CXXXII.—*The Preparation and Characterisation of Ethylenebromohydrin.*

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ACCORDING to the somewhat scanty references available in the literature, it appears that ethylenebromohydrin has hitherto been prepared only in an impure condition. This remarkable fact in the case of so simple a substance is to be attributed not so much to instability as to the nature of the preparative methods adopted. Thus, in the older methods ethylene glycol was utilised as the starting point, the second reagent being either ethylene dibromide (Lourenço, *Ann. Chim. Phys.*, 1863, [iii], **67**, 275), hydrogen bromide (Henry, *Jahresber.*, 1872, 304), or phosphorus tribromide (Demole, *Ber.*, 1876, **9**, 48); whereas, more recently, application has been made of the interaction of ethyleneiodohydrin and bromine (Henry, *ibid.*, 1889, 1321), and the direct addition of hypobromous acid to ethylene (Mokievski, *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 900). Of the principles involved in these methods the last is undoubtedly to be preferred, as least liable to give rise to impurities in the resultant ethylenebromohydrin, and the advance which has lately been made in the experimental application of this principle (Read and Williams, *T.*, 1917, **111**, 240; this vol., p. 359) has now enabled us to undertake the preparation of pure ethylenebromohydrin in quantity. At the same time, further study has been directed to the course of the reaction between ethylene and dilute bromine water, the investigation being facilitated by the observation that, as anticipated, the amount of bromohydrin formed during definite intervals may be estimated with sufficient accuracy by a titrimetric determination of the accompanying hydrogen bromide, produced in accordance with the following scheme:

The results indicate a remarkable preponderance of bromohydrin in the initial stages of the reaction; thus, when the concentration of bromohydrin has reached 0.2*N* the molecular ratio of ethylenebromohydrin to ethylene dibromide is about 10:1, and in more dilute solutions the value is still higher.

The characteristics of the pure ethylenebromohydrin now obtained differ markedly from the data recorded by previous observers, the density at 20°, for instance, being 1.7629, as compared with the value 1.7195 at 18.6°, given by Henry (*loc. cit.*). In view of the specific interest of this substance as a simple derivative of ethyl alcohol and of its general potentialities as a synthetic agent, it seemed important to establish its main physical and chemical characteristics, and the present paper records some of the results of inquiries directed towards these ends.

EXPERIMENTAL.

Preparation of Pure Ethylenebromohydrin.

Bromine vapour and ethylene were passed into 1500 c.c. of distilled water under the conditions described previously (T., 1920, 117, 359), the operation being continued for several days, until 450 grams of bromine had reacted. The rate of absorption of the bromine, which was slow at first, increased appreciably as the reaction progressed. Ultimately the liquid was neutralised in the cold by the addition of solid sodium carbonate, and the aqueous layer was separated from ethylene dibromide. The latter, of which nearly half the total yield had volatilised in the course of the experiment, was shaken once with water in order to extract dissolved bromohydrin, and dried over calcium chloride; the yield amounted to 80 grams. The amount of hydrogen bromide produced in the reaction, estimated by titration with standard silver nitrate solution, corresponded with 35 per cent. of the bromine added, and thus indicated a 70 per cent. yield of ethylenebromohydrin. In order to allow of the eventual recovery of the bromine present as bromide, the aqueous solution was saturated at the ordinary temperature with anhydrous sodium sulphate rather than with sodium chloride or calcium chloride. Extraction of the bromohydrin was accomplished with three successive quantities of 250 c.c. of ether, and after drying over anhydrous sodium sulphate the ether was expelled on the water-bath.

Repeated distillation of the residual crude ethylenebromohydrin (180 grams) under atmospheric pressure demonstrated the impracticability of effecting an adequate purification by such a method.

The results were, however, of interest as throwing some light upon the varying boiling points, ranging from 147° to 155° , recorded for this substance by earlier investigators. On distillation, the temperature rose gradually to 145° , and the bulk of the liquid distilled between 145° and 150° , although distillation was incomplete even at 155° . The distillates were pale yellow and the residue dark brown, and an appreciable amount of hydrogen bromide was produced during the distillation. After several redistillations the purest material obtained in this way distilled between 146° and 150° (n_D^{20} 1.4925; D_4^{25} 1.7655, vacuum standard). On dilution with water to 60 per cent. strength a slight opalescence appeared, whilst at 50 per cent. a distinct second phase collected, and this persisted on further dilution. The second phase at 35 per cent. had n_D^{20} 1.496, and was shown to contain ethylene dibromide. The purest ethylenebromohydrin obtainable by this method thus contains both ethylene dibromide and hydrogen bromide, as well as traces of water.

By conducting the distillation of the crude ethylenebromohydrin under diminished pressure, however, these impurities are readily eliminated. After the original removal of the ether, a little pure sodium carbonate is added, if necessary, to correct any acidity, and on distilling under diminished pressure a sharp delimitation occurs between the portion of low boiling point and the main fraction. In three different preparations the latter boiled smoothly and constantly at $53.5^{\circ}/14$ mm., $54.5^{\circ}/14$ mm., and $48.5^{\circ}/13$ mm. respectively, and no colour was developed during the distillation. The pure substance is neutral to litmus, and gives no opalescence when diluted with water or silver nitrate solution. As a rule, one distillation under diminished pressure yields a product conforming to these criteria, but sometimes a second distillation is necessary. The average primary yield of pure ethylenebromohydrin obtainable from 450 grams of bromine, in the manner outlined above, is about 120 grams, and further quantities may be extracted from the distillate of low boiling point and the original aqueous liquid. It may be mentioned that the extraction with ether from the aqueous solution is rendered more complete by previously saturating it with sodium sulphate at about 30° instead of at the ordinary temperature. Under such conditions a second phase, consisting mainly of ethylenebromohydrin, separates from the solution concerned, that is, from an approximately 1.2*N*-solution of ethylenebromohydrin containing also sodium bromide. This observation is in conformity with Gomberg's experience with aqueous solutions of ethylenechlorohydrin (*J. Amer. Chem. Soc.*, 1919, **41**, 1426). The volume of ethylene required in practice for this preparation amounts, accord-

ing to our experience, to between twice and thrice the calculated quantity.

Conditions affecting the Course of the Reaction between Ethylene and Dilute Bromine Water.

The effect upon the course of the reaction utilised in the foregoing preparation of certain factors which may be subjected to variation has been discussed in former communications (*loc. cit.*); supplementary work of a quantitative nature has now been carried out in three directions in order to establish the influence upon this process of (1) concentration of the reaction-products, (2) temperature, and (3) light.

(1) For the purpose of ascertaining accurately the amounts of ethylenebromohydrin produced at various stages of the reaction, the determination, from time to time, of hydrogen bromide in an aliquot part of the reaction mixture proved to be satisfactory. In a control experiment, bromine vapour was passed into 500 c.c. of water under the usual conditions, the current of ethylene being replaced by one of air; after an interval of seven hours, during which a pale yellow tint had been maintained in the liquid, the volume of $N/10$ -silver nitrate solution required by 5 c.c. was less than one drop, showing that no measurable decomposition of hypobromous acid into hydrogen bromide and oxygen had taken place under the conditions adopted.

In the succeeding preparations of ethylenebromohydrin the customary procedure was observed, except that the bromine was introduced in stages, the amount used being determined in each case by direct weighing. At the end of each stage the liquid was stirred for ten minutes after it had become colourless, and 5 c.c. of the liquid was then withdrawn and titrated with standard silver nitrate solution. Some of the results of two independent series of experiments are tabulated below. The calculations take into account the changes in volume which occur throughout the process, but it was considered unnecessary to apply a correction for the slight loss of bromine by diffusion. The original volumes of water used were 530 c.c. and 550 c.c. respectively, and in the second series a higher final concentration was attained than in the first series. The two sets of results are instructive as illustrating the order of the numerical discrepancies which may occur in determinations of this kind. It should be added that the temperature of the solution, which was ice-cooled, varied from about 7° to 9° , and that the experiments were conducted in diffused daylight.

Stage.	Total bromine present (grams).	Total bromine present as $\text{C}_2\text{H}_4\text{Br}\cdot\text{OH}$ + HBr (grams).	Percentage of total bromine reacting to form $\text{C}_2\text{H}_4\text{Br}\cdot\text{OH}$ + HBr .	Concentration of ethylenebromohydrin.	
				Grams per litre.	Normality.
<i>Series I.</i>					
1	4.26	4.05	95.1	5.9	0.048
2	12.95	11.85	91.5	17.5	0.140
5	52.56	44.02	83.8	65.0	0.520
8	100.66	76.73	76.2	112.4	0.899
12	160.44	111.00	69.2	161.8	1.294

Series II.

