THE HALOGENATION OF THE PARAFFIN HYDROCARBONS[1]

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I. INTRODUCTION

The halogens, with the exception of iodine, are among the few chemical substances which react readily with the paraffin hydrocarbons. Fluorine reacts with avidity, chlorine very vigorously, and bromine, while less energetic in action, usually substitutes with no great difficulty. Iodine, as a rule, does not react with the paraffins, but one instance of iodination has been reported.

Direct fluorination has been studied only in the case of methane. Chlorination makes up the most voluminous, as well as the most important, chapter in the halogenation of the paraffins. The action of chlorine on all the normal hydrocarbons from methane to octadecane and a number of the compounds isomeric with these has been studied. Some of this work is of questionable value, because the supposedly pure hydrocarbons used were petroleum fractions. No matter how carefully prepared, there is reason to doubt the purity of such fractions, especially those of higher molecular weights, unless there is proof that they are chemical individuals.

Although failure to react with bromine is used as a diagnostic property of the paraffin hydrocarbons, it is found that on vigorous treatment, as with the aid of light, heat, or such catalysts as iron, charcoal, or iodine, substitution by bromine generally takes place. It has been claimed that the reactivity of the hydrocarbons towards this halogen decreases with the increase in the length of the carbon chain. No certain evidence of this has been offered, although the hydrocarbons above decane that have been studied have been reported to show little or no reaction with bromine.

Due to the availability of the lower paraffins, which abound in natural gas and petroleum, and the cheapness of chlorine, a considerable amount of study has been given to the industrial application of chlorination. To some extent the chlorine derivatives of methane, particularly methyl chloride, are now manufactured from the hydrocarbon. The chlorination of pentane has developed a new source of amyl alcohol, amyl acetate, and isoprene.

In general, halogenation has been brought about by direct contact of the substituting element with the hydrocarbon, the latter in either gas or liquid form. Actinic light, heat, and catalysts have been extensively used to accelerate the reaction. Only a small amount of study has been given to the action on hydrocarbons of reagents containing loosely bound halogen, such as the chlorides and bromides of non-metallic elements.

Considerable difficulties are encountered in halogenating hydrocarbons, either for scientific purposes or in industrial practice. Chief among these are: the simultaneous formation of isomeric halides, rather than a single substance; the production of undesired polysubstitution products where monosubstitution is desired; and with chlorine, the danger of explosive reaction. Proper control of concentrations, temperature, and catalytic influences minimizes, though it does not entirely overcome, the first two difficulties; chlorination in the liquid phase, dilution of the hydrocarbon with carbon dioxide, nitrogen, steam, hydrogen chloride, or already chlorinated substances, and accurate regulation of the rate of addition of halogen greatly reduce the risk of explosion.

Herzfelder (62) has made certain generalizations in regard to chlorination and bromination:

> "When into a monohalogen compound a second halogen atom is introduced, it always attaches itself to that carbon atom which is situated next to the carbon atom already united with halogen. In the case of further substitutions this rule only holds for bromine, of which it is never possible, by other than violent means, to attach more than one atom to each atom of carbon. On the other hand, when a third atom of chlorine is introduced, it frequently attaches itself to a carbon atom that is already united with chlorine.
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> "Bromides that already contain one atom of bromine united with each atom of carbon can not be easily further brominated; chlorides, however, take up more chlorine. A normal hydrocarbon, when brom-

inated by ordinary means, takes up as many atoms of bromine as it contains atoms of carbon; this was shown in the case of methane, ethane, propane, and also, although not with absolute certainty, in that of butane, hexane, and octane."

A study of the available experimental data on halogenation, however, leads one to the opinion that there is not sufficient evidence to justify such a sweeping statement.

In this review hydrocarbon fractions have been presented as individual compounds with the names given them by the original investigators. Boiling ranges and densities have been cited wherever possible and comparison of these with the constants of the pure hydrocarbons allows one to estimate to some extent the validity of conclusions drawn from the experimental work.

In many cases with both the hydrocarbon starting materials and the chlorinated products, the published identifications are not accurate. Recent work in hydrocarbon chemistry has shown how treacherous are hydrocarbon fractions, particularly from petroleum, when one is endeavoring to obtain pure substances, and how far they may be from single compounds even though boiling over narrow ranges and giving analytical values in harmony with supposed molecular composition.

II. FLUORINATION

The data available on the reaction of the paraffin hydrocarbons with fluorine are confined to two studies on methane. By passing a current of fluorine through a platinum tube into an atmosphere of this hydrocarbon Moissan (116) obtained a mixture of fluorine compounds from which he isolated carbon tetrafluoride. The reaction was accompanied by incandescence and deposition of carbon.

Later Moissan and Chavanne (117) observed that on coming in contact with liquid fluorine at −187°C. solid methane reacted with a bright flash and violent explosion. It was impossible to identify the products because the glass reaction tubes were "pulverized."

III. CHLORINATION

1. *Methane and natural gas*

Chlorination of methane results in the formation of all the possible products—methyl chloride, dichloromethane, chloroform, and carbon tetrachloride. Bedford (14) reported that at low temperatures in the presence of actinic light each of these compounds forms in turn from the preceding member of the series, chlorine showing a slight preference for chloromethanes over the hydrocarbon itself. As a result, the product of reaction is usually not a single substance, but a mixture of several compounds. The relative proportions of the derivatives obtained are determined largely by the ratio of chlorine to hydrocarbon in the mixture of reacting gases. Other conditions, such as small changes in temperature or the presence of catalysts, have influence in lesser degree.

Martin and Fuchs (108) endeavored to calculate from thermochemical data the ratios which may be expected between the chloromethanes after the reaction of chlorine and methane. They believed that under the same conditions the ratio of the velocity constants of the successive stages of chlorination should be proportional to the number of hydrogen atoms displaced by chlorine. On the basis of these theoretical ratios (4:3:2:1), the course of the chlorination of methane with time was calculated. The theoretical and experimental results were in agreement in the neighborhood of 300°; at higher temperatures, especially in the presence of catalysts which presented large surfaces, the more highly chlorinated products were formed in greater proportions than was demanded by theory. The work of other investigators has not borne out the hypothesis of Martin and Fuchs.

Müller (120) has suggested that in chlorination the methane and chlorine may first combine to form an addition compound, which then splits to a chlorine derivative and hydrochloric acid. During chlorination there is also a condensing action, resulting in the formation from methane of halogen derivatives of higher hydrocarbons, especially of ethane.

If the chlorination is not controlled, but allowed to cause a considerable elevation of temperature by reason of its exothermic nature, the course of the reaction changes. Substitution gives way to a disruptive process, producing free carbon and hydrogen chloride according to the equation:

$$CH_4 + 2Cl_2 = C + 4HCl$$

The chlorination of methane has been accelerated in many different ways. Actinic light has been used frequently. Some investigators have employed catalysts, or used a chlorine hydrocarbon mixture raised to temperatures as high as 600°, or subjected the mixture to the silent electrical discharge. At times two or more of these methods of stimulating reaction have been allowed to act simultaneously.

Photochemical chlorination. (*a*) *Methane.* Sunlight, diffused daylight, light from a carbon arc, from a metallic filament and from a mercury-vapor lamp, have been used to promote the chlorination of methane. In one study on natural gas (12) an interesting comparison of the influence of light of different wave lengths on chlorination was made. Blue light had by far the greatest accelerating effect. Most other colors, even ultra-violet, were ineffective. Some workers have recommended "ultra-violet lamps" as a source of activating light in chlorination. It is quite probable, however, that light from these lamps of wave lengths other than those of ultra-violet is the effective agent assisting reaction with the halogen.

In most of the experimental work that has been reported the halogen and hydrocarbon were treated at room temperature. According to patent claims, however, where methyl chloride is sought the reaction chamber may be cooled, and in some work the chlorination has been carried out in the interstices between ice cakes.

Dumas (42) observed that while methane and chlorine could be mixed in all proportions in the dark without any immediate action, the mixing of three volumes of chlorine and one of methane in daylight, even when diffused, produced a violent explosion. If the methane, however, was first diluted with an equal volume of carbon dioxide, the chlorine could be added without danger, and when methane was permitted to diffuse downward into chlorine in the presence of sunlight, the reaction proceeded smoothly. Carbon tetrachloride and a smaller amount of chloroform were produced under these conditions. Attempts to produce methyl chloride by the action of either gaseous chlorine, antimony pentachloride, or phosphorus pentachloride upon methane were unsuccessful.

Bischoff (18) found that a mixture of methane with twice its volume of chlorine exploded in bright sunlight, producing carbon and hydrogen chloride. If the light intensity was weakened by clouds, while the reaction occurred, carbon was not deposited and the residual gas had the odor of turpentine. Berthelot (16) also observed that the use of diffused sunlight was necessary in order to obtain normal chlorination, as direct sunlight nearly always caused explosion.

A little later, Kolbe and Varrentrap (82) noted that in diffused light equal volumes of dry methane and chlorine were converted into equal volumes of hydrogen chloride and a chlorine-containing, combustible gas. They were unable to decide whether this was "actually methyl chloride or an isomeric compound."

In contrast with previous observations, Phillips (129) reported that "a mixture of methane and chlorine was exposed over water to bright sunshine on a July day without undergoing any noticeable contraction in volume or change in color." He claimed that chlorine attacked methane only at temperatures considerably above 100°.

Whiston (192) mixed chlorine and methane in various proportions in the dark and exposed the mixtures to daylight admitted through glass windows. In a mixture of 2.75 volumes of methane to 1 volume of chlorine, he found that not more than 25 per cent of the chlorine reacting went to form methyl chloride, while from a mixture of equal volumes of the two gases only 10 to 13 per cent of the chlorine appeared in the monohalogenated product. Whiston did not determine the amounts of dichloromethane, chloroform, and carbon tetrachloride produced.

In preliminary experiments Whiston (192) found that in mixtures containing two volumes of methane to one of chlorine there was no action in the dark, a slow combination under the influence of light from an ordinary 60-watt metallic filament lamp placed 30 cm. from the reaction vessel, and a much more rapid reaction when an arc light was used. If a very small amount of nitrosyl chloride was present, practically no action took place even in the strongest light.

Römer (138) found that methane when illuminated was chlorinated more readily than hydrogen in a mixture of the two gases. He found it impossible, however, to predict the partition of the chlorine between the gases from a study of the velocity of their individual reactions.

(*b*) *Patents on photochemical chlorination of methane.* The industrial interest taken in the photochemical chlorination of methane is shown by the number of patents which have been issued on this subject. Elworthy and Lance (46) claimed to be able to prepare chloroform by mixing "suitable proportions" of methane and chlorine, adding an inert diluent as nitrogen or carbon dioxide, and subjecting the mixture to the action of sunlight or other suitable illumination in a series of thick-walled glass tubes. The dilution was said to eliminate all danger of explosion.

By Walter's process (189) methane was mixed with a corresponding quantity of chlorine and exposed in air-cooled glass tubes to light of gradually increasing intensity. It was stated that the reaction could also be carried out satisfactorily in a tower-like reaction chamber in which the light source was overhead. Walter claimed that by working with a gas mixture consisting of one volume of methane to four of chlorine about 45 per cent of the weight of chlorine was used, and methyl chloride, dichloromethane, and chloroform as well as carbon tetrachloride were formed, the proportions varying with the quantity of chlorine and the reaction temperature.

Snelling (172) introduced mixtures of methane and chlorine, which would ordinarily be explosive, into dome-shaped glass vessels two feet in diameter and five feet high, and exposed them to intense light. He claimed that explosion was prevented by convection currents set up by the heat liberated in the reaction.

The reaction was started at a low rate of gas flow, and after it had commenced the mixture of methane and chlorine was admitted at rates up to 60 liters per minute with complete and quiet combination. The products were dichloromethane, chloroform, and carbon tetrachloride.

In a variation of this process, Snelling (170) passed mixtures of methane and chlorine through three parallel series of transparent, dome-shaped reaction vessels (171). As the gas advanced through the apparatus it was exposed to actinic light (as from mercury-vapor lamps) of gradually increasing intensity.

According to another patent (173) of Snelling, chlorine was mixed with an excess of methane, reaction brought about, and the resulting gases brought in contact with a solvent for removing the methyl chloride, such as oil or carbon tetrachloride, which is a relatively poor solvent for the unhalogenated hydrocarbon. The residual methane was then retreated, and the circulation continued.

Riesenfeld (136) developed an apparatus for chlorinating methane with provision for preventing sudden increase or stoppage of the flow of the gas-mixture into and out of the reaction chamber, which would be likely to cause explosion. He also claimed that he could regulate the chlorinated product by varying the speeds of flow of methane and chlorine. Reaction of equal volumes of the gases was said to give 80 per cent of methyl chloride, 10 per cent of dichloromethane, and small amounts of chloroform, carbon tetrachloride, and hexachloroethane. When the chlorine-methane ratio was between 3:1 and 5:1, the product consisted of 5 per cent of chloroform, 42 per cent of carbon tetrachloride, and 10 per cent of chloroethanes.

Leiser and Ziffer (99) aimed to obtain mainly methyl chloride by rapidly passing a mixture of one volume of chlorine to six of methane through four reaction chambers of progressively increasing size. During the passage, the reacting gases were exposed to light from mercury-vapor lamps extending axially through the chambers. Addition to the gas mixtures of small amounts of hydrogen chloride proved advantageous, while a small amount of water vapor seemed to prevent the undesired disruptive reaction to hydrogen chloride and free carbon.

The Goldschmidt A.-G. (56) patented a process for the production of methyl alcohol and dichloromethane, which consisted in chlorinating methane and treating the chlorinated product under pressure with milk of lime. Methyl alcohol was formed by action of the milk of lime on methyl chloride and was carried away dissolved in the lime suspension, while the dichloromethane was carried by the gas stream and later separated by cooling to low temperature.

(c) *Natural gas.* By employing Dumas's method (42) of allowing chlorine and the hydrocarbon gas to mix slowly by diffusion while exposed to sunlight, Melsens (109) prepared carbon tetrachloride from marsh gas and thus proved its identity with methane produced from the acetates.

Baskerville and Riederer (12) made the study already referred to concerning the wave length of light used to speed the reaction of natural gas and chlorine mixtures. The radiation from a "Uviol" ultra-violet lamp was found to have no noticeable effect on the chlorination. Light from either an unscreened carbon arc or from the arc screened with blue accelerated the reaction, but the interposition of green, yellow, or red screens decreased the rate of chlorination almost immediately. When the blue screen replaced these, the reaction was at once reaccelerated. The screening-out of the other colors was of no assistance to the chlorination, as the inactive red, yellow, and green rays had little, if any, interfering influence. In other experiments natural gas mixed with chlorine was heated and passed into a reaction chamber consisting of a cruciform glass tube, through two opposite arms of which a quartz tube containing iron terminals was inserted, across which an arc was struck. A yield of approximately 20 to 25 per cent of the methane as chloroform and carbon tetrachloride mixture was obtained.

Tolloczko (182) chlorinated natural gas in the outer jacket of an ultra-violet lamp constructed in the form of a Liebig condenser. The reaction proceeded continuously at 80–100° without explosion, even with equal volumes of natural gas and chlorine, but more slowly with the lamp than in sunlight (183). An excess of natural gas (natural gas: chlorine $=1.2:1$) gave with double passage of the gases between the walls of the ultra-violet lamp, a yield of 1.53 grams of oil and 0.38 grams of gaseous products per liter of natural gas. The volatile products consisted mainly of methyl chloride and dichloromethane. The oily portion was separated into dichloromethane and chloroform, which in nearly equal amounts made up 75 per cent of the oil, carbon tetrachloride, dichloroethane, ethylene dichloride, and tetrachloroethane. Chlorination with an excess of halogen yielded solid hexachloroethane as well as oily products.

Bedford (14) exposed a mixture of natural gas and chlorine, confined over water at room temperature, to light from a "white flame arc," and then cooled the gas by shaking with the water. He found that for the production of the lower chloro derivatives of methane, the chlorine should be added in small increments, and after each addition the reaction should be completed and the heat of reaction dissipated before more chlorine was used.

In order to obtain better cooling and to prevent the formation of carbon tetrachloride, Bedford later carried out the chlorination in the interstices between cakes of ice in a large Woulff bottle. The reaction was started by means of the white flame arc in a mixture containing about 12.5 per cent by volume of chlorine. The hydrocarbon gas and chlorine were then admitted in regulated amounts to the Woulff bottle while the reaction proceeded. Bedford obtained 166 cc. of a mixture of dichloromethane and chloroform from 2.6 cubic feet of natural gas. This was equivalent to about 17 gallons per 1000 cubic feet.

In a large wooden reaction chamber provided with a plate glass window through which the mixture was exposed to light from the white flame arc, 250 cubic feet of natural gas was consumed at a rate of 14 to 30 cubic feet per hour, and gave several gallons of product, which was separated under water. The product contained 35 per cent by volume of dichloromethane, 35 per cent of chloroform, 5 per cent of carbon tetrachloride, and 20 per cent of chloroethanes. About 14 per cent of the reaction product dissolved in the water resulting from the melting of the ice by the heat of the reaction. This portion of the product contained 61 per cent of dichloromethane, 28 per cent of chloroform, 1.5 per cent of carbon tetrachloride and 6 per cent of chloroethanes.

Bedford (15) patented the process of chlorination in the interstices between cakes of ice. He claimed that methyl chloride was the main product when the reaction chamber was full of cakes of ice. The use of finely cracked ice reduced the speed of chlorination and favored the formation of dichloromethane. Higher average temperature produced approximately half dichloromethane and half chloroform.

Patents of Snelling (167, 168) employed actinic light, the intensity of which increased as the gases moved through the apparatus. Natural gas containing ethane and propane as well as methane was passed, together with chlorine, toward sunlight or some artificial actinic light in reaction vessels containing a series of transparent baffles. In this way the mixture richest in chlorine was exposed to light of the least intensity. The temperature within the reaction cell was controlled and the reaction mixture diluted if desired by an inactive gas such as steam, carbon dioxide, nitrogen, or highly chlorinated (169) hydrocarbons.

Thermal chlorination. In some methane chlorinations, particularly processes covered in patents, reaction has been assisted by heat. The low limit of effectiveness of heat appears to be about 250°, and work has been reported up to as high as 500°. In the presence of light the reacting gases have also sometimes been heated, but to lower temperatures.

Jones, Allison and Meighan (76) reported the beginning of chlorination in the dark at 250°. Lacy (88) stated that a chlorinated product consisting mainly of methyl chloride was obtained by passage of an excess of methane mixed in the cold with chlorine (a ratio of ten volumes of methane to one of chlorine was suggested) through a reaction vessel of glass, quartz, porcelain, or earthenware maintained at a temperature of about 400°.

In further patents Lacy (89, 95) claimed that both methyl chloride and dichloromethane were formed by the use of from four to eight volumes of methane to one of chlorine. Moreover the heat developed by the reaction was sufficient to maintain the gas mixture at a temperature of 400–600°. Use of a porous contact material in the reaction chamber accelerated the heating of the incoming gases and increased the velocity of reaction.

Lacy (96, 97) also found that reaction could be effected by mixing chlorine at ordinary temperatures with an excess of methane, and then introducing an additional quantity of the hydrocarbon at an elevated temperature. An apparatus (92) was proposed which comprised an iron shell lined with "acid tile" brick or silica, surrounded by a flue, and heated by gas. A filling of ground flint was placed between the shell and the lining. Conditions and temperatures were regulated so that any chlorine which diffused into the flint filling reacted with methane before reaching the iron shell. The operating temperature suggested was 400–500°. In an example (93) chlorine was mixed with five times its volume of methane at ordinary temperature, while ten volumes of methane was heated separately to 370°, and mixed with the cold chlorine-methane mixture. Methyl chloride and a small amount of dichloromethane were produced.

According to Carter and Coxe (31) the more highly chlorinated products of methane were produced by passing a mixture of methyl chloride, methane, and chlorine through a reaction chamber kept at a high temperature, usually about 400–500°. The limiting temperatures for the reaction were stated to be from 350° to somewhat below 800°.

The reaction was started by heating a mixture of the three substances. It was kept in operation by continuously adding to the system chlorine and methane in the volume ratio of 2:1. From the reaction products the dichloromethane, chloroform, and carbon tetrachloride were removed by condensation; the methyl chloride and residual methane were recirculated with the added gases. The product removed contained about 80 per cent of dichloromethane, 15 per cent of chloroform, and 5 per cent of carbon tetrachloride.

In a patent of Payne and Montgomery (123) one volume of moist hydrocarbon gas—still gas, natural gas, or a mixture—was brought into contact with three or more volumes of chlorine at 150° in the presence of porous solid material made by chlorinating (122) a light paraffinic oil until it ceased to evolve hydrogen chloride. The gas was then run in, and the vessel illuminated. It was claimed that even with the high proportion of chlorine used and the large amounts of higher paraffins and unsaturated hydrocarbons in the gas treated, practically no solid compounds, such as hexachloroethane, were formed.

Catalytic chlorination. The chlorination of methane has been carried out in the presence of a variety of catalysts, including salts, notably halides, metals, and carbonaceous materials. The results obtained, however, cannot be attributed solely to the catalysts, since most of the chlorinations have been carried out at temperatures of 300° and above, where heat alone can cause reaction. No systematic work has been reported showing accurately the effect these catalysts have on the course or speed of the chemical action.

(*a*) *Metallic salts and metals.* Halides of the metals have been employed more than any other class of catalytic substances to facilitate the chlorination of methane or natural gas. The substances which have been used are ferric chloride, silver chloride, "partially reduced" cupric chloride, aluminum chloride, manganous chloride, antimony pentachloride, molybdenum pentachloride, coke impregnated with the chlorides of platinum, zinc, cadmium, tin, and lead, and nickel nitrate. In patents the use of alkaline earth chlorides, zinc chloride, and thallic chloride is claimed; and sodium, cadmium, zinc, arsenic, or phosphorus in vapor form, are specified as chlorination catalysts.

(1) Methane. Pfeifer, Mauthner and Reitlinger (127) reported a series of experiments on the chlorination of nearly pure methane in the presence of antimony pentachloride and ferric chloride. The hydrocarbon was free from olefins and thoroughly dry, but contained small amounts of oxygen and nitrogen. It was mixed with chlorine and reacted by passage through a quartz tube heated in an electric oven at 360–400°. The gaseous products of the reaction were passed through two spiral condensers (the first cooled by water and the second by alcohol and solid carbon dioxide at a temperature of $-35°$ to $-45°$). The distillate which collected in the first receiver consisted of dichloromethane, chloroform, and carbon tetrachloride, while that in the second receiver was mainly methyl chloride. The results are summarized in table 1.

In the presence of ferric chloride, with methane and chlorine in the volume ratio of 2:1, 85 per cent of the chlorine entered the reaction and gave 30.1 per cent of the possible yield of methyl chloride calculated on the basis of chlorine. Dichloromethane and chloroform were also formed in about equal amounts. By increasing the methane-chlorine ratio to 3:1, the yield of methyl chloride was brought up to 40 per cent of the theoretical, calculated on the basis of chlorine used.

To obtain carbon tetrachloride as the chief product, a large excess of chlorine was necessary. But since the use of more chlorine than methane when the gases were mixed by themselves caused explosion, the chlorine was diluted with nitrogen. With a gas mixture of one volume of methane, two of nitrogen, and three of chlorine, carbon tetrachloride and chloroform only were obtained.

TABLE 1

Catalytic chlorination of methane

(Pfeifer, Mauthner and Reitlinger)

CATALYST	RATIO OF CH_4 TO Cl_2	CHLORINE REACTING	CHLORINE IN PRODUCTS PER CENT OF TOTAL USED			
			CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
		per cent				
$SbCl_5$	1:2	64	0	5.8	20.3	5.9
$FeCl_3$	1:2	83.6	Trace	13.25	22.2	6.35
$FeCl_3$	1:1	86.4	5.8	15.7	21.7	0

Schleede and Luckow (141) passed mixtures of methane and chlorine through quartz or glass tubes (electrically heated at about 400°) with and without catalysts. When the gases were mixed in molecular proportions, inflammation occurred at first, but the flame gradually died out. The flame remained when an excess of chlorine was used. In an excess of methane ignition was not observed, but the chlorine was utilized quantitatively only if the temperature was below a certain value, which depended on the composition of the mixture and its rate of flow. These investigators obtained all the chloromethanes and, in addition, considerable amounts of chlorine derivatives of higher hydrocarbons. If the rate of flow was considerably below that causing the ignition, an increased production of chloroform, carbon tetrachloride, or substances of similar boiling point, at the expense of methyl chloride and dichloromethane, was observed.

The results were not modified appreciably when the minimum reaction temperature was exceeded by as much as 100°, when the heating zone was increased or diminished, or when ferric chloride, molybdenum pentachloride, or antimony pentachloride were present as catalysts. The relative proportions of the chlorinated methanes were not those to be expected according to the relationship of Martin and Fuchs (108).

These workers considered that the most probable reason for the difference was that the reactions followed a route different from the step-wise series of substitutions usually postulated. Methane might first dissociate, and chlorine then react with the fragment. Methane might also react with a chlorinated derivative to give a homolog according to the following equations:

$$CH_3Cl + CH_4 = C_2H_6 + HCl$$
$$CH_2Cl_2 + CH_4 = CH_3CH_2Cl + HCl$$
$$2CH_3Cl = CH_3CH_2Cl + HCl$$
$$CH_2Cl_2 + CH_3Cl = ClCH_2CH_2Cl \text{ (or } CH_3CHCl_2) + HCl$$

This explanation would account for the presence of halogen derivatives of the higher paraffins among the reaction products.

Tanaka (178) observed silver chloride to be an effective catalyst for the chlorination of methane in the presence of ultra-violet light.

In Boswell and McLaughlin's (21) study on the optimum yield of methyl chloride, 80 per cent or more, on the basis of the chlorine used, was obtained when moist nitrogen, methane, and chlorine in the volume ratios 70:7:1 were passed at 450° over pumice impregnated with cupric chloride. The catalyst was previously "reduced about three-quarters of the way to the cuprous condition" by nine hours heating at 450° in a current of moist nitrogen. From 10 to 15 per cent of the chlorine went to form dichloromethane, but the formation of chloroform or carbon tetrachloride was negligible.

Carbon tetrachloride in 90 per cent yield, free from other chloromethanes, was obtained by passing methane and chlorine in approximately theoretical proportions (1:4) over a fresh sample of the cupric chloride catalyst prepared as stated.

(2) Patents. Pfeifer and Mauthner (126) obtain all the chlorine derivatives of methane by causing mixtures of chlorine and this hydrocarbon, proportioned according to the product desired, to react at a temperature of 150–500° in the presence of free metals or salts of metals which exhibit two valencies, such as iron, copper, or antimony.

The Holzverkohlungs Industrie A.-G. and Roka (64, 66, 137) used as catalysts cupric chloride, ferric chloride, and halides of the alkaline earth metals, particularly calcium or magnesium chloride, employing the salts either alone or diluted with a porous carrier. They used steam as a diluent to moderate the violence of the reaction and at the same time to supply, when necessary, heat for its initiation. From two to five volumes of steam per volume of chlorine were mixed with sufficient methane to give the products desired. The reaction temperature was kept between 100° and 650°, being usually about 400–500°. Other diluents (68, 69) recommended were hydrogen chloride, carbon dioxide, and nitrogen.

According to another patent (67) of the same firm, methane and chlorine were passed into a liquid medium of high boiling point,—for instance, fused zinc chloride or potassium bisulfate, or mixtures of the chlorides of the alkali or alkaline earth metals of suitable melting point. The chlorination was aided by addition of catalysts such as ferric chloride or cupric chloride. The gases were mixed without a diluent and were kept below the temperature of reaction until they entered the fused medium. With proper regulation of the gas stream and use of suitable reaction vessels to prevent local overheating, the reaction proceeded quietly and gave good yields. From one mole of chlorine and two moles of methane, passed into a reaction vessel containing potassium bisulfate at 320°, about half of the theoretical yield of methyl chloride was obtained, together with relatively small quantities of dichloromethane and chloroform.

Polányi and von Bogdandy (131) claimed to produce methyl chloride by adding a small amount of sodium, cadmium, or zinc in vapor form to a mixture of methane and chlorine. The use of arsenic and phosphorus (132) was reported in another patent. It was assumed that the reaction was due to the liberation of atomic chlorine by the action of the metal vapor.

(3) Natural gas. Tolloczko and Kling (183) chlorinated natural gas at as low a temperature as possible in the presence of pumice, alone or impregnated with cupric or manganous chloride. In experiments with an excess of chlorine, a Jena glass tube 1 meter long was filled with pumice and heated to 400° in an electric furnace. At a gas velocity of 2.5 liters per hour, the yield of chlorinated material was about two grams per liter. The chlorinated products were separated by distillation into two main fractions, one boiling from 75–150°, and the other above 150°. The more volatile fraction consisted of 78 per cent of carbon tetrachloride, 14 per cent of tetrachloroethane and smaller amounts of hexachlorobenzene and hexachlorobutadiene.

Natural gas was also chlorinated in the presence of pumice soaked with cupric or manganese chloride. The copper salt proved the better catalyst, allowing a considerable lowering of temperature and increase in speed of gas flow over that feasible when no catalyst was present. From two passages of the gas mixture through a tube at 300° using half as much chlorine as natural gas, and passing the mixture twice through the apparatus, there was obtained, per liter of natural gas, 0.79 gram of oil and 0.35 gram of gaseous products. In the latter methyl chloride and dichloromethane predominated, with a little ethyl chloride also present. The oil contained chloroform, carbon tetrachloride, tetrachloroethylene, and acetylene tetrachloride, and in the fraction boiling above 165°, dichloroethane. The presence of its higher homologs was thought to induce the chlorination of methane, since only a slight reaction was said to take place when the pure hydrocarbon was used in place of natural gas.

Garner (53) reported that 1000 cubic feet of natural gas when passed through a tube containing clay, pumice, infusorial earth, or aluminum chloride as catalyst at a temperature of 270–290° and treated with 526.4 pounds of chlorine gave 51.34 pounds of carbon tetrachloride, 189.8 pounds of chloroform, 62.86 pounds of dichloromethane and 13.06 pounds of methyl chloride. With metallic iron or ferric chloride as catalyst both dichloromethane and methyl chloride could easily be converted into chloroform and carbon tetrachloride.

Gault and Benlian (55) have published preliminary results on the chlorination of natural gas of Vaux, France. Equal volumes of the gas and chlorine were passed over a ferric chloride catalyst in the dark at temperatures ranging from 245–415°. They obtained a mixture of the four chloromethanes.

Jones, Allison and Meighan (75, 76) chlorinated Pittsburgh natural gas, which contained 89.5 per cent of methane, 10.1 per cent of ethane, and 0.4 per cent of nitrogen, by passing mixtures with chlorine over such catalysts as metals, salts, and carbon in a glass tube heated in an electric furnace. The reaction began when the catalyst temperature was slightly below 250°. At this temperature the chlorine reacted with the ethane in preference to methane. The most suitable temperature found was 400°. After the reaction had started, very little application of heat was necessary to maintain the temperature. The greater the rate of gas flow, the less the heating required.

If the temperature of the reaction chamber rose above 500°, the velocity became explosive and the only products were carbon and hydrogen chloride. These investigators stated that "the heat control of the reaction is the important phase of the problem that must be solved before the work can be placed on a plant basis."

The catalysts most suitable for chloroform production were coke, impregnated with nickel nitrate or with chlorides of platinum, zinc, cadmium, iron, or tin. Using platinized coke, 50 per cent of the natural gas was converted into chloroform and 34 per cent into other chlorinated products. The highest yield of methyl chloride, 31 per cent of that possible on the basis of the natural gas used, was obtained by the use of two volumes of chlorine to one of natural gas in the presence of cokes impregnated with nickel, tin, or lead. Addition to the gas of a small amount of moisture, up to about 1 per cent, was said to promote the chlorination, although the data reported showed no decided effect.

(*b*) *Carbonaceous materials.* Activated charcoal, animal charcoal, and animal charcoal mixed with finely divided calcium oxide have been used in methane and natural gas chlorination, at temperatures up to 400°. The effectiveness of these materials appears due in part, at least, to their ability to absorb large quantities of chlorine.

(1) Methane. Schleede and Luckow (141) observed that the production of carbon tetrachloride and of highly chlorinated derivatives of higher hydrocarbons from methane at 400° was increased by the use of activated charcoal.

Curme (37) also reported the chlorination of methane by passing it mixed with chlorine over activated charcoal. The proportion of chlorine, which was usually from 5 to 30 per cent of the gas mixture, was varied according to the product desired.

Huff (70) pointed out that in the chlorination of methane in the presence of a charcoal catalyst the absorption of the heat developed presents difficulty because of the high reaction heat and the low thermal conductivity of charcoal. As a possible solution of this problem, he suggested that the catalyst be mounted upon the inside of a reaction tube surrounded by a liquid of high heat capacity kept in motion, or that use be made of the latent heat of vaporization of an atomized liquid carried into the reaction chamber by the gas. He favored, however, making the contact time of the gas with the catalyst brief, and alternating with cooling periods. He employed a short electrically heated contact grid to hold the catalyst.

A process of Mallet (107) carried out the reaction of chlorine with methane at a temperature between 30° and 90° in the presence of animal charcoal or other porous material, to give chloroform, dichloromethane, and carbon tetrachloride.

According to Yoneyama and Ban (197) methyl chloride was prepared easily without explosion by passing dry methane and chlorine at the respective rates of 3 and 5.5 liters per minute, over a catalyst composed of a mixture of animal charcoal and finely divided calcium oxide at 250°.

(2) Natural gas. Phillips (130) caused natural gas (containing 95.4 per cent of methane) and chlorine to react in glass combus-

tion tubes, empty or containing bone-black, sand, or asbestos. Usually the tubes were heated to the lowest temperature which would cause the color of the chlorine to disappear. Phillips found that the tendency was always toward the formation of methyl chloride and carbon tetrachloride, and that dichloromethane and chloroform were normally produced in relatively small quantities. He believed, therefore, that the manufacture of chloroform from natural gas would prove difficult.

At about 400° and using a large excess of chlorine and activated charcoals or "batchite" (98) (a material made from anthracite), Jones, Allison and Meighan (76) also obtained from natural gas large amounts of carbon tetrachloride and hexachloroethane, and relatively small quantities of chloroform.

MacKaye (105, 106) claimed to be able to produce chlorohydrocarbons, including chloroform and carbon tetrachloride, continuously on a commercial scale, by mixing natural gas or methane and chlorine at a controlled temperature in a chamber containing granulated porous material such as coke, which had been treated to remove its sulfur and iron content. The mixture was then drawn into a reaction zone also containing this catalyst material, where it was subjected to a temperature of between 250° and 600°, depending upon the speed of gas flow and the relative purity of the reactants. The proportions of methane and chlorine and the temperature of the reaction chamber were adjusted according to the product desired. Cooling means were provided to prevent the return of reaction products into the mixing chamber.

Garner and Clayton (54) mixed natural gas with chlorine at room temperature in the first half of a reaction chamber filled with freshly calcined vegetable or animal charcoal, and then passed the gaseous mixture over more of the catalyst in the second section of the chamber, heated to about 300°. In an example, 50 volumes of natural gas containing 84.7 per cent of methane, 9.4 per cent of ethane, 3.0 per cent of propane, and smaller amounts of other paraffins were allowed to react with 33 volumes of chlorine. All of the chloromethanes and derivatives of ethane as well were obtained.

Sper (175) covered very indefinitely the chlorination of saturated hydrocarbons, including methane and ethane, by mixing them with sufficient chlorine to produce the desired derivative and passing the mixture through a reaction chamber filled with small pieces of graphite and maintained at "the temperature necessary for the reaction."

(c) *With chemical chlorinating agents.* A few patents cover the chlorination of methane by reagents which liberate chlorine. Phosgene, sulfuryl chloride, or antimony pentachloride have been mixed with the hydrocarbon and the mixtures exposed to temperatures within the range of 250–450°, producing chiefly methyl chloride. Cupric chloride alone and hydrochloric acid in the presence of oxygen are also used similarly.

For the preparation of methyl chloride Hochstetter (63) proposed to conduct a mixture of methane and phosgene, in the volume ratio 3:2, over finely divided charcoal in porcelain tubes maintained at 400°. The reaction product was cooled, passed through water to absorb the hydrogen chloride, and the methyl chloride condensed by cooling under pressure.

Electrochemische Werke, Bosshard, Steinitz und Strauss (44) pass sulfuryl chloride and methane mixed in the ratio of 16:135 by weight, through an iron tube containing a catalyst, such as charcoal, metals, or metal halides, at a temperature of 300–450°. It is stated that the substances produced can be separated easily: hydrogen chloride and sulphur dioxide may be removed by absorption in water, chloroform and carbon tetrachloride by condensation at ordinary pressure, and methyl chloride and dichloromethane by condensation under increased pressure. By this process a conversion of 30 to 35 per cent of the methane used into methyl chloride, and 15 to 20 per cent into a mixture of dichloromethane and chloroform, is claimed.

The Holzverkohlungs-Industrie A.-G. (65, 85) allows methane to react with antimony pentachloride at temperatures of 300–350° in the presence of refractory clay or pumice to aid contact of the two substances. The product is largely methyl chloride with small amounts of dichloromethane and chloroform. The antimony trichloride formed during the chlorination is condensed, rechlorinated, and returned to the reaction chamber. The use of catalysts permits the temperature to be lowered to 250°. Among the catalysts usable are the chlorides (85) of iron, copper, or calcium, preferably precipitated upon substances presenting a large surface, such as charcoal, refractory clay, or pumice.

Krause and Roka (86) reported the chlorination of methane, alone or mixed with other gases, by treating it with a mixture of hydrogen chloride, steam, and oxygen at temperatures between 300° and 650°, preferably at 450–550°. Reaction was promoted by carbon, cupric chloride, ferric chloride, thallic chloride, the chlorides of the alkaline earths and of the rare earth metals. From 60 to 80 per cent of the chlorine of the acid used appeared in the chloromethanes produced.

The I. G. Farbenindustrie A.-G. (71) also claimed to produce chloromethanes by passing a mixture of methane, oxygen, and hydrogen chloride over cupric chloride at 300–450°.

Tizard, Chapman and Taylor (181) passed methane over cupric chloride heated at 430–500°. When the halide became inactive through conversion to cuprous chloride it was regenerated by treatment with chlorine. The four chloromethanes were formed in proportions depending upon the temperature employed and the rate of flow of hydrocarbon. Slow flow and high temperature favored the formation of carbon tetrachloride and chloroform.

Electrical chlorination. The silent electrical discharge and electric sparks have been used to some extent as activating agents in the chlorination of methane or natural gas.

(*a*) *Methane.* Pfeifer and Szarvasy (128, 177) proposed in a patent the employment of the silent discharge with methane. Either chlorine or a substance which would liberate the halogen (128) in the discharge space was used and the discharge was sometimes aided by light, heat, or catalysts. Under this treatment a mixture of equal volumes of methane and chlorine was reported to produce all the chloromethanes.

(*b*) *Natural gas.* Baskerville and Riederer (12) observed that a mixture of chlorine and natural gas, saturated with water, burned continuously when directed into a spark between carbon terminals, but the yield of chlorinated products obtained was too small for their identification. According to a patent of Colin (36) methyl chloride, dichloromethane, and chloroform were made by burning natural gas and chlorine in a reaction chamber through which an electric spark was passing. One volume of chlorine was used for each atom of hydrogen which it was desired to replace. If chloroform was to be produced the reaction chamber was kept at a temperature of 100–200°. In the production of methyl chloride the chamber was cooled by passage of air around it, which prevented the formation of carbon tetrachloride. This process (11) went as far as an unsuccessful experimental plant at Allegheny, Pennsylvania.

2. Ethane

Ethane is reported to react with chlorine more readily than methane. It is stated that ethane will chlorinate in a natural gas containing but 10 per cent of this hydrocarbon with scarcely any formation of chloromethanes. Like its lower homolog, however, ethane does not change when in contact with chlorine in the dark at ordinary temperatures. To bring about reaction, diffused daylight and artificial light have been used. Catalysts, notably charcoal and cupric chloride, have found some use, particularly in the production of chloroethanes from natural gas.

From the reaction of pure ethane and chlorine only two products, ethyl chloride and dichloroethane have been identified. From natural gas a trichloroethane, a tetrachloroethane, and hexachloroethane have also been obtained.

Photochemical chlorination. Kolbe and Frankland (83) employed chlorination in their early work on the structures of ethane and other paraffin hydrocarbons. When dry ethane was mixed with an equal volume of chlorine in the dark, and the mixture exposed to diffused daylight, ethyl chloride was produced. By the reaction of two volumes of chlorine with one of ethane (51) some ethylene dichloride was obtained. A substance resembling camphor (83) resulted when ethyl chloride mixed with a large amount of chlorine was exposed to sunlight.

Schorlemmer (146) found that ethane, obtained either by electrolysis of potassium acetate or by the action of strong sulfuric acid on mercury diethyl, whether dry or moist (147, 148) gave the same products when mixed with an equal volume of chlorine in the dark and then exposed to diffused daylight at 5°. These products were chiefly ethyl chloride, with a small amount of ethylene dichloride. Schorlemmer used this fact to prove that the hydrocarbons from these two sources were identical.

Darling (38) also obtained ethyl chloride and ethylene dichloride by exposing equal volumes of chlorine and ethane, mixed in the dark, to diffused daylight.

In the treatment of natural gas with an excess of chlorine in the presence of light from an ultra-violet lamp, Tolloczko (182) obtained, as has already been noted, hexachloroethane and an oily product which was not identified.

The chlorination of ethane and higher paraffins in the presence of artificially produced light rich in chemically active rays, has been claimed in a patent of the Badische Anilin und Soda Fabrik (7). Graul and Hanschke (57) chlorinated mixtures of chlorine with ethane and higher hydrocarbons by exposing them to light from a mercury-vapor lamp.

Tompkins (184) claimed the preparation of chloroethanes from ethane, obtained from coal gas by liquefaction, with the aid of actinic light. He also found it possible to chlorinate the crude oil gas, containing about 20 per cent of ethane, by the use of actinic light of gradually increasing intensity, so that the chlorination of methane was avoided, and only derivatives of ethane were formed. The intensity of the light was controlled either by passing the gas through the apparatus so arranged that the distance of the gas from the light source was gradually diminished, or so that it was screened from the light by paper or other translucent material of gradually diminishing thickness.

Snelling (168) chlorinated ethane, as he had chlorinated methane, in an illuminated chamber provided with transparent baffles, using an excess (173) of the hydrocarbon and circulating the gas mixture from the reaction vessel into contact with a solvent for the halogenated products, such as oil or carbon tetrachloride.

Thermal chlorination. When using a reaction vessel of silica, earthenware, or brick, maintained at a temperature of from 300° to 550°, Lacy (90) claimed that a large excess of hydrocarbon, such as eight volumes of ethane to one of chlorine, restricted the product to monochloroethanes. According to another method (91) the dried reaction product containing crude ethyl chloride was passed over calcium oxide at 250° to 450° to produce ether.

Catalytic chlorination. In most of the published work on the catalytic chlorination of ethane, charcoal catalysts have been used. In the presence of war-gas charcoal, Jones, Allison and Meighan (75, 76) found that the ethane present in natural gas (10 per cent of ethane with 90 per cent of methane) was chlorinated in preference to the methane and at a lower temperature. Hexachloroethane was the chief product, with some ethyl chloride, dichloro-, trichloro-, and tetrachloro-ethane.

Mallet (107) mixed ethane and chlorine and passed them through a layer of animal charcoal or other porous contact material at a temperature between 30° and 90°. Curme (37) chlorinated ethane, among other hydrocarbons, by contact with chlorine in the presence of activated charcoal. Garner and Clayton (54) proposed the formation of chloroethanes by passing mixtures of natural gas and chlorine through charcoal at 300°.

Tolloczko and Kling (183), by chlorinating natural gas in the presence of pumice, or pumice impregnated with cupric chloride at 400°, produced hexachloroethane when chlorine was in excess, and ethyl chloride, dichloro-, and tetrachloro-ethane when an excess of natural gas was used.

Electrical chlorination. A mixture of ethane and chlorine is exposed to the influence of the silent electric discharge in a modification (8) of a process patented earlier by the Badische Anilin und Soda Fabrik (7).

3. Propane

This hydrocarbon, like methane and ethane, is not acted upon by chlorine in the dark, but from experiments with mixtures it appears to be more readily chlorinated than methane. In sunlight, *n*-propyl chloride, 1,2-dichloropropane, and more highly chlorinated products may be obtained, the extent of the reaction depending upon the intensity of the light and the time of exposure. Under extreme conditions, such as the use of iodine chloride at 250°, chlorinating agents can break down the hydrocarbon structure, producing halogen derivatives of lower carbon content.

In the study of the structure of propane, Schorlemmer (152) investigated the chlorination of this hydrocarbon. He found that a mixture of chlorine with slightly more than an equimolecular proportion of propane reacted in diffused daylight, and yielded a product consisting of a low-boiling fraction which was 1,2-dichloropropane with small quantities of *n*-propyl chloride, and a mixture of more highly chlorinated products boiling between 100° and 200°. To effect further chlorination, a considerable amount of the fraction boiling above 80°, mainly dichloropropane and higher products, was exposed to direct sunlight while chlorine was passed into it for several days. After this treatment the greater portion of the product boiled between 150° and 160°. While it was impossible to isolate a fraction having a constant boiling point, the chemical behavior, boiling point range, and chlorine content of this fraction showed that it consisted of trichloropropane mixed with more highly chlorinated products.

The residual liquid, after further chlorination in direct sunlight for several days, was composed partly of a liquid and partly of a fraction boiling between 200° and 205° which solidified in the receiver as a white, crystalline mass, which after recrystallization had the chlorine content of tetrachloropropane. The liquid from this chlorination, which boiled between 205° and 250°, was acted upon very little by chlorine even in the brightest sunlight in the presence of iodine. Treatment with potassium chlorate and fuming hydrochloric acid also had little immediate effect, but by exposure to these reagents for several days, the boiling range of the liquid was raised to between 220° and 250°. From this liquid hexachloropropane was obtained, a substance which had a camphor-like odor and boiled at about 250°.

Mereshkowsky (111) reported the formation of tetra-, penta-, and hexa-bromides by the action of bromine on propane in the presence of iron, but gave no experimental details.

Snelling (167, 168) chlorinated propane in the reaction chamber provided with transparent baffles, already described, through which a stream of mixed gases passed toward a source of actinic light. The products (173) were removed from the reaction vessel, as in the case of the other hydrocarbons chlorinated in this way, by a solvent in which the unchanged hydrocarbon was sparingly soluble.

Herzfelder (62) studied the further chlorination of seven di- and tri-chloropropanes by antimony pentachloride at varying temperatures up to 190°. He reported products as shown in table 2.

TABLE 2

Products obtained by chlorination of chloropropanes by antimony pentachloride

INITIAL SUBSTANCE	PRODUCT
1,1-Dichloropropane	1,1,2-Trichloropropane
1,2-Dichloropropane	1,1,2-Trichloropropane
1,3-Dichloropropane	1,1,3-Trichloropropane
2,2-Dichloropropane	1,2,2-Trichloropropane
1,2,3-Trichloropropane	1,1,2,3-Tetrachloropropane
1,2,2-Trichloropropane	1,2,2,3-Tetrachloropropane
1,1,2-Trichloropropane	Pentachloropropane

4. Butanes

n-Butane. A number of studies have been made of the chlorination of butane, which, like its lower homologs, does not react with chlorine in the dark, but readily undergoes reaction in sunlight or artificial illumination. The only products that have been identified are a butyl chloride and a dichlorobutane.

Eighty years ago, Frankland (50) observed that a dry mixture of chlorine with butane reacted immediately on exposure to diffused daylight. Butane did not react with antimony pentachloride even in direct sunlight.

