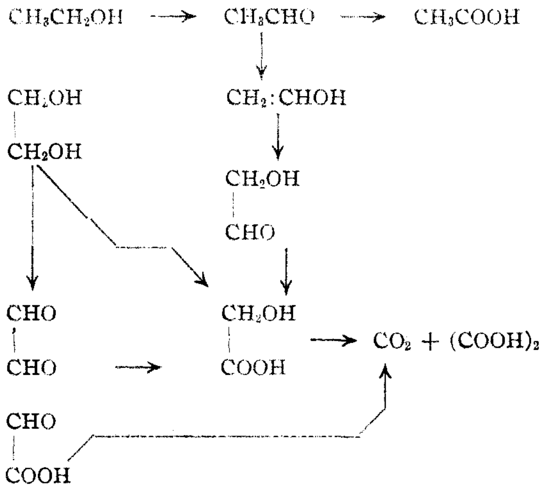

COLUMBUS, OHIO.

ETHYLENE CHLOROHYDRIN AND β,β-DICHLOROETHYLSULFIDE.[1]

BY M. GOMBERG.

Received June 21, 1919.

Within a few days after the so-called "mustard gas" was introduced as a means of offense in warfare (July 12–13, 1917), it was definitely identified as β,β-dichloroethylsulfide. There was reason to believe that it had been manufactured from ethylene chlorohydrin, according to the method described some 30 years previously by V. Meyer.[2] A second possible method,—the reaction between ethylene and the mono- or dichloride of sulfur,—was also given some consideration, but on the basis of preliminary experiments in several laboratories, was not looked upon at that time as promising.[3]

The directions in the literature for the preparation of dichloroethylsul-

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[1] This article has been approved for publication by the Director of the Chemical Warfare Service. The experimental work was done at the Chemical Laboratory, University of Michigan, under the auspices of the Bureau of Mines, War Gas Investigations. The results were reported to the Bureau of Mines in three reports—March 9, April 8, and June 28, 1918.

[2] *Ber.*, **19**, 3260 (1886).

[3] In the light of subsequent and the more recent events, it seems almost certain that Guthrie actually did have in his hands some dichloroethylsulfide, as a result of his experiments with this reaction. He says: "Its smell is pungent and not unpleasant, resembling that of oil of mustard; its taste is astringent and similar to that of horseradish. The small quantities of vapor which it diffuses attack the thin parts of the skin, as between the fingers and around the eyes, destroying the epidermis. If allowed to remain in the liquid form on the skin, it raises a blister." (*Quart J. Chem. Soc.*, **12**, 117 (1860).)

fide from chlorohydrin seemed sufficiently explicit to furnish the basis of a reliable technical process. The reactions are as follows: (1) Ethylene chlorohydrin, in solution, reacts with sodium sulfide and gives dihydroxyethylsulfide in good yields; (2) this product, harmless in itself, gives the highly toxic dichloroethylsulfide when treated with phosphorus pentachloride (V. Meyer) or with conc. hydrochloric acid.[1]

$$2HOCH_2CH_2Cl + Na_2S = HOCH_2CH_2 - S - CH_2CH_2OH + 2NaCl.$$

$$(HOCH_2CH_2)_2S + 2HCl = ClCH_2CH_2 - S - CH_2CH_2Cl + 2H_2O.$$

The fundamental difficulty was how to get the chlorohydrin itself. The methods in the current scientific literature for the preparation of this substance seemed wholly inadequate for a technical process. These methods fall within two classes: (*a*) the addition of hypochlorous acid to ethylene,[2] (*b*) the action of sulfur monochloride,[3] of hydrochloric acid,[4] or of chlorine[5] upon pure ethylene glycol. For the preparation of chlorohydrin merely on a laboratory scale it has been found more desirable to use pure ethylene glycol,—in itself not readily obtainable,—as the starting point, and this is the method usually recommended. But from the practical standpoint, for a technical method, the hypochlorous acid addition reaction seemed to offer more promise, notwithstanding the discouraging facts that alkaline hypochlorites as such are known to have no action on ethylene, that free hypochlorous acid can only be prepared in solutions from 1 to 3%, and that the best yield of chlorohydrin by this reaction was known to be only about 30% of the theoretical amount (Butlerow).

The most feasible source of hypochlorous acid for technical operation was deemed to be bleaching powder. It was suggested, in various reports from abroad that ethylene could be passed into a suspension of bleaching powder in water, and dil. mineral acid, or carbon dioxide under pressure, could be used to liberate hypochlorous acid at the rate that the latter is being used up by the ethylene. Whether chlorohydrin has actually been made by the above method on a technical scale, the writer does not know. Our own experience in this direction on laboratory scale gave poor yields of chlorohydrin.

In view of the many difficulties connected with the use of bleaching powder, several investigators independently of each other attempted to utilize as the source of hypochlorous acid the solution of chlorine in water, *i. e.*, bringing chlorine and ethylene into reaction in presence of water. As is well known, the reaction between chlorine and water yields but very

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[1] H. T. Clarke, *J. Chem. Soc.*, **101**, 1583 (1912).

[2] Carius, *Ann.*, **126**, 197 (1863); Butlerow, *Ibid.*, **144**, 42 (1867).

[3] Carius, *Ibid.*, **124**, 257 (1862); Fittig u. Ström, *Ibid.*, **267**, 191 (1892).

[4] Ladenburg, *Ber.*, **16**, 1407 (1883).

[5] Donciu, *Monatsh.*, **16**, 3 (1895).

little hypochlorous acid. This is due not merely to the inherent proneness of the acid towards decomposition with liberation of oxygen, but even more so to the presence of the hydrochloric acid.

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl.$$

The equilibrium is thus very much on the left-hand side of the equation. Consequently, it was generally assumed that since the amount of hypochlorous acid as compared with the amount of free chlorine must at best be but small, the tendency would therefore be greater towards the formation of ethylene chloride rather than of chlorohydrin.

$$CH_2{:}CH_2 + HOCl = HOCH_2.CH_2Cl.$$
$$CH_2{:}CH_2 + Cl_2 = ClCH_2.CH_2Cl.$$

Various procedures were suggested in order, presumably, to obviate, or to overcome this difficulty. Some[1] have proposed to pass ethylene and chlorine into a solution of sodium borate,—the borax, through its interaction with the hydrochloric acid, should keep down the hydrogen ion concentration; sodium hydroxide is added at intervals in order to bring back into solution the boric acid which has separated. Others have used copper oxy-chloride, alternately saturating the solution with chlorine and with ethylene, catalytic influence being claimed as additional advantage for the copper salt.[2] Some[3] have proposed to pass the unsaturated hydrocarbon into an aqueous bath in which "chlorine or hypochlorous acid is generated electrolytically." Others[4] have carried on the reaction between ethylene and chlorine in presence of steam, or at temperatures slightly under 100°, introducing the two gases simultaneously or alternately. Obviously, of the procedures mentioned above, only those that employ borax or copper oxychloride actually tend to depress the hydrogen ion concentration[5] and thus do affect the equilibrium in favor of the hypochlorous acid, and, presumably, in favor of chlorohydrin. But, as will be shown in this paper, the accumulation of the sodium chloride in solution is more harmful than that of hydrochloric acid and is distinctly detrimental to the favorable progress of the reaction. The procedures based upon the interaction of ethylene, chlorine and water at, or near to, 100° can hardly favor the reaction between chlorine and water in favor

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[1] J. B. Conant, in report to the Bureau of Mines. Williamson, in 1845, used disodium acid phosphate (*Ann.*, **54**, 133 (1845)).

[2] J. C. Irvine, of St. Andrews University, in report at Bureau of Mines.

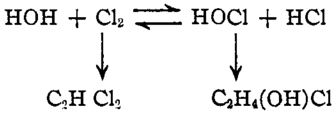
[3] McElroy, *U. S. pat.* 1,253,615, *C. A.* **12**, 702 (1918).

[4] E. P. Kohler, in report to the Bureau of Mines; McElroy, *U. S. pat.* 1,253,616, *C. A.* 12, 703 (1918); Commerc. Research Co., *Br. pats.* 113,954 and 113,955, *C. A.*, 12, 1469 (1918); Eldred, *Can. pat.* 186,634, *C. A.*, 12, 2325 (1918).

[5] It must not be forgotten that by the use of those bases which produce soluble chlorides the concentration of the hydrogen ion is depressed, but not that of the chlorine ion. Hence, the improvement due to the use of such bases is limited. See Jakowkin, *Z. physik. Chem.*, **29**, 613 (1889).

of hypochlorous acid. In all probability they give lower yields of chlorohydrin,—the hypochlorous acid is less stable at that temperature, the ethylene is less soluble, etc. The surmised advantage of such methods is that chlorohydrin is being removed from its dil. aqueous solution as soon as produced, by virtue of the fact that it tends to form with water a constant boiling mixture possessing a low boiling point, as will be shown further on. But chlorohydrin of itself is of least influence as a factor in depressing the concentration of the desired product attainable in this reaction, which also will be shown later.

The premises which the writer used for the working out of his procedure were of somewhat different nature from those as above described.[1] They were suggested by the excellent paper by John Read and Margaret M. Williams,[2] on the action of bromine water on ethylene. Substituting chlorine for bromine we can express, as they have done, the relationship between water, chlorine and ethylene schematically in the following manner:



$$\begin{array}{ccc} HOH + Cl_2 & \rightleftharpoons & HOCl + HCl \\ \downarrow & & \downarrow \\ C_2H\ Cl_2 & & C_2H_4(OH)Cl \end{array}$$

In other words, the principal factor which is likely to determine the ratio of ethylene chloride to chlorohydrin must lie, after all, in the relative velocities of the two reactions,—between ethylene and chlorine on the one hand, and between ethylene and hypochlorous acid on the other. In case the second reaction occurs with greater velocity than the first, then we should be dealing with a case of mobile equilibrium, and the principal product would be chlorohydrin,—provided that care be taken to maintain stirring, so that ethylene reacts only with the chlorine in solution and not with the gaseous chlorine. Experiments proved that such is actually the case. Very little ethylene chloride is produced until a concentration of 6 to 8% of chlorohydrin has been attained.

A brief study has been made of some factors which influence the rate of chlorohydrin formation, the concentration of chlorohydrin attainable, also of the practical means of separating the chlorohydrin from its aqueous solution. Some data concerning the preparation of β,β-dichloroethylsulfide from chlorohydrin, and of unsuccessful attempts to prepare it from ethylene chloride, are given at the end of this paper.

I. Chlorohydrin.

Ethylene.—The unsaturated hydrocarbon was prepared from alcohol by the use of aluminum sulfate as the catalyst.[3] The hydrated aluminum

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[1] None of the above mentioned processes was known to the writer at the time his own work was being done.

[2] *J. Chem. Soc.*, 111, 240 (1917).

[3] Sabatier and Mailher, *Ann., chim. phys.*, [8] 20, 300 (1910); Senderens, *Ibid.*, 25, 491 (1912).

salt was heated in an iron dish till the water was driven off The porous residue was granulated, the larger lumps reduced to about $^1/_8$ inch in diameter, and the fine powder was removed by sifting through a 20-mesh sieve. The granular salt was placed in a 30-inch brass tube through a length of about 25 inches, and the tube placed in an electrically heated furnace. The alcohol was led into the tube in the form of vapor, previous preheating of the vapor having been found to be without advantage in our small scale experiments. The issuing gases were passed through a condenser and receiver and collected as usual over water. Best results were obtained with a temperature of 420 to 460°. The yield of ethylene varied, 60 to 80% of the calculated amount being produced. The ethylene is 95 to 97% pure. The aluminum sulfate gradually becomes reduced and at the same time coated with a layer of carbon, but on reheating in the furnace and passing air over it, the catalyst becomes white and resumes its former activity.

Procedure.—From one to three liters of water was placed in a wide-mouth bottle which was provided with a tightly fitting stopper with 4 holes. One opening carried a glass tubing for the introduction of ethylene; the second, for the introduction of chlorine; the third is for an efficient stirrer, and the fourth carried a tube for connection with a trap, in order to indicate whether any uncombined gas was escaping,—ethylene or chlorine, and also for the purpose of carrying on the reaction under slight pressure when this was desired. The rate at which the gases were introduced was carefully noted, and the relative quantities of each were so regulated that practically no gas left the reaction chamber. The ethylene was kept just enough in excess over chlorine to keep the solution colorless. At the end of the experiments the aqueous solution was separated from the ethylene chloride if any had been formed, and the amount of chlorohydrin in solution was carefully determined in an aliquot portion. The method of estimation is based upon the difference between the indices of refraction of water (1.333) and pure chlorohydrin (1.442). The indices of refraction of known concentrations of chlorohydrin were determined in an Abbe refractometer, and plotted, the result being a straight line. In order, therefore, to determine the quantity of chlorohydrin in a given solution, some of the latter is carefully neutralized with sodium carbonate and distilled. From the index of refraction of the distillate, previously diluted in order to throw out any ethylene chloride that might be present in solution, the per cent. of chlorohydrin in the distillate is read off at once. The method is rapid and readily accurate within 0.5%.

Rate of Formation, and the Concentration Attainable.—The rate at which the gases could be introduced was found to depend very much upon the efficiency of the stirring arrangement. At the outset of the operation they were often passed in at the rate of 20 to 25 liters each per hour, the solution being kept at about 10 to 12°, which gave almost as good results as 0°. But such rates cannot be kept up for long, and with the progress of the reaction the rate of combination between the two gases slows down. Up to a concentration of chlorohydrin equal to 5%, and 2.5% hydrochloric acid, there is hardly any ethylene chloride being formed. But when the concentration of chlorohydrin has reached about 8% the absorption of the reacting gases becomes markedly slower, even when employing vigorous stirring and working under a pressure of 2 to 3 inches mercury. But by continuing to pass in the gases at a slow rate it is possible to attain concentrations of chlorohydrin equal to 14 to 15%. Such high concentrations are reached, however, only at the expense of a good deal of ethylene, since with the increase of concentration in chlorohydrin proportionately more and more ethylene chloride is produced.

Salts of mercury, because of their capacity to unite with ethylene, were tested as possible favorable catalysts for this reaction. The results, however, did not indicate any particular influence in this respect.

Effect of Neutralizing the Acid.—The attempt to depress the amount of hydrochloric acid, which might otherwise accumulate in the reaction mixture, by the addition of powdered marble or precipitated calcium carbonate resulted unfavorably. The aqueous solution soon became saturated with carbon dioxide; this, apparently, greatly diminished the solubility of ethylene, and after a while the reaction slowed down very considerably. Much better results were obtained when the neutralization was done at intervals by successive small additions of calcium hydroxide in amounts corresponding to the quantity of the acid formed, as judged from the amount of ethylene used up. By this procedure solutions containing 14 to 15% of chlorohydrin were obtained. Thus, the neutralization of the acid is of little effect as regards the concentration of chlorohydrin attainable. Nor was there any evidence that the rate of reaction was improved; on the contrary, it rather seemed as if the rate of combination was somewhat slower than when the acid was left unneutralized, which effect might have resulted from the probable decrease in solubility of the gases in water containing calcium chloride, or any other salts, for that matter.

Ratio between Chlorohydrin and Ethylene Chloride.—It was found that when the operation is limited to the production of only 6 to 8% of chlorohydrin there is comparatively little ethylene chloride produced, from 0 to 10%. Higher concentrations, particularly 14 to 15%, are obtained, as indicated above, only by using a good deal of ethylene, which is lost in the formation of ethylene chloride. When ethylene, chlorine and water alone are used, the by-product is hydrochloric acid; if this acid is progressively neutralized with borax, sodium hydroxide, or calcium hydroxide, the corresponding salts are produced. Experiments were carried out with the object of getting some idea as to the influence which these various products exert on the ratio of chlorohydrin to ethylene chloride, *i. e.*, the influence of chlorohydrin, of hydrochloric acid, and of the different salts. As has been mentioned, very little ethylene chloride is ordinarily produced when the concentration of chlorohydrin is 8% or lower, *i. e.*, when the concentration is equal to a *N* solution or less. Under these circumstances, the concentration of the acid, or of the salts resulting on its neutralization, is approximately similar. Obviously, then, the pronounced influence of each of the factors mentioned comes into play only after the normal concentration is reached, as not until then does the formation of ethylene chloride commence to be appreciable. Accordingly, the experiments were arranged in this manner: One liter of water was taken, chlorine and ethylene passed into it, and at intervals the content of chlorohydrin and ethylene chloride produced was determined; this was continued until the concentration of the former was considerably above normal. Then experiments under as nearly similar conditions as possible were carried out, with water which contained, to begin with, an amount of chlorohydrin, or of acid, or of the salts, to make *N* or 2 *N* of each, respectively. The following table gives the results obtained. The initial strength of the various solutions, as well as the concentration of the

TABLE I.

	Chlorohydrin produced.		Ethylene dichloride.		Ethylene distribution.	
Solution.	Concentration. *N*.	Ethylene consumed. G.	Cc.	Ethylene consumed. G.	In chlorohydrin. %.	In ethylene chloride. %.
Water	0.92	25.8	0.0	0.0	100	0
	1.25	35.0	10.0	3.62	91	9
	1.62	45.4	22.0	7.96	85	15
Chlorohydrin, *N*	0.92	25.8	1.0	0.36	99	1
Chlorohydrin, *N*	0.54	15.1	0.0	0.0	100	0
	0.63	19.0	3.5	1.27	94	6
Hydrochloric acid, 2 *N*	0.23	6.44	0.0	0.0	100	0
	0.47	13.20	2.0	0.72	96	4
	0.94	26.40	12.0	4.35	86	14
Hydrochloric acid, 2 *N*	0.40	11.2	1.0	0.36	97	3
	0.69	19.3	8.0	2.90	87	13
Calcium chloride, 2 *N*	0.46	12.9	7.0	2.53	84	16
	0.75	21.0	17.0	6.15	77	23
	1.04	29.1	36.0	13.00	69	31
Calcium chloride, 2 *N*	0.40	11.2	9.0	3.26	77	23
	0.69	19.3	18.0	6.52	75	25
	0.96	26.9	34.0	12.50	70	30
Magnesium chloride, 2 *N*	0.43	12.1	3.5	1.27	90	10
	0.66	18.5	18.0	6.52	74	26
Sodium chloride, 2 *N*	0.46	12.9	14.0	5.07	72	28
Sodium chloride, 2 *N*	0.36	10.1	9.0	3.26	76	24
	0.56	15.7	28.0	10.14	61	39

chlorohydrin actually produced in the experiment, are expressed in terms of normality factor.

Fig. 1 shows more graphically the influence exerted by the various factors upon the ratio of ethylene consumed in chlorohydrin formation to that consumed in ethylene chloride formation.

It is not safe to draw decided conclusions from so few experiments, but the above results, as far as they go, seem to indicate: (1) hydrochloric acid, by itself, even when in concentration 2 *N*, does not hinder the conversion of ethylene exclusively into chlorohydrin. But when the concentration of the latter has reached about 3 % (HCl = 2.3 *N*) ethylene chloride commences to be produced in considerable amounts. (2) Chlorohydrin, by itself, even in *N* concentration, has no bad influence upon chlorohydrin formation. On the contrary, the presence of some chlorohydrin in the solution at the beginning of the operation, seems to increase the speed of the absorption of ethylene. When, however, in the course of the reaction the concentration on chlorohydrin becomes about 2 *N*, the acid at the same time becoming about *N*, ethylene chloride commences to form. (3) The combined effect of chlorohydrin and acid is of far greater influence than the individual influence of each would lead one to expect. A *N* concentration of each, when simultaneously present, favors the formation of ethylene chloride. (4) Neutralization of hydrochloric acid during the course of the reaction would appear to be harmful rather than beneficial. The salts thus produced show a more deleterious effect than the acid in chlorohydrin formation. Neutralization by calcium or magnesium hydroxide is likely to prove less harmful than by sodium hydroxide.

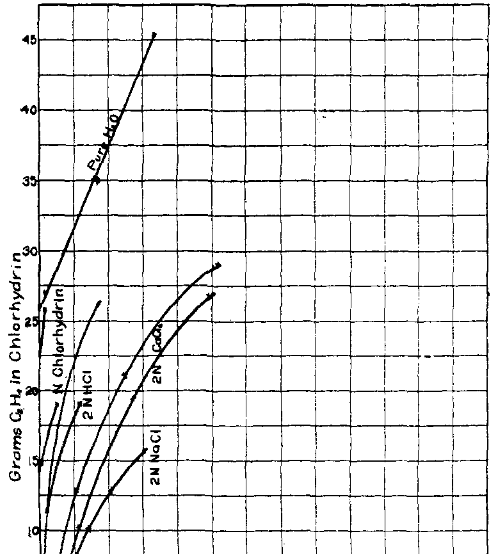

Fig. 1.—Curves showing effects of acids, salts, etc., on the formation of CH_2OHCH_2Cl and $C_2H_4Cl_2$.

The additional small amount of free acid, simultaneously produced with the chlorohydrin in the course of the tests with the salts, is not taken into account.

Thus, it would seem, that for practical purposes it is not advisable to go beyond 7 or 8% of chlorohydrin concentration, although very good stirring may raise this somewhat. It also seems best not to neutralize the acid while the reaction is progressing, unless this becomes desirable in order to prevent corrosion of the apparatus.

Fractional Distillation of Chlorohydrin Solutions.—Pure chlorohydrin is described in the literature as possessing a boiling point between 128° and 132°. In our experience, chlorohydrin, known from its analysis to be pure, boils at 128° to 128.5°, under 730-735 mm. pressure. Although the difference in the boiling points of chlorohydrin and water is greater than that of water and alcohol, yet in the past the separation of chlorohydrin from water by fractional distillation was not attempted, for the reason, presumably, that chlorohydrin was believed to distil all with the water. Carius' early observation[1] that chlorohydrin distils over with the first portions of the water, has apparently never been utilized by subsequent workers. That statement is correct only when the concentration of chlorohydrin is within certain limits, as will be shown below. We, too, found that with 10 to 15% solutions of chlorohydrin, the hydrin distils over almost wholly with the first half of the water, the thermometer usually indicating 98° to 99°. But when the distillate was collected in small fractions and these were examined with the refractometer, we found that the first fractions were richest in chlorohydrin, the strength rapidly dropping off as the distillation proceeded. From a series of experiments it was determined that chlorohydrin and water, in the proportion of 42.5% of the former and 57.5% of the latter, make a constant boiling mixture which boils at 95.8° under 735 mm. (Fig. 2). Consequently, when a solution richer than the constant-boiling mixture is distilled, the latter comes over first, and almost pure chlorohydrin towards the last (Fig. 3, 50% Solution). On the other hand with solutions poor in chlorohydrin content, the very first fractions on distillation will tend to approach in their composition the constant boiling mixture, and will consequently be the richest. This was verified on concentrations of 5, 10 and 15% of

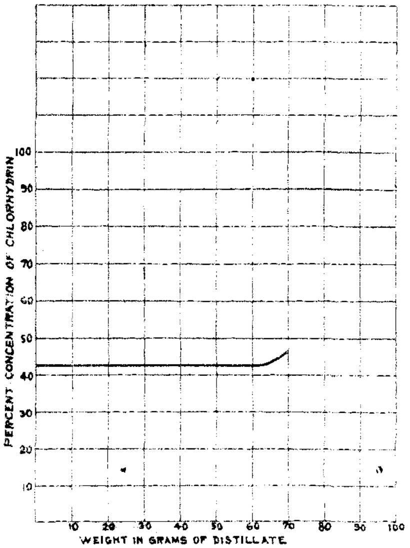

Fig. 2.—Constant-boiling mixture. Original concentration, 43.7%

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[1] *Ann.*, **126**, 198 (1863).

chlorohydrin, respectively (Fig. 4). It is apparent that the more dilute the solution is, the greater, relatively, is its tendency to enrich itself in the first fractions on distillation. By the time $^1/_2$ of the total original solution had distilled, it carried over 80%, and more, of all the chlorohydrin, and the concentration in this distillate was now almost double that of the original solution.

It should be mentioned that J. C. Irvine[1] arrived at similar conclusions, based upon similar findings. He, too, employed the refractometer in the course of distillation of aqueous solutions of chlorohydrin.

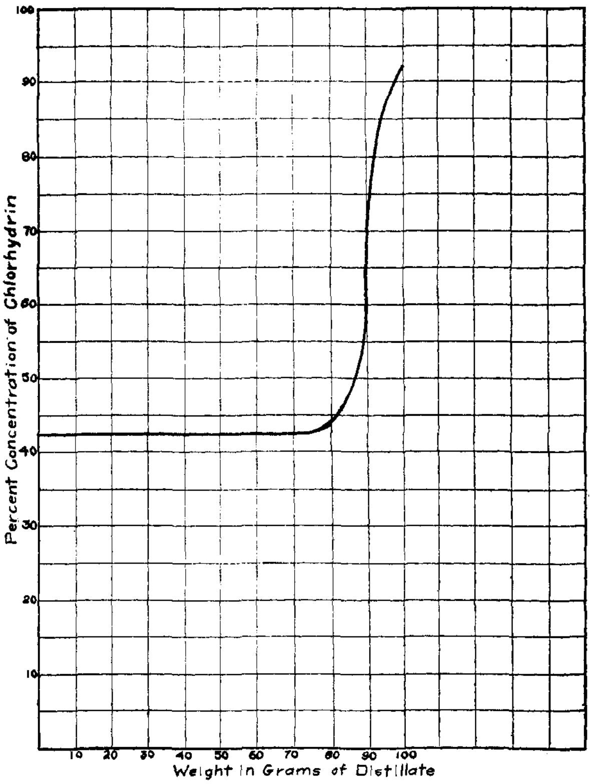

Fig. 3.—Curve for 50% solution.

Effect of Hydrochloric Acid and of Salts upon the Course of the Distillation.—When chlorohydrin is prepared as described, there is produced as a by-product an equivalent amount of hydrochloric acid, or, if progressively neutralized, an equivalent amount of some salt. The separation of chlorohydrin from the acid solution can be accomplished through fractional distillation just as readily as from a neutral solution, and neutralization of the acid is not necessary unless it be desirable to avoid the corrosive action of the acid upon the distillation vessel.

The refractive indices of dil. hydrochloric acid solutions are almost identical with those of chlorohydrin when of the same molecular concentrations. Also, the refractive index of a mixture consisting of acid and chlorohydrin is an additive quantity, as we found by experiment. Consequently, by determining in the course of a fractional distillation the refractive indices of the fractions on the one hand, and by titration the acid content on the other hand, one may follow the progress of separation of chlorohydrin

[1] Report at the Bureau of Mines.

from acid by distillation. In the following experiment 25 cc. of 2 *N* chlorohydrin solution was mixed with 25 cc. of 2 *N* hydrochloric acid, the resulting mixture approximating what is usually obtained in actual practice, *i. e.*, a solution containing about 8% of chlorohydrin. The mixture was distilled, using an ordinary fractionating column with 3 bulbs, and the distillate was collected in 9 fractions.

TABLE II.

			Acid.		Chlorohydrin.		
Fraction.	Weight. G	Refr. index.	Cc. 0.1 *N*.	Combined % of total.	G.	Concentration in %.	Combined % of total.
1..........	5.9	1.361	0.00	..	1.52	25.7	40.3
2..........	8.1	1.3486	0.03	..	1.16	14.3	71.1
3..........	5.1	1.343	0.03	..	0.47	9.2	83.5
4..........	6.0	1.339	0.00	..	0.33	5.5	92.3
5..........	5.0	1.337	0.00	..	0.185	3.7	97.3
6..........	5.0	1.335	0.03	..	0.05	1.0	98.4
7..........	5.0	1.337	3.8	3.3	0.05	1.0	100.0
8..........	5.1	1.373	57.8	51.4	...	..	...
9..........	2.8	1.3776	31.2	80.1	...	..	...

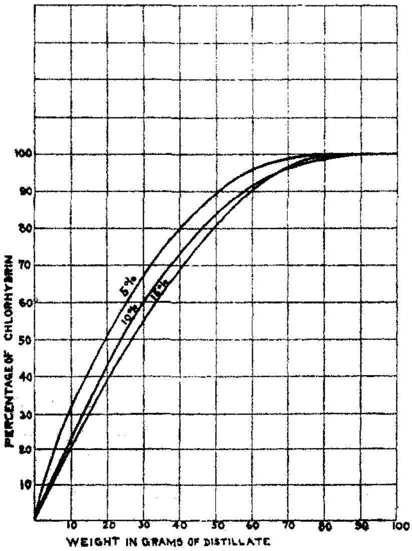

Fig. 4.—Superimposed curve of 5%, 10%, 15% solutions.

Fig. 5 shows in a very striking manner how readily and completely chlorohydrin may be distilled from the dil. hydrochloric acid solution, leaving all the acid behind.

As to the effect of salts, experiments have shown that a solution containing 5% of chlorohydrin and only an equivalent amount of sodium or calcium chloride is but slightly affected by the presence of the latter. But in a 10% solution the influence becomes apparent after the first $^1/_{10}$ of the solution has distilled over, and is quite appreciable after the first $^1/_8$ has gone over. Again, if such a solution is saturated with calcium chloride, the first fraction of the distillate, which is equal in volume only to $^1/_3$ of the original solution, contains 95% of all the chlorohydrin originally present. In other words, the 10% solution becomes now a 30% solution of chlorohydrin with practically no loss of the product. These facts are shown in Fig. 6.

It is not possible to get as concentrated distillates by saturating dilute solutions of chlorohydrin with salt as when saturating with calcium chlo-

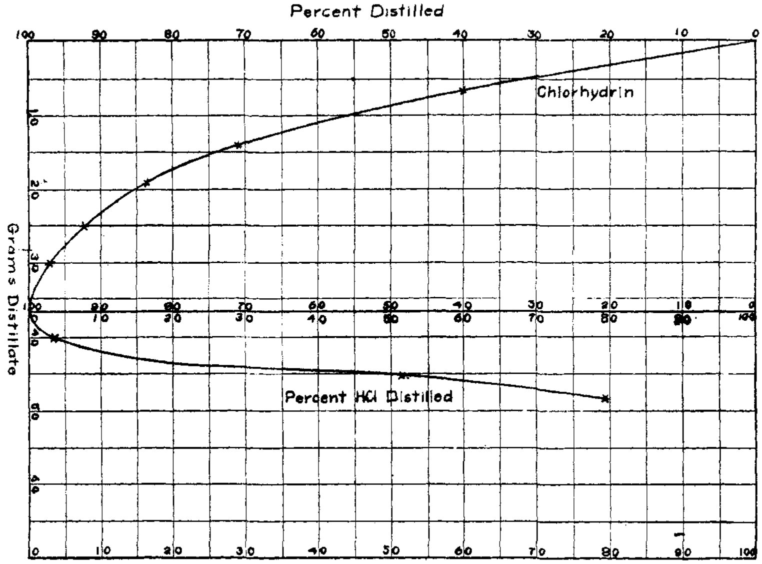

Fig. 5.—Curve for fractionation of equivalent parts of chlorohydrin and HCl in H_2O.

ride, due to the great difference in the solubility of the two chlorides. The following examples show what can be accomplished by a successive combination of the salts. About 8 liters of water was treated with ethylene and chlorine until a 7.3% concentration of chlorohydrin was produced. This mixture, 9 liters, was neutralized with lime and distilled until 4 liters was collected. The distillate was now saturated with salt and again distilled and 1600 cc. collected. This distillate was now saturated in the cold with commercial calcium chloride, and distilled until one liter was collected. The strength of the final solution was 64% of chlorohydrin. Thus, by three distillations, all the chlorohydrin originally present in 9 liters, was concentrated into one, with practically no loss of the product.

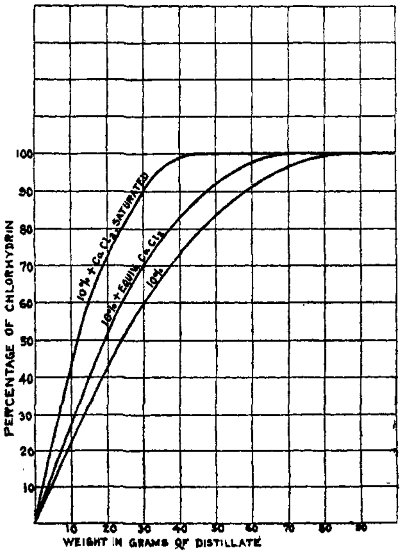

Fig. 6.—Superimposed curves of 10% solutions, one containing an equivalent quantity of $CaCl_2$, and one saturated with $CaCl_2$.

Salting Out the Chlorohydrin.—Carius, in describing the properties of chlorohydrin, makes the statement that chlorohydrin readily separates on the addition of soluble salts to its aqueous solution. The statement is misleading, and this may account for the fact that, subsequently, this property has not been utilized for the separation of chlorohydrin. The nature of the salt, the concentration of the chlorohydrin, the temperature of the solution,—each of these constitute a very important factor in this operation. Thus, with sodium chloride, very little, if any, chlorohydrin is thrown out of a solution, unless more than 16 to 18% is present, for water saturated at room temperature simultaneously with both salt and chlorohydrin, retains 16 to 17 g. of the latter per 100 cc. of liquid. By raising the temperature, more salt will be dissolved, but on the other hand, the solubility of chlorohydrin in water increases also to such an extent that no chlorohydrin is separated even from a 50% solution. If now such a solution is allowed to cool down slowly to room temperature, an oil rich in chlorohydrin will appear on the top. It is evident, therefore, that it would hardly be advisable to resort to salting out chlorohydrin with ordinary salt, unless the solution contains 30 to 35% of the hydrin. Under such circumstances, about $^1/_2$ of the total separates as an oil on the surface; its composition is about 30% water, 70% chlorohydrin, and it carries 7.2 g. sodium chloride per 100 cc. of oil.

Sodium sulfate gives far more satisfactory results than sodium chloride. Saturation with the sulfate at ordinary room temperature has very little effect, but at slightly higher temperatures, 32 to 33°, a great deal more of the sulfate goes into solution. The separation of the oil commences when the solution contains 7 g. of the sulfate per 100 cc., and the amount of oil continues to increase until the aqueous solution is saturated, at that temperature, with the sulfate, containing 25 g. of it per 100 cc. The aqueous solution is now only about 7% chlorohydrin, while the composition of the oil is about 68% chlorohydrin and 32% water, and it carries only about 0.65 g. of sodium sulfate per 100 cc. of oil. Obviously, sodium sulfate at 32 to 33° is decidedly a more suitable salting out agent than sodium chloride at room temperature.

The following procedure may be employed when working on a laboratory scale: After all the chlorohydrin has separated on saturating the solution at 32° with sodium sulfate, the mixture is cooled down without disturbing the liquids. If now a crystal of the salt is dropped in, crystallization in the supersaturated aqueous solution ensues at the point of juncture of the two liquids. So dense is the mass of crystals at the juncture that the oil can be decanted readily, free from contamination with the lower layer.

A combination of the two salts may be employed with advantage. Stopping slightly short of saturation with sodium chloride, and then finishing with just a small amount of sodium sulfate, all at room temperature, a satisfactory separation may be had, the aqueous solution being only 10% strong in chlorohydrin.

Magnesium sulfate, ammonium sulfate, aluminum sulfate, were found to induce separation; magnesium chloride and calcium chloride, on the other hand, proved ineffective. The subject of salting out deserves very careful attention, and more work, of greater accuracy, needs to be done in this connection.

In addition to distillation and salting out, we still have the old standard method of extraction with immiscible solvents. On a technical scale, benzene would offer decided advantages over ether, which has been used generally in the past for the extraction of chlorohydrin from its aqueous solutions. Ethylene chloride, the by-product in the manufacture of chlorohydrin, could also be employed for this purpose.

It is obvious that the isolation of chlorohydrin from its dilute aqueous solution, can be accomplished advantageously by a judicious combination of all three methods,—distillation, salting out and extraction with immiscible solvents in a continuous extraction apparatus.

Hydrolysis of Chlorohydrin.—The hydrin is very slowly hydrolyzed during the distillation of its dilute solution in water. The following data give some idea of this loss through hydrolysis. A solution of chlorohydrin, 2.706 *N* (21.6%), was boiled under a reflux condenser, and the acid produced was estimated from time to time.

TABLE III.

Time, hours.	Acid concentration, *N*.	% hydrolyzed.
0	0.0164	0.0
1	0.0452	1.06
2	0.0822	2.43
5	0.1946	6.60
10	0.3330	12.30
16	0.441	16.30

2. β,β-Dichloroethylsulfide.

The conversion of the hydrin into dichloroethylsulfide involves only two steps and the employment of the very simple, readily accessible materials, namely, sodium sulfide and hydrochloric acid.

Thiodiglycol.—We found that it was unnecessary to employ such a large excess of sodium sulfide as was recommended by V. Meyer and by H. T. Clarke in order to convert chlorohydrin into ethyl sulfide.

$$2HOC_2H_4Cl + Na_2S = HO.CH_2CH_2.S - CH_2CH_2OH + 2NaCl.$$

Instead of 4 mols. of the sulfide, 1.5 mol., and less, was found to be not only sufficient, but preferable, in that a purer product resulted. Another point of significance, in considering the technical possibilities of the process, is the fact that for good yields it is not essential to employ very concentrated solutions of chlorohydrin; 20% solutions gave results as good as the 80 or 100% solutions. Large scale operations alone could have decided whether it be preferable to get rid of the water before conversion of the chlorohydrin into thiodiglycol or after its conversion, but at the one or the other stage that would have to be done. Of course, less evaporation is entailed in obtaining concentrated solutions of chlorohydrin than would be required in obtaining equivalent concentrations of thiodiglycol. On a laboratory scale it was found convenient to employ 40 to 80% chlorohydrin solutions. The weighed amount of the solid sodium sulfide containing water of crystallization is added directly to the chlorohydrin solution, and the reaction is completed by heating the mixture for a short time. The solution is now neutralized, sulfuric acid being preferable to hydrochloric in that it introduces no additional amount of water, and the water evaporated, reduced pressure being safely used as the glycol is not volatile. The residual salts are impregnated with the syrupy oil of the glycol, and the next problem is to separate the glycol from the salts. On a large scale probably centrifuging, followed by washing with a little alcohol, would prove serviceable. In the laboratory, the glycol can be extracted with alcohol, and is obtained pure on the evaporation of the solvent.

The yield of the glycol is very satisfactory, being easily 90 to 95% of the calculated amount, and frequently even better than that. It is a thick, syrup, non-volatile even at 200°, non-distillable under reduced pressure without decomposition. It is immiscible with most of the organic solvents, but is soluble in chloroform. The only certain way of determining the purity of a technical sample of glycol is to determine how much mustard gas it yields. An attempt was made to prepare the glycol pure by extracting its aqueous solution with chloroform. But on drying this with calcium chloride it was found that nearly all the glycol had combined with the salt. It behaves in this respect like the ordinary alcohols.

Dichloroethylsulfide.—The usual methods of replacing alcohol hydroxyl groups by chlorine can be applied to this problem, but the simplest procedure is to heat the thiodiglycol with conc. hydrochloric solution.[1] With this procedure in view it becomes unnecessary to isolate the thiodiglycol as such, and the two steps, the preparation of the glycol and the dichloride, can then readily be combined into one operation. To the solid sodium sulfide containing water of crystallization the required amount of 70 to 80% chlorohydrin is added. The solution process of the sulfide is endothermic, the reaction with chlorohydrin is exothermic, and the two just about balance each other. When the reaction is over, the excess of sodium sulfide is neutralized with 90% sulfuric acid. To this, *without previous evaporation*, concentrated hydrochloric acid is added, and the precipitated sodium salts are filtered off by suction and washed with

[1] H. T. Clarke, *Loc. cit.*

more acid. On warming the clear, yellow hydrochloric acid solution of the glycol to 60–75°, the dichloroethylsulfide separates as a heavy, yellow oil. The acid solution is separated and can be used again after being fortified with hydrogen chloride. The oil is washed with water, and after filtering through a layer of calcium chloride or sodium chloride, it is sufficiently pure for all purposes, unless a C. P. article is desired. We have repeatedly obtained yields from 90 to 98%, based upon the amount of chlorohydrin taken for the experiment.

The undistilled material retains very little moisture and hardly any hydrochloric acid. In fact, passing hydrogen chloride into pure mustard gas, the latter takes up, under the most favorable conditions, not more than 1.5% of its weight, and this can be swept out readily with a little dry air.

If further purification is desired, distillation under reduced pressure gives the best results. A slight decomposition occurs when the product is subjected to prolonged heating, as when distilling large amounts of the material. The distilled and pure product is absolutely colorless, and remains colorless on long exposure to light. A sample which has been exposed for almost a year shows no trace of coloration.

The dichloride is readily hydrolyzed by alkalies, silver nitrate solution, and even to a slight extent with cold water. Consequently, the reaction between the diglycol and hydrochloric acid is a reversible one.

$$(HOC_2H_4)_2S + 2HCl \rightleftarrows (ClC_2H_4)_2S + H_2O.$$

It was found that the conversion of the glycol into the dichloride is done best at 65–75°, and that at the end of the operation the supernatant acid solution at 70° should still remain saturated with hydrochloric acid, *i. e.*, it should contain 33% of acid. Under such conditions, one drop of pure glycol gives, with 25 cc. acid, a fairly visible amount of mustard gas. With a concentration of acid of 30%, even two drops fail to give any dichloride; with 25% several tenths of a cubic centimeter are required, while with acid 20% strong, even 2 cc. do not produce turbidity. It may be mentioned that the above equilibrium between acid and glycol is not readily established when starting from the other end, *i. e.*, hydrolyzing mustard gas with solutions of hydrochloric acid of various strengths. For instance, 0.5 cc. of mustard gas was heated at 70° with 15 cc. of 20% hydrochloric acid for a week, with frequent stirring,—but not more than half of the oil disappeared. Apparently the hydrolysis of the dichloride must proceed at a much slower rate than the formation of the dichloride from the glycol.

To summarize, with the problem of producing ethylene on a scale hitherto unattempted, solved in a satisfactory manner[1] and with the conditions for the successful manufacture of chlorohydrin determined, the

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[1] Dorsey, *J. Ind. Eng. Chem.*, 11, 286 (1919).

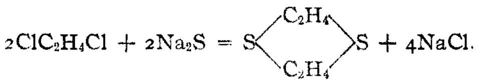
foundation of a process for producing mustard gas on a technical scale was assured. Another process, however, namely, the one based upon the sulfur chloride reaction, was ultimately adopted in this country.

3. Action of Sodium Sulfide on Ethylene Chloride.

The possibility of making mustard gas from ethylene chloride according to the equation,

$$2Cl_2C_2H_4Cl + Na_2S = (ClC_2H_4)_2S + 2NaCl$$

has been studied, but the results were negative. The reaction was found to proceed further than desired, even when at room temperature.



$$2ClC_2H_4Cl + 2Na_2S = S\langle{}^{C_2H_4}_{C_2H_4}\rangle S + 4NaCl.$$

The ill-smelling, but non-toxic, crystalline disulfide was produced, or one of its two polymers,[1] in either case only comparatively small amounts being formed, from 1 to 5% of the theoretical amount. Ethylene bromide gave the same product, but in larger yields. With the object in view to keep down the mass of the reacting metal sulfide, attention was turned to the use of insoluble sulfides, such, however, as possess the tendency to form soluble chlorides. Zinc sulfide, ferrous sulfide, etc., were tried, but they gave no better results.

General considerations concerning the reactivity of halogen derivatives of this group of compounds suggest that the dichloroethylsulfide is likely to prove more reactive than ethylene dichloride. Compare ethyl chloride with ethylene dichloride, and we notice the stabilizing effect of the second halogen. On the other hand, compare ethyl chloride with glycol chlorohydrin and we notice, if anything, the opposite effect of the oxygen atom. Now, in mustard gas the sulfur atom is with respect to the halogen in the same position as the oxygen in chlorohydrin, and we may expect a similar influence by sulfur as by oxygen. Experiments with pure mustard gas gave results which were quite decisive: sodium sulfide converts dichloroethylsulfide *very readily* into the disulfide. In the following experiments one cc. (1.3 g.) of mustard gas was taken in each case, mixed with sodium sulfide and allowed to stand at room temperature. Curiously enough, the more dilute the solution of sodium sulfide employed in the experiment, the quicker did the reaction set in, and the larger the final yield of the disulfide in a given time. This difference in action may be due to the greater alkalinity of the conc. sodium sulfide solutions, and the consequent more extensive hydrolysis of the dichloride. With the dilute solution, the precipitation of the disulfide begins in about an hour, when cold, and much quicker when heated.

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[1] V. Meyer, *Loc. cit.*

	Strength of sodium sulfide solution.	Days standing.	Yield in g.	Calc. yield, g.
I	20%	5	1.10	1.30
II	30%	8	0.72	1.30
III	50%	10	0.45	1.30

The greater velocity of reaction toward sodium sulfide possessed by dichloroethylsulfide than by ethylene dichloride precluded the possibility of obtaining mustard gas by this reaction, and the work in this direction was not pursued further.

4. Summary.

1. It has been shown that ethylene chlorohydrin can readily be prepared from ethylene and chlorine in presence of water, at comparatively low temperatures, 0–20°. It was found unnecessary, and apparently undesirable, to keep down, through neutralization, the amount of hydrochloric acid which is being produced in the course of this reaction.

2. Concentrations as high as 15% of chlorohydrin have been obtained, but it was found not advisable to go beyond 8%, on account of the proportionately increasing amounts of ethylene chloride produced at the expense of chlorohydrin. Some factors which affect adversely the yield of chlorohydrin were determined and they can be arranged in order of their increasing influence: chlorohydrin, hydrochloric acid, magnesium chloride, calcium chloride, sodium chloride; also deficient stirring.

3. It has been found that chlorohydrin and water, 42.5% of the one and and 57.5% of the other, make a constant boiling mixture, 95.8°. In virtue of this property, it has been shown, dilute solutions of chlorohydrin can be readily enriched by distillation, especially when salt or calcium chloride is added to the solutions to be distilled. From the concentrated solutions pure chlorohydrin, b. p. 128°, can be obtained.

4. Methods for salting out chlorohydrin from its aqueous solutions have been described, and it is shown that about 70% strong solutions can be obtained in this manner. By combining the 3 processes, distillation, salting out and extraction with immiscible solvent, chlorohydrin can be readily obtained pure.

5. The conditions have been determined which permit an almost quantitative conversion of chlorohydrin into mustard gas, starting with either dilute or concentrated aqueous solutions of chlorohydrin.

6. It was found impossible to get mustard gas by the action of metal sulfide upon ethylene chloride. The reason therefore was found to lie in the much greater reactivity towards these metal sulfides possessed by the mustard gas itself than by ethylene chloride.

To Mr. F. W. Sullivan, Jr., and Mr. F. H. Kranz the writer wishes to express his great obligation for their able assistance in the course of the work described in this paper.

ANN ARBOR, MICH.