitive to the initial amount of water. It was decided to fix on the ratio 3 to 1 water-acetaldehyde because purification distillations were not complicated with tarry residue, as they tended to be when the ratio was lower.

To improve further the efficiency of chlorine dispersion, the apparatus shown in Figure 2 was built. The novelty consisted of introducing the gas in between two centrifugal pumps connected in series. The analysis of a typical run is given in Table I. Subsequently, the water in the starting mix of 3 moles of water and 1 mole of aldehyde was replaced by 36% hydrochloric acid (Table I).

The apparatus shown in Figure 3 was used to determine the results of carrying out the chlorination on a continuous basis. A 3 to 1 water-acetaldehyde mix was fed continuously into the first flask at about 0° C., and the final product was collected from the fourth flask, which was kept at about 90° C. A typical result is given in Table II.

Before the obvious difficulties of continuous third-stage chlorination were considered, a series of runs was made, chlorinating to dichloroaldehyde continuously, using the two-pump dispersion system and finishing the third stage batchwise. In this appara-

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Table I. Large Scale, Single-Stage, Batchwise Runs

	Conversion to Aldehyde, %
Chloral	62.6
Butyl chloral	1.4
Dichloroaldehyde	5.6
Acetic acid	28.7
Dichloroacetic acid	1.7
36% HCl at Start	
Chloral	80.2
Butyl chloral	6.7
Dichloroaldehyde	6.0
Acetic acid	5.0
Dichloroacetic acid	2.1

Table II. Small Scale, Four-Stage, Continuous Runs

	Conversion to Aldehyde, %
Chloral	63.0
Butyl chloral	0
Dichloroaldehyde	20.9
Acetic acid	5.0
Dichloroacetic acid	11.1

Table III. Large Scale, Three-Stage, Semicontinuous Runs

	Conversion of Aldehyde, %	
Chloral	91.0	84.0
Butyl chloral	0.4	1.7
Dichloroaldehyde	6.8	10.8
Acetic acid	0	1.4
Dichloroacetic acid	1.8	2.1

Table IV. Large Scale, Third-Stage, Batchwise and Continuous Runs

	Conversion of Aldehyde, %	
	Batch	Continuous
Chloral	92.0	91.0
Butyl chloral	2.9	2.6
Dichloroaldehyde	3.0	2.9
Organic acids as acetic	2.1	3.5

tus, stage 2 consisted of a 5-liter flask fitted with a sintered-glass diffuser for the chlorine gas. The inlet for the overflow from stage 1 was at the bottom of the flask near the diffuser and the overflow was near the top of the flask. A series of six runs was made, each representing 20 liters of crude product. Conversion of acetaldehyde to chloral ranged from 84 to 91%; the limiting analyses for the runs are shown in Table III.

To carry out the third stage continuously, modifications were made in the apparatus to adjust the holdup time. A determination of reaction rate constants gave $K = 0.009$ min.$^{-1}$ down to 3% dichloroaldehyde; thereafter, $K = 0.003$ min.$^{-1}$ Experimental data were also considered in terms of equations given by *MacMullin and Weber* (*5*), who dealt theoretically with the degree of completion to be expected from a first-order reaction carried out continuously in one kettle. The agreement was very good and using these data the optimum third-stage holdup time was determined to be 32 hours.

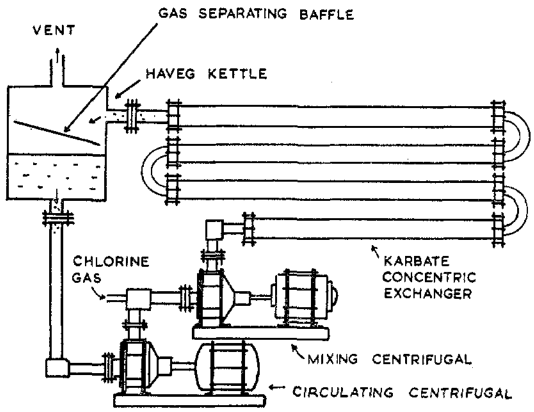


Figure 2. Apparatus for Large Scale, Single-Stage, Batchwise Runs

Using samples of stock crude dichloroacetaldehyde made on the continuous basis, the third stage was now completed continuously and batchwise for comparison (Table IV).

