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DEVELOPMENTS IN THE CHLORINATION OF SATURATED HYDROCARBONS

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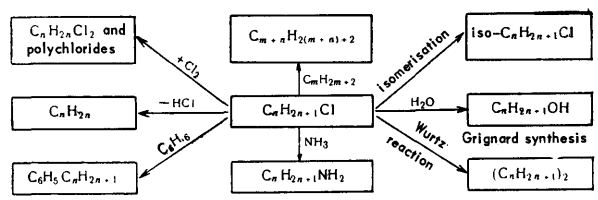
INTRODUCTION

The present article is a review of work published on the chlorination of saturated hydrocarbons in the USSR and abroad from 1947 to 1958.

Ellis[1] has reviewed the literature in this field up to 1934, and Hass and McBee[2] and Nelles[3] have also considered certain aspects of the chlorination of saturated hydrocarbons in their reviews. The literature from 1937 to 1947 has been reviewed by Solodar' and Markin[4].

A considerable expansion of the chemical industry in the USSR is planned for the period 1958–1965, particular attention being directed towards the necessity of utilising natural and industrial petroleum gases as raw material for the chemical industry. The saturated hydrocarbons in natural and industrial gases can be converted into useful products by various methods, chiefly by chlorination.

Diagram of possible conversions of alkyl halides



Chlorinated hydrocarbons find very wide application in industry and agriculture as solvents, refrigerants, synthetic intermediates, insecticides, herbicides, etc. At the present time the production of chlorinated hydrocarbons is growing continuously; thus in the USA the production of chlorine, hydrogen chloride, and chlorine-containing chemicals increased considerably in 1955 by comparison with 1954 [5] (Table 1).

TABLE 1. Production of chlorinated hydrocarbons in the USA (tons).

Product	1953	1954	1955	1956
Cl_2	—	2 622 298	3 091 628	—
HCl	—	672 889	764 419	—
CH_3Cl	18 300	—	16 500	—
CH_2Cl_2	28 000	—	31 000	—
$CHCl_3$	11 500	—	18 300	—
CCl_4	117 000	—	130 500	136 200
$C_2H_4Cl_2$	—	—	213 600	249 700
C_2H_3Cl	234 000	—	245 900	28 600

Chlorinated hydrocarbons may be obtained by various methods, the chief being:

1. Hydrochlorination and chlorination of unsaturated hydrocarbons:

$$C_nH_{2n} + HCl \rightarrow C_nH_{2n+1}Cl.$$

2. Chlorination of saturated hydrocarbons:

$$C_nH_{2n+2} + Cl_2 \rightarrow C_nH_{2n+1}Cl + HCl.$$

Both methods have considerable theoretical and practical interest.

The classic work of Butlerov and Markovnikov[6] on the mutual influence of atoms in organic molecules and the formulation of rules for the chlorination of alkanes has made a large contribution to the theoretical basis of the hydrochlorination of unsaturated hydrocarbons and the chlorination of saturated hydrocarbons. The ten general rules for the chlorination of saturated paraffinic hydrocarbons formulated by Hass et al.[7] represent a further development of Markovnikov's rules for the replacement of hydrogen atoms in hydrocarbons of the methane series.

Tishchenko's experimental data[8] confirm Markovnikov's theoretical propositions; in the chlorination of a saturated hydrocarbon the chlorine atom is more easily attached to a carbon atom already substituted by chlorine. By analysing published data[10-13], Ewell[9] has established a connection between the rate of replacement of hydrogen in the chlorination of saturated and unsaturated hydrocarbons, and the molecular structure of the hydrocarbon.

Later work by Soviet chemists on the chlorination of saturated hydrocarbons[14-29] shows that this field of chemistry is of great significance both for the further development of the Butlerov theory of the structure of organic compounds, and in practical application in Soviet industry.

I. THE CHAIN MECHANISM FOR THE CHLORINATION OF SATURATED HYDROCARBONS

In the theoretical and experimental study of the chain mechanism, much credit is due to Semenov and his school[14,15,16,29], who proved the chain mechanism for the chlorination of saturated hydrocarbons and explained the mechanism in the light of modern theory. The chain mechanism for the photochlorination reaction must be considered as firmly established, in agreement with Hass[30], who connects the initial formation of chain centres with the photochemical decomposition of chlorine:

$$Cl_2 + h\nu \rightarrow Cl\cdot + Cl\cdot .$$

The photochemical reaction between hydrogen and chlorine, which proceeds at room temperature, has been the most studied. Comparison of the number of light quanta absorbed with the number of molecules reacted shows that each molecule activated by light produces up to 10^5 molecules of hydrogen chloride. The reaction chains commence with chlorine atoms:

$$\left.\begin{array}{ll} 1) & Cl_2 + h\nu \rightarrow Cl\cdot + Cl\cdot , \\ 2) & Cl\cdot + H_2 \rightarrow HCl + H\cdot , \\ 3) & H\cdot + Cl_2 \rightarrow HCl + Cl\cdot , \end{array}\right\} \text{repeated.}$$

The photochemical chlorination of hydrocarbons is completely analogous to the reaction between hydrogen and chlorine. This has been confirmed experimentally by Jones and Bates[31] and Stewart and Weidenbaum[32], who studied the photochlorination of pentane in the liquid phase; they give the reaction mechanism as follows:

$$\left.\begin{array}{ll} 1) & Cl_2 + h\nu \rightarrow Cl\cdot + Cl\cdot , \\ 2) & Cl\cdot + C_5H_{12} \rightarrow C_5H_{11}\cdot + HCl, \\ 3) & C_5H_{11}\cdot + Cl_2 \rightarrow C_5H_{11}Cl + Cl\cdot , \end{array}\right\} \text{repeated.}$$

Numerous Soviet and foreign investigators have studied the mechanism of the chlorination of alkanes[10,29-35].

From experimental data, Pease and Walz[33] and others consider the chlorination of saturated hydrocarbons to be a chain reaction:

$$\left.\begin{array}{ll} 1) & Cl_2 \rightarrow Cl\cdot + Cl\cdot , \\ 2) & Cl\cdot + RH \rightarrow R\cdot + HCl, \\ 3) & R\cdot + Cl_2 \rightarrow RCl + Cl\cdot , \end{array}\right\} \text{chain.} \qquad (I)$$

However, thermal chlorination could proceed by a different mechanism:

$$\left.\begin{array}{ll} 1) & Cl_2 \rightarrow Cl\cdot + Cl\cdot , \\ 2) & RH + Cl\cdot \rightarrow RCl + H\cdot , \\ 3) & H\cdot + Cl_2 \rightarrow HCl + Cl\cdot , \end{array}\right\} \text{chain.} \qquad (II)^{36}$$

The fact that hydrogen has not been detected in the reaction products throws grave doubts on mechanism (II). The type (I) mechanism is supported by Vaughan and Rust[10], who showed that the chlorination of, for instance, propane is greatly accelerated in the presence of compounds which can furnish free radicals under the experimental conditions. The authors of the present review consider that the following may be adduced as proof of mechanism (I): reaction (2) of mechanism (I) is exothermic, while reaction (2) of mechanism (II) is endothermic, so that mechanism (I) is thermodynamically more probable.

Experimental data[10,29,31-35,37-42] indicate that the chlorination of methane may be represented as follows:

$$Cl_2 + h\nu \rightarrow Cl\cdot + Cl\cdot \quad -57.8 \text{ kcal},$$

1) $Cl\cdot + CH_4 \rightarrow HCl + CH_3\cdot$ (-101 + 102) + 1.0 kcal,

2) $CH_3\cdot + Cl_2 \rightarrow CH_3Cl + Cl\cdot$ (-57.8 + 83.5) + 25.7 kcal,

3) $CH_3Cl + Cl\cdot \rightarrow HCl + CH_2Cl\cdot$ (-97.4 + 102) + 4.6 kcal,

4) $CH_2Cl\cdot + Cl_2 \rightarrow CH_2Cl_2 + Cl\cdot$ (-57.8 + 78.5) + 20.7 kcal,

5) $CH_2Cl_2 + Cl\cdot \rightarrow HCl + CHCl_2\cdot$ (-93.2 + 102) + 8.8 kcal,

6) $CHCl_2\cdot + Cl_2 \rightarrow CHCl_3 + Cl\cdot$ (-57.8 + 73.5) + 15.7 kcal,

7) $CHCl_3 + Cl\cdot \rightarrow HCl + CCl_3\cdot$ (-89 + 102) + 13.0 kcal,

8) $CCl_3\cdot + Cl_2 \rightarrow CCl_4 + Cl\cdot$ (-57.8 + 68.4) + 10.6 kcal.

If the reaction is exothermic, according to the Polanyi–Evans rule[43]

$$E = 11.5 - 0.25\,g,$$

where E is the energy of activation and g the heat of reaction. Calculating the energy of activation for each stage of the reaction, we obtain

$$E_1 = 11.5 - 0.25 \times 1 = 11.25 \text{ kcal},$$
$$E_3 = 11.5 - 0.25 \times 4.6 = 10.35 \text{ kcal},$$
$$E_5 = 11.5 - 0.25 \times 8.8 = 9.3 \text{ kcal},$$
$$E_7 = 11.5 - 0.25 \times 13.0 = 8.25 \text{ kcal}.$$

The rates of reaction are for example:

$$v_1 = k_1 P_{CH_4} P_{Cl}$$
$$v_3 = k_3 P_{CH_3Cl} P_{Cl}$$
$$k_1 = f_1 z_1 e^{-\frac{E_1}{RT}}$$
$$k_3 = f_3 z_3 e^{-\frac{E_3}{RT}},$$

where k_1 and k_3 are the velocity constants of the corresponding reactions, f_1 and f_3 are the steric factors, and z_1 and z_3 are the collision numbers.

Therefore $\frac{v_1}{v_3} = \frac{k_1 P_{CH_4}}{k_3 P_{CH_3Cl}}$; and, when $\frac{P_{CH_4}}{P_{CH_3Cl}} = 1$ and with $f_1 = f_3$ and $z_1 = z_3$,

$$\frac{v_1}{v_3} = e^{\frac{E_3 - E_1}{RT}}$$

It follows from these calculations that the rates of chlorination of methane and its chlorinated derivatives are in the order

$$CHCl_3 > CH_2Cl_2 > CH_3Cl > CH_4.$$

The catalytic chlorination takes place by the general cationic substitution mechanism, i.e. the chlorine anion combines with the proton, and the chlorine cation with the hydrocarbon anion[44]:

$$\geq C - H \rightarrow \geq \overline{C} + H^+ \rightarrow \xrightarrow{CH + Cl^-} \geq C - Cl + HCl.$$

In initiated chlorination, the chlorine molecules are split into atoms by introducing into the reaction zone substances capable of forming free radicals, which then initiate the chain:

$$R - R \rightarrow 2R\cdot,$$

$$R\cdot + Cl_2 \rightarrow Cl\cdot + RCl,$$

$$Cl\cdot + C_nH_{2n+2} \rightarrow C_nH_{2n+1}^{\cdot} + HCl,$$

$$C_nH_{2n+1}^{\cdot} + Cl_2 \rightarrow C_nH_{2n+1}Cl + Cl\cdot, \text{ etc.}$$

Surfaces have a great influence on gas-phase chain reactions. The breaking of the chains on the wall of the reaction vessel, discovered by Semenov and his coworkers early in the development of the theory of chain reactions, must apparently be considered as the capture of a radical by the solid surface, forming a chemical compound (perhaps unstable) with it[45]. The wall may have a retarding influence on the chain reaction. The formation of a bond between the radical and the solid surface requires a certain energy of activation, which depends on the radical and the nature of the surface and sometimes reaches comparatively high values of the order of 9–10 kcal. The ability of various surfaces to combine with the active centres causes large changes in the general kinetics of the process.

The heterogeneous retardation of a homogeneous reaction was first studied experimentally by Trifonov[46], who established that in the photochemical reaction of hydrogen with chlorine, chlorine atoms are captured by the wall.

In addition to the breaking of chains, the solid surface has a large influence on the initiation of chains. Changes occurring in the reaction surface suggest a two-fold influence of the surface on the rate of chlorination. After the surface becomes covered with alkyl groups, the rate of reaction increases; the surface film may be more effective than clean Pyrex in initiating chains in thermal chlorination.

The accelerating effect of glass walls on the chlorination of ethane, studied by Vaughan and Rust[10], shows that chains are initiated on the surface in thermal chlorination.

Chambers and Ubbelohde[47] have observed that a film which does not contain chlorine compounds is formed on the wall of the reaction vessel in the chlorination of hydrocarbons. Since the film is removed by oxidation, it must be formed by the attack of the glass surface by alkyl radicals, with the formation of Si–O–R groups. These workers also showed that the rate of reaction of chlorine atoms with paraffinic hydrocarbons increases as the chain length of the hydrocarbon increases.

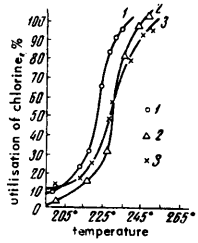


Fig. 1. Influence of the degree of branching of hydrocarbons on the relative rates of their thermal chlorination.
1) *n*-hexane; 2) 2, 3-dimethylbutane; 3) 2, 2, 4-trimethylpentane.

Fig. 1 shows that the rate of chlorination decreases with increased branching of the hydrocarbon chain.

II. THERMAL CHLORINATION OF SATURATED HYDROCARBONS

The thermal chlorination of paraffinic hydrocarbons is carried out industrially at 400°–600°, a temperature range which ensures a fairly fast reaction, usually under conditions of complete utilisation of the chlorine, thus avoiding the need to purify the reaction products from free chlorine. It appears that homogeneous bimolecular reactions also occur, in addition to chain reactions[10].

It is known that pyrolysis of the starting materials and the chlorination products takes place to a greater or lesser extent during the thermal chlorination of saturated hydrocarbons at sufficiently high temperatures; some isomerisation of the intermediate products also occurs. Polychlorides may therefore be produced not only by further chlorination of the monochloride, but also by chlorination of the products of pyrolysis and isomerisation.

1) Thermal Chlorination of Methane

In the chlorination of saturated hydrocarbons, that of methane has been most studied, because methane is abundant and because all its chloro-derivatives are economically important.

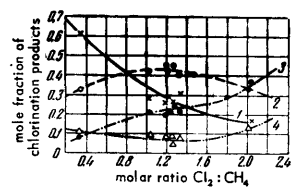


Fig. 2. Composition of the chlorination products of methane.
1) CH_3Cl; 2) CH_2Cl_2; 3) $CHCl_3$; 4) CCl_4.

It is known from the literature and from practical data that a number of difficulties arise in the industrial chlorination of methane due to complications connected with removal of heat and the necessity of having large cooling surfaces for complete condensation of the products when a considerable volume of gas is recirculated.

The chlorination products usually contain all four chloroderivatives of methane, and it is impossible in practice to carry out the reaction so as to produce only one of them.

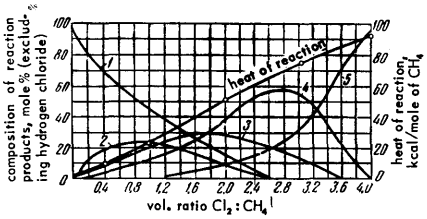


Fig. 3. Dependence of the composition of the chlorination products of methane and the heat of reaction on the volume ratio $Cl_2 : CH_4$. 1) CH_4; 2) CH_3Cl; 3) CH_2Cl_2; 4) $CHCl_3$; 5) CCl_4.

Fig. 2 shows that all ratios of chlorine to methane produce a mixture of chlorinated methanes, the methyl chloride content of which is greater as the proportion of methane in the feed mixture is increased[48].

Fig. 3, constructed from literature data, shows that evidently it is possible to obtain predominantly carbon tetrachloride if the molar ratio of chlorine to methane is greater than 3.0 : 1. Methylene chloride is produced industrially using a chlorine to methane ratio of 0.25–0.3 : 1; the heat of reaction in this case is 8 kcal/mole of methane (Fig. 3). When CCl_4 is produced, using a chlorine to methane ratio of, for instance, 3.5 : 1, the heat of reaction is more than 85 kcal/mole of methane.

Kiprianov and Kusner[49] have studied various methods for removing the heat evolved in the reaction and establishing standard conditions for the chlorination of methane to CCl_4. Dilution of the reacting gases with hydrogen chloride formed in the chlorination was the most effective.

The principle of recirculating the reacting gases in the chlorination of methane to maintain given temperature conditions has been employed in more recent years in a number of industrial establishments in the USSR, Germany, Italy, and other countries[50]. The recirculation of two-thirds of a reaction mixture consisting of 200 m^3 of CH_4 and 4.5 m^3 of Cl_2 at 350°–380° produces in 1 h 5 kg of CH_3Cl, 2.5 kg of CH_2Cl_2, 1 kg of $CHCl_3$, and 0.25 kg of CCl_4.[51]

The main requirement for the successful chlorination of hydrocarbons is the correct feed-rate and thorough mixing of the chlorine with the hydrocarbon, together with sufficiently effective removal of heat to avoid the explosive reaction

$$CH_4 + 2Cl_2 \rightarrow C + 4HCl.$$

Pease and Walz[33], Deanesly[34], Hass et al.[52], and Vaughan and Rust[10] have established that the thermal chlorination of lower paraffins begins only from 250° upwards. To obtain the maximum yield of methyl chloride a considerable excess of methane over chlorine and a fairly high temperature are required, while the production of carbon tetrachloride requires excess chlorine and the presence of active catalysts[53–58].

If chlorine is introduced into the reactor so that there is always an excess of methane or its partial chlorination products, mixtures can be obtained which contain from 90% methyl chloride to 100% carbon tetrachloride[55]. The optimum chlorination temperature is 400°–440°. In all cases 93–96% of the chlorine is converted.

Methane is chlorinated in Germany on a large scale to produce methyl chloride and methylene chloride[59]. One mole of chlorine is mixed with five moles of 99.5% methane and the mixture passed into a large internally cemented reactor externally heated to 390°–410°. The condensate consists of 50% of methyl chloride, 35% of methylene chloride, and 15% of higher chlorinated products. To obtain methylene chloride as the main product, the methyl chloride is returned to the reactor with the original gas mixture, in amounts up to 20% of the total gas feed.

For the chlorination of methane Wilson and Howland[48] used natural gas (2.5% C_2H_6, 88.5% CH_4, 9% N_2) or a gas containing 87.4% CH_4, 4.1% CO_2, 0.2% CO, 2.5% O_2, and 5.8% N_2. With a methane feed-rate of 150 litres/h, a temperature of 400°–440°, and chlorine to methane ratios of 0.37–2.02, the yield was 92.5–98.8% with respect to chlorine. The gas mixture contained 41.2–48.0% of chlorinated methanes and 49.6–52.8% HCl. On separating the chloromethanes, they were shown to consist of 16.9–61.0% CH_3Cl, 32.2–44.8% CH_2Cl_2, 7.6–36% $CHCl_3$, and 4.6–13.9% CCl_4. The quantity of carbon obtained was 0.038–0.121 g/h. With feed rates of 150 litres/h of CH_4 and 17 litres/h of Cl_2 at 440° and a nozzle diameter of 1.06 mm, a yellow flame was observed at the point of entry of the mixture, and carbon separated. With a feed rate of 75 litres/h of Cl_2 and a nozzle diameter of 2.5 cm a red glow appeared, with much formation of soot. With chlorine to methane ratios of 0.1, 0.3, 0.5, and 0.65, the amounts of carbon which separated were 2, ~3, ~8.0, and ~25 mg/h respectively.

A method has been described for the preparation of chlorinated methanes and hydrogen chloride by chlorinating the methane–hydrogen mixture obtained as a by-product in the cracking of kerosine[60]. The process is carried out in three tubes connected in series, 2 m high and 5 cm in diameter, each containing a layer of sand kept in turbulent motion. The methane–hydrogen mixture (40.5% H_2) is fed in at a rate of 370 litres/h, and the chlorine is fed into the three tubes at rates of 215, 403, and 277 litres/h respectively, the temperatures in the tubes being maintained at 350°, 360°, and 413°. Before condensation, the exit gas contained 1.3% of chlorine and 83% HCl. The residual gas contained 8.5% of the starting methane–hydrogen mixture. 99% of the methane fed was found in the chloromethanes and the residual gas.

A Japanese Patent[61] has described a method for the manufacture of lower chlorinated hydrocarbons and carbon tetrachloride. Aliphatic hydrocarbons are treated with 1.2–5 moles of Cl_2 and 1 mole of gaseous HCl at high temperature. At 500°–700°, a mixture of 1 mole of CH_4, 2 moles of Cl_2, and 1 mole of HCl gave 0.23 mole of CH_3Cl, 0.2 mole of CH_2Cl_2, 0.11 mole of $CHCl_3$, and 0.01 mole of CCl_4; 0.45 mole of CH_4 was recovered.

Stegner, Marczewska, and Treszczanowicz[62] carried out a series of experiments designed to increase the yield of CCl_4. The chlorination was carried out without a catalyst at 390°–400° with a methane to chlorine ratio of 5–6 in a mild steel reactor faced with bentonite. It was shown that the CCl_4 content of the reaction product could be increased to 50% by raising the reaction temperature to 420°–440° and the condensation temperature to 20°, but the C_2Cl_6 content also increased greatly; the vapour condensation temperature should be kept below 7°–10° to avoid large wastage of CH_4 and Cl_2 on side reactions, even though the CCl_4 content does not then exceed 20–30%. Best results were obtained by adding a 1 : 1 mixture of CH_2Cl_2

and $CHCl_3$ to the circulating gas; at a reaction temperature of 435° and a condensation temperature of 13°, a product containing 65% CCl_4 was obtained.

Developments in the industrial production of chloroform and carbon tetrachloride include the use of a two-stage process[63], comprising the gas-phase chlorination of methane to produce predominantly methylene chloride, and the liquid-phase photochemical chlorination of the latter to chloroform and carbon tetrachloride.

The thermal chlorination of methane to obtain tetrachloroethylene[64-67] and carbon tetrachloride is today of great importance. Thus 1 mole of CH_4 and 5 moles of Cl_2 are mixed with 9 moles of hot CCl_4 and the mixture passed into a reactor at 500°–700° to produce 96% C_2Cl_4.[64] Ethane or propane may be used instead of methane.

Chlorination on a fluidised-bed heat exchanger merits attention as a method for removing the heat of reaction and creating conditions which ensure thorough chlorination of methane, with CCl_4 as the main product.

In chlorinating a mixture of methane and hydrogen to give chloroform and carbon tetrachloride as the main products, Johnson[68] used a finely ground fluidised inert material in three series-connected reactors, without recirculation. Choporov and Tishchenko[23] showed that it is possible to chlorinate methane to produce CCl_4 as the main product by using as cooling agent a chemically inert granulated moving heat carrier at 390°–500°, with a molar ratio of chlorine to methane of 2.6–3.6 : 1. The reaction product contained the three higher chlorinated methanes, the contents of which could be changed within wide limits by regulating the reactant ratio. Increasing the chlorine to methane ratio within the above limits reduces the methylene chloride content of the product from 11.0 to 6.0% and the chloroform content from 40.4 to 24.5%, the carbon tetrachloride content increasing from 42 to 64%. With increase of the chlorine to methane ratio, the amount of unreacted chlorine rises from 2.7 to 8.0%, and the amount of chlorine required to produce 1 g of product rises from 2.8 to 3.2 g, the reaction temperature being 460°–480°.

Viriot[69] proposed the use of a special apparatus and a molar ratio $Cl_2 : CH_4 + CH_3Cl$ below 0.5. Brown, Colton, and Landau[70] chlorinated C_1–C_4 hydrocarbons at 500°–700°; for instance $1CH_4 + 3Cl_2 \rightarrow 4HCl + 0.48\ C_2Cl_4$; $1C_2H_6 + 5Cl_2 \rightarrow 6HCl + 0.94\ C_2Cl_4$.

Foster and Frankish[71] recommend the production of polychloromethanes by causing a mixture of Cl_2 with CH_3Cl, CH_2Cl_2, and $CHCl_3$ vapour in the molar ratio chloromethane : chlorine = 0.9–4 : 1 (the presence of CH_2Cl_2 is not essential) to come into contact with finely ground (50–100 mesh) inert material in turbulent flow at 250°–390°. Separation of the chloromethanes gave 3.5% CH_3Cl, 21.5% CH_2Cl_2, 51.0% $CHCl_3$, 23.0% CCl_4, and 1% of high-boiling product.

Chlorination of methane in the USSR[72]. Thermal chlorination is carried out on a large scale in the USSR. In the thermal process, destructive chlorination takes place, in addition to the formation of the chlorinated methanes, $CH_4 + 2Cl_2 = C + 4HCl$; as experience has shown, this reaction becomes noticeable at temperatures above 570° (with a methane to chlorine ratio of 3 : 1). In deciding on the chlorination conditions and the construction of the chlorinator, much attention is given to reducing side reactions to a minimum. The methane–hydrogen fraction, which is the waste gas from the separation of pyrolysis gas is used as raw material. Its composition is methane 72, hydrogen 23, ethylene 2, carbon dioxide 0.5, oxygen 0.5, and nitrogen 2.0 vol.%.

The technological process is as follows. Chlorine, mixed with the methane–hydrogen fraction in the ratio 1 : 3, is fed to the chlorinator, where the temperature is maintained at 500°–520° by the exothermic nature of the reaction. The temperature is regulated by changing the proportions of the gases fed to the reactor. The reaction mixture, containing chloromethanes, 25% of hydrogen chloride, excess methane, hydrogen, and nitrogen, is freed from hydrogen chloride, given an alkaline purification, and dried with a calcium chloride solution cooled to -15° with boiling ammonia. Before drying, the neutralised gas has the following composition: methyl chloride 10–12, methylene chloride 6–7, chloroform 1.5–2, residue (as carbon tetrachloride) 0.1, and methane + hydrogen + nitrogen 80 vol.%.

On drying, part of the chlorinated products is condensed and separated from the mixture. This portion of the products has the composition: methyl chloride 20, methylene chloride 50, chloroform 25, and carbon tetrachloride and other chlorides 5 vol.%. After being dried, the gases are compressed to 10 atm. and cooled to -40°; the main bulk of the chlorides condenses, the condensate containing 45 vol.% of methylene chloride, 13 vol.% of chloroform, and 2 vol.% of carbon tetrachloride and other chlorides. The excess of methane, containing a little methyl chloride, is recirculated to the chlorinator. The mixture of chlorides is rectified on three successive columns to separate methyl chloride (b.p. -23°), methylene chloride (b.p. 42°), and chloroform (b.p. 61.2°).

Production of methylene chloride in England[73] *. When methane separated from coke-oven gas is chlorinated methylene chloride is the main product, with chloroform and methyl chloride as by-products.

Unpurified coke-oven gas contains 15–15.2% H_2, 6–7% CO, 24–25% CH_4, 2–3% CO_2, 2–8% C_2H_6, and 10–12% N_2. After aqueous and alkaline purification and separation of hydrogen, 99.5% methane is obtained.

The chlorinator is a welded cylindrical pot lined internally with cement, 4580 mm high, with 1200 mm internal diameter, and 15 mm walls. The top 1 m is packed with 25 mm porcelain rings. In the centre of the pot is a cement tube 2400 mm long, into the top of which projects a nickel feed tube. 480 m^3 of chlorine and 240 m^3 of methane are fed per hour; the methane mixes with the circulating gas, which contains 20–25% N_2 and 5% CH_3Cl, the remainder being methane. The temperature is 410° above and below the chlorinator, and ~380°–400° in the centre. 53 000 m^3 of coke-oven gas per month are required for heating six reactors, or 13 m^3/h for one reactor. The reactor is shown in Fig. 4.

After cooling, the mixture of chlorides contains 48% CH_3Cl, 14% $CHCl_3$, 35% CH_2Cl_2, and 3% CCl_4. On rectification, CH_3Cl is obtained as final product (300–400 kg/h);

* This section is in fact a summary of a BIOS report[73] describing the chlorination of methane at the I.G. Höchst plant in Germany; the main product is methyl chloride. Some minor errors in the Russian text have been corrected to agree with the report[73] (Ed. of Translation).

TABLE 2. Raw materials, energy required, and yield of products per ton of methylene chloride.

Raw materials, source of energy, and products	Units	Per ton of CH_2Cl_2
Chorine	tons	4.08
Methane–hydrogen mixture	m^3	950
Electrical energy	kWh	1500
Steam	Mcal	6.20
Chloroform	tons	0.45
Hydrochloric acid, calculated as hydrogen chloride	tons	1.85

after removal of CH_3Cl, the chloride mixture contains 67–75% CH_2Cl_2 and 33–25% $CHCl_3$.

Preparation of methylene chloride in East Germany [74]. Methylene chloride is prepared technically by two methods: 1) thermal chlorination of methane with elementary chlorine; 2) esterification of methanol with hydrochloric acid and chlorination of the resulting methyl chloride with chlorine.

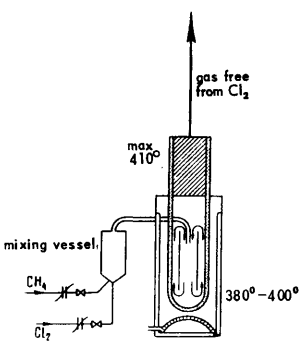


Fig. 4. The reactor.

For 30 years the first method has been that predominantly used in Germany. Methane from Ruhr gas is chlorinated to produce methyl chloride, methylene chloride, chloroform and carbon tetrachloride.

The electrochemical works at Bitterfeld uses the second method (Fig. 5), which is more profitable because of the smaller amounts of chlorine required. The chlorination of methane requires 2 moles of chlorine to produce 1 mole of CH_2Cl_2, $CH_4 + 2Cl_2 = CH_2Cl_2 + 2HCl$, while starting from methanol only one mole is required:

$$CH_3OH + HCl = CH_3Cl + H_2O,$$

$$CH_3Cl + Cl_2 = CH_2Cl_2 + HCl.$$

The resulting hydrogen chloride may be utilised for the first step. Here again the chlorination does not stop at the formation of methylene chloride; chloroform and a small amount of carbon tetrachloride are also formed.

A similar reaction starting from ethanol produces 1,1-dichloroethane, 1,1,1-trichloroethane, and 1,1,2-trichloroethane [75].

The Bitterfeld electrochemical works has developed and tested on a pilot-plant scale two methods for utilising the chloroform. The first is its chlorination to carbon tetrachloride, which is conveniently carried out in the liquid phase [76], and the other possibility is the reduction of chloroform to methylene chloride.

An adiabatic method has been proposed [77] for the chlorination of CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, or their mixtures, which may contain inert gases, below the decomposition temperature of the chlorination products.

The starting mixture and the reaction products, with a final temperature of 380°–420°, are fed through a cylindrical nozzle into the reactor in a volume ratio of more than 3 : 1 ("circulation coefficient"). Chlorine reacts almost quantitatively, any residue of it reacting in an auxiliary chamber (inside or outside the reactor), so that the exit gases contain less than 0.05% Cl_2. The starting gas may be fed to the reactor at a temperature between -20° and +320°. The reactor and other parts of the apparatus which come into contact with the reaction mixture are made of nickel or high-nickel steel. Before commencing the reaction, the reactor is heated to the initial reaction temperature, the hot circulation gas containing CH_4 or its chlorinated derivatives being passed through it at the same time. When the initial reaction temperature is reached the feeding of chlorine is commenced. With a mixture containing 18 vol.% Cl_2, 56.8 vol.% CH_4, 7.9 vol.% CH_3Cl, 0.4 vol.% CH_2Cl_2, and 16.9 vol.% of inert gas (temperature at the reactor inlet 15°, circulation coefficient 5 : 1), the reaction product contains 20.3 vol.% CH_3Cl, 52.5 vol.% CH_2Cl_2, 26.1 vol.% $CHCl_3$, and 1.1 vol.% CCl_4; with a mixture containing 9.2 vol.% Cl_2, 67.2 vol.% CH_4, 9 vol.% CH_3Cl, 0.3 vol.% CH_2Cl_2, and 14.3 vol.% of inert gas (temperature at the reactor inlet 190°, circulation coefficient 5 : 1), the product contains 25.2 vol.% CH_3Cl, 58.4 vol.% CH_2Cl_2, and 16 vol.% $CHCl_3$.

This method of chlorination has the following advantages. The absence of external heating of the reactor prevents the deposition of carbon on the walls. Since the reaction is independent of external heating, the reactor may be enlarged to any dimensions. The possibility of regulating the circulation coefficient ensures the maximum utilisation

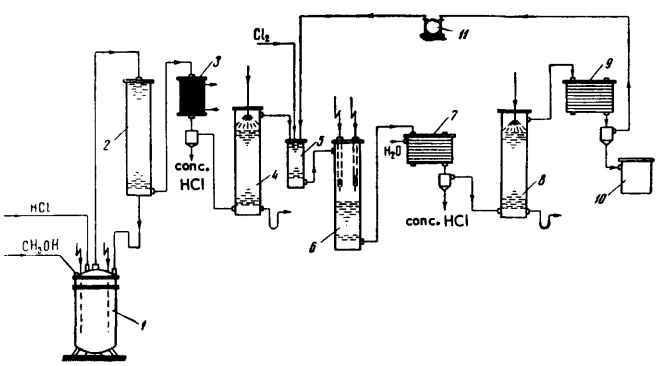


Fig. 5. Production of methylene chloride at the Bitterfeld electrochemical works.
1) Hydrochlorinator supply vessel; 2) hydrochlorinator; 3) condenser; 4) scrubber; 5) mixing vessel; 6) chlorinator; 7) HCl absorber; 8) scrubber; 9) low-temperature condenser; 10) receiver for crude product; 11) pump for gas recycle.

of the heat of reaction: thus with a circulation coefficient of 5 : 1, 83.3% of the heat of reaction is transmitted to the fresh gas, only 16.7% being carried away by the reaction products.

The results of works studies on the production of chloromethanes by the direct chlorination of natural gas have been published[78]. The natural gas is mixed with Cl_2 to give a molar ratio $Cl_2 : CH_4 = 0.2-0.5$, and the mixture fed to an externally heated reaction chamber, where chlorination takes place at 400°–420°, giving a mixture of all the chlorinated methanes.

A new process for the production of carbon tetrachloride. Carbon tetrachloride has usually been prepared by the action of elementary chlorine on carbon disulphide[78,79], but this process has recently been replaced by the thermal or photochemical chlorination of methane[80]. The thermal chlorination of methane developed in Rumania has been described[81]. High-purity natural gas and electrolytic chlorine are reacted in a cast iron vessel lined inside with acid-resistant cement with a high content of finely ground quartz.

The temperature in the reactor is held at 380°–400°. The reaction product contains 0.020 mole CH_4, 0.1410 mole $CHCl_3$, 0.9369 mole CCl_4, and 4.1671 moles HCl. The yield of chlorinated products is 95% based on chlorine. The chlorine is completely utilised, and the gases after scrubbing contain only 1.5–2.5% of methane.

The same process may be used to produce other chlorination products, such as methylene chloride and tetrachloroethylene, in high yield.

2) Thermal Chlorination of Ethane

The chlorination of the other gaseous paraffins (ethane, propane, and the butanes) has been much less studied than that of methane.

The thermal chlorination of ethane, which takes place at 600°, has also been used industrially[59]. The following processes occur:

a) $C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$,

b) $C_2H_6 + 2Cl_2 \rightarrow C_2H_4Cl_2 + 2HCl$,

c) $C_2H_5Cl \rightleftharpoons C_2H_4 + HCl$,

d) $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$.

In spite of the side reactions, the main product is ethyl chloride. Small amounts of vinyl chloride are formed by the pyrolysis of the dichloroethane. Ethane is chlorinated so much more easily than methane that it is possible to chlorinate it in a mixture of 10% ethane and 90% methane without substantial formation of chloromethanes[82].

Vaughan and Rust have studied the thermal and partial catalytic chlorination of ethane[83,84].

An American patent[85] describes the chlorination of hydrocarbons containing 2–6 carbon atoms by a two-stage process. The first stage comprises the simultaneous metaleptic chlorination of the hydrocarbon or partially halogenated hydrocarbon and the pyrolytic decomposition of the halogen derivative. The quantities of reactants may be so chosen that the products from the first stage are the starting materials for the second stage. Thus the addition of chlorine to acetylene produces tetrachloroethane, which is mixed with chlorine and ethane and used as starting material for the production of tetrachloroethylene and trichloroethylene in the first stage; part of the tetrachloroethylene and trichloroethylene is converted to pentachloroethane and hexachloroethane in the second stage.

The chlorination or bromination of ethane and higher paraffins is carried out in a vertical tube heated to 350° and filled with sodium chloride and/or bromide[86]; a mixture of SO_3 and the hydrocarbon is passed continuously into the tube. In this way ethane gave 1-chloro-2-bromoethane and 1-chloro-1-bromoethane. In a similar reaction using only NaBr at 300°–325°, ~91% of ethyl bromide was obtained.

3) Thermal Chlorination of Propane and Other Saturated Hydrocarbons

Propane is chlorinated more easily than methane and ethane, forming mono- and polychlorides.

Studies of the chlorination of propane confirm Hass's rules, according to which the rates of substituting hydrogen by chlorine at 300° on primary, secondary, and tertiary carbon atoms are in the ratio 1.00 : 3.25 : 4.43. When 2 moles of propane are chlorinated with 1 mole of chlorine the latter reacts completely to give a fraction containing 52.4% of 2-chloropropane and 47.6% of 1-chloropropane. Propane contains 6 hydrogen atoms attached to primary carbon atoms and 2 attached to the secondary carbon atom; hence the ratio of 1-chloropropane to 2-chloropropane in the reaction product should be $\frac{6 \times 1.00}{2 \times 3.25}$, which corresponds to 48% of 1-chloropropane and 52% of 2-chloropropane. With a propane to chlorine ratio of 2 : 1, ~15% of polychlorides is formed; with a ratio of 8 : 1 the quantity of polychlorides falls to 5%; in both cases the relative proportions of the monochlorides remain the same. Further chlorination of the 1- and 2-chloropropanes produces a mixture of 1,1-, 1,2-, 1,3-, and 2,2-dichloropropanes. From 1,3-dichloropropane, the important anaesthetic cyclopropane can be obtained; previously it had been prepared from trimethyleneglycol[59].

Mason and Wheeler studied the purely thermal chlorination of propane, using an excess of the hydrocarbon over the chlorine, high temperatures, and high linear velocities of the reactants[53]; under these conditions the degree of chlorination can be limited to produce monochloride as the main product.

Fruhwirth[87] produced a mixture of perchloroethylene and carbon tetrachloride by chlorinating hydrocarbons. A mixture of gaseous aliphatic hydrocarbons containing more than 2 carbon atoms (excluding C_4), or the corresponding halogen derivatives, was treated at 300°–800° (preferably 500°–600°) with approximately the theoretical amount of chlorine; when the starting hydrocarbon mixture contained an odd number of carbon atoms a mixture of perchloroethylene and carbon tetrachloride was obtained in 92% yield. The starting material may be propane, a mixture of propane, propylene, butane and isobutane, or a mixture of methylpentane, hexane and methylcyclopentane.

Krentsel', Topchiev, and Il'ina[19] studied the chlorination of propane in a continuous system with the molar ratio $C_3H_8 : Cl_2 = 1 : 2$ and space velocity 30 h^{-1}. Chlorination commences at 180°; as the temperature is increased, the conversion of chlorine also increases, this being more rapid in a tube filled with pieces of glass rod than in an empty reaction tube due to the chain nature of the reaction.

TABLE 3.

Temp., °C	Duration, min	Molar ratio $C_3H_8 : Cl_2$	Space velocity, h^{-1}	Composition of product, wt.%		
				mono-chlorides	di-chlorides	tri-chlorides
310	265	0.94:1	46	48.2	41.0	10.8
315	220	0.80:1	75	34.0	55.0	11.0
314	730	1:1	11	51.7	41.0	7.3
314	410	0.95:1	42	47.9	40.5	11.6
310	348	3.80:1	85	89.0	11.0	—
310	600	3.90:1	28	84.7	15.3	—
310	300	1.39:1	57	69.5	24.7	5.8
317	360	1.47:1	28	69.6	26.9	3.5
320	340	1.46:1	37	53.5	38.4	8.1

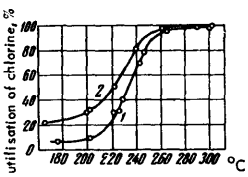


Fig. 6. Utilisation of chlorine as a function of temperature. 1) Empty tube; 2) packed tube.

The results of this study are given in Table 3. It is seen that altering the space velocity within the limits studied has little effect on the relative proportions of the various chloropropanes obtained.

Fig. 6 shows that in the thermal chlorination of propane the chlorine is completely utilised at 300°; changing the space velocity within the limits 11–85 h^{-1} has little influence on the composition of the chlorination products. With the ratio $C_3H_8 : Cl_2 = 4:1$ the relative proportions of mono- to dichloropropanes are almost independent of temperature; the reaction product contains 81.2 to 83.9% of monochloropropanes (comprising 57.2% of 1-chloro- and 42.8% of 2-chloropropane) and 16.1–18.8% of dichloropropanes (containing all possible isomers). With the ratio $C_3H_8 : Cl_2 = 2:1$ increase of the reaction temperature from 310° to 398° increases the dichloropropane content from 20.2 to 34.3% and the trichloropropane content from 1.5 to 7.7%. Fig. 7 shows the influence of the propane to chlorine ratio on the composition of the reaction products. Increasing the molar excess of the hydrocarbon in the reaction mixture causes a decrease in the yield of di- and trichloropropanes (Fig. 7).

Topchiev and Krentsel'[88] chlorinated propane in a small-scale apparatus[23], with mullite as a fluidised-bed heat exchanger. The starting propane contained 95.3 wt.% C_3H_8, ~4.2 wt.% C_2H_6, and ~0.5 wt.% C_4H_{10}. The experiments were carried out at 360°–395° with a space velocity of 60–180 h^{-1}. It was found that changing the chlorine to propane ratio from 1.58 to 2.1 leads to a slight decrease in the yield of di- and trichloropropanes and an increase in the yield of polychloropropanes; further increasing the ratio to 2.38 at sufficiently high space velocities causes an increase in the yield of di- and trichloro derivatives to 80–81%, as against 68–73% with a chlorine to propane ratio of 2.1. Only a small quantity of monochloropropanes is formed (1–4%), and this remains almost constant as the chlorine to propane ratio is increased from 1.58 to 2.38. On distilling the separate fractions, 1,1- and 1,2-dichloropropanes, 1,1,2- and 1,2,3-trichloropropanes, and 1,1,1,2- and 1,1,2,2-tetrachloropropanes are obtained.

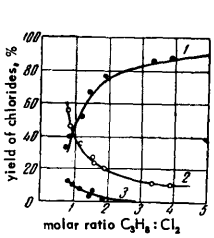


Fig. 7. Influence of the $C_3H_8 : Cl_2$ ratio on the composition of the reaction products. 1) Monochlorides; 2) dichlorides; 3) trichlorides.

The experiments on the extensive chlorination of propane on a fluidised-bed heat exchanger have shown that this process may be used to produce more highly chlorinated propanes and for the destructive chlorination of the reaction products to obtain carbon tetrachloride and perchloroethylene.

According to the German Federal Republic Patent 946,891[89] chlorinated derivatives are obtained by chlorinating saturated, unsaturated, or chlorinated hydrocarbons containing not less than two carbon atoms. Thus a mixture of 9 vol.% Cl_2 and 91 vol.% of propane at an initial temperature of 250° and the reaction chamber at 360° gives a chlorinated product containing 18.2 wt.% of isopropyl chloride, 34.6 wt.% of *n*-propyl chloride, 43.2 wt.% of 1,2-dichloropropane, and 4.0 wt.% of 1,2,3-trichloropropane.

Krentsel' and Pokatilo[90] studied the thermal chlorination of *n*-butane as the first step in the production of butyl alcohols by way of monochlorobutanes. They used 98–98.5% *n*-butane obtained by rectifying technical butane-isobutane fractions. From many experiments they showed that *n*-butane is chlorinated with 100% utilisation of chlorine at temperatures above 250°, and that filling the reaction tube with glass packing lowers the temperature at which chlorination commences, but does not lower the temperature at which there is complete utilisation of the chlorine. Monochlorides are obtained at space velocities of up to 500 h^{-1} with a 4.5 fold molar excess of butane in the reaction mixture. With a smaller excess of the hydrocarbon the yield of monochlorides does not exceed 80% at any space velocity. The monochlorides obtained contained ~60% of s-butyl chloride and ~40% of *n*-butyl chloride. At 400° the 1-chlorobutane content increases to 50%.

Topchiev, Andreev, and Krentsel'[91] carried out a series of experiments on the thermal chlorination of an isobutane fraction containing 66.5 vol.% of isobutane, 25.8 vol.% of *n*-butane, 5.8 vol.% of butylene, 0.9 vol.% of propane, 0.6 vol.% of isopentane, 0.3 vol.% of *n*-pentane, and a residue of 0.1 vol.%. 100% utilisation of chlorine with this fraction occurs at the same temperatures as with *n*-butane, but there is a higher yield of polychlorides at the same hydrocarbon to chlorine ratios. Chlorination of *n*-butane with a four-fold excess of hydrocarbon gives 100% yield of monochlorides, but in the case of isobutane, even with a greater hydrocarbon to chlorine ratio, the yield of monochlorides is only ~94%.

Topchiev, Krentsel', and Andreev[92] calculated from experimental data the energy of activation for the chlorination of the isobutane fraction to be 20 000 cal/mole, and for the chlorination of *n*-butane under the same conditions, 39 000 cal/mole. This might explain the higher yield of polychlorides in the chlorination of isobutane.

Nametkin and Serebrennikova[93] carried out experimental studies on the chlorination of alkanes as the first stage in

the production of alcohols. An interesting method for the thermal vapour-phase chlorination of *n*-pentane and isopentane to amyl chlorides is described by Ayres[94] and Clark[95].

Koch, Stallkamp, and Burrel[96], Dobryanskii and Gurevich[97], and Lemke and Tishchenko[98] chlorinated *n*-pentane in the vapour and liquid phase to obtain dichlorides. Dobryanskii and Gurevich[97] showed that vapour-phase chlorination is preferable for the synthesis of monochlorides.

Davydova, Papkina, and Tishchenko[99] were the first to chlorinate synthetic isopentane in the liquid phase at 18°–−20° and in the vapour phase in the apparatus described by Kursanov[100]. With 2 moles of chlorine and 1 mole of isopentane, the reaction product contained ~30% of monochlorides, 60% of dichlorides, and 10% of trichlorides. 2,3-dichloro-2-methylbutane, 2,4-dichloro-2-methylbutane, and 1,4-dichloro-2-methylbutane were found in the products.

Markovnikov[6], who chlorinated *n*-hexane in an atmosphere of dry and of moist chlorine, showed that the best yield of monochloride is obtained with moist chlorine.

Studies on the chlorination of hexanes have not fully revealed conditions for obtaining monochlorides as the main product with complete utilisation of the chlorine.

Galanina[101], continuing the work of Nametkin and Serebrennikova[93], chlorinated *n*-hexane from petroleum. She achieved complete utilisation of chlorine with a maximum yield of monochloride at 235°, with the ratio $C_6H_{14}:Cl_2$ = = 10:1 and space velocity 0.73 litre/h per litre of reactor volume. Higher temperatures did not give improved results, and a lower temperature gave a lower yield of monochloride. With hexane to chlorine ratios of 3:1 and 6:1, there were frequent flashes in the reactor, which caused local overheating and deposition of carbon on the walls. The monochloride was separated on a rectification column into a fraction of b.p. 122°–125°, corresponding to 2-chlorohexane, and a fraction of b.p. 134°–136°, corresponding to 1-chlorohexane. The resulting monochloride was again chlorinated, producing under certain conditions dichlorohexane in a yield of 98.7%.

Galanina and Nekrasov[27] chlorinated *n*-heptane in the vapour phase at high temperature in an attempt to attain the maximum yield of monochloride with complete utilisation of the reacting chlorine. The chlorine was in excess. The monochloride which formed was immediately removed from the reaction zone. Their experiments showed that increase of temperature increases the yield of monochloride, and that the chlorine reacts completely to give monochloride in 96.5% yield at 260°, with space velocity 0.72* and reactant ratio 10:1.

McBee and Hass[102] chlorinated propane, *n*-butane, isobutane, *n*-pentane, isopentane, and *n*-heptane at atmospheric pressure. They established the following rules.

1) If an aliphatic hydrocarbon is chlorinated at an elevated temperature or under the influence of light, all the isomers theoretically possible are formed.
2) At low temperatures hydrogen atoms attached to secondary and tertiary carbon atoms are substituted more rapidly than those on primary carbon atoms.
3) At 600° and above the chlorination is not selective, and all hydrogen atoms are substituted at the same rate; under these conditions the yield of primary isomers is ~90 vol.% of the total monochlorides in the case of isobutane, 60 vol.% in the case of *n*-butane, and 75 vol.% in the case of propane.

McBee, Hass, and coworkers[103] studied the thermal chlorination of hydrocarbons in the vapour phase under pressure and at an elevated temperature. At 500° and 500 atm with a large excess of chlorine, pentane gave 90% of the theoretical quantity of CCl_4 and 10% of hexachloroethane. At 300°–360° and 100 atm hexane or octane produced CCl_4 and hexachlorobutadiene. There was no deposition of carbon.

Nekrasova and Shuikin[104] studied the possible thermal chlorination of *n*-hexane, *n*-heptane, *n*-nonane, and *n*-decane, and established the optimum conditions and the main features of the process. The hydrocarbons were chlorinated thermally in the absence of light, when the reaction may be limited to the formation of primary or secondary monochlorides or dichlorides. A study of the way in which the temperature influenced the chlorination showed that for each of the hydrocarbons there are certain most favourable conditions for the formation of mono- and dichlorides. Thus the optimum temperature for the formation of 1-chlorohexane is 197°, for 1-chlorononane 317°, for 1-chloropentane 257°, for 1-chlorooctane 277°, and for 1-chlorodecane 357°. The optimum time of contact is 0.2 to 0.3 sec, and the optimum hydrocarbon to chlorine ratio from 6:1 to 10:1, depending on the hydrocarbon. The conditions for obtaining high yields of secondary alkyl chlorides were also established; the optimum temperatures are *n*-hexane 77°, *n*-heptane 137°, *n*-octane 177°, *n*-nonane 187°, and *n*-decane 197°. 1-Chlorohexane and 1-chloroheptane could be thermally chlorinated to produce the corresponding dichlorides in almost quantitative yield.

This study thus provides a method for synthesising chloroalkanes in simple and available apparatus, simply by altering the reaction conditions. The authors called this method directed thermal chlorination.

III. CATALYTIC CHLORINATION OF SATURATED HYDROCARBONS

Catalytic and photochemical chlorination have received much less attention than thermal chlorination, and most work in this field relates only to methane and ethane.

Catalytic chlorination has been studied with a view to the possible reduction of the chlorination temperature by using various solid catalysts. Up to the present, homogeneous catalysis in the chlorination of hydrocarbons has received little attention, although the use of homogeneous catalysts in radical reactions gives very interesting results, as Topchiev and Ananiya have shown[105].

It is known that various metal chlorides (ferric chloride, silver chloride, partially reduced cuprous chloride, aluminium chloride, manganous chloride, antimony pentachloride, and platinum, zinc, cadmium, tin and lead chlorides impregnated on carbon), and various adsorbent materials mixed with finely ground calcium oxide, may be used as catalysts[106-111].

The conditions for chlorinating paraffinic hydrocarbons to produce specified products depend not only on the nature of the catalyst, but also on the hydrocarbon to be chlorinated.

* Litre/h per litre of reactor volume. (Ed. of Translation)

No noticeable influence on the relative rates of substitution of hydrogen attached to primary and secondary carbon atoms in the photochemical chlorination of paraffins is shown by such catalysts as the chlorides of antimony, tin, aluminium, titanium, and bismuth, nor by iodine and sulphur.

1) Catalytic Chlorination of Methane

Among inorganic catalysts, cupric chloride has attracted most attention.

Boswell and McLaughlin[112] and Deanesly[109] have demonstrated the use of cupric chloride in the catalytic chlorination of methane to methyl chloride. This work has been confirmed and extended by Mamedaliev and his coworkers[113], who showed that in the preparation of methyl chloride from natural gas, best results are obtained with a catalyst of cupric chloride on pumice promoted with cerium chloride. Catalysts which have a high adsorptive capacity for chlorine are unsuitable for the production of methyl chloride, but favour the formation of more highly chlorinated products, particularly CCl_4, probably because the catalyst surface adsorbs chloromethanes to a greater extent than methane, thus producing more extensive chlorination[112-116].

Polanyi and Bogdandy have shown in their patent[117] that it is possible to obtain methyl chloride by adding small amounts of sodium, cadmium, or zinc vapour to the mixture of chlorine and methane, while Martin and Lux[118] have chlorinated methane in the presence of the vaporised lower chlorides of polyvalent elements which are capable of forming higher chlorides, for instance, antimony trichloride. Sper[119] has described the chlorination of saturated hydrocarbons (including methane) in a heated reaction chamber filled with graphite lumps. The use of catalysts in the chlorination of methane has also been discussed in several other papers[50].

The published data on the catalytic chlorination of methane lead to the conclusion that in order to obtain an optimum yield of CH_3Cl it is necessary to use a considerable excess of methane over chlorine and a fairly high temperature in the reaction tube (empty or filled with a porous material). To obtain CCl_4 it is necessary to have first of all an excess of chlorine over methane as well as active catalysts; the tendency of the reacting gases to explode is reduced by introducing gases such as carbon dioxide and nitrogen into the reaction zone. In the chlorination of methane the hydrogen chloride formed accounts for 50% of the reacting chlorine for each atom of chlorine which combines with methane; hence the search for new methods of chlorinating hydrocarbons with the minimum formation of hydrogen chloride is of theoretical and practical interest[120-122].

Chlorination in the presence of chlorine carriers (melts of certain, mainly copper, salts) can bring about oxidative chlorination of hydrocarbons, as well as the normal chlorination, with simultaneous utilisation of the hydrogen chloride[24].

$$RH + 2CuCl_2 \rightarrow RCl + Cu_2Cl_2 + HCl$$

$$Cu_2Cl_2 + 2HCl + \tfrac{1}{2}O_2 \rightarrow 2CuCl_2 + H_2O.$$

In this process the heat of chlorination is partly compensated by the endothermic regeneration of the cupric chloride, the temperature of the chlorination being thereby more easily controlled. Pure cupric chloride or a eutectic salt mixture, e.g $Cu_2Cl_2 + KCl + CuCl_2$, is used as chlorine carrier. The use of salt melts simplifies the removal of heat, but causes other difficulties, because of the necessity of circulating a melt at high temperature in the reaction system. Detailed studies of the kinetics of the chlorination of methane in the presence of salt melts have appeared in recent years[123].

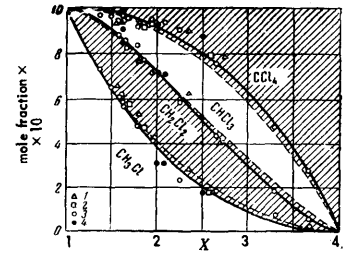


Fig. 8. Distribution of chlorinated methanes in the reaction product. X is the ratio of g-atoms of chlorine to moles of chlorinated product.
1) HCl - air - CH_4; 2) HCl - O_2 - steam - CH_4; 3) Cl_2 - - air - CH_4; 4) CH_4 - Cl_2.

Meisner and Thode[124] reported the existence of local overheating when a fixed catalyst (cupric chloride on pumice) is used for the chlorination of methane at 440°–550° in the presence of hydrogen chloride and oxygen. They carried out experiments on the oxidative chlorination of methane with the following systems: 1) HCl–air–methane; 2) HCl–oxygen–steam–methane; 3) chlorine–air–methane. Analysis of the experimental results showed that the reaction mixtures contain all four chloromethanes, but their proportions differ in the different systems (Fig. 8).

The same effect was noticed by Wilson and Howland[48], who showed that the variation in the proportions of the products in the different systems may be explained by equilibrium between CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4 in accordance with the equations

$$CH_3Cl + CHCl_3 \rightleftharpoons 2CH_2Cl_2, \quad (1)$$

$$CH_2Cl_2 + CCl_4 \rightleftharpoons 2CHCl_3. \quad (2)$$

Meisner and Thode found that when chlorine is mixed with methane and air, its conversion by the reaction

$$2CH_4 + Cl_2 + \tfrac{1}{2}O_2 = 2CH_3Cl + H_2O$$

was 70–90%, and the conversion of hydrogen chloride by the reaction

$$CH_4 + HCl + \tfrac{1}{2}O_2 = CH_3Cl + H_2O$$

was 65–80%. 10–40% of the methane is converted, and, depending on the reaction conditions, 20–50% of the methane is burnt on the overheated parts of the catalyst, because of poor removal of heat from the reaction zone.

Soviet[24] and foreign[125] workers have shown that methane can be subjected to oxidative chlorination in a continuous system with a heterogeneous catalyst of a porous material. Under certain conditions CCl_4 can be obtained as the main product (up to 75% of the total chlorinated methanes).

Churchill and Thomas[125] prepared chlorinated hydrocarbons from organic compounds, particularly lower aliphatic alcohols, by using melts of NH_4Cl and chlorides, bromides, and fluorides of metals of Groups I and II of the Periodic System, e.g. Cu_2Cl_2, NaCl, $ZnCl_2$, and KCl, at 250°–500°. With a melt of Cu_2Cl_2, NH_4Cl, and $ZnCl_2$ the reactions were carried out at 335°–347°.

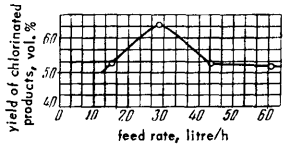


Fig. 9. Dependence of the yield of chloroderivatives on the rate of flow of the gas mixture. Temperature 460°; $CH_4 : O_2 : Cl_2 = 1 : 0.175 : 0.240$.

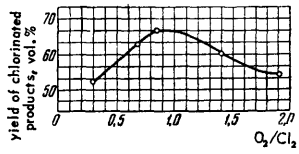


Fig. 10. Dependence of the yield of chloroderivatives on the oxygen to chlorine ratio. Temperature 460°; rate of flow of gas 30 litre /h.

Corin[126] showed that $HgCl_2$ may also be used as the chlorine carrier, the reaction being carried out in the vapour phase at 500°–650° in accordance with the equation

$$HgCl_2 + CH_4 \rightarrow CH_3Cl + HCl + Hg.$$

Vdovichenko, Galenko, and Sarishvili[25] studied the possibility of direct oxidative chlorination of natural gas in a melt of KCl and $ZnCl_2$ containing $CuCl_2$ as catalyst; the studies were made on methane–oxygen–chlorine and methane–air–chlorine gas mixtures.

The experiments showed that the content of unreacted chlorine in the exit gases decreases from 2.5 vol.% at 360° to 0 vol.% at 500°. The optimum reaction temperature is 450°; at lower temperatures the yield of chlorinated products decreases because of the larger amount of unreacted chlorine in the reaction products, and at higher temperatures the yield falls because of destructive chlorination of the methane to hydrogen chloride and soot, which can be observed visually. The maximum yield of chlorinated methanes is obtained with a reactant feed rate of ~30 litres/h (Fig. 9). At 460° and a feed rate of 30 litres/h, the yield of chlorinated derivatives reaches 60–68% with an oxygen to chlorine ratio of 0.68–0.85 (Fig. 10). Thus in the oxidative chlorination of methane in a $KCl–ZnCl_2–CuCl_2$ melt under optimum conditions, the yield of chloromethanes, calculated with respect to chlorine, reaches 60–64%, which is 11–15% greater than the yield obtained in the vapour-phase thermal (non-oxidative) chlorination.

In the direct oxidative chlorination of methane in a $KCl–ZnCl_2–CuCl_2$ melt, the resulting chloromethanes contain 85–90 mole % of methyl chloride, 9–14 mole % of methylene chloride, 2–5 mole % of chloroform, and up to 1 mole % of carbon tetrachloride.

Bijawat, Patel, and Potnis[127] have described the application of a fluidised-bed catalyst for the chlorination of methane. They used activated carbon, pumice, and copper chloride on pumice, comparing their activity with that of sand as an inert material. The methane contained 90% CH_4, 9.4% CO_2, 0.2% CO, and traces of H_2 and N_2; O_2 was absent. Carbon tetrachloride was obtained as the product. The apparatus used is shown in Fig. 11. The experiments were carried out with a chlorine to methane ratio of 4:1, a rate of chlorine feed of 0.5–2.2 moles/h, and reaction temperature 250°–500°.

At all feed rates, the yield of CCl_4 rose to a maximum as the temperature increased, and then fell (Fig. 12). The highest yield of CCl_4 was obtained with activated carbon as catalyst, and the lowest with sand. The yield was 90% of the theoretical calculated with respect to chlorine (Fig. 13).

Mickley and Trilling[128] found that the heat transfer coefficient in fluidised layers is 3–70 times as much as in empty tubes. Gilliland and Mason[129] assert that, because of heat transfer by the solid particles, a comparatively homogeneous temperature is maintained in a fluidised layer throughout its volume, in spite of the large variations in the

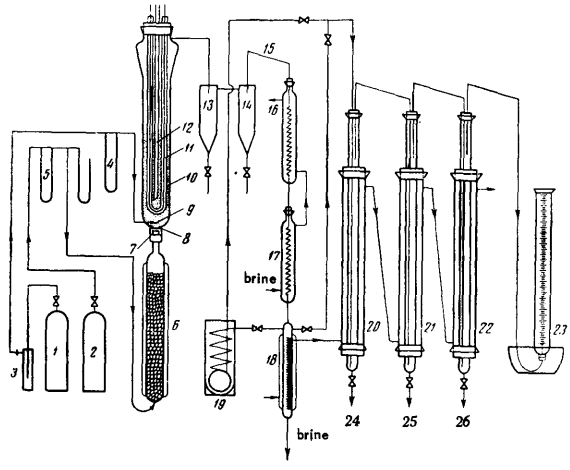


Fig. 11. Apparatus for the chlorination of methane: 1), 2) gas cylinders; 3) sulphuric-acid bottle; 4) manometer for methane; 5) manometer for chlorine; 6) preheater; 7), 12) Chromel-Alumel thermocouple; 8) distribution plate; 9) inlet pipe 2.5 cm above the distribution plate, fixed to the bottom of the reactor; 10) reactor with fluidised layer; 11) internal nichrome wire heater; 13) dust trap; 14) cyclone; 15) air condenser; 16), 17) spiral condensers; 18) straight tube condenser; 19) additional condenser; 20), 21), 22) absorbers; 23) graduated cylinder; 24)-26) valves for the removal of the chloromethanes.

heat liberated at different heights; hence it would appear that a reactor with a fluidised layer is more suited to a chlorination reaction than is an empty tube or a fixed-bed reactor.

Pie[130] has patented an apparatus for the chlorination of methane in which the reagents are passed through a zone of gradually increasing catalytic activity; the inlet end of the reaction chamber is cooled, and the outlet end heated. It is asserted that this construction enables the reaction to be easily controlled without any sudden increases of temperature, while retaining a high reaction rate.

Methane can be chlorinated in the presence of CCl_4 at 345°–400° on a fluidised-bed catalyst with a gas flow of 6–30 cm/sec and a chlorine to methane ratio of 1:10; higher yields of chloroform and carbon tetrachloride are obtained[131].

Another patent[132] describes the preparation of CCl_4 and C_2Cl_4 in a combined yield of 90% at 300°–370° with a feed of 1 mole of CH_4 to 3.6–4 moles of Cl_2; the catalyst is an untreated material of low density, such as wood charcoal, silica gel, or Fuller's earth.

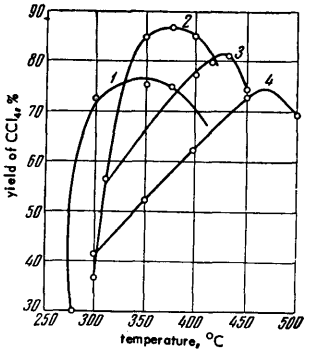


Fig. 12. Influence of temperature and rate of chlorine feed on the yield of CCl_4. activated carbon as the fluidised solid. Rate of chlorine feed, moles/h: 1) 1.01; 2) 1.31; 3) 1.93; 4) 3.20.

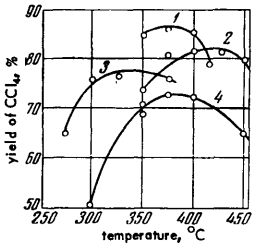


Fig. 13. Influence of the nature of the fluidised solid on the yield of CCl_4;
Fluidised solid; 1) activated carbon; 2) pumice; 3) cupric chloride on pumice; 4) sand.

Joseph and Pye[133] carry out the oxidative chlorination of hydrocarbons (e.g. methane and ethane) in a reaction chamber containing a carrier such as diatomaceous earth and copper chloride. Copper chloride is oxidised by air in the first zone to copper oxychloride, which is converted by HCl in the second zone to $CuCl_2$; this is reduced to CuCl by the hydrocarbon.

Kuntz, Cocherell, and Disberger[134] passed a mixture of CH_4 and Cl_2 (in molar ratio 1:3.6–1:4) through a reactor at 300°–370° over a fluidised-bed catalyst [wood charcoal, synthetic $Al_2(SiO_3)_3$, synthetic silica-alumina gel, silica gel, or Fuller's earth, 60–100 mesh] maintained in the fluidised state by the stream of gas, velocity 0.03–0.3 m/sec at the above temperature in an empty reactor. After separating the catalyst, the reaction products contained CCl_4 and C_2Cl_4.

Ketslakh, Rudkovskii, and Suknevich[135] prepared methylene chloride by chlorinating methane in glass tubes 60 mm long and 15 mm in diameter. The reaction space (50 cm^3) was filled with glass rings or $CaCl_2$, and the methane to chlorine ratio was 1:2. The yield of methylene chloride was practically constant over the temperature range 380°–450°. Chloroform and carbon tetrachloride are formed when the rate of flow of the gases is reduced. It was shown that it was best to use methane containing methyl chloride, the yield of methylene chloride then being 73.6% with respect to chlorine and 34% with respect to methane.

Iserson[136] prepared CCl_4 in 60–70% yield by reacting $COCl_2$ with PCl_5 at 350° under pressure with activated carbon as catalyst.

Thomas and Hundley[137] passed a mixture of 2.2 parts of CH_4 and 1 part of Cl_2 through a vertical reactor filled with glass beads and containing S_2Cl_2 at a rate of 45 g/h at 20°, and obtained 36 g of CH_3Cl per hour with traces of CH_2Cl_2. With the ratio $CH_4:Cl_2$ = 3.6:1 at 70° they obtained 215 g of CH_3Cl and 113 g of CH_2Cl_2 per hour. Methane conversion was 78%. 14 moles of $CHCl_3$ were obtained for 100 moles of CH_3Cl; CCl_4 was not formed. Methylene chloride may be prepared analogously from methyl chloride and chlorine[138].

2) Catalytic Chlorination of Ethane and Other Saturated Hydrocarbons

The catalytic chlorination of ethane and other saturated hydrocarbons has been less studied than that of methane.

Mamedaliev[113] obtained hexachloroethane in 70% yield by chlorinating ethane over activated carbon at 350°–400°. Foster[139] prepared ethyl chloride from 5 volumes of ethane and one volume of chlorine with a $CuCl_2$–Al_2O_3 catalyst at 450°–500° with a contact time of 0.3–0.5 sec, the yield being 80% with respect to chlorine.

Other workers[140] have chlorinated ethane in the vapour phase in the presence of suspended graphite powder; the composition of the chlorination product varied with the experimental conditions. With this catalyst at 400°, a contact time of 0.19 sec and gas feed of 7.6 g/h, Furr and Neher[141] obtained a product containing 0.4% CH_2 = CHCl, 60.29% C_2H_5Cl, 29.2% CH_3CHCl_2, and 6.4% CH_2ClCH_2Cl and $ClCH_2CHCl_2$. The degree of conversion of ethane to ethyl chloride reached 44%. The chlorination of 1,1-dichloroethane on graphite at 450° with a contact time of 8 sec gives trichloroethylene in 81.4 mole % yield[142].

McBee and Bittles[143] chlorinated ethane in the vapour phase in the presence of fluorine at room temperature or below in a current of nitrogen as diluent, and obtained ethyl chloride and dichloroethane in 90–100% yield with complete utilisation of the chlorine.

Topchiev, Krentsel', and Andreev[144] studied a number of heterogeneous catalysts for the chlorination of technical *n*-butane in a continuous system, and found an iron catalyst, which considerably lowered the apparent energy of activation, to be the most active. A high yield of polychlorinated derivatives was obtained with these catalysts, the yield of monochlorides not exceeding 50% of the total.

Krentsel', Topchiev, and Il'ina[145] studied the continuous chlorination of propane on silica gel impregnated with $CuCl_2$, an iron catalyst in the form of a spiral of stainless steel, and in the presence of oxides of nitrogen. They showed that the iron catalyst is the most effective, the chlorination commencing at a low temperature and more than 30% of the chlorine reacting at 40°. Under comparable conditions, the yield of di- and trichloro derivatives was considerably higher with the copper chloride impregnated silica gel than with the iron catalyst. The addition of 1–2% NO_2 has a strong catalytic effect, giving a higher chlorine utilisation than in the purely thermal process.

Topchiev and Alaniya[105] were the first to show that chlorine is a homogeneous catalyst for the nitration of hydrocarbons with oxides of nitrogen in the vapour phase; in addition to the nitrated hydrocarbons which are the main product, chlorides are also formed. This suggested that with certain proportions of chlorine and oxides of nitrogen it should be possible to direct the reaction so as to produce chlorides as the predominant product, thus using the nitrogen oxides as catalysts for the chlorination. To confirm this suggestion, butane was chlorinated in the usual continuous system with the addition of 2% NO_2 to the reaction

mixture; the chlorination commenced at a lower temperature, and at 150° the utilisation of chlorine reached 44%, while in the absence of NO_2 there is no reaction at all at this temperature.

The reaction of NO and Cl_2 with methane in the vapour phase from room temperature (25°–30°) to about 300° has also been studied, with the ratios $CH_4:NO = 4:1$ and $CH_4:Cl_2 = 1:3$. In addition to nitration and chlorination products, oxidation products of methane were also observed: small amounts of formaldehyde were detected in the gaseous products, and were absorbed in ammonia to form hexamethylenetetramine. Under identical conditions, there was no reaction between chlorine and methane in the absence of oxides of nitrogen, and no nitration of methane by nitrogen oxides in the absence of chlorine. Only the simultaneous action of chlorine and nitrogen oxides on methane at elevated temperatures can provide a series of products under fairly mild conditions.

Nekrasova and Shuikin[20] studied the reaction products in the vapour-phase (265°–400°) and liquid-phase (123°–213°) chlorination of *n*-alkanes from C_6H_{14} to $C_{12}H_{26}$ with a molar ratio of alkane to chlorine = 1:1, with 2% NO_2 as catalyst in the presence of 1% of unsaturated hydrocarbons as chain initiators. They also[21] studied the chlorination of *n*-dodecane in the vapour and liquid phases in the presence of NO_2, the use of which enables the reaction temperature to be lowered by 70°–100° and produces monochlorides in high yield.

Profft[146] carried out the simultaneous chlorination and nitration of propane and pentane. A stream of nitrogen was passed through the hydrocarbon, heated almost to boiling, and the hydrocarbon vapour mixed with HNO_3 vapour and N_2, and then with Cl_2, after which the mixture was heated to 240°–400°; in the case of pentane the final product contained 3.5% N and 31% Cl.

The catalytic action of small quantities of olefines on the chlorination of saturated hydrocarbons is of much interest.

Thus Stewart and Weidenbaum[147] showed, in agreement with Deanesly's patent[110], that the chlorination of pentane (and also propane and butane) is quite strongly accelerated in the presence of ethylene, and (significantly) practically no dichloroethane is formed. Stewart and Weidenbaum conclude that this "initiation" of the hydrocarbon chlorination is a chain process and suggest the following reaction mechanