Chemistry. — "*Researches on the Addition of Gaseous Hydrochloric Acid and Hydrobromic Acid to Ethylene and Propylene under the Influence of Catalysts.*" By J. P. WIBAUT, J. J. DIEKMANN, and A. J. RUTGERS. (Communicated by Prof. S. HOOGEWERFF).

(Communicated at the meeting of June 28, 1924).

In this communication further researches are discussed on addition reactions to ethylene and propylene. On the addition of water to these compounds a preliminary communication has already appeared in these Proceedings[1]).

I have been able to carry out this investigation by the aid of a support granted me out of the HOOGEWERFF-fund: for this kindness I express again my heartfelt thanks to the Board of Trustees of the HOOGEWERFF-fund.

The experiments on the addition of hydrochloric acid and hydrobromic acid to ethylene and propylene were undertaken by me in conjunction with Mr. DIEKMANN. When it had already been found that these reactions can be realized by means of the catalysts to be described below, Mr. DIEKMANN was obliged to interrupt this work on account of his military duties. I then continued the investigation in conjunction with Mr. RUTGERS.

The researches described here were already completed for the greater part in September 1923; with a view to the filing of a patent the publication was postponed[2]).

J. P. WIBAUT.

§ 1. *Introduction.*

It is a characteristic property of the olefines that these substances can combine with hydrogen halide. This reaction takes place most readily with hydriodic acid; hydrobromic acid also reacts smoothly in many cases, whereas the addition of hydrochloric acid in general proceeds much more slowly. In general the addition of hydrogen halide to the higher olefines takes place more readily than to the lower terms of the series.

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[1]) WIBAUT and DIEKMANN, These Proceedings 26, p. 321—328.

[2]) French patent 574.800; Dutch patent filed on January 12th, 1923; English patent 209.722.

About the addition of hydrogen halide to ethylene an investigation of BERTHELOT ¹) was known when we started our experiments. This investigator heated ethylene with a saturated solution of hydrobromic acid at 100° C. in a sealed glass bulb for 100 hours; ethylbromide was formed. A solution of hydriodic acid reacted somewhat more rapidly under the same circumstances.

If the same experiment was made with ethylene and concentrated hydrochloric acid, only traces of a neutral substance containing chlorine were formed, which could not be identified. From this it appears that the addition of hydrochloric acid to ethylene proceeds very slowly under these circumstances.

If propylene was heated with aqueous hydrochloric acid in the same way at 100°, the hydrochloric acid was completely absorbed after 70 hours with formation of isopropylchloride.

We have set ourselves the task of examining the reaction between gaseous hydrochloric acid and hydrobromic acid and ethylene, resp. propylene. These olefines are now available in great quantities as components of coal gases (coke-oven gas and gases of the coal distillation at low temperature) and in the gases obtained in the preparation of light hydrocarbons from heavy petroleum-distillates (cracking process). Therefore an investigation on the possibility of transforming the ethylene resp. propylene out of these gas mixtures into the corresponding alkylchlorides looked promising, as these alkylchlorides, in particular ethylchloride, find various applications in chemical industry. As will appear from what follows, we have actually attained our end.

In the mean time several investigations have become known bearing on the same problem. In a German patent of the "Farbenfabriken vorm. FR. BAYER and Co." (D. R. P. 361041) it is stated that ethylene and gaseous hydrochloric acid combine to ethyl chloride at temperatures between 200° and 300°, when a mixture of these gases passes over indifferent substances, as fragments of stone, charcoal, pumice, and similar substances; these substances would serve to transmit the heat. Oxides of heavy metals, in particular "roasted pyrites", might serve as catalysts in this reaction. In a patent of the chemical factory WEILER TER MEER (D. R. P. 369702) another method for the preparation of ethylchloride from ethylene and gaseous hydrochloric acid is protected. These substances are pressed in an autoclave filled with charcoal. At 100°—200° and at a pressure

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¹) Compt. r. Acad. d. Sc. **44**, 1350; **50**, 612.
Lieb. Ann. **104**, 184 (1857) en **115**, 114 (1860).

of 25—50 atmospheres ethylchloride is said to be formed in a quantitative yield.