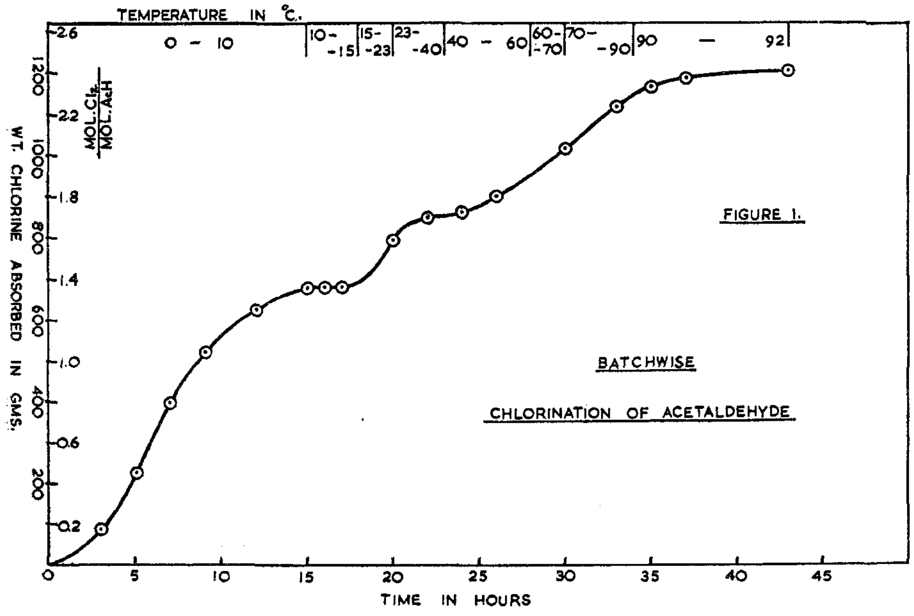
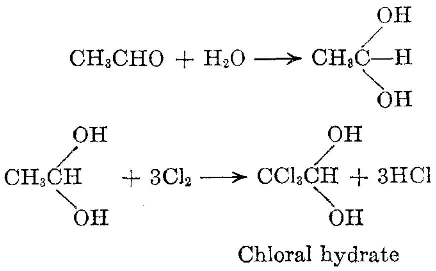


FIGURE 1.

Discussion

From the trials with the small scale single-stage, batchwise apparatus it was clear that water acted effectively to block the reactive —CHO group to permit chlorination only at the α-carbon atom. Moreover, the data in Figure 1 indicated that the chlorine substitution occurred in three distinct steps characterized by specific temperature limits. The reaction, therefore, was as follows:

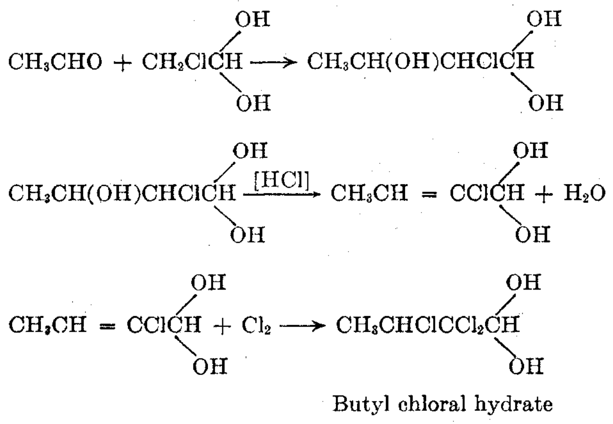


$$\mathrm{CH_3CHO + H_2O \longrightarrow CH_3\overset{OH}{\underset{OH}{C}}{-}H}$$

$$\mathrm{CH_3\overset{OH}{\underset{OH}{C}}H + 3Cl_2 \longrightarrow CCl_3\overset{OH}{\underset{OH}{C}}H + 3HCl}$$

Chloral hydrate

The analyses indicated the main by-product of the reaction was butyl chloral, and it was clear that to improve further the conversion of aldehyde to chloral the nature of this competitive reaction would have to be understood. The pronounced beneficial effect of increasing the rate of input of chlorine at 0° to 10° C. suggested that the side reaction must involve unchlorinated aldehyde and monochloroaldehyde. The probable reaction was visualized as follows:



$$\mathrm{CH_3CHO + CH_2ClCH{<}^{OH}_{OH} \longrightarrow CH_3CH(OH)CHClCH{<}^{OH}_{OH}}$$

$$\mathrm{CH_3CH(OH)CHClCH{<}^{OH}_{OH} \xrightarrow{[HCl]} CH_3CH = CClCH{<}^{OH}_{OH} + H_2O}$$

$$\mathrm{CH_3CH = CClCH{<}^{OH}_{OH} + Cl_2 \longrightarrow CH_3CHClCCl_2CH{<}^{OH}_{OH}}$$

Butyl chloral hydrate

Favorable conditions were therefore defined as those which increased the probability of aldehyde reacting with chlorine and decreased the probability of aldehyde reacting with monochloroaldehyde.

It was with this conclusion in mind that the two-pump dispersion system (shown in Figure 2) was built. The results in Table II were therefore anticipated regarding butyl chloral. This by-product had been effectively avoided. However, the very large increase in acetic acid was a new and undesirable feature. It seemed most likely that the oxidation was accomplished through the agency of a too large excess of chlorine:

$$\mathrm{Cl_2 + H_2O \rightleftarrows HOCl + HCl}$$

$$\mathrm{HOCl \rightleftarrows HCl + (O)}$$

Assuming this explanation to be true, the water in the starting mix was replaced with 36% hydrochloric acid to suppress the formation of hypochlorous acid. The data of Table I indicated that the production of acetic acid was significantly reduced, but an increase in the formation of butyl chloral was also evident. Therefore, although the presence of hydrochloric acid appeared to have suppressed hypochlorous acid formation, it also served to enhance the condensation reaction leading to butyl chloral. Nonetheless, using a low initial temperature (~0° C.) and an excess of chlorine, and having hydrochloric acid present in the starting mix, an 80% conversion of aldehyde to chloral was shown to be possible batchwise. To examine what further possibilities might be inherent with a continuous process, the apparatus of Figure 3 was constructed. From the data of Table II it is seen that butyl chloral was reduced to less than 1%. This was the result expected, as the concurrent introduction of aldehyde and chlorine offered the best conditions for the prevention of the condensation reaction. The acetic acid figure was no higher than the batchwise trials using 36% hydrochloric acid to start with, so that stage 1 at 0° to 10° C. appeared to have operated very satisfactorily.

The dichloroaldehyde and dichloroacetic acid figures, however, indicated that the other two stages at 20° to 30° and 70° to 90° C. were not properly managed. Going back to the explanation for the presence of acetic acid, it was expected that the dichloroacetic acid indicated too great an excess of chlorine in stage 2 and possibly 3. To find out whether this explanation was tenable, a solution of 75% chloral and 25% water was held at 85° C. for 13 hours, while chlorine was passed through the solution through a sintered-glass diffuser. Thirteen per cent trichloroacetic acid was separated (from the high boiling residue) as a pink-white solid melting at 50–55° C. Thus it appeared that the excess of chlorine had to be carefully controlled to prevent substantial oxidation of the aldehyde in all three stages, even though hydrochloric acid was present in saturation amounts. The high dichloroaldehyde figure indicated that the holdup time for stage 3 was insufficient.

Working on the problem of reducing the amount of dichloroacetic acid, trials were made with the larger apparatus with the two-pump system.

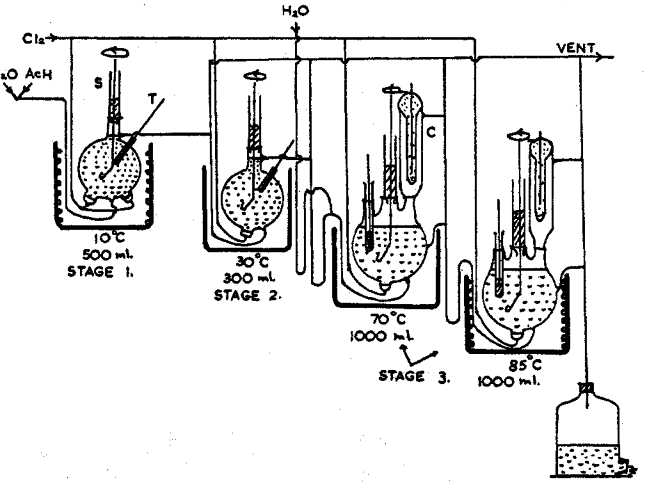


Figure 3. Apparatus for Small Scale, Four-Stage, Continuous Runs

C. Condenser
S. Mercury seal stirrer
T. Thermometer

As can be seen from Table III, the objective of the trials was successfully achieved with the best conversion figures of 90% for chloral and less than 3% for all other by-products, with the exception of dichloroaldehyde which ran at 7%.

Having discovered a means of controlling the condensation and oxidation side reactions, a final attempt was made to determine whether a completely continuous operation could be used.

Bell and Longuet-Higgins (*1*) have considered the halogenation of acetone, using alkaline hypobromite, and found that the reaction was of zero order respecting the hypobromite and of first order respecting acetone. In this investigation, as the rate of chlorination is independent of the concentration of chlorine, it is assumed to be of first order respecting the concentration of dichloroaldehyde. On this basis the reaction rate constants were determined experimentally to be $K = 0.009$ min.$^{-1}$ down to 2.7% by weight of dichloroaldehyde and $K = 0.003$ min.$^{-1}$ below this amount. This result was confirmed by substituting the experimentally determined degree of completion of the reaction in stage 3 in the equations of MacMullin and Weber. A reaction velocity constant of 0.009 min.$^{-1}$ was the answer found.

Table IV shows that when the holdup time was properly adjusted, results were entirely comparable with batchwise trials. The lowest practical limit of dichloroaldehyde was shown to be near 3% on the basis of aldehyde conversion.

Conclusions

In the chlorination of acetaldehyde or paraldehyde in the presence of water it is possible to exceed 90% conversion to α,α-dichloroaldehyde or α,α,α-trichloroaldehyde. The main competing reaction appears to involve the condensation in the presence of hydrochloric acid of a molecule of acetaldehyde with a molecule of monochloroaldehyde and produces finally α,α,β-trichlorobutyraldehyde. Another side reaction involves the oxidation, through the agency of hypochlorous acid, of the aldehydes to the corresponding acetic acid, dichloroacetic acid, and trichloroacetic acid. Both types of side reaction can be controlled through proper arrangement of temperature and conditions pertaining to the introduction of chlorine. The chlorination can be carried batchwise, but is most efficiently managed on a semicontinuous or completely continuous basis.

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Kinetics of Coal Gasification

Proposed Mechanism of Gasification

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IN THE course of work in the development of the synthetic liquid fuels program, attention has been centered primarily on coal as a source material for the necessary synthesis gas or hydrogen.

Gasification of coal has been undertaken in a number of ways; most of the work of the Bureau of Mines has been concentrated on the reaction in dilute suspension of powdered coal with oxygen and steam.

Over a period of years, considerable scientific labor has been devoted to small-scale studies of certain single reactions that are a part of the complex reaction system comprising coal gasification. Isolation of these reactions was, of course, necessary to obtain adequate and accurate data on reaction mechanism and rate, although in many cases competing reactions and the inherent difficulties of high temperature measurement required very ingenious experimental methods.

Although such studies serve as a basis for the understanding of the nature of the reactions involved, they do not integrate the kinetics of the individual reactions with the heat transfer and mass transport phenomenon, which are necessarily a part of the gasification process.

Because of the significant influence of size on these phenomena, bench-scale work has not been adequate for application to commercial-size units. On the other hand, empirical treatment of data obtained from the observation of pilot plant scale gasifiers has resulted in considerable information regarding the operation and performance of each individual unit but does not clarify the complex physical processes involved and does not permit the design of other gasifiers in other than empirical fashion.

For these reasons, it was decided to make this work an engineering study of the gasification process as a whole. An extensive search of the literature was made to obtain available rate data and to suggest a suitable mechanism of the over-all process, including heat and mass transfer. Theoretical equations expressing the kinetic changes in gasification were derived and applied in the calculation of conversion and product distribution to be expected in the gasification of powdered coal with such variable operating conditions as steam-coal ratio, oxygen-coal ratio, gasifier heat loss, and steam preheat. The results of this theoretical approach were then compared with data obtained experimentally from operation of suitable gasifiers.

The theoretical calculations depend on the results of the literature survey, but not to the extent that might be thought. Three specific rate constants are involved, but the accuracy of these constants does not affect the form of the equations derived, and consequently does not affect the correlation of the chemical reactions and thermal and mass transfer involved in gasification.

An extensive bibliography of the gasification literature has been published (*44*).

The thermodynamics of the gasification system have been fairly well defined and may serve as a guide in choosing the variables to be studied and to indicate the limits toward which a reacting system may progress. Numerous papers have presented

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