Schöyen (162) found that chlorine and butane did not react in the dark, but when butane over water in a flask of white glass was quickly mixed with an equal volume of chlorine, and the flask placed in bright daylight, reaction took place immediately with the formation of hydrochloric acid and a liquid insoluble in water, which was a mixture of butyl chloride, butylene chloride, and a more highly chlorinated liquid. Even in very weak sunlight reaction occurred.

Ronalds (139) found that butyl chloride was formed when butane from American petroleum reacted with two volumes of chlorine in the presence of light.

From ten volumes of butane and nine volumes of chlorine, exposed to daylight, Butlerov (26, 27) obtained a product containing somewhat more chlorine than called for by the formula $C_4H_8Cl_2$.

Patents owned by the Badische Anilin und Soda Fabrik (57, 73) cover the production of chlorine derivatives from butane and the other low-boiling paraffin hydrocarbons such as pentane, hexane, and heptane in the vapor phase in the presence of ultraviolet light. Snelling (173) mixed chlorine with an excess of butane in a reaction vessel from which the gaseous mixture could be circulated and brought into contact with oil or carbon tetrachloride, as a solvent for the halogenated products, and a second solvent to remove hydrogen chloride.

Butyl chloride was one of the halogen derivatives obtained by Brooks, Essex and Smith (24) by chlorination of a gasoline fraction boiling between 25° and 45° in the presence of actinic light.

Mabery and Hudson (103) chlorinated a number of petroleum fractions boiling within the range $-10°$ to 20°, but in no case did they isolate *n*-butyl chloride.

A petroleum distillate boiling between 5° and 10° which Pelouze and Cahours (124) treated with chlorine in diffused light, yielded a product which boiled between 65° and 70° and possessed the properties and composition of butyl chloride.

Isobutane. Only a few studies have been made of the chlorination of pure isobutane. In bright sunlight the reaction is violent and explosive; in diffused light it can be controlled and yields both monohalides and more highly chlorinated products. Work on petroleum fractions has also yielded isobutyl halides.

By exposing a mixture of ten volumes of isobutane and nine of chlorine to the action of daylight, Butlerov (26) produced *tertiary* butyl chloride and a chlorinated liquid very similar to that which he had obtained by the same method from butane. It contained slightly more chlorine than does a dichlorobutane.

A naphtha fraction boiling from −2° to 2°, from Pennsylvania and Ohio petroleum, was observed by Mabery and Hudson (103) to react violently with chlorine in bright sunlight with the appearance of a flame and separation of carbon. To obtain smooth reaction and highest yield of monochloro derivative, they worked in the cold with a sheet of newspaper interposed between the reaction vessel and the sun. Chlorine was slowly passed into a 2-liter bottle which contained from 100 to 200 cc. of oil. The delivery tube for introduction of halogen extended half way from the top of the bottle to the surface of the liquid. Continuous operation during 10 to 12 days was required to chlorinate 100 grams of naphtha. The reaction was stopped while a small amount of the unchanged hydrocarbon remained. After twenty fractionations, 80 per cent of the product was collected at 68–69°, and by reason of the properties of the acetate, alcohol, and sulfide into which it was converted it was thought to be an isobutyl chloride. By prolonged fractional distillation one other chlorobutane was obtained, which distilled at 121–122° and was shown by analysis to be a dichlorobutane.

Aschan (3) chlorinated in the presence of water a petroleum fraction which boiled at 10–12°. The formation of a chloride, C_4H_7Cl, with a boiling range of 60–70°, as the main product, indicated that butanes were among its components. The presence of isobutane was established; *n*-butane appeared to be either absent or present in only small quantity.

Without describing any details of his experiment, Mereshkowsky (111) stated that he formed tetra-, penta-, and hexa-bromides by the action of bromine on isobutane in the presence of iron.

Krafft and Merz (84) reported that heating isobutane with iodine chloride at 250° caused decomposition of the hydrocarbon and yielded the same products as did similar treatment of propane, namely, hexachloroethane and carbon tetrachloride.

In the combustion of isobutane in a mixture of oxygen and chlorine, Schlegel (142) observed that the hydrogen combined preferentially with chlorine and the carbon with oxygen.

5. Pentanes

The work done on chlorination of pentanes has as a rule not been carried out on the normal hydrocarbon or on an isomer in pure form, but on "pentane" fractions from petroleum, some sufficiently closely fractionated to be pentane or isopentane in nearly pure form, others boiling over a considerable range and probably containing all three pentanes and perhaps higher hydrocarbons as well. The chlorination of the fractions has had commercial success, and is a source of amyl chlorides, from which the alcohols, acetates, and other derivatives can be made.

From pure *n*-pentane have been obtained *primary* and *secondary* amyl chlorides and unidentified more highly chlorinated substances. Isopentane appears to chlorinate more easily than the normal hydrocarbon. As products from isopentane all of the four possible monochlorides have been identified. Mixed pentane fractions, which have usually been chlorinated at elevated temperature, and often in the presence of light and catalysts, have yielded chiefly monochloropentanes, the reaction normally being controlled so as to avoid the formation of higher products. In several studies mention is made of the fact that the presence of moisture aided chlorination.

n-Pentane. Cahours and Demarcay (28) found that pentane (boiling at 32–35°, whereas the accepted boiling point of pentane is 36.2°), separated from an oil produced by distilling crude fatty acids with superheated steam, absorbed chlorine rapidly in diffused light. When the action was not continued too long a liquid was produced which boiled at about 100° and had the characteristics of amyl chloride.

Lachowicz (87) obtained two monochloropentanes by passing a slow stream of chlorine into the vapors of *n*-pentane at room temperature. The retort in which the reaction took place was provided with a well-cooled reflux condenser. After the reaction had started it was accelerated by heating to boiling on a water bath. Two amyl chlorides were formed, the one which was formed in larger quantity boiling at 106°, and the other, apparently a *secondary* chloride, boiling at 104°.

When Schorlemmer (156) passed a strong current of chlorine into the vapors of a petroleum fraction boiling at 37–39°, he obtained a mixture of amyl chlorides boiling between 95° and 110°; the main fraction distilled at 100–102°.

Aschan (3) identified 1-chloropentane and secured a second amyl chloride which boiled at 96–98° from petroleum pentane. The best results were obtained when the hydrocarbon was thoroughly dry during chlorination.

The Badische Anilin und Soda Fabrik (5) raised pentane to its boiling point in an enamelled vessel provided with a fractionating column, mixed the vapors with chlorine, and subjected them at 40–50° to the influence of the silent electric discharge. They recommended that two volumes of vapor be mixed with one volume of chlorine. Diminished pressure (9) was said to promote the action.

Bauer (13) found that when chlorine was passed for several hours into pentane a product was formed which boiled between 230° and 240° and to which he gave the formula $C_5H_8Cl_4$. The pentane absorbed chlorine and evolved hydrogen chloride so rapidly that sufficient heat was produced to raise the liquid to the boiling point.

Isopentane. Aschan (3) found that isopentane from petroleum reacted more readily with chlorine than did pentane. Chlorination of the dry hydrocarbon yielded a mixture of the four monochloroisopentanes (monochloro-2-methylbutanes) together with dichlorides. Chlorination of moist isopentane produced large amounts of the *primary* isoamyl chlorides, small quantities of *secondary* isoamyl chloride and no *tertiary* product. The best yields of monochloropentanes, however, were obtained when the isopentane was dry. Aschan also investigated the conversion of these isopentane derivatives into isoprene.

Pelouze and Cahours (124) observed that an isopentane fraction from petroleum, boiling at 30–32°, absorbed chlorine rapidly at ordinary temperature even in diffused light. By avoiding an excess of chlorine and stopping the reaction while a part of the hydrocarbon remained unchanged, they obtained an amyl chloride boiling at 98–103°.

Lachowicz (87) obtained monochloro derivatives of isopentane by the action of a slow stream of chlorine on isopentane (b. p. 29–30°), obtained from Galician petroleum. The reaction was started at room temperature and after some of the chloride had been formed, was continued at the boiling point of the hydrocarbon. The chloroisopentanes boiled at 99.8–100.5°, and had a specific gravity of 0.8703 at 20°.

Mabery and Hudson (103) exposed several hundred grams of a distillate of boiling point 29–30°, obtained from Pennsylvania and Ohio petroleum, to the action of chlorine until they obtained about 200 cc. of substitution products. As in the chlorination of butane, the reaction was carried out in the presence of sunlight subdued by passing through newspaper. After eighteen distillations of the chlorinated products about 85 per cent of it boiled at 96.5° and was proved to be isoamyl chloride.

The only other constant boiling fraction that could be obtained from the chlorination products was collected at 144–145° after fifteen distillations. It amounted to about 5 grams, and had the composition of a dichloropentane.

Mott and Bedford (119) observed that at room temperature mixtures of chlorine and isopentane reacted twice as rapidly when exposed to light from a white flame arc as when exposed to that from a quartz mercury-vapor lamp. The white flame arc was rich in blue light, which has been shown to be more suitable than ultra-violet for chlorination.

According to patents controlled by Badische Anilin und Soda Fabrik (6, 74) a mixture of chlorine and an excess of isopentane is exposed to radiation from a mercury-vapor lamp. A mixture of two monochloroisopentanes is obtained from which isoprene may be produced. A process apparently identical with that of the Badische Company (74) is outlined in a patent of Graul, Hanschke and Webel (58).

According to a patent of the Chemische Fabrik auf Aktien (32), a mixture of four isoamyl chlorides boiling between 85° and 105° was obtained by chlorinating isopentane. The Badische Anilin und Soda Fabrik (9) prepares dichloropentane from isopentane under diminished pressure.

Tetramethylmethane. Tissier (180) obtained the monochloro derivative by allowing a mixture of chlorine and this hydrocarbon to stand in ordinary light at room temperature.

Pentane mixtures (petroleum fractions). (*a*) *Photochemical chlorination.* Brooks, Essex and Smith (24, 25) prepared amyl chlorides from a pentane fraction (boiling range 25–45°) from petroleum. Chlorine was introduced into the hydrocarbon material in the dark at a temperature just sufficient to vaporize it completely. The resulting mixture was then passed through glass tubes illuminated by an ultra-violet lamp. Once started, the chlorination proceeded smoothly in diffused daylight and the lamp was unnecessary. The highest yields of monochloro derivatives were obtained when the chlorine-hydrocarbon mixture contained a large excess of hydrocarbons, namely, 2 to 4 times the ratio necessary to form the monochloro compounds. When employing mixtures containing three moles of hydrocarbon to one of chlorine, amyl chlorides made up 88 per cent of the chlorinated product. They had difficulty in regulating the ratio of hydrocarbon vapors to the chlorine introduced, and for this reason obtained the formation of dichloro and trichloro derivatives as well. The hydrogen chloride formed in the reaction was absorbed in water to prevent loss of pentane vapor.

When chlorinating in the liquid phase, 90 to 94 per cent of the chlorinated product consists of monochloropentanes. The chlorine was passed through a large number of small orifices into cold pentane, and the chlorination stopped before the concentration of chlorine derivatives became greater than about 20 per cent of the mixture. The process was controlled by observing the specific gravity of the mixture. The presence of moisture seemed to aid the chlorination. Although illumination of the reaction mixture was not absolutely necessary, at the start these workers used light from a high-power tungsten bulb in the upper part of the reaction chamber. In order to prevent excessive vaporization of pentane, the temperature was not allowed to rise above 10°. From the chlorinated products a monochloropentane fraction suitable for conversion into amyl acetate was obtained.

About the time this information was published (1918), Gardner (53) described a similar process in which a natural gasoline fraction boiling between 40° and 70° was chlorinated in the presence of ultra-violet light to produce amyl chloride.

Dobryanskii and Gurevich (40) chlorinated a pentane cut (boiling at 31–38°) from aviation gasoline in the gas phase using artificial light. The highest yield of monochloride (35 per cent) was obtained at 60–70°. Wet chlorine increased the formation of polychlorides, and also led to explosion and separation of carbon.

Sparre (174) claimed the chlorination in the presence of light of a naphtha fraction boiling between 28° and 69° and said to consist of "pentanes, isopentanes, hexanes, and isohexanes."

The patent of Boyd (22) specified the chlorination of pentane, as well as of others of the first eight paraffins above methane, by treating the hydrocarbon in the liquid phase with chlorine, and then exposing the vapors from this step to actinic light in a separate reaction chamber. Superatmospheric pressure was considered advantageous in the vapor phase stage of the chlorination.

Lacy (94) disclosed a method of chlorinating pentane and other hydrocarbons by dissolving chlorine in the hydrocarbon floating on water, and then exposing the solution to light from a quartz mercury-vapor lamp. The hydrogen chloride produced was absorbed by the water.

Patents controlled by the Badische Anilin und Soda Fabrik (57, 73) already referred to under the chlorination of butane, claim applicability to the chlorination of pentane in the presence of ultra-violet light.

(*b*) *Photochemical-catalytic chlorination.* As catalysts to assist the photochemical chlorination of pentane charcoal, batchite, and silica gel have been used, and, in addition, the use of ferric chloride and iron is covered by patents.

Koch and Burrell (80) found that in the vapor phase, chlorination of a pentane fraction from natural gasoline was difficult to control, and di-and tri-chloropentane were formed, as well as the desired amyl chloride. Accordingly an apparatus (79, 81) was devised in which it was possible to carry out chlorination on an industrial scale in the liquid phase at any desired rate without danger of explosion or formation of di- or tri-chloro derivatives. The apparatus consisted of a vertical tube of lead-free glass provided at the lower end with a screen through which a chlorine-injecting nozzle projected. A tube of the same material, of smaller diameter and about half as long, with its lower end spread out in the form of a funnel, was supported within the larger tube, so that the funnel was a short distance above the bottom screen. The chlorinating catalyst, which was activated charcoal, silica gel, batchite, or other porous substances with large power of gas absorption, was placed on the bottom screen in the large tube to the depth of about three inches. In carrying out the process, the large tube was filled three-fourths full of pentane, and a regulated stream of chlorine admitted by the injector at the bottom. The chlorine passed through the layer of activated charcoal and carried a portion of the catalyst with it up through the percolator tube. While flowing upward the catalyst absorbed large amounts of chlorine.

Upon passing from the top of this tube the carbon dropped on the outside of the inner tube to the bottom of the large reaction tube. In falling it passed through a reaction zone where the absorbed chlorine reacted with the pentane under the influence of the light from the mercury-vapor lamps. The catalyst was continuously cycled while any pentane passing off as vapor was refluxed to the reaction tube.

To keep the formation of di- and tri-chloropentanes at a minimum it was necessary to stop the chlorination when the derivatives amounted to 20 to 25 per cent of the total volume of liquid. Yields of monochloropentanes were 78 per cent in actual plant practice. The residue, consisting of di- and tri-chloro derivatives, amounted to about 5 per cent.

Only 20 per cent of monochloride was obtained when Dobryanskii and Gurevich (40) chlorinated pentane from aviation gasoline in the liquid phase in the presence of activated charcoal.

In the process of Blanc (20) a stream of chlorine was introduced directly into pentane cooled by an ice bath to about 10° and exposed to daylight, sunlight, or light from a tungsten lamp, gas light, electric arc, or mercury-vapor lamp. An aqueous solution of iron chloride was added as a halogen carrier. The presence of moisture, even in small amounts, was favorable to the chlorination. To produce dichloropentane, a slower rate of passage of the reaction mixture through the apparatus was used than that found suitable for producing monochloropentane.

Dow (41) proposed conversion of pentane, present in coal distillation products, into chlorine or bromine derivatives in order to increase its boiling point and enable the hydrocarbon to be separated from carbon disulfide.

(*c*) *Thermal chlorination.* The Sharples Solvents Corporation (4, 45, 52, 78) at Charleston, W. Va., produces chloropentanes on a commercial scale from a 28° to 37° fraction of natural-gas gasoline by chlorination at elevated temperatures. The process used (4), which in the patents is claimed for paraffins containing more than two carbon atoms, consists in mixing the hydrocarbon material in vapor form at about 100° with 1/15th to 1/20th part of chlorine, and passing the mixture at high velocity through a tubular reactor, such as a gas-fired pipe still (33), kept at 315° to 371°.

Clark (33) states that by the Sharples process monochloro derivatives of pentanes are produced in approximately the following proportions:

	per cent		*per cent*
1-Chloropentane	24	1-Chloro-2-methylbutane	30
2-Chloropentane	8	2-Chloro-2-methylbutane	5
3-Chloropentane	18	4-Chloro-2-methylbutane	15

Ayres (4) reports very similar data from the same process: "One-half of the monochloride formed from *n*-pentane is *primary* and the other half is *secondary*. Of the *secondary* fraction there is much more 3-chloropentane than 2-chloropentane. . . . . In the commercial synthesis isopentane yields 85 per cent *primary* isoamyl chlorides and 15 per cent *tertiary* amyl chloride. No *secondary* isoamyl chloride is formed. (It will be noted that Aschan did obtain this substance.) Of the *primary* chlorides, one-third is 4-chloro-2-methylbutane, and two-thirds is 1-chloro-2-methylbutane." Below 100° in either vapor or liquid phase it was stated that light or catalysts are required to bring about chlorination, and yields of *primary* chlorides are low. Use of iodine, sulfur chloride, or red phosphorus as catalysts causes excessive production of polychlorides. High monochloride yields in either liquid or vapor phase were produced when insoluble and non-volatile metallic chlorides were used as catalysts, but these materials were reported to cause transposition of *primary* to *secondary* or *tertiary* chlorides.

Dichloropentanes were identified as follows:

Dichloro derivative	*Amount present*
1,1-Dichloropentane..........	"Almost none"
1,2-Dichloropentane..........	"Present in minor proportion"
1,5-Dichloropentane..........	"Almost none"
2,3-Dichloropentane..........	"Major constituent"
1,2-Dichloro-2-methylbutane	"Present in minor proportion"
2,3-Dichloro-2-methylbutane	"Formed, but is mostly destroyed by polymerization."

6. *Hexanes*

The chlorination of hexane can be readily controlled to yield monochloro, dichloro, or more highly chlorinated products. In most of the work reported the main products have been by choice hexyl chlorides, rather than more completely substituted derivatives. The hexane has been in some cases synthetic material, but more usually a closely cut petroleum fraction has been used. Light and catalysts have been employed to a considerable extent to aid reaction. Catalysts, as a rule, encourage the formation of polysubstituted compounds. A small amount of work has been done with diisopropyl, producing monochloro derivatives.

n-Hexane. Schorlemmer (154, 155, 158) made a series of investigations of the chlorination of hexane from petroleum to determine the conditions governing the formation of the *primary* or the *secondary* chloride.

The hexane was treated with chlorine under the following conditions: (1) chlorine was passed into the well-cooled hydrocarbon in diffused daylight; (2) chlorination was carried out in the cold in the presence of iodine; (3) chlorine alone was passed into the vapors of the boiling hydrocarbon; (4) chlorine was passed into the hydrocarbon vapors in the presence of iodine. In all four cases, the bulk of the product was a mixture of *primary* and *secondary* hexyl chlorides. When chlorine acted on liquid hexane either in the presence or absence of iodine, large quantities of more highly chlorinated products also formed, but by chlorination of the vapors, the formation of the higher halogen derivatives was avoided almost completely.

By passing chlorine into the vapor of gently boiling petroleum hexane, and fractionating the product, Schorlemmer (158) obtained monochlorohexanes which distilled at 125–126°. Chlorination of the vapor of hexane, prepared by reduction of hexyl iodide (158, 160), gave a product which distilled largely at 126–128.5°, with a smaller portion boiling at 128.5–130°. More highly chlorinated substances were also formed but in smaller quantity. "It appeared," Schorlemmer (158) stated, "that by the action of chlorine upon the hydrocarbon (hexane) one-sixth is converted into the *primary* chloride and five-sixths into the *secondary.*"

Several researches made prior to that of Schorlemmer are of historical interest. Wanklyn and Erlenmeyer (190) had noted that the chlorination of hexane was aided by iodine. Riche (134) stated that hexane, obtained by treating *n*-heptoic acid with barium oxide and boiling at 58° (*n*-hexane boils at 69°), was attacked briskly by chlorine with formation of substitution products.

From American petroleum, Pelouze and Cahours (124) obtained a fraction boiling at 68° which they showed consisted essentially of hexane, and which on chlorination in diffused light yielded mainly a monochlorohexane boiling at 125–128°.

A chlorohexane with the same boiling range was formed when Cahours and Demarcay (28) chlorinated hexane (boiling point 68–70°, d_{13} 0.667) which they had separated from an oil produced by distilling crude fatty acids in the presence of superheated steam. In diffused light the continued (124) action of chlorine on the monochloride of Pelouze and Cahours formed a dichlorohexane boiling at 180–184°, density 1.087; a trichlorohexane boiling at 215–218°, density 1.193; and a tetrachlorohexane. Further chlorination with the aid of heat and sunlight yielded a hexachlorohexane, a stable product which boiled at 285–290° and had a density of 1.598. Schorlemmer (153) also produced a hexachlorohexane by passing chlorine into hexane from petroleum as long as any action could be observed, first in diffused light and afterwards in direct sunlight. This product could not be distilled without decomposition.

Morgan (118) chlorinated hexane from petroleum (b. p. 68–70°) in the vapor phase by Schorlemmer's method (158). Nine-tenths of the hydrocarbon was converted into a mixture of monochlorides boiling at 120–134°, while the remainder formed more highly chlorinated products.

Michael and Turner (115) passed chlorine into boiling hexane in diffused daylight and obtained a mixture containing about 10 per cent of 1-chlorohexane, a small amount of 2-chlorohexane, and still less 3-chlorohexane.

The following researches are of more recent date.

Faragher and Garner (47) chlorinated isohexane and hexane fractions (boiling at 61–64°, and 67.5–70°, respectively, and obtained from Pennsylvania straight-run gasoline) in the vapor phase by the method suggested by Schorlemmer (158). They introduced the chlorine at about the middle point of a tube into which the hydrocarbon was being refluxed. Monochloro derivatives were the principal products, with small amounts of dichlorohexanes and more highly chlorinated compounds. The chlorination was carried out in diffused light, as in full daylight a flame appeared and carbon was formed. In order to obtain good yields, it was necessary to absorb the issuing hydrogen chloride or to cool it to a low temperature, so that none of the chlorinated products should be carried away and lost.

A fraction which was obtained from the chlorinated *n*-hexane, distilling at 120–124° after four fractionations, corresponded in properties to 2-chlorohexane. From isohexane was obtained a mixture of monochlorohexanes distilling at 119–123°.

According to patents controlled by the Badische Anilin und Soda Fabrik (57, 73) an excess of hexane vapor mixed with chlorine is led from below into a vessel in the middle of which a mercury-vapor lamp is placed. The vapors from this reaction vessel are passed through a condenser where the chlorohexane and hexane are condensed and from which they are siphoned into the distillation vessel, while the hydrogen chloride escapes. Most of the chlorohexane remains in the reaction vessel until the end of a run.

Vivas (188) claims the catalytic chlorination of a purified gasoline presumably consisting mainly of hexane. The hydrocarbon material is introduced into a reaction vessel together with carbon tetrachloride, aqueous ammonia, and catalysts, such as aluminum or ferric chloride, and chlorine is bubbled through the reaction mixture. The product is said to be suitable for cleaning purposes or as an ingredient in paints.

According to the International Fireproof Products Corporation (72) a compound $C_6H_7Cl_7$ is obtained by bubbling chlorine through gasoline, consisting mainly of hexane, in the presence of aluminum chloride or ferric chloride.

2,3-Dimethylbutane (diisopropyl). Schorlemmer (151) found that diisopropyl (prepared from isopropyl iodide), with a boiling point of 58° and specific gravity of 0.6701 at 17.5°, reacted with chlorine readily in the cold. If the reaction was stopped before all the hydrocarbon had reacted, the chief product was a monochloride which boiled at 122° and had a specific gravity of 0.8874 at 22°. When iodine was present, no monochloride was formed, but the main product consisted of dichlorodiisopropyl, a solid which melted at 160°.

In the presence of iodine, Silva (165) obtained from diisopropyl both of the chlorides described by Schorlemmer (151). When the reaction was carried out in sunlight (166) two monochlorides were formed: one was that of Schorlemmer (151), the other boiled at 118°. In the absence of iodine the lower boiling monochloride and a liquid dichloride which boiled at 160° were formed.

Aschan (2) subjected diisopropyl (a 57–59° fraction of Baku petroleum) to chlorination in a retort cooled externally with ice water and provided with reflux condenser. In order to avoid the formation of more highly chlorinated products, at frequent intervals the portion boiling above 100° was separated by distillation, and the chlorination of the remainder continued. By fractionation of the final product two liquids were obtained, one of which boiled at 117–119° and was the *tertiary* chloride, while the other, which boiled at 123–125° was an unidentified monochloro derivative. Later Aschan (3) reported the formation of both these substances and a third monochlorohexane of undetermined structure on chlorinating a 58–69° petroleum fraction.

7. *Heptanes*

From the published work on heptane chlorination, it is apparent that the halogen and either the normal hydrocarbon or its isomers react readily in diffused daylight, or in the dark in the presence of catalysts such as iodine. Bright sunlight is likely to cause a disruptive action with separation of carbon. Some of the investigations reported have been made with synthetic heptane, but there is doubt sometimes of the purity of the material used, as reported boiling points do not agree with the accepted value. Many of the workers employed petroleum fractions, which had such wide boiling ranges that considerable amounts of hydrocarbons other than those designated must have been present.

Usually chlorination has been stopped when only monochloro derivatives were produced. There is no difficulty, however, in producing higher products by prolonging the action, especially when using catalysts. In several cases there is doubt as to the exact structure of the chloroheptanes produced. 1-Chloro- and 2-chloro-heptane have been identified, but in some investigations the workers have been content to simply report the production of monochloroheptanes and to give boiling points and densities.

n-Heptane. In one of the early studies of paraffin hydrocarbons Schorlemmer (143) observed that when chlorine was passed into heptane, "hydride of heptyl," the liquid became warm and hydrogen chloride was evolved. From the products of the reaction he isolated a monochloride which boiled at 150–152° and had a specific gravity of 0.891 at 19°. Smaller amounts of higher boiling chlorine compounds were formed, but they were not identified. He produced the same monochloride (144) by a method of Müller (121) in which an excess of chlorine was avoided and the reaction catalyzed by a small amount of iodine.

Schorlemmer (149) also chlorinated a heptane, "ethyl amyl," prepared by the action of sodium on a mixture of ethyl and amyl iodides which boiled at 90–91° (accepted b. p. of heptane is 98.4°) and had a specific gravity of 0.6819 at 17.5°. (These constants are closer to those of 2-methyl- or 3-methyl-hexane than to those of *n*-heptane.) In diffused daylight chlorine was absorbed by this hydrocarbon without apparent change. The liquid then suddenly became hot, and the chlorine reacted vigorously with the evolution of hydrogen chloride. A monochloroheptane boiling at 150°, "identical with chloride of heptyl" which he had described previously (143), and a dichloropentane boiling at about 190° were found in the products. If a little iodine was added, the action continued even in the dark, with production of more highly chlorinated products. In direct sunlight the reaction took place with great vigor and separation of carbon occurred.

Schorlemmer (149) observed that heptane from petroleum gave a monochloride which boiled at 149° and had a specific gravity of 0.8965 at 19°. The monochloro derivative of heptane prepared by heating azelaic acid with barium hydroxide boiled at 151–153° and had a specific gravity of 0.8737 at 18°.

Schorlemmer and Thorpe (161) found that the product obtained by passing chlorine into the vapors of boiling *n*-heptane from *Pinus sabiniana* boiled between 143° and 157°, and consisted of 1-chloro- and 2-chloro-heptane.

Pelouze and Cahours (124) found that chlorine attacked warm heptane from American petroleum, boiling at 92–94°, with formation of a monochloroheptane which boiled at 148–152° and had a specific gravity of 0.890 at 20°.

Heptane which Morgan (118) isolated from petroleum (boiling at 96–99°) yielded a mixture of monochlorides boiling at 144–156°.

From Pennsylvania straight-run gasoline Faragher and Garner (47) separated a *n*-heptane fraction boiling at 97–100°, which they chlorinated in the liquid phase at a temperature of 20° to 25° until an increase in weight of 50 to 75 per cent of that which would be produced by complete conversion into monochloroheptane was realized. Three fractions of the product produced a monochloroheptane fraction which boiled at 150–160° at atmospheric pressure and a dichloroheptane fraction boiling at 90–100° at 15 mm.

According to a patent of Perkin, Weizmann, and Davies (125), a stream of chlorine is passed into *n*-heptane at 90° exposed to ultra-violet rays. When chlorine was added to 300 grams of heptane until the weight of the reaction mixture had increased 50 grams, 225 grams of monochloroheptane and 10 grams of dichloroheptane were obtained. The chlorination reaction could be accelerated by heat, light, or such catalysts as phosphorus compounds or iodine.

2-Methylhexane (isoheptane). Schorlemmer (157) showed that a petroleum fraction contained small quantities of a heptane boiling at 90.4° which yielded a monochloro derivative boiling at about 150°.

Grimshaw (59) applied Schorlemmer's method (158) of halogenating in the vapor phase to the chlorination of heptane prepared from ethyl and isoamyl bromides. He observed that it was necessary to protect the reaction mixture from excessive illumination, as in strong light combustion of the chlorine-hydrocarbon mixture took place. Nearly the whole of the product boiled between 140° and 150° and consisted of monochloroheptanes. In addition, small quantities of more highly chlorinated products were always formed. Grimshaw concluded that 2-methylhexane was acted upon by chlorine in exactly the same manner as are the normal paraffins.

The photochemical halogenation process of the Badische Anilin und Soda Fabrik (9, 57, 73) has been applied to the chlorination of a fraction from Galician petroleum boiling at 88–92° and consisting mainly of isoheptane. The hydrocarbon liquid was vaporized at a pressure of 50 mm. of mercury, mixed with chlorine, and then passed through a vessel containing mercury lamps. When seven parts of chlorine to ten of hydrocarbon were used, the products consisted chiefly of a monochloroisoheptane, boiling at about 140°.

Probably the first record of the action of a chlorinating agent on isoheptane is that of Wurtz (194), who found that at its boiling point the hydrocarbon was acted upon slowly by phosphorus pentachloride and that the action became vigorous in a sealed tube at 100°. Because the tube exploded no product was identified.

8. Octanes

Octanes appear to react slowly with chlorine in the cold, and much more rapidly if heated or illuminated. As with the heptanes, not much work has been done with pure octanes, but the raw material in most cases has been more or less closely-cut petroleum fractions. Usually chlorination experiments have been carried only to the monochloro derivative stage. More highly chlorinated products can readily be formed, however, and under extreme conditions may even break down the carbon chain of the hydrocarbon.

n-Octyl chloride and 2-chlorooctane are the only chlorine derivatives that have been positively identified. In many cases only the boiling point and density of chlorination products have been given, and structures are undetermined.

n-Octane. Riche (134) found that normal octane, prepared by distilling sebacic acid with barium oxide, was attacked slowly by chlorine and formed a viscous mixture of products. Schorlemmer (143) noted that the action of chlorine on octane, "hydride of octyl," yielded a monochlorooctane boiling at 170–172° and having a specific gravity of 0.892 at 18°, and also other products which could not be identified because they decomposed on distillation.

Pelouze and Cahours (124) found that the octane fraction from American petroleum, boiling at 116–118° (*n*-octane boils at 124.6°) and having a specific gravity of 0.725 at 15°, was attacked by chlorine slowly in the cold and more rapidly at 40–50°. When an excess of chlorine was avoided the main product consisted of a monochlorooctane boiling at 168–172° and having a specific gravity of 0.895 at 16°.

Schorlemmer (153) prepared from petroleum octane (boiling 122–125°) an octyl chloride which was a colorless liquid with the odor of oranges; it boiled at 173–176°, and by conversion into the alcohol was shown to be essentially 2-chlorooctane. Chlorination of the octane formed by replacing the hydroxyl group in methylhexylcarbinol by hydrogen also yielded mainly a liquid boiling at 174–176°; it proved on conversion to the corresponding alcohols to be a mixture of the *primary* chloride with a small quantity of a *secondary* chloride thought to be 3-chlorooctane. It was not identical with the chlorooctane obtained from petroleum.

An octane which Cahours and Demarcay (28) separated from an oil produced by distilling crude fatty acids with superheated steam yielded *n*-octyl chloride boiling at 182°. Mabery and Hudson (103) chlorinated at ordinary temperature the vapor of an octane (b. p. 119.5–120°, specific gravity 0.7243) separated from Ohio petroleum by thirty-three fractional distillations. The best yield of monochlorooctanes was obtained when the quantity of chlorine absorbed was 50 per cent in excess of the amount theoretically required to form the monochloride. Even with this excess, a small amount of the octane remained unchanged. Fractionation of the chlorination product yielded a large quantity of a monochlorooctane boiling at 164–166°. These investigators also produced a monochlorooctane which distilled at 173–174° from a petroleum distillate boiling at 124–125°. A small amount of higher boiling material was produced which was apparently more highly chlorinated.

Other octanes. Wurtz (194) observed that hydrogen chloride was evolved when chlorine acted upon an octane (b. p. 106°, specific gravity 0.7057) prepared by the action of sodium on a butyl iodide. Antimony pentachloride also reacted with this octane, with the evolution of hydrogen chloride and the formation of a chlorine-containing product which was not investigated further. Butyl chloride, phosphorus trichloride, and hydrogen chloride were formed when phosphorus pentachloride was heated with the hydrocarbon for a long time. Later (195) Wurtz found that an octane (probably 4-methylheptane), boiling at 115–118° and having a specific gravity of 0.728 at 0°, yielded a monochloride which boiled at 167°.

Schorlemmer (151) chlorinated what was apparently diisobutyl, obtained by treating a mixture of isopropyl and amyl iodides with sodium and boiling between 109° and 110° (diisobutyl boils at

109.2°). He obtained a chlorooctane boiling at 165° and having a specific gravity of 0.8834 at 10.5°. Carleton-Williams (30) obtained a mixture of *primary* and *secondary* chlorides when diisobutyl, prepared by the action of sodium on isobutyl bromide, was chlorinated by Schorlemmer's method (158) of passing a current of dry chlorine into the vapor in diffused sunlight. The chlorinated product, which remained liquid at −17°, had no constant boiling point and could not be separated into single compounds even by repeated fractionation.

Hartmann (61) treated diisobutyl with dry chlorine under reflux, first in the cold and then at the temperature of the water-bath, as long as hydrogen chloride was evolved. The product was freed from hydrogen chloride and uncombined chlorine by placing it under a partial vacuum. It was then transferred to tubes, and iodine and antimony pentachloride added. A vigorous reaction ensued. When this had ceased, the tubes were sealed and heated at 50° and for four hours at 190–200°. They were then opened, the antimony pentachloride regenerated by passing in dry chlorine, and the tubes heated further, the temperature ultimately reaching 450°. The product consisted mainly of carbon tetrachloride, with small amounts of hexachloroethane and hexachlorobenzene.

Ahrens (1) reported, without mentioning the methods used, that the action of chlorine on an octane prepared from coal oil produced mono-, di-, and tri-chlorooctanes. The monochloride was a colorless oil boiling at 164–166°, and the dichloride a yellow oil boiling at 122–124° at 49 mm. pressure. The trichloride was not described.

9. *Nonane*

Both synthetic nonane and petroleum fractions falling within the nonane boiling range have been chlorinated, usually to monochlorononanes, but in no case has the structure of the product been proved.

Pelouze and Cahours (124) obtained a fraction of American petroleum, boiling at 136–138° and with a specific gravity of 0.741 at 15°, which from analysis and vapor density they judged to be made up of nonane. Chlorine attacked this nonane when gently heated. A monochlorononane boiling at 196° and with a density of 0.899 at 16° was isolated.

Thorpe and Young (179) passed a stream of dry chlorine through purified nonane under reflux in direct sunlight. Action appeared to start at once, with darkening of the liquid and evolution of hydrogen chloride. "The chlorine on passing into the heated liquid appeared to burn, a flash of light appearing at the end of the delivery tube as each successive bubble of gas passed into the hydrocarbon." The passage of chlorine was stopped occasionally and the liquid distilled in order to prevent, as far as possible, the formation of highly chlorinated products. After each fractionation, the portion which distilled below 200° was exposed to further action of chlorine. Ultimately the greater part of the liquid boiled between 200° and 230°, about 40 per cent of the product boiling above 230°. A nonyl chloride fraction was obtained which boiled at 190–198° and had a specific gravity of 0.8962 at 14°; it was thought to be a mixture of *primary* and *secondary* monochlorononanes. A fraction which boiled at about 245° and was too small for analysis, was believed to be dichlorononane.

By treatment with chlorine at below 65° Lemoine (100) produced from nonane (which boiled at 132° under 759 mm. pressure and had a density of 0.730 at 23.8°) a monochlorononane distilling between 180° and 184° and having a density of 0.911 at 23.3°. He prepared monochloro derivatives from a number of other saturated hydrocarbons in the same way.

10. Decanes

n-Decane. As with other paraffins, most of the study of the chlorination of decane has been done on petroleum fractions, and very little on synthetic material. Two sorts of fractions have been used, one boiling at about the true boiling point of decane, the other at near the boiling point of isodecane. In work with fractions of both types, mono- and di-chloro derivatives have been reported, but in no case has the structure of a product been ascertained.

Besides chlorine, phosphorus pentachloride and antimony pentachloride have been used as agents of chlorination.

Decane boiling at 173–174°, which Mabery (101, 104) separated from Pennsylvania petroleum by fractional distillation, reacted rapidly with chlorine in sunlight even when the intensity of the light was diminished by interposing a sheet of newspaper. The product was fractionated *in vacuo.* After the fourth distillation, a small quantity of liquid was collected between 130° and 140° at 80 mm.; analysis indicated it to be monochlorodecane. A further fraction, distilling at 170–171° under 80 mm. pressure and at 235–240° at 747 mm. pressure and having a specific gravity of 1.0126, was shown to be a dichlorodecane.

Normal decane (101), obtained from Ohio petroleum and boiling at 173–174° gave a product boiling at 134–136° at 80 mm. and having the composition of monochlorodecane. It had a specific gravity of 0.8895 and distilled under atmospheric pressure with some decomposition at 205–210°. The chlorinated material also yielded a higher fraction, boiling from 170–180° at 80 mm., and under atmospheric pressure at 240–243° and having a specific gravity of 1.03, whose chlorine content was that of a dichlorodecane.

Decane (101) boiling at 173°, obtained from Canadian petroleum, similarly produced a monochloride, containing some dichloride, which boiled at 205–210°.

Schultz and Hartogh (164) found that chlorine acted so readily on normal decane, obtained from coal tar, that it was best to dilute the chlorine with carbon dioxide. From decane subjected to the action of diluted chlorine until the contents of the reaction flask had increased in weight about 25 per cent, they obtained a monochlorodecane fraction boiling at 180–190° at 720 mm. When decane was treated in the same manner until twice as much chlorine as in the first experiment had been absorbed, dichlorodecane was obtained, boiling at 245–250°.

The patent of Strauss (176), covering chlorination in the vapor phase under diminished pressure of petroleum hydrocarbons, brown coal tar oils, and the like, includes, as an example, the halogenation of paraffin hydrocarbon mixtures boiling between

173° and 238° and containing decane. The use of an amount of chlorine not in excess of that theoretically required to produce the monohalide, an average reaction temperature double the boiling point temperature, and the addition to the reaction mixture of a small amount of iodine are recommended.

2, 7-Dimethyloctane and decanes of unknown structure. When Wurtz treated synthetic diisoamyl (195, 196), or "diamyl," at its boiling point with chlorine, a product was obtained which distilled from 165° to above 200°. An analysis of the fraction passing over between 190° and 200° showed that it contained a monochlorodecane. By heating diisoamyl with phosphorus pentachloride, he obtained a dichloride boiling between 215° and 220° and possibly also a tetrachloride. He also found that antimony pentachloride attacked this decane.

From American petroleum Pelouze and Cahours (124) obtained a fraction, supposedly diisoamyl, with specific gravity 0.757 at 15°, and boiling point 160° (the boiling point of diisoamyl) with which, when warm, chlorine readily reacted. The first substitution product boiled at 200–204° and was shown by analysis to be a monochlorodecane.

Schorlemmer (145) found that when chlorine was passed into diisoamyl ("amyl"), a liquid resulted which boiled at about 200° and had the composition of monochlorodecane. He stated that this chloride was identical with that prepared by Pelouze and Cahours (124) from decane obtained from American petroleum.

By passing chlorine into the hydrocarbon exposed to diffused daylight, Schorlemmer (150) obtained from synthetic diisoamyl which boiled at 158–159° a monochlorodecane distilling at 203–205°. Decane, "hydride of decatyl," isolated from rectified American petroleum (b. p. 157–159°) yielded a monochloride which also boiled at 203–205°.

Grimshaw (60) passed dry chlorine into the vapor of boiling diisoamyl, using the methods he had employed with 2-methylhexane and had described in an earlier paper (59). In the presence of an excess of chlorine or of too much light there was more danger of decomposition and ignition of the decane vapor than during treatment of the heptane. The chlorinated product distilled entirely between 198° and 217°, giving two main fractions, one boiling at 198–202° and the other at 208–213°.

Mabery (101) chlorinated decane from Pennsylvania petroleum (boiling at 163–164°) in sunlight moderated by passing through a sheet of paper. Seventeen grams of chlorine reacted with 45 grams of the hydrocarbon. The chlorine was absorbed as fast as it was passed over the surface of the liquid, and hydrogen chloride was evolved. The reaction generated sufficient heat to maintain the temperature at about 70°. After ten distillations at 80 mm. pressure 6 grams of a monochlorodecane was collected at 125–130°. It had a specific gravity of 0.8914 at 20°, and at atmospheric pressure distilled at 197–203°. Eight fractionations of the higher chlorinated products yielded 15 cc. of an oil which was collected at 160–170° under 80 mm. pressure, had a specific gravity of 1.0187 at 20° and according to analysis was a dichlorodecane.

Similarly 46 grams of decane boiling at 163°, from Ohio petroleum (101), was exposed to the action of chlorine until the weight had increased 11 grams. After the chlorinated product had been fractionated twelve times at 80 mm., 15 cc. was collected at 130–135°; the fraction boiled at 200–208° under atmospheric pressure, and was shown to have the composition of a monochlorodecane. Twelve further distillations of the chlorinated product yielded 10 cc. boiling between 160° and 170° at 80 mm. The analysis indicated a dichlorodecane.

A distillate from Canadian petroleum (101), boiling at 160–161°, behaved toward chlorine as did the corresponding fractions from Ohio and Pennsylvania oils. At atmospheric pressure the monochlorodecane produced boiled at 200–204°. A distillate from Berea grit petroleum boiling at 162° also yielded a monochlorodecane, which boiled at 120–130° at 80 mm. pressure.

Lemoine (100) found that when decane with a boiling point of 155° and density of 0.908 at 19° was treated with chlorine at a temperature below 65°, it yielded a monochlorodecane which boiled at 201–203° .

Cloëz (34) obtained, among other hydrocarbons, "decane" boiling at 155–160° by the action of hydrochloric acid on cast iron, and found that the decane reacted with chlorine.

Hartmann (61) treated diisoamyl first with chlorine and then with antimony pentachloride in sealed tubes at 360°, and obtained about equal parts of carbon tetrachloride, hexachloroethane, and hexachlorobenzene, with a trace of perchloromesole, C_4Cl_6 (hexachlorobutadiene).

11. Undecane

When heated gently and treated with chlorine, undecane readily undergoes substitution. Monochloro and dichloro derivatives of the products have been separated, but no structures have been established.

From the fractionation of American petroleum, Pelouze and Cahours (124) reported an "undecane" boiling at 180–182° and having a specific gravity of 0.765 at 16°. Chlorine reacted with the hydrocarbon when heated gently. The product, a slightly amber-colored liquid, boiled mainly at 200–224°.

An undecane, boiling at 178–180° and having a specific gravity of 0.769, was separated by Cloëz (34) from the oil produced by the action of hydrochloric acid on manganiferous cast iron. Chlorine was said to act on this undecane and form substitution products, but these were not described.

Mabery (101) prepared chlorine derivatives of undecane obtained from Pennsylvania petroleum, and boiling at 196°, by allowing 40 grams of oil to absorb 14 grams of chlorine. Substitution began with the greatest readiness as soon as the chlorine came in contact with the hydrocarbon. After five distillations of the product, 10 cc. collected at 145–150° under 80 mm. pressure and distilled without decomposition between 225° and 230° at 747 mm. Its analysis corresponded to that of a monochloroundecane. Mabery believed that a dichloroundecane was also formed in the chlorination, since in the distillation at 80 mm. pressure, about 5 cc. collected at 190–200° and gave a percentage of chlorine only 2 per cent below the theoretical value for this compound.

Undecane (101), derived from Ohio petroleum and boiling at 196° gave, when subjected to chlorination, a halide which was obtained in small quantity and boiled at 150–155° under 80 mm. pressure.

To Mabery the high boiling point was evidence that the chlorination had gone so far that the monochloroundecane could not be separated completely from the dichloro derivative. From a fraction of Canadian petroleum boiling at 196°, Mabery (101) isolated a monochloroundecane fraction which boiled at 145–150° at 80 mm. and at 220–228° at atmospheric pressure.

Strauss's process (176) of chlorinating petroleum hydrocarbon vapors under diminished pressure was said to be applicable to hydrocarbon mixtures which boiled between 173° and 238° and contained undecane.

12. Dodecane

The work to date on dodecane, like that on other hydrocarbons near it in molecular weight, is fragmentary and indefinite, due to the use of petroleum fractions as starting material, and failure to identify individual products. Mainly the formation of mono- and di-chlorododecanes has been reported.

Pelouze and Cahours (124) separated from American petroleum a "dodecane" fraction which boiled at 196–200° and had a specific gravity of 0.778 at 20°. They chlorinated it with the aid of gentle heating, stopping the reaction before all of the hydrocarbon had been acted upon, and obtained as a large proportion of the product a monochloride boiling at 242–245°.

Mabery (101) allowed a dodecane, obtained from Pennsylvania petroleum and distilling completely at 214–216°, to react with chlorine until 95 grams of the hydrocarbon had absorbed 30 grams of the halogen. After six fractional distillations at 80 mm. pressure, 20 cc. of the product was collected at 142–153°. It distilled at 230–235° under atmospheric pressure. Analysis and molecular weight determinations showed it to be a monochlorododecane.

A fraction from Ohio petroleum (101), boiling at 212–214° and having a specific gravity of 0.7728, reacted readily with chlorine, and fractional distillation of the product at 80 mm. pressure yielded two main fractions, one collected at 150–160° and the other at 190–200°. The chlorine content of the 150–160° distillate was about 0.7 per cent lower than that of a dichlorododecane.

Strauss (176) claimed that paraffin hydrocarbon mixtures containing dodecane could be converted into the monochloro derivatives by treatment under diminished pressure at a temperature approximately double that of the boiling point of the hydrocarbon and preferably with the addition of a small amount of iodine.

Cloëz (34) found that chlorine attacked dodecane (density 0.782, b. p. 195–198°) obtained by treating manganiferous cast iron with hydrochloric acid. Brazier and Gossleth (23) found that in diffused daylight *n*-dodecane was attacked vigorously by chlorine and was converted rapidly into a viscous mass which could not be purified for analysis.

13. Tridecane

The work which has been done on tridecane is very indefinite, both as regards the purity of the starting material and the identity of the products formed, which usually had the chlorine content of monochloro derivatives. From American petroleum Pelouze and Cahours (124) isolated a "tridecane" fraction boiling at 216–218°, which they chlorinated in diffused light. The first substitution product boiled at 258–260°, and on the basis of a chlorine determination was called a monochlorotridecane.

After thirty-two fractional distillations, Mabery (102) obtained from Pennsylvania petroleum a hydrocarbon material boiling at 226°, which after purification had a specific gravity of 0.7834, and about the molecular weight of a tridecane. Chlorine was allowed to act on this hydrocarbon in screened sunlight over water, care being taken to avoid an excess of the halogen. After the product had been fractionally distilled several times under a pressure of 12 mm. a considerable portion was collected at 135–140°. This fraction, which had a specific gravity of 0.8974 at 20°, had the chlorine content of a monochlorotridecane.

Strauss's patent (176) gives as an example of his process for preparing monohalogen derivatives of higher paraffin hydrocarbons the reaction of a hydrocarbon mixture containing tridecane in the vapor phase under diminished pressure with a controlled quantity of chlorine.

14. Tetradecane

Pelouze and Cahours (124) chlorinated a fraction from American petroleum boiling between 236° and 240° (b. p. of tetradecane is 252.2°) and having a density of 0.809. Chlorine reacted readily and formed an amber-colored liquid which boiled at 280°, and by reason of its carbon and hydrogen content (a very poor criterion) was thought to be a monochlorotetradecane.

By twenty-four distillations at 50 mm. pressure, Mabery (102) obtained from Pennsylvania petroleum a fraction which boiled at 236–238° at atmospheric pressure. Chlorination and distillation of the product at 20 mm. gave a fraction boiling at 150–153° (specific gravity of 1.9185) which had a chlorine content 0.4 per cent higher than that of a monochlorotetradecane. A higher boiling fraction which was collected at 175–180° under 17 mm. and had a specific gravity of 1.032, had the chlorine content of a dichlorotetradecane. It should be borne in mind, however, that the differences in chlorine content of two homologous compounds, say of a chlorotetradecane and a chloropentadecane, is only 0.6 per cent, an amount so small that the halogen determinations frequently cited in proof of the identity of chlorine derivatives are almost valueless, particularly in view of the fact that the chloride fraction usually boiled over a considerable range and was made from an impure hydrocarbon material.

15. Pentadecane

As far as showing anything about the properties of pentadecane is concerned, the work which has been reported on material supposed to contain this hydrocarbon is worthless.

Chlorination by Pelouze and Cahours (124) of a fraction of American petroleum boiling between 255° and 260° (pentadecane boils at 270.5°) and having a specific gravity of 0.825 at 19°, gave a number of products, of which the lowest boiling fraction, the only one studied, was thought to be a monochloropentadecane.

The pentadecane fraction which Mabery (102) isolated by fractionating Pennsylvania petroleum distilled at 256–257° under 760 mm. pressure. After treatment with fuming sulfuric acid, its specific gravity was 0.7896 at 20°. Mabery did not succeed in obtaining a monochloride, perhaps, in part, because he had only a small amount of the starting material. The chlorinated product boiled mainly at 175–180° under 50 mm. pressure. Chlorine and molecular weight determinations gave approximately the values for a dichloropentadecane.

Foote and Kremers (48) reported that "appreciable amounts of chlorination products" resulted from the action of nitrosyl chloride on pentadecane from *Kaempferia Galanga L.*

16. Hexadecane

A substance supposed to be hexadecane, which Mabery (102) separated from Pennsylvania petroleum and which boiled at 275–276° under 760 mm. pressure (the accepted b. p. of *n*-hexadecane is 287.5°), yielded what was apparently a dichloro derivative, distilling between 205° and 210° under 16 mm. pressure and having a specific gravity of 1.0314 at 20°.

17. Heptadecane

The fraction which boiled, after Mabery's (102) forty-second distillation of Pennsylvania petroleum, at 188–190° at 50 mm. pressure and at 288–289° at atmospheric pressure (accepted b.p. of heptadecane is 303°), and had a specific gravity of 0.800, was thought from its analysis and molecular weight to be heptadecane. The main portion of the product of its chlorination boiled at 175–177° under 15 mm. pressure, had a specific gravity of 0.8962 at 20°, and the chlorine content of a monochloroheptadecane.

18. Octadecane

Mabery (102) obtained from Pennsylvania petroleum a fraction which distilled, for the most part, at 300–301° and had a specific gravity of 0.8017. Molecular weight determinations and combustion analyses gave the data corresponding to octadecane (accepted b.p. 317°). The product obtained by the action of chlorine boiled at 185–190° under 15 mm. pressure, and had a specific gravity of 0.9041 at 20°, with the chlorine content of a monochlorooctadecane. By bringing chlorine into contact with octadecane mixed with an alkali metal or arsenic and phosphorus, Polányi and von Bogdandy (132) claimed to produce chlorinated substances which by hydrolysis and oxidation could be converted into soap acids.

IV. BROMINATION

In general, bromination of the paraffins takes place with considerably more difficulty than chlorination. Moreover, the formation of polybromo derivatives of the paraffins proceeds to a smaller degree than does the formation of compounds containing several atoms of chlorine. Vigorous chlorination, at least of the lower paraffins, can replace the hydrogen atoms entirely; bromination, however, generally proceeds only until each carbon atom has a single bromine atom attached. Further bromination can be brought about only by most vigorous methods, which are likely to rupture the carbon chain.

The published work on bromination of these hydrocarbons is fragmentary and incomplete. On the gaseous paraffins almost no work has been done, nor is the data on the higher members of the series at all satisfying. Often only a single, monobromo derivative has been isolated, and no study given to higher products.

Schorlemmer (159) concluded "that by the action of bromine on normal paraffins only *secondary* bromides of the general formula $C_nH_{2n+1}CHBrCH_3$ are produced, but not a trace of *primary* bromide. In addition to the *secondary* bromides other products are formed, which on distillation either decompose completely, or are resolved into hydrogen bromide and unsaturated hydrocarbons which are probably olefins." However, some workers have reported the formation of *primary* bromo paraffins.

Mereshkowsky (110, 111) has attempted to coördinate the available results on the bromination of the paraffins.

> "It is known from the author's experiments (bromination of propylene, isobutylene, tribromoisobutane, tetrabromoisobutane, and later tribromoisopentane) and previous work on this subject that specific catalysts not only influence the rate and initial direction of halogenation, but also determine the simultaneous production of different end-products, if the reaction is allowed to continue; the production of polyhalogenated isomerides may therefore be selectively catalysed.

The catalysts used are shown to form the following series in the order of decreasing production of the more symmetrical isomeride: (1) pure bromine without a catalyst; (2) metallic iron; (3) metallic aluminum or aluminum tribromide; (4) ferric bromide.

"The substitution rules of Markovnikov, Städel, and V. Meyer are combined and extended as follows:

(1) If the number of carbon atoms in the hydrocarbon is n, then, either with or without a catalyst at temperatures below 100°, $n - 1$ halogen atoms will become successively attached to carbon atoms on which substitution has not yet occurred.

(2) If $n - 1$ atoms of the hydrocarbon already carry a halogen atom, a further halogen atom will enter partly on the remaining halogen-free carbon atom, and partly on that one of the other carbon atoms which carries the greatest number of hydrogen atoms.

(3) Further substitution generally occurs on the carbon atom bearing the greatest number of hydrogen atoms.

(4) Substitution always occurs in several directions depending on the catalyst."

While these rules may be correct, sufficient experimental data are not available so that they may be considered proven. Except in the case of a few of the lower members of the series, the structure of the successive bromine derivatives of the individual paraffins has not been accurately determined.

1. Methane

Except in patents, there seems to be no report of a direct action of bromine on methane. Schroeter (163) patented a process for producing methyl bromide by passing a mixture of bromine and methane, or gas mixtures containing methane, over iron or other catalysts at a temperature above 200°. The iron catalyst could be replaced by small quantities of copper, copper oxide, copper carbonate, or copper bromide, by nickel, cobalt, or mixtures of these metals, or by compounds of other metals having more than one valence.

When a small amount of bromine was used, the product was reported to be about one-half unchanged methane and the remainder methyl bromide and hydrogen bromide; methylene bromide and bromoform were also formed if more bromine and a higher temperature was used.

The Elektrochemische Werke, Bosshard, Steinitz und Strauss (43) claimed the bromination of methane by mixing it with a current of gaseous bromine in the absence of catalysts, under atmospheric or elevated pressure at 300–450°. For example, 1 part of methane and 12 parts of bromine passed through quartz tubes at 400° yielded about 3.1 parts of methylene bromide, 3.1 parts of bromoform, and a small amount of carbon tetrabromide. It was reported that any of the four bromine derivatives could be obtained in predominating amount by varying the proportion of bromine to methane.

Merz and Weith (113) concluded from experiments on the bromination of methyl iodide that methane would be changed into carbon tetrabromide by direct bromination at 180°.

2. Ethane

An early patent by Mallet (107) claimed the production of bromine derivatives of ethane by passing a mixture of hydrocarbon and the halogen through a layer of animal charcoal or other porous contact material at a temperature between 30° and 90°.

That ethane would be converted into ethylene tetrabromide and hexabromoethane by the action of bromine in the presence of iodine at 200–250° was predicted by Merz and Weith (113) from experiments on ethyl iodide.

3. Propane

By using elevated temperatures, Snelling (173) was able to apply his patented chlorination process to the bromination of propane. The halogen and excess hydrocarbon reacted in a vessel from which the gas mixture was circulated into contact with a solvent to remove the halogenated product.

Merz and Weith (113) believed that they could forecast, from work on allyl bromide, the behavior of propane on energetic bromination. This substance at 210°, using iodine as a bromine carrier, yielded a liquid pentabromo derivative, which at still higher temperatures gave carbon tetrabromide, hexabromoethane, and tetrabromoethylene.

4. Butanes

n-Butane. Butane treated with bromine under exposure to sunlight and gentle heat produced liquids consisting mainly of polybrominated compounds. Heating butane and bromine for several hours at 100° gave butylene dibromide and unidentified products.

Frankland (50) observed that bromine reacted with butane if both gases were exposed to direct sunlight and heated gently. Carius and Lisenko (29) heated bromine and butane several hours at 100° in a sealed bulb. They obtained a colorless liquid which had the bromine content of a butylene dibromide, and distilled without decomposition between 155° and 162°.

Butlerov (26, 27) obtained no decisive results from the action of one mole of bromine per mole of butane in daylight, but as a product obtained a heavy, oily, difficultly volatile material which consisted mainly of polybrominated substances.

Merz and Weith (113) continued their conjectures regarding hydrocarbon bromination by stating that because butyl bromide gave tetrabromoethylene by the action of bromine at 160–250° the same results would necessarily follow from butane. They believed that bromination would be easier than chlorination of this hydrocarbon.

Isobutane. Butlerov (26, 27) obtained no definite products from the reaction of equimolecular amounts of isobutane and bromine. As with *n*-butane, a heavy, high-boiling liquid was obtained consisting mostly of highly brominated derivatives. The bromine reacted more readily with the isobutane than with the normal hydrocarbon. Merz and Weith (113) secured from isobutyl bromide at 175° a hexabromoisobutane and at 300–340° hexabromoisobutylene. They thought they would have obtained the same results from isobutane.

5. Pentanes

Only one report of bromination of pentane has been published. Poni (133) found bromopentanes in the products of bromination of a fraction of Colibasi petroleum boiling at 0–10°. The hydrocarbon material and bromine were in contact from four to fourteen days in the presence of water and diffused sunlight. The bromopentanes identified and their properties were as shown in table 3.

As has been mentioned, Dow (41) suggested chlorination followed by distillation to separate pentane from carbon disulfide. He also proposed bromination in the presence of iron for this purpose.

A number of workers have reported that bromine has no action on pentane; among them are Pelouze and Cahours (124), Lachowicz (87) and Routala (140).

6. *Hexanes*

n-Hexane. While more work has been done on the bromination of hexane than of its lower homologs, the results are sketchy and far from satisfactory. Apparently bromine reacts slowly, if at all, in the cold without light, but in sunlight, at higher temperatures, or in the presence of catalysts, reaction is quite rapid. Monobromohexanes have been isolated in pure form; dibromo derivatives also form readily, while under extreme conditions oxidation seems to take place with the formation of derivatives of benzene.

TABLE 3

Bromination of Colibasi petroleum fraction boiling between 0° and 10°

(Poni)

PRODUCT	BOILING POINT
2-Bromo-2-methylbutane	108–109° at 745 mm. with decomposition
1-Bromo-2,2-dimethylpropane	89–91° at 749 mm.
1,1-Dibromo-2,2-dimethylpropane[2]	64–65° at 43 mm.
1,3-Dibromo-2,2-dimethylpropane	82–83° at 49 mm.

In 1860, Riche (134) observed that bromine attacked briskly a substance supposed to be *n*-hexane (b.p. 58°, specific gravity 0.688 at 0°; accepted b.p. of *n*-hexane 69°) obtained by the action of barium oxide on *n*-heptoic acid, and substitution products were

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[2] The constitution of the last two substances was deduced from the rule that the lower boiling of two disubstituted derivatives has the two substituting atoms closer together (Henry).

formed. Pelouze and Cahours (124) found that bromine reacted with liquid hexane and produced dibromohexane, but no monobromide could be isolated even when not more than an equimolecular quantity of bromine was used. The amount of bromine used reacted with half of the hydrocarbon present forming the dibromide, which boiled between 210° and 212°.

Wanklyn and Erlenmeyer (190) found that bromine acted with great difficulty on a hexane which boiled at 68.5–70°. When six volumes were sealed with one volume of bromine and exposed to bright sunlight for many hours, no reaction took place, nor was any effected by heating to 120°, although a change took place slowly when the mixture was exposed to sunlight after heating. Wanklyn and Erlenmeyer did not describe the products of the bromination but simply stated that "torrents of hydrobromic acid escaped" when the tube was opened.

Merz and Weith (112) assumed that hexane would brominate readily—they believed more readily than it would chlorinate—because hexyl iodide brominated smoothly at 120–130° to hexabromohexane, octabromohexane, octabromohexylene, and a compound C_6Br_8.

In order to avoid the formation of polybromohexanes, Schorlemmer (159) allowed bromine to vaporize into gaseous hexane in the sunlight, and stopped the action when half of the hydrocarbon had reacted. The chief product was proved by conversion to the corresponding alcohol, which on oxidation with chromic acid gave acetic and butyric acid, to be 2-bromohexane.

Michael and Garner (114), using Schorlemmer's method, dropped bromine slowly into the upper part of a reflux condenser while hexane was kept boiling in a flask below. In sunlight, reaction took place instantly. The main product, boiling at 143–146°, consisted of 2-bromohexane and 3-bromohexane together with a small amount of higher boiling oil. These workers had previously found that heating hexane and bromine in sealed tubes produced polybromohexanes in considerable quantities.

Herzfelder (62) brominated *n*-hexane heated on a water bath under reflux in the presence of a spiral of iron wire. Hexabromohexane was produced when bromine and hexane were used in the molar proportions of 7:1. Herzfelder assumed that one bromine atom combined with each carbon.

Blair, Ledbury and Wheeler (19) found that when *n*-hexane vapor was passed into bromine containing a little water, p-dibromobenzene, and *trans*-benzene hexabromide formed. The mechanism of the reaction was not clear, but since benzene volatilized into bromine by means of nitrogen yielded results identical with those given by hexane, these investigators thought it possible that, due to oxidation of the hexane by bromine, cyclohexane and then benzene were formed, and the benzene was then converted by the excess of bromine into the hexabromide and the dibromo compound.

Kaufmann and Hansen-Schmidt (77) found that 0.1 *N* solutions of bromine in carbon tetrachloride, carbon disulfide, and methylalcohol containing sodium bromide, left in contact with hexane in the dark remained unchanged for two weeks. When the same systems were exposed to diffused daylight for 22 days, 28 per cent of the bromine in the carbon tetrachloride solution combined with the hexane while but 3 per cent of the bromine disappeared from each of the other two solutions.

Lachowicz (87) reported that hexane withstood the action of bromine in the cold.

2,3-Dimethylbutane (diisopropyl). Silva (165) observed that if bromine and diisopropyl were permitted to react at a "mild" temperature and in sunlight a crystalline dibromo derivative was formed, but no monobromide was isolated.

7. Heptanes

Bromination of heptane is more satisfactory than that of any of the lower paraffins. Reaction with bromine does not occur in the dark, even in the presence of iodine or aluminum bromide, but it is rapid at water-bath temperature or in sunlight. The first product is apparently 2-bromoheptane. More highly brominated products form, but are difficult to identify because of their instability.

n-Heptane. Pelouze and Cahours (124) noted that heptane from American petroleum (b.p. 92–94°; accepted b.p. of *n*-heptane

98.4°) was not acted upon by bromine at ordinary temperature and pressure.

Schorlemmer (144) observed that hydrogen bromide was evolved slowly when a mixture of bromine and heptane, "hydride of heptyl," was exposed to direct sunlight or heated in sealed tubes in the water-bath. The action, much less energetic than that with chlorine, was hastened by the addition of a little iodine. On distillation the products decomposed with evolution of hydrogen bromide and separation of a tarry mass in the flask.

Schorlemmer (159) found that heptane was attacked slowly in artificial light, but more readily than was hexane. A bromo derivative was obtained which distilled at 165–167° and was found to be 2-bromoheptane. Much of the products decomposed during distillation into carbonaceous matter, hydrogen bromide, and heptene.

The work of Venable (186) showed that bromine did not act appreciably in the cold on normal heptane from *Pinus sabiniana* even in the presence of iodine or aluminum bromide. On the other hand, hydrogen bromide was evolved copiously when bromine was dropped into the gently boiling hydrocarbon. Best results were obtained by the addition of 75 per cent of the theoretical quantity of bromine required for the monobromide. The product was separated by distillation into three fractions: unchanged heptane; a main fraction of heptyl bromide, equivalent to about 33 per cent of the heptane; and a high-boiling mixture of other brominated and decomposition products. The monobromide boiled under ordinary pressure at 165–167°, and appeared to be identical with Schorlemmer's 2-bromoheptane. The higher boiling products were difficult to separate, since they could not be distilled without decomposition. A very unstable fraction boiling at 182–185° was not investigated. If the fraction boiling above 170° was distilled after being allowed to stand for some time, it evolved hydrogen bromide and yielded a "fair proportion" of a liquid boiling at 164–167°, which was similar to heptyl bromide.

Later, Venable (187) found when the theoretical amount of bromine for a monobromoheptane was added as rapidly as it could be absorbed by hot heptane, the yield of *secondary* bromide was about as before, from 25 to 30 per cent of the theoretical.

Wheeler (191) made several unsuccessful attempts to increase Venable's yield of *secondary* heptyl bromide. His method was the same except that during the bromination he imposed an increase in pressure on the boiling heptane equivalent to 190 mm. of mercury. He also used more bromine than Venable, and by this means increased the yield of *secondary* bromide by 18 per cent, obtaining at the same time a "much greater increase" in the bromides of higher boiling point.

Francis and Young (49) treated a fraction from American petroleum, boiling between 96.5° and 102°, with bromine in the presence of aluminum bromide. Polybromo derivatives of both paraffin and polymethylene hydrocarbons were formed, but no monobromides could be isolated from the product. Without the catalyst, a petroleum fraction boiling from 93.5° to 102° was heated with bromine, and yielded a substance reported as *n*-heptyl bromide.

Cohen and Dakin (35) found that in the presence of an aluminum-mercury couple, bromine acted rapidly on a heptane fraction from light petroleum boiling at 95–100°. On fractionation of the product, a liquid boiling at 110–120° under 100 mm. pressure distilled over, which they stated was "probably heptylic bromide." The residue in the flask, on cooling, formed a colorless crystalline mass with a strong camphor-like odor. From this, two crystalline substances were obtained. The first, recrystallized from alcohol, melted at 88–90° and from its bromine content appeared to be tetrabromoheptane. The second, only slightly soluble in alcohol, crystallized from glacial acetic acid in colorless needles melting at 250°. As it contained the same percentage of bromine as the first product, it was thought that it might be polymeric with the low-melting substance. The possible structure of such a polymer was not explained.

Isoheptane. Francis and Young (49) produced an isoheptyl bromide, boiling at 83–84° under 70 mm. pressure, by heating bromine with a petroleum fraction boiling between 93.5° and 102°, and rich in isoheptane. That it was an isoheptyl derivative was proved by its reduction to isoheptane by the zinc-copper couple and hydrochloric acid.

8. Octane

Riche (134) found that bromine slowly attacked octane, prepared by distilling sebacic acid with barium oxide, and produced a viscous mixture of substitution products. On the other hand, Pelouze and Cahours (124) stated that bromine had no effect on an octane fraction from American petroleum. The octane of Pelouze and Cahours boiled between 116° and 118° (accepted b.p. of *n*-octane 124.6°) and had a density of 0.725 at 15°.

9. Decanes

n-Decane. Lachowicz (87) found that under the influence of direct sunlight, the action of bromine on normal decane was very brisk and hydrogen bromide was evolved copiously. When decane was heated to 55° with bromine it ignited and burned with a luminous flame. Berthelot (17) observed that bromine did not act on the decane obtained by the hydrogenation of "diamylene."

2,7-*Dimethyloctane (diisoamyl).* Lachowicz (87) reported that bromine acted very slowly on diisoamyl in diffused light, but vigorously in direct sunlight. Bromine vapor was carried by a stream of dry carbon dioxide into a reaction vessel, equipped with a reflux condenser, where the halogen mixed with the vapors of boiling diisoamyl. No brominated substance could be isolated because the product split into decylene and hydrogen bromide on distillation.

10. Dodecane

In 1851 Brazier and Gossleth (23) stated that even in sunlight bromine had practically no action on dodecane ("caproyl"), boiling at 202° (accepted b.p. of dodecane 216°), which they obtained by electrolysis of the potassium salt of *n*-heptoic acid. A supposed dodecane, boiling at 196–200° and having a specific gravity of 0.778 at 20°, which Pelouze and Cahours (124) obtained by the fractionation of American petroleum, was also unattacked by bromine in the cold. Later, Cloëz (34) found that a "dodecane" which boiled at 195–198° reacted with bromine, but he did not describe the conditions of the experiment or the products obtained.

11. Tridecane

The "tridecane" which Pelouze and Cahours (124) separated from American petroleum had a specific gravity of 0.796 at 20° and boiled at 216–218° (accepted b.p. of tridecane 234°). This "tridecane" did not react with bromine. Barbier (10) also stated that tridecane was not attacked in the cold. On the other hand, Cloëz (34) found that while an aqueous solution of bromine had no effect on this hydrocarbon, bromine itself would react with liberation of hydrogen bromide.

12. Pentadecane

Berthelot (17) reported that pentadecane did not react with bromine. Later, van Romburgh (185) found that the pentadecane which he isolated from the essential oil of *Kaempferia galanga L.* was unattacked by a solution of bromine in chloroform. Willstätter, Mayer, and Huni (193) observed that bromine did not attack a pentadecane which was produced in small amount from phytol.

V. IODINATION

It is generally stated that iodine will not react with the paraffins. This failure to substitute is attributed by Richter (135) to the reversibility of the reaction, the hydrogen iodide formed serving to reduce the alkyl iodides. This hypothesis is borne out by the fact that Datta and Chatterjee (39) were able to obtain a small amount of iodohexane by heating hexane under reflux with iodine and concentrated nitric acid, which no doubt destroyed the hydriodic acid. A "good deal" of iodohexane was hydrolyzed by the nitric acid as soon as formed. Richter (135) also states that in the presence of other substances capable of decomposing or uniting with hydriodic acid, such as iodic acid or mercuric oxide, substitution by iodine may be brought about.

VI. SUMMARY

Table 4 is a résumé of the products which have resulted from the action of chlorine and bromine upon the paraffin hydrocarbons.

TABLE 4

Substances identified in the products of the action of chlorine and of bromine on paraffin hydrocarbons

HYDROCARBON	SOURCE	PRODUCT REPORTED FROM ACTION OF	
		Chlorine	Bromine
Methane	Synthetic and from natural gas	Methyl chloride, dichloromethane, chloroform, and carbon tetrachloride	Methyl bromide, dibromomethane, bromoform, and carbon tetrabromide
Ethane	Synthetic	Ethyl chloride and dichloroethane	Hexabromoethane and tetrabromoethylene
	Coal gas and natural gas	Ethyl chloride, di-, tri-, and hexa-chloroethane	
Propane	Synthetic	*n*-Propyl chloride, 1,2-dichloropropane, a trichloropropane, a tetrachloropropane (m.p. 177–178°), and hexachloropropane. Also carbon tetrachloride and hexachloroethane from action of chlorine and heat	
Butane	Synthetic	Butyl chloride, butylene dichloride, and "higher" products	Butylene dibromide, b.p. 155–162°
	American petroleum	Butyl chloride	
2-Methylpropane (isobutane)	Synthetic	Carbon tetrachloride and hexachloroethane	"Highly brominated derivatives"
	Pennsylvania petroleum	Isobutyl chloride and a dichlorobutane boiling at 121–122°	

TABLE 4—*Continued*

HYDROCARBON	SOURCE	PRODUCT REPORTED FROM ACTION OF	
		Chlorine	Bromine
Pentane	Synthetic	$C_5H_8Cl_4$ boiling at 230–240°	
	American petroleum	A monochloropentane	
	Natural gasoline	Amyl chlorides, di- and tri-chloropentanes	
	Galician petroleum	*Primary* and *secondary* monochloropentanes	
2-Methylbutane (isopentane)	Galician petroleum	Monochloro derivatives	
	Ohio and Pennsylvania petroleum. "Mineral" Oil	An isoamyl chloride and a dichloropentane By dry chlorination 1-, 2-, 3-, and 4-chloro-2-methylbutane By chlorination in presence of moisture—*primary* isoamyl chloride	
	Colibasi petroleum		2-Bromo-2-methylbutane
2,2-Dimethylpropane (tetramethylmethane)	Colibasi petroleum		1-Bromo-; 1,1- and 1,3-dibromo-2,2-dimethylpropane
Hexane	Synthetic	1-, 2-, and 3-chlorohexane	2- and 3-bromohexanes, hexabromohexane, *p*-dibromobenzene and benzene hexabromide
	American petroleum	Mono-, di-, tri-, tetra-, and hexa-chlorohexane	Dibromohexane, b.p. 210–212°
2,3-Dimethylbutane (diisopropyl)	Synthetic	Mono- and di-chlorodiisopropyl	Dibromodiisopropyl
	Baku petroleum	*Primary* and *secondary* monochlorodiisopropyl	

TABLE 4—*Continued*

HYDROCARBON	SOURCE	PRODUCT REPORTED FROM ACTION OF	
		Chlorine	Bromine
Heptane	Synthetic	A monochloride	2-Bromoheptane, b.p. 165–167°
	Pinus sabiniana	1- and 2-Chloroheptane	Monobromide, b.p. 165–167°
	Petroleum	A monochloride and small amounts of higher chlorides	
	Light petroleum		Mono- and tetrabromoheptane
2-Methylhexane (isoheptane)	Synthetic	A mono- and a dichloroisoheptane	
	Petroleum		Isoheptyl bromide, b.p. 83–84° at 70 mm.
Octane	Synthetic (distillation of sebacic acid)	Mixture of chlorooctanes	Viscous mixture of products
	Petroleum	2-Chlorooctane	
2,5-Dimethylhexane (diisobutyl)	Synthetic	Mixture of *primary* and *secondary* diisobutyl chlorides	
	Synthetic (treated with antimony pentachloride)	Carbon tetrachloride, hexachloroethane, and hexachlorobenzene	
Nonane	American petroleum	A monochlorononane	
Decane	Synthetic		Vigorous action in sunlight, but product was not identified
	Pennsylvania, Ohio, and Canadian petroleums	A mono- and a di-chlorodecane	

TABLE 4—*Continued*

HYDROCARBON	SOURCE	PRODUCT REPORTED FROM ACTION OF	
		Chlorine	Bromine
2,7-Dimethyloctane (diisoamyl)	Synthetic	A monochlorodecane	Slow reaction in diffused light, vigorous action in sunlight
	Synthetic (treated with antimony pentachloride)	Carbon tetrachloride, hexachloroethane, hexachlorobenzene, and perchloromesole (C_4Cl_6)	
	American petroleum	A monochlorodecane	
	Pennsylvania and Ohio petroleums	A mono- and a dichlorodecane	
Undecane	Pennsylvania, Ohio, and Canadian petroleums	A mono- and a dichloroundecane	
Dodecane	Synthetic (electrolysis of *n*-heptoic acid)	Viscous substitution products	Only slight substituting action observed
	American petroleum	A monochloride, b.p. 242–245°	
	Pennsylvania petroleum	A monochloride, b.p. 230–235°	
	Ohio petroleum	A mono- and a dichlorododecane	
Tridecane	American petroleum	A monochlorotridecane, b.p. 258–260°	Did not react
	Pennsylvania petroleum	A monochlorotridecane, b.p. 135–140° at 12 mm.	
Tetradecane	American petroleum	A monochlorotetradecane	
	Pennsylvania petroleum	A monochlorotetradecane, b.p. 150–153° at 20 mm. A dichlorotetradecane, b.p. 175–180° at 17 mm.	

TABLE 4—*Concluded*

HYDROCARBON	SOURCE	PRODUCT REPORTED FROM ACTION OF	
		Chlorine	Bromine
Pentadecane	Oil of *Kaempferia galanga L.* and also phytol		No action produced
	American petroleum	A monochloropentadecane	
	Pennsylvania petroleum	A dichloropentadecane, b.p. 175–180° at 50 mm.	
Hexadecane	Pennsylvania petroleum	A dichlorohexadecane, b.p. 205–210° at 16 mm.	
Heptadecane	Pennsylvania petroleum	A monochloroheptadecane, b.p. 175–177° at 16 mm.	
Octadecane	Pennsylvania petroleum	A monochlorooctadecane, b.p. 185–190° at 15 mm.	

VII. SUGGESTED PROBLEMS FOR FURTHER RESEARCH

As a field for further study, the halogenation of the paraffins has great possibilities, and results of great interest and value can be predicted with certainty. Work is particularly needed on the liquid members of the series, using substances of known purity and accurately locating the halogen atoms in the products.

Fluorination has scarcely been attempted; chlorination has been studied considerably but not exhaustively; bromination has been investigated only in a most cursory manner; iodination is reported in but one case. All the halogens offer opportunities for fruitful research.

The following are some problems which are suggested as being worthy of consideration:

1. Chlorination in the liquid phase at low temperature, in the presence of light and with or without catalysts, in an endeavor to secure better control of the reaction.

2. Chlorination by bubbling the hydrocarbon gas or vapor through a chlorine solution or through liquid chlorine.
3. Extension of the work with chemical chlorinating agents such as antimony pentachloride, phosphorus pentachloride, sulfuryl chloride, phosgene, phosgene-aluminum chloride complexes, etc.
4. Similar investigation of the action on paraffin hydrocarbons of antimony pentabromide, phosphorus pentabromide, sulfuryl bromide, and carbonyl bromide.
5. Determination of the mechanism by which halogens convert paraffins, such as hexane, into aromatic compounds.
6. Separation of hydrocarbons by selective chlorination, possibly with the aid of catalysts.
7. Investigation of the effect of chain branching on chlorination or bromination, and determination of the reactivity of *primary, secondary,* and *tertiary* hydrogens toward halogens.
8. To determine whether catalysts change the point of attack of a halogen.
9. Measuring the relative rates of reaction of chlorine and bromine.
10. A study with particular thoroughness of the halogenation of hydrocarbons easily available—methane, ethane, propane, butane, and pentane.
11. Determination of the extent to which iodine substitution products can be obtained by the action of iodine on the paraffins at elevated temperatures and in the presence of substances decomposing hydrogen iodide.
12. To determine whether, as has been stated, the reactivity of paraffin hydrocarbons to bromine decreases on ascending the series.
13. Further work on chlorination with carriers or promoters for the purpose, in part, of discovering new aids to reaction.
14. Further work on the action of active chlorine on paraffin hydrocarbons.
15. Determination of the relative ease of chlorination of individual paraffin hydrocarbons and their lower chlorine derivatives.

16. A study of the effect of the chloro derivatives first formed on the further course and extent of the halogenation.

17. Observation of the effect of halogenation in the presence of aqua regia and of mixtures of nitric and hydrobromic acids on paraffin hydrocarbons.

18. Determination of the action of bromine vapor on vapors of boiling, individual, paraffin hydrocarbons with and without solid finely-divided or porous catalytic contact materials.

19. Halogenation in the presence of silent discharge under low temperature conditions.

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