We had already found in our preliminary experiments that when a mixture of ethylene and gaseous hydrochloric acid is passed over asbestos, over granules of burned clay or over charcoal, no formation of ethylchloride takes place between 100° and 270°. This is, therefore, in conflict with the statement of the just-mentioned patent of Bayer. Between gaseous hydrobromic acid and ethylene there appeared to proceed a slow addition reaction at 140°—170° in the presence of asbestos.

If the thermic effect of the formation of ethyl chloride from hydrochloric acid and ethylene is considered, this reaction appears to be strongly exothermic. The heat of combustion of ethyl chloride has been determined by Thomsen and by Berthelot. In the experiments of these two investigators the products of combustion formed were: carbonic acid, liquid water, hydrochloric acid and very little free chlorine. In Thomsen's experiments part of this hydrochloric acid occurred in the gaseous state. Berthelot burned gaseous ethylchloride with oxygen in his calorimetric bomb; the hydrochloric acid gas dissolved in the water, which had been put in the bomb. Both Berthelot and Thomsen have determined the quantity of free chlorine and recalculated the results for the case that only hydrochloric acid should be formed in the combustion; for this calculation the heat of formation of hydrochloric acid and that of water must be known. In the case of ethylchloride this correction is small.

The heat of combustion of ethylene has been determined both by Thomsen and by Berthelot. Hence the heat that is liberated when hydrochloric acid combines with gaseous ethylene can be calculated from these results, provided that the heat of solution of hydrochloric acid in water is taken into account, since in the combustion of ethylchloride an aqueous solution of hydrochloric acid is formed. In this way Thomsen and Berthelot have calculated the thermic effect of the reaction:

$$\underbrace{C_2H_4 + HCl \rightarrow C_2H_5Cl}_{\text{gaseous.}}$$

Berthelot finds for the thermic effect 31,9 cal., Thomsen gives 10,8 cal. Thomsen has calculated the heat of reaction at constant volume, whereas Berthelot's value is valid for constant pressure, but the ensuing difference is comparatively small. In the combustion of ethylbromide both hydrobromic acid and free bromine is formed in considerable quantity, which rendered the experiments and the calculation still more complicated. Below we give the values for the heats of reaction of some of these reactions as these values have been given on one side by THOMSEN, on the other side by BERTHELOT.

	THOMSEN [1]	BERTHELOT [2]
$C_2H_4 + HCl$	10.84 Cal.	31.9 Cal.
$C_3H_6 + HCl$	11.96 „	
$C_4H_8 + HCl$	12.13 „	
$C_2H_4 + HBr$	12.87 „	29.1 „
$C_3H_6 + HBr$	14.91 „	

It is seen that the values of THOMSEN and of BERTHELOT differ greatly. We shall not enter into a discussion of the question which of these values are reliable, and how great the accuracy should be estimated, which would be very difficult for want of experimental details, but we will only conclude from these data that the addition of halogen hydrogenic acid to olefines is a clearly exothermic reaction.

In virtue of these thermic data it might be expected that the addition of hydrochloric and hydrobromic acid to ethylene and propylene can proceed rapidly enough at the ordinary temperature resp. at a slightly raised temperature, if one has a suitable catalyst at one's disposal. It is natural to look for catalysts for this reaction among the metal chlorides, in order to avoid secondary reactions; for instance when metal oxides are used, the chlorides would be formed from this through the action of hydrochloric acid gas.

In the literature only few data were to be found to decide in which groups of the periodic system one had to find such a catalyst. SABATIER and MAILHE [3]) have studied the decomposition of alkylchlorides and alkylbromides in halogen hydrogenic acid and the corresponding olefine. They found that this reaction is catalytically accelerated by the chlorides of bi-valent metals as $NiCl_2$, $CoCl_2$, $FeCl_2$, $PbCl_2$, and $BaCl_2$. When ethylchloride or propylchloride is led over barium chloride at 300° C. a smooth decomposition takes place into hydrochloric acid gas and ethylene. The chlorides of sodium potassium or of silver do not promote this reaction according to SABATIER and MAILHE; in the presence of these substances there

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1) These values are those calculated by THOMSEN from the heats of formation; see Thermochemische Untersuchungen, Bd. IV, 372.

2) Annales de Chimie et de Physique (5), t. **23**, 238 (1881).

3) Compt. r. Acad. d. Sc. **141**, 238 (1905).

is no decomposition even at 350°. According to SENDERENS[1]) also aluminium oxide, silicum dioxyde, aluminium sulphate are catalysts for the splitting off of hydrochloric acid from alkylchlorides. We have tried if barium chloride, which according to SABATIER and MAILHE is the most suitable catalyst for the decomposition of alkylhalides, would act catalytically on the addition of hydrochloric acid to ethylene or propylene, but have not been able to find the slightest influence of barium chloride on this reaction.

GUSTAVSON[2]) has investigated the action of hydrobromic acid on ethylene in the presence of aluminium bromide. This investigator led a mixture of hydrobromic acid gas and ethylene over anhydrous aluminium bromide. At 60°—70° there took place a vigorous reaction in which, however, a complex reaction product was formed, wherein besides a substance which seemed to be a compound of aluminium bromide with a hydrocarbon, also saturated hydrocarbons occurred. If the reaction was carried out at 0°, a pretty large quantity of ethylbromide was formed, according to GUSTAVSON (quantitative data are not given), but even at this temperature other reactions occurred.

As it appeared from GUSTAVSON'S experiments, which are not described very clearly, that aluminium bromide causes a complicated reaction process, we have not included this substance in our investigation.

We have found that bismuth trichloride and antimonytrichloride resp. the corresponding bromides are excellent catalysts, which cause the addition of hydrochloric acid and hydrobromic acid to ethylene and propylene to take place rapidly.

Recently a paper has been published by E. BERL and J. BITTER[3]) on the addition of hydrochoric acid gas to ethylene. These investigators used anhydrous aluminium chloride as a catalyst, after it had appeared to them that in an empty glass tube the addition of hydrochoric acid to ethylene does not take place. They find that in the presence of aluminium chloride the addition of hydrochloric acid to ethylene proceeds at temperatures from 100° C. upwards; only a small quantity of by-products was formed. These investigators have not carried out experiments with hydrobromic acid, neither with propylene.

§ 2. *Experimental part.*

We have prepared the ethylene required for these experiments according to SENDERENS' method, by conduction of the vapour of

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[1]) Bull. Soc. chim. d. France (4), 3, 823 (1908).

[2]) Journ. f. prakt. Chemie (2) 34, 161 (1886).

[3]) Ber. d. deutsch. chem. Ges. 57, 95 (1924).

ethyl alcohol over heated aluminium sulphate. SENDERENS gives a very extensive description of the best way in which the catalyst for this reaction is to be prepared. According to our experience no special care need be taken to obtain a suitable catalyst for this reaction. We have soaked asbestos with a strong solution of aluminium sulphate; the evaporated mass was dried at 130° and powdered. With such a catalyst we have obtained excellent results. The best temperature for the reaction was 370°—380°. The propylene was always prepared from propylalcohol, which is much cheaper than isopropylalcohol, and yields equally good results. The ethylene and propylene obtained in this way, always contains a little hydrogen dependent on the temperature of reaction and the particular properties of the catalyst. Since this quantity of hydrogen had no injurious influence in our experiments, we have not removed the hydrogen, but determined the percentage of olefine of each gas mixture used. In this way, we have indeed often obtained a gas with 99,5 °/₀ olefine.

The reaction space consisted of a glass tube of a length of 100 cm. A wire of chromium nickel was wound round this tube immediately on the glass, which wire was connected with the electrical circuit. By means of a suitable resistance any required temperature between 100° and 300° could be kept constant in the reaction tube. Round the reaction tube a wider glass tube was placed concentric with it, which served for heat-insulation. This electrical furnace has the advantage that the inside of the reaction space can be watched during the experiment. The temperature of the reaction was measured by means of a thermo-element, which was mounted inside the reaction tube. The ethylene came from a graduated glass gasholder, passed through a *U*-tube with calciumchloride, and washing-bottle with strong sulphuric acid, which at the same time served as gas-bubble counter, and then entered the reaction tube. In the experiments with propylene, the washing-bottle was filled with 90 °/₀ sulphuric acid. Hydrochloric acid gas was developed from sulphuric acid and ammonium chloride, also passed through a washing-bottle with sulphuric acid, and mixed with the olefine before the reaction space was reached. The proportion between hydrochloric acid gas and olefine was approximately determined by counting the gas bubbles in the washing bottles, which were of the same demensions.

Hydrobromic acid was prepared by leading a mixture of hydrogen and bromine vapour over heated platinum; then the reaction mixture was led through tubes with anthracene in order to remove unchanged bromine vapour. With some practice a pretty constant stream of hydrobromic acid gas can be obtained in this way, which mixed with the olefine and entered the reaction tube.

The gases issuing from the reaction tube were freed from unchanged hydrogen halide by means of *U*-tubes filled with soda-lime, and then the halogen alkyl was condensed in a convenient way. In the case of ethyl chloride a spiral cooled in carbonic acid and alcohol was required for this. In order to drive all the halogen alkyl present in the reaction tube into the receiver, air was passed through the reaction tube and the *U*-tubes for two hours after the experiment. The *U*-tubes were heated to a suitable temperature in the case of ethylbromide and of the isopropyl halogenides.

The yield of halogen alkyl was measured in most experiments by the weight of the distilled alkyl halide. In our preliminary experiments on the addition of hydrochloric gas we have followed another method. The gas mixture which had been carefully freed from hydrogen halide passed by way of control through a washing bottle filled with a solution of silver nitrate, then through a drying tube, after which it entered a quartz tube heated to redness. There the ethyl chloride or iso-propylchloride was decomposed and hydrochloric acid was split off. The quantity of this was determined by the titration of the chlorine ion. This method has rendered us good services to test the addition of hydrochloric acid during an experiment, especially in the experiments with illuminating gas which will be mentioned later. BERL and BITTER have applied the same method independently of us in the said paper. In the subjoined tables we shall now give a survey of the results, in which only a number of typical experiments are mentioned out of the great number of experiments made.

In the first column is found the number of the experiment; in the 2nd column is indicated the contact substance with which the reaction tube was filled; the third column contains the numbers of litres of gas used in the experiment, and the percentage of olefine of this gas mixture; the 4th column gives the duration of the experiment; the 5th column the temperature. In the 6th column the result is recorded and the yield of alkylhalogenide is calculated with respect to the quantity of olefine.

In all the experiments a reaction tube of the same dimensions was used, which was filled over the same length with catalyst or indifferent substance. Accordingly the experiments are comparable inter se. The gas volumes given have been reduced to 0° and 760 mm. These volumes have, however, not been measured accurately; the errors may amount to some percentages, the same uncertainty prevails, therefore, in the values indicating the yield. A greater accuracy in the measurement of the gas volumes was not necessary, as comparatively small differences in the yield are also caused by the oscillations in the velocity of the current of the gas mixture, by differences in the filling of the tube and similar causes, which we could not perfectly control with the arrangement of our experiments.

The differences between the behaviour of ethylene and propylene, of hydrochloric and hydrobromic acid, the characteristic action of catalysts are, however, very evident in these comparatively rough experiments.

In the gas volumes given, the volume of the admixed halogen hydrogen gas is *not* included. In the case of hydrochloric acid gas the volume of this was about 30—50 °/₀ more than the volume of the olefine. In the case of hydrobromic acid gas the quantity of this was more difficult to ascertain. The hydrobromic acid gas was, however, always present in excess. (See the table on the next page).

It appears clearly from table I that bismuth chloride is a specific catalyst for the addition of hydrochloric acid gas to ethylene. Whereas in the presence of indifferent substances as asbestos, charcoal carbon, granules of burned clay, no ethylchloride is formed even at 220°—270°, or at least very little (experiment 92), the reaction takes place slowly already at room temperature in the presence of $BiCl_3$ (experiment 76); at 120°—200° with bismuth trichloride as a catalyst the reaction takes place pretty rapidly, and a good yield is therefore obtained. The transformation of ethylene in ethylchloride proceeds still smoothly when the ethylene is mixed with a great excess of air, as appears from experiment 142. In this experiment the ethylchloride formed was isolated from the gaseous reaction product through absorption with active charcoal, after unchanged hydrochloric acid had first been removed, and then the ethylchloride had been obtained through distillation from the active charcoal. It has appeared to us that a number of experiments can be performed with the same mass of catalyst, without any decrease of activity being perceptible. (Compare the series of experiments 72—79: this same catalyst was also used in later experiments. Compare table II).

We have often verified the purity of the ethylchloride obtained in these experiments by distillation. The greater part of the reaction product distilled from 12°—12°,8. Except for a little dissolved ethylene, the reaction product seemed to contain no impurities. Substances which boiled at a higher temperature than ethylchloride were not present in appreciable quantity.

TABLE I. (Ethylene and gaseous hydrogen chloride).

Number	Filling of the reaction tube	Quantity of gas in litres	Duration of the experiment in hours	Temperature	Result
92	Asbestos	4.2 l. 97 $^0/_0$ C_2H_4	6	220°	About 0.04 gr. C_2H_5Cl i.e. 0.3 $^0/_0$
93	"Bayer A—Kohle"	3.2 l. 97 $^0/_0$ C_2H_4	2	220°	No C_2H_5Cl formed
94	Granules of burned clay	3.3 l. 97 $^0/_0$ C_2H_4	2	270°	„ „ „
97	Granules of burned clay	3.3 l. 97 $^0/_0$ C_2H_4	2	250°	„ „ „
103	Asbestos soaked with $BaCl_2$	2.5 l. 97 $^0/_0$ C_2H_4	3.5	170°	„ „ „
72	Asbestos soaked with $BiCl_3$	4.1 l. 99 $^0/_0$ C_2H_4	5	150°	8.8 gr. C_2H_5Cl = 74.5 $^0/_0$
73	The same catalyst as in 72	1.5 l. 99 $^0/_0$ C_2H_4	$3^2/_3$	120°	3.5 gr. C_2H_5Cl = 81 $^0/_0$
76	The same catalyst as in 72	3.8 l. 99 $^0/_0$ C_2H_4	6	15°	0.65 gr. C_2H_5Cl = 6 $^0/_0$
77	The same catalyst as in 72	2 l. 99 $^0/_0$ C_2H_4	$4^1/_2$	120°	4.7 gr. C_2H_5Cl = 84 $^0/_0$
78	The same catalyst as in 72	2.5 l. 95 $^0/_0$ C_2H_4	5	150°	5.1 gr. C_2H_5Cl = 75 $^0/_0$
79	The same catalyst as in 72	3.8 l. 92 $^0/_0$ C_2H_4	3	200°	7.4 gr. C_2H_5Cl = 73 $^0/_0$
142	Asbestos soaked with $BiCl_3$	43 l. of a mixture of 9.5 $^0/_0$ of C_2H_4 and 90.5 $^0/_0$ of air	57	200°	8.6 gr. C_2H_5Cl = 73 $^0/_0$

Berl and Bitter obtained yields of ethylchloride of 18—36 $^0/_0$ with respect to the ethylene used. The highest yield was 36.7 $^0/_0$ at a reaction temperature of 130°. They worked with a mixture of equal volumes of hydrochloric acid gas and ethylene. It is not possible to make a reliable comparison between the catalytic activity of aluminium chloride and bismuth chloride, because the rate at which the gas was flowing and the dimensions of the reaction tube in Berl and Bitter's experiments were different from those in our experiments. It seems to us that bismuth chloride is a more active catalyst than aluminium chloride. At 120° we have obtained conversions to 84 %; this is a much higher yield than the two investigators mentioned.

The reaction between ethylene and hydrochloric acid is reversible. **Berl** and **Bitter** give a calculation of the equilibrium constant:

$$K_p = \frac{PC_2H_4 . PHCl}{PC_2H_5Cl}$$

admitting a value of 14.2 Cal. for the heat of reaction. They have calculated this value for the heat of reaction from the values for the energy of the atomic linkings as they are given by **Fajans** and by **Martin** and **Fuchs**. As we have seen already in the introduction the result of the measurements of the heats of combustion does not give any reliable value for the heat of reaction.

By the aid of **Nernst**'s well-known approximative formula **Berl** and **Bitter** have calculated the values of K_p for some temperatures; they do not state, however, what numerical values they use for this calculation, besides the value for the reaction heat. For 200° C. they find $K_p = 5,25$. The equilibrium concentration of ethylchloride which would correspond to this value of K_p, is, however, much smaller than the quantity of ethylchloride which is formed according to our experiments and according to the experiments by **Berl** and **Bitter** themselves.

We shall not enter further into this question, as in this case no great importance can be attached to the calculation of the equilibrium concentrations on account of the uncertainty in the value of the heat of reaction.

It appears from table II that the reaction between propylene and hydrochloric acid gas proceeds smoothly at 150°. However bismuth trichloride appears to be a powerful catalyst. In the presence of this substance a rapid reaction takes place at the ordinary temperature, with notable generation of heat. The formation of isopropyl chloride proceeds rapidly, even when the propylene is mixed with excess of air (experiment 51).

Antimony trichloride acts as catalyst in the same way.

The product formed is chiefly isopropylchloride, as was, indeed, to be expected according to **Markonikov**'s rule for the addition to olefines. The reaction product of experiment 84 was subjected to fractionated distillation at 755 mm. The following quantities were obtained: 8,5 gr. of 32°—35°, 55 gr. of 35°.5—36°,5, and 10 gr. of 36°.5—38°5.

TABLE II. (Propylene and gaseous hydrogen chloride).

Number	Filling of the reaction tube	Quantity of gas in litres	Duration of the experiment in hours	Temperature	Result
32	Asbestos soaked with $BiCl_3$	6.3 l. 99 % C_3H_6	2	Initial temp. 20°	Rapid reaction in which the temp. of the catalyst rose to 70°: 15.5 gr. of isopropylchloride, boiling-point 36—37°. Yield 68 %.
51	Asbestos soaked with $BiCl_3$	6 l. of a mixture of 18.6% C_3H_6 and 81.4% air	4	18°	About 80 % isopropylchloride formed (determined by titration of the split off hydrochloric acid.)
56	Asbestos soaked with $SbCl_3$	6.3 l. 98.5% C_3H_6	3¾	Initial temp. 18°	Rapid reaction in which the temperature of the catalyst rose to 60 to 70°: 14 gr. of isopropylchloride = 70%: almost the whole quantity distilled from 36.4—36°.8.
81	Asbestos soaked with $BiCl_3$: the same catalyst was already used in the experiments 72—80	11.7 l. 96% C_3H_6	6	100°	31.6 gr. of crude isopropylchloride = 80 %: the greater part distilled from 36—37°.
83	The same catalyst as in N°. 81	Mixture of 5 l. C_3H_6 and 12 l. of air	4½	80°—100°	15.5 gr. of crude isopropylchloride = 92 %. The greater part distilled at 35—37°.
84	The same catalyst as in N°. 81	27.1 l. 96 % C_3H_6	10	80°—90°	82 gr. of crude isopropylchloride = 92%.
106	Pure asbestos	3.1 l. 90 % C_3H_6	3	150°	6.5 gr. of isopropylchloride = 66 %.
107	Pure asbestos	1.9 l. 90 % C_3H_6	2	150°	3.5 gr. of isopropylchloride = 58 %.
109	Asbestos soaked with $BaCl_2$	1.3 l. 90 % C_3H_6	1.5	150°	2.2 gr. of isopropylchloride = 55 %.

Whether a little propylchloride is still present in this last fraction, has not yet been ascertained. At any rate the quantity of this substance cannot be large. Besides, the reaction product, which was obtained in the experiments with propylene, contained still a very small quantity of a liquid that did not boil at 100°.

It appears from table III that the addition of hydrobromic acid to ethylene in the presence of asbestos proceeds very slowly at 140°—170°, though there is some ethylbromide formed. Accordingly the addition of hydrobromic acid takes place ceteris paribus more readily than the addition of hydrochloric acid (compare N°. 92, 93, 94, 97, 103 of table I). Bismuth tribromide is again a vigorous catalyst for this reaction: in the presence of this substance a pretty rapid reaction takes place already at the ordinary temperature.

TABLE III. (Ethylene and gaseous hydrogen bromide).

Number	Filling of the reaction tube	Quantity of gas in litres	Duration of the experiment in hours	Temperature	Result
121	Pure asbestos	1.9 l. 90 % C_2H_4	2	140°	0.5 gr. $C_2H_5Br = 6\,\%$
128	Pure asbestos	3 l. 93 % C_2H_4	4	20°	No C_2H_5Br formed
129	Pure asbestos	1.95 l. 93 % C_2H_4	2	170°	0.8 gr. $C_2H_5Br = 9\,\%$
133	Asbestos soaked with $BiBr_3$	1.2 l. 93 % C_2H_4	2½	90°—100°	4.5 gr. $C_2H_5Br = 84\,\%$
134	The same catalyst as in 133	1.7 l. 93 % C_2H_4	2½	20°	6.6 gr. $C_2H_5Br = 84\,\%$
136	The same catalyst as in 133	0.84 l. 93 % C_2H_4	2	170°	3.4 gr. $C_2H_5Br = 88\,\%$

TABLE IV. (Propylene and gaseous hydrogen bromide).

Number	Filling of the reaction tube	Quantity of gas in litres	Duration of the experiment in hours	Temperature	Result
30	Glass wool on which $BiBr_3$	7.4 l. 96 % C_3H_6	2	Initial temp. 20°	34.6 gr. of crude isopropylbromide = 89 %. 30 gr. of this distilled from 59°—60°. The temp. rose during the experiment to 40° C.
122	Pure asbestos	2.4 l. 96 % C_3H_6	4	170°	7 gr. of isopropylbromide = 55 %. The greater part distilled at 60°
126	Pure asbestos	2.0 l. 96 % C_3H_6	2	170°	5.7 gr. of isopropylbromide = 55 %
125	Pure asbestos	2.6 l. 96 % C_3H_6	3½	20°	8.6 gr. of isopropylbromide = 61 %. The greater part distilled at 60°
139	Asbestos soaked with $BiBr_3$	1.9 l. 96 % C_3H_6	½	20°	8.7 gr. of isopropylbromide = 93 %. The temp. rose to 80° C. at the spot where the mixture of propylene and HBr struck the catalyst

The reaction product from the experiments 129, 134, and 136 was fractionally distilled; the greater part went over from 38°—40°. There was left only a very small residue. The product is, therefore, almost pure ethyl bromide.

It appears from table IV that the addition of hydrobromic acid to propylene proceeds already pretty rapidly at 20° in the presence of asbestos. In the presence of bismuth tribromide, the velocity of the reaction becomes, however, much greater, as appears from the experiments 30 and 139; in these experiments the propylene flowed at a rate of 4 litres per hour, and round 90 °/$_0$ of isopropylbromide could be obtained from this, whereas in experiment 125 with a rate of flow of about, 0,7 L. of propylene per hour, the yield was only 61 °/$_0$.

§ 3. *Summary of the Results.*

We can give the following summary of these results. The addition of hydrogen chloride to ethylene does not take place between 170° and 270° without catalyst or, if it does, the velocity of the reaction is very small; in the presence of bismuth chloride, on the other hand, a perceptible reaction takes already place at the ordinary temperature; between 120° and 200° the reaction proceeds rapidly in the presence of $BiCl_3$, and without formation of by-products. The addition of hydrogen bromide to ethylene proceeds somewhat more readily than the addition of hydrogen chloride. Yet in the absence of a catalyst no addition takes place at 20° under the circumstances of the experiment; this reaction does not become perceptible until the neighbourhood of 140° is reached. In the presence of bismuth bromide however the reaction proceeds rapidly even at 20° C.

The addition of hydrogen halide to propylene takes place much more quickly than that to ethylene, which is apparent both in the addition of hydrogen chloride and of hydrogen bromide. Under the circumstances of these experiments the reaction evidently takes place much more rapidly than in the experiments of BERTHELOT, who worked with an aqueous solution of hydrochloric acid.

Hydrogen bromide appears to react with propylene at lower temperatures than hydrogen chloride. Bismuth trichloride or antimony trichloride resp. bismuth tribromide are powerful catalysts for the reaction between propylene and hydrogen chloride resp. hydrogen bromide; in presence of these substances the reaction proceeds rapidly at the ordinary temperature, while much heat is liberated.

Some interesting questions arise, among others whether in this reaction there is formed any *n*-propylchloride, resp. *n*-propylbromide, and whether the quantity of this varies with the temperature. From the experiments of table II and IV it appears that chiefly isopropylchloride is formed both at 20° and at 100°, resp. chiefly isopropylbromide at 20° and 170°, but it might perhaps be worth while investigating this point more closely. It will probably be possible to investigate the equilibrium of the reaction:

$$\text{olefine} + \text{halogen hydrogen} \leftrightarrows \text{alkylhalogenide}$$

at very divergent temperatures, now that a vigorous catalyst is at our disposal.

Another question is whether hydrogen halide might be added to aromatic hydrocarbons in this way. Ethylene combines with hydrogen to ethane under the influence of finely divided nickel or platinum, while under the same circumstances cyclohexane is formed from benzene. Would it now be possible that e.g. tribromcyclohexane is formed from benzene vapour and gaseous hydrogen bromide under the influence of bismuth bromide?

Preliminary experiments in this direction with toluene, which is somewhat more easily accessible to addition reactions than benzene, have yielded negative results. We have not been able to find an indication of an addition of hydrobromic acid.

We have finally also made some orientating experiments on the addition of hydrochloric acid gas to acetylene in the presence of bismuth chloride. We have, however, not yet succeeded in realizing this reaction.

§ 4. *Preparation of Ethyl chloride from Coal-gas.*

We have applied the method found by us to convert the ethylene present in illuminating gas in small quantities, into ethylchloride. We shall not give a detailed description of these experiments, as they do not open any essential new points of view. What *has* appeared from them is, that this reaction can be successfully applied to gas mixtures with a small ethylene-content. The Amsterdam illuminating gas used by us contained[1]) from 1 to 1,8 °/₀ of ethylene.

The illuminating gas was first freed from benzene vapour by washing with creosote oil, then passed through a gas-meter and drying-tubes, after which it was mixed with a small quantity of hydrochloric acid gas. The mixture of illuminating gas and hydro-

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[1]) Determined by absorption with fuming sulphuric acid in the gas that had previously been freed from benzene vapour. Hence also other olefines are included in this: the quantity of them is, however, very small in illuminating gas.

chloric acid gas was conducted over the bismuth trichloride catalyst between 150° and 200° C. The apparatus was arranged in such a way that the experiment could be continued day and night, without interruption and required little supervision. The ethylchloride formed, which was present only in small concentration in the issuing gas mixture, was isolated by absorption with active charcoal, after the hydrogen chloride that was still present, had been removed. The chief constituents of the illuminating gas were not adsorbed by the charcoal, and left the adsorption-apparatus unchanged. In order to be able to verify in the course of the experiments, whether the charcoal still adsorbed ethylchloride, resp. whether ethylchloride was still being formed in the reaction tube, we made use of the method of analysis mentioned in the beginning, which is based on the splitting off of hydrochloric acid from ethylchloride. From the active charcoal we liberated the adsorbed ethylchloride by heating, and then condensed it by cooling.

In the paper cited, **Berl** and **Bitter** have also applied the adsorption of ethylchloride by means of active charcoal.

To give an example we obtained 5,8 gr. of pure ethylchloride from 360 litres of illuminating gas, which quite distilled over from a water bath of 15° C., besides a very small quantity of higher-boiling alkyl chlorides. This corresponded to about 50 °/₀ of the quantity of ethylene present in the illuminating gas.

We have also mixed illuminating gas with a little propylene, and obtained a very good yield of isopropyl chloride from this in the same way.

It is of importance that prolonged experiments were made with the same catalyst without this decreasing in activity.

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