1	4.00	3.77	94.3	5.3	0.043
2	12.10	11.09	91.7	15.8	0.126
4	51.36	43.26	84.2	61.7	0.494
7	97.67	75.06	76.9	106.6	0.853
10	167.90	111.29	70.5	156.9	1.255
15	230.41	148.31	64.4	207.6	1.661

These data show that the relative velocity of reaction between bromine and ethylene and hypobromous acid and ethylene respectively is displaced to the advantage of the former reaction as the products accumulate, a result which is probably connected with the great difference in solubility of ethylene dibromide and ethylenebromohydrin, and the separation of the dibromide as a distinct phase. Notwithstanding the change which has just been noted, the molecular ratio of bromohydrin to dibromide (which in the first stage was about 20:1) remained greater than unity throughout the range of concentrations investigated.

By plotting concentrations of ethylenebromohydrin in terms of normality factor (x) against the corresponding percentages (y) of bromine reacting to form ethylenebromohydrin and hydrogen bromide a regular curve is obtained (Fig. 1), the major portion of which is closely defined by two linear equations, namely, (i) $y = 94.37 - 20.48x$, and (ii) $y = 89.99 - 15.47x$. These equations embrace, respectively, the portions of the curve corresponding with (i) $x = 0.125$ to 0.853 , and (ii) $x = 0.853$ to 1.661 . The approximate yield of ethylenebromohydrin obtainable from a given amount of bromine, over this range of concentrations, is thus capable of ready calculation.

Attention was also directed to the rate of absorption of the bromine in these experiments; this was found, on the whole, to increase with the concentration of the solution, although irregularities were noticed. Twenty-one successive portions of 8 grams of

bromine took the following respective times, expressed in hours, for complete absorption when introduced with ethylene under the usual conditions into a volume of water originally measuring 530 c.c.: 1.9, 1.6, 1.6, 1.1, 1.1, 1.1, 1.2, 1.0, 0.9, 1.1, 1.1, 1.1, 1.3, 0.8, 0.8, 0.6, 0.5, 0.5, 0.5, 0.5, 0.5. The gradual acceleration in the rate of absorption may perhaps be attributed to an enhanced solvent action of the bromohydrin solutions on the ethylene, that is, to a progressive increase of the molecular concentration of this reagent. In other series of experiments the corresponding times were noticeably different, and it seems possible that the acceleration or retardation was due to the presence of small amounts of foreign substances.

(2) In order to test the influence of temperature on the reaction

FIG. 1.

it was conducted at 35° , after a preliminary control experiment had been carried out at the same temperature according to the principle indicated above. A constant volume of 250 c.c. was maintained throughout the experiment, water being added to replace the loss by evaporation. The volume of $N/10$ -silver nitrate solution required by 5 c.c. of the liquid after the control experiment had been continued for four hours was 0.08 c.c. Thus, at 35° there appears to be a very slow decomposition of hypobromous acid into hydrogen bromide and oxygen, and a corresponding correction was introduced. It was also found necessary, when working at this temperature, to apply a correction for the loss of bromine by diffusion, which amounted to 1.20 grams in the control experiment.

On passing bromine vapour and ethylene into 250 c.c. of water

under the conditions of the control experiment, the amount of bromine utilised in the preparation of a 0.437*N*-solution of ethylenebromohydrin was 28.2 grams, after correcting for the loss by diffusion. Of this amount, 62 per cent. reacted to form ethylenebromohydrin and hydrogen bromide, as compared with 85.4 per cent. reacting in this way, for the same concentration, in the ice-cooled solution. The time taken was 14.5 hours, the corresponding time at the lower temperature being 10.0 hours. It is therefore apparent that by raising the temperature the reaction takes place more slowly, and that at the same time the molecular ratio of ethylenebromohydrin to ethylene dibromide is materially lessened.

The effects just noticed were accentuated at still higher temperatures, but owing to the considerable loss of bromine by diffusion at temperatures much above 35° quantitative examination was rendered difficult in such cases. From further experiments, to be described below, the second effect is somewhat more pronounced than indicated by the above figures, which take no account of the slow hydrolysis of ethylenebromohydrin occurring in warm aqueous solutions. The slower rate of reaction between ethylene and bromine water in warm solutions is probably to be attributed to the diminishing solubility of ethylene in water as the temperature rises.

(3) In the addition of hypochlorous and hypobromous acids to unsaturated substances it has usually been assumed that the reaction is favoured by conducting the operation not only at a low temperature but also in diffused light, or, preferably, in the dark. It was therefore of interest to investigate the influence of light upon the additive reaction between hypobromous acid and ethylene. In the short series of experiments summarised below, the ice-cooled water (530 c.c.) was exposed to direct sunlight during the passage of the bromine vapour and ethylene, and the progress of the reaction was followed in the manner already described. The result of a control experiment indicated that no appreciable decomposition of hypobromous acid took place under the conditions laid down.

Stage.	Total bromine present (grams).	Total bromine present as $C_2H_4Br\cdot OH$ + HBr (grams).	Concen- tration of ethylene- bromohydrin (<i>N</i>).	Percentage of total bromine reacting to form $C_2H_4Br\cdot OH + HBr$.	
				In sunlight.	In diffused light.
1	4.12	3.81	0.045	92.5	93.5
2	12.38	10.97	0.130	88.6	91.7
3	20.35	17.80	0.212	87.5	90.0
4	36.59	30.75	0.368	84.0	86.8

From the last two columns of the table it is seen that the values obtained in this series of experiments for the molecular ratio of

ethylenebromohydrin to ethylene dibromide are slightly lower than the values corresponding with the original conditions; the differences, however, are not marked. The time taken for the absorption was 2.75 hours, which is appreciably less than any corresponding period observed for an experiment conducted in diffused light. On the whole, therefore, the rather remarkable conclusion is reached that sunlight exerts an advantageous rather than a detrimental influence upon the additive reaction between hypobromous acid and ethylene.

Physical Properties of Pure Ethylenebromohydrin.

Ethylenebromohydrin is a colourless, mobile liquid, miscible with water in all proportions. Demole's statement (*loc. cit.*) that it is only sparingly soluble in water indicates contamination with ethylene dibromide. The solubility in water decreases considerably in the presence of certain salts, such as, for example, sodium chloride, calcium chloride, and sodium sulphate. The aqueous solutions possess a sweet, burning taste. The vapour of the pure substance or of its aqueous solutions, down to about 5 per cent. strength, produces a painful irritation of the eyes and nostrils shortly after inhalation. Ethylenebromohydrin dissolves readily in most of the common organic solvents, but forms a distinct phase when added to light petroleum. It distils unchanged under diminished pressure at the temperatures noted above; when the pure substance is heated under atmospheric pressure, however, it darkens as the temperature approaches the boiling point, and decomposition occurs with the production of hydrogen bromide. Distillation commences at about 150°, but the temperature fluctuates and the boiling point is indefinite.

The refractive index of several specimens was determined with the Abbé refractometer at 20° for the *D* line; the results were practically identical, the mean value being 1.4915. When the liquid was exposed for a few seconds on the prism this value sank in a typical instance to 1.479; this observation illustrates the pronounced hygroscopicity of ethylene bromohydrin. The observed molecular refractive power at 20° was 34.84, which stands in close agreement with the calculated value, 34.76.

Determinations of specific gravity (reduced to a vacuum) were as follows:

$$D_4^0 \text{ 1.7902, } D_4^{15} \text{ 1.7696, } D_4^{20} \text{ 1.7629, } D_4^{25} \text{ 1.7560, } D_4^{30} \text{ 1.7494.}$$

The mean coefficient of dilatation between 0° and 30°, calculated from the data obtained in the above determinations, is 0.00078.

The Relationship between the Refractive Index and the Concentration of Aqueous Solutions of Ethylenebromohydrin.

It has been shown by Irvine that measurements of refractive index provide a rapid and convenient method for the determination of the approximate strengths of aqueous solutions of ethylenechlorohydrin; the method has also been adopted, with useful results, by Gomberg (*loc. cit.*, p. 1418). For this reason, and also in view of certain interesting thermal changes and related phenomena which occur during the dilution of ethylenebromohydrin with water, it was considered advisable to undertake a refractometric examination of a series of aqueous solutions of this substance. Solutions of different concentrations were made by direct weighing of the constituents, and in each case the refractive index was determined with the Abbé instrument at 20° for the D line. Some of the observations are tabulated herewith:

Percentage by weight of ethylenebromohydrin.	n_D^{20} .	Percentage by weight of ethylenebromohydrin.	n_D^{20} .
100.000	1.4915	49.179	1.3915
95.340	1.4801	40.372	1.3790
90.032	1.4671	30.999	1.3667
80.007	1.4454	22.441	1.3561
72.201	1.4299	18.810	1.3517
60.586	1.4095	10.010	1.3422
53.620	1.3980	3.361	1.3358
		0 (water)	1.3330

When the whole of the data are represented graphically, the resulting points lie on a regular curve which does not approximate to a straight line (Fig. 2). The character of the curve indicates that the refractive index of aqueous solutions of ethylenebromohydrin is always less than the value calculated from the admixture formula, that is, on mixing ethylenebromohydrin with water there is a contraction in volume. It is also to be observed that the value of the refractive index does not pass through a maximum, as in the case of ethyl alcohol (Doroshevski and Dvorschantschik, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 908). It is evident that the above curve furnishes a ready means of determining, with close accuracy, the concentrations of aqueous solutions of ethylenebromohydrin.

The Distillation of Aqueous Solutions of Ethylenebromohydrin.

From the general characteristics of ethylenebromohydrin it seemed probable that its dilute aqueous solutions, such as are obtained in the method of preparation outlined above, might be

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concentrated by fractional distillation. In order to test this point, solutions of known strength were submitted to this operation, the various fractions being examined refractometrically. In the case of a 5 per cent. solution a first fraction, containing 3 per cent. of the total bromohydrin, had a concentration of 12 per cent. The concentrations of succeeding fractions were lower; when 20 per cent. of the total bromohydrin had been collected, the concentration of the next few drops of distillate was 9.5 per cent., and after the collection of 50 per cent. the corresponding value was 7.0 per cent.

FIG. 2.

The boiling point was originally $100.0^\circ/766$ mm., and it rose eventually to 100.1° . The boiling point of water at the same pressure is 100.22° .

With a 30 per cent. solution a first fraction, containing 11 per cent. of the total bromohydrin, had a concentration of 34.0 per cent., and when two-thirds of the total bromohydrin had passed over the concentration of the next few drops of distillate was identical with that of the original solution, that is, 30 per cent. Meanwhile, the boiling point had risen from 99.0° to 99.4° ; the barometric height was 768.5 mm., corresponding with a boiling point of 100.31° for water.

These observations suggested that ethylenebromohydrin forms a mixture of constant boiling point with water at a concentration in the vicinity of 34 per cent. A similar distillation of a 34 per cent. solution confirmed this conclusion, the actual concentration of the constant-boiling mixture being 35.0 per cent., as is evident from the following table:

Fraction.	Boiling point.	Weight of fraction (grams).	n_D^{20} .	Concentration per cent. of bromohydrin in fraction.	Percentage of total bromohydrin in fraction.
1	99.1	0.90	1.3718	35.1	3.0
2	99.1	2.06	1.3720	35.2	6.9
3	99.1	2.96	1.3717	35.0	9.8
4	99.1	3.22	1.3717	35.0	10.7
5	99.2	3.38	1.3716	34.9	11.2
6	99.2	3.44	1.3714	34.8	11.3
7	99.2	4.24	1.3708	34.3	13.7
8	99.5	4.35	1.3700	33.7	13.9
residue	—	6.11	1.3700	33.7	19.5

The constant boiling point of a 35.0 per cent. aqueous solution of ethylenebromohydrin is therefore $99.1^\circ/762.4$ mm., the corresponding boiling point of water being 100.06° . The residue from the above distillation possessed a faint yellow colour, and was distinctly acid; titration with standard silver nitrate solution showed that it contained 0.1491 gram of hydrogen bromide, evidently produced by partial hydrolysis of the bromohydrin during the distillation. The distillates contained a mere trace of the acid, and thus the percentage amount of the total bromohydrin hydrolysed in the course of the operation was 2.2.

Very interesting results were obtained by distilling more concentrated solutions of the bromohydrin, and a typical series of data is accordingly summarised below for the case of a 74.9 per cent. solution. The barometric height was 755 mm., corresponding with a boiling point of 99.82° for water.

Fraction.	Boiling point.	Weight of fraction (grams).	n_D^{20} .	Concentration per cent. of bromohydrin.	Percentage of total bromohydrin in fraction.
1	99.5°	1.08	1.3798	41.0	2.0
2	100.0—101.0°	3.03	1.3838	43.9	6.1
3	101.0—102.8	3.70	1.3880	47.0	8.0
4	102.8—109.1	3.84	1.3982	53.9	9.5
5	109.1—137.0	3.81	1.4332	74.0	12.9
6	137.0—147.4	4.51	1.4840	97.0	20.0
7	147.4—149.0	5.26	1.4912	99.9	24.0
residue	—	3.83	1.4905	99.7	17.5

When concentrated aqueous solutions of ethylenebromohydrin are distilled the water thus passes over in the initial stages of the operation, and eventually almost pure bromohydrin distils. In the

experiment described it was ascertained by titration that 0.9 per cent. of the total bromohydrin present was hydrolysed during the distillation. Of the hydrogen bromide formed it is interesting to note that 5 per cent. remained in the distilling flask, and 5 per cent. was present in fraction 5; the bulk was found in fractions 6 (60 per cent.) and 7 (30 per cent.). As fractions 6 and 7 thus contained 1.7 and 0.7 per cent. of hydrogen bromide respectively, the purity was distinctly lower than indicated by the refractive index. From these investigations it is seen that dilute aqueous solutions of ethylenebromohydrin might be concentrated by fractional distillation, but that in dealing with large quantities of such solutions the loss by hydrolysis would be considerable. This objectionable feature could be partly eliminated by conducting the distillation under diminished pressure.

The Hydrolysis of Ethylenebromohydrin.

The slight decomposition noticed during the distillation of aqueous solutions of ethylenebromohydrin seemed to indicate a greater susceptibility of this substance towards hydrolysing agents than is exhibited by ethylenechlorohydrin, and accordingly further observations were made in order to settle this point.

In the first place, when aqueous solutions of ethylenebromohydrin of concentrations ranging from 95 per cent. to 3 per cent. were prepared and examined at regular intervals no decomposition could be established until several weeks had elapsed. As a typical example, a 50 per cent. solution after remaining for a month at the ordinary temperature had developed a perceptible content of hydrogen bromide, corresponding with the hydrolysis of about 0.3 per cent. of the bromohydrin originally present; in the same period the refractive index had declined by 0.0007. With a 3 per cent. solution the amount hydrolysed in the same time approached 1 per cent. of the bromohydrin, and in general this very slow hydrolysis was most apparent in dilute solutions. At higher temperatures the velocity of hydrolysis in aqueous solution was much accelerated; on boiling a 6.25 per cent. solution for thirty minutes under reflux, 19 per cent. of the bromohydrin was hydrolysed, and in ninety minutes 44 per cent. was hydrolysed.

Silver nitrate produced no immediate reaction with cold aqueous solutions of the bromohydrin, but in dilute solutions an opalescence developed after fifteen or twenty minutes, and quantitative estimations made after longer intervals showed that the hydrolysis had undergone appreciable acceleration.

Seeing that ethylenebromohydrin is prepared in acid solution, it was of interest to ascertain the effect of acid on the rate of hydro-

lysis. A 1·8*N*-solution of hydrochloric acid containing 9·0 per cent. of ethylenebromohydrin was examined twenty-four hours after being prepared, but no perceptible hydrolysis had occurred in the cold. By boiling this solution for thirty minutes, 51 per cent. of the bromohydrin was hydrolysed, the presence of acid having therefore accelerated the reaction.

It was to be anticipated that alkali would exert a much more pronounced acceleration than acid, and, in fact, a 4·5 per cent. solution of ethylenebromohydrin, containing about two equivalent proportions of potassium hydroxide, was hydrolysed to the extent of 47 per cent. when allowed to remain at the ordinary temperature for thirty minutes. By boiling a similar solution for thirty minutes, 97 per cent. of the bromohydrin was hydrolysed, and ninety minutes' boiling brought about complete hydrolysis.

Lastly, an analysis of a pure specimen of ethylenebromohydrin by alkaline hydrolysis may be quoted: 0·2935 gram, after boiling for ninety minutes with an excess of sodium hydroxide solution, required 23·5 c.c. of *N*/10-AgNO₃. Br=64·0. Calc., Br=64·0 per cent.

Summary.

1. Pure ethylenebromohydrin has been prepared in quantity by the action of cold dilute bromine water on ethylene, this method having been found preferable to any other which has been described for the purpose.

2. In the above reaction the molecular ratio of ethylenebromohydrin to ethylene dibromide decreases continuously with increasing concentration of ethylenebromohydrin and hydrogen bromide in the solution, and also with rise of temperature, but it is not influenced markedly by sunlight. The reaction is hastened by cooling or by exposure to sunlight.

3. The main physical characteristics of ethylenebromohydrin, and also the relationship between the concentration and refractive index of its aqueous solutions, have been established.

4. Ethylenebromohydrin and water form a mixture of constant boiling point (99·1°/762·4 mm.) at a concentration of 35·0 per cent.

5. Ethylenebromohydrin is hydrolysed more readily than ethylenechlorohydrin. In cold aqueous solutions the hydrolysis is perceptible, although extremely slow; it is greatly accelerated by heat, also by the presence of acid, and, notably, of alkali.

Cognate investigations are in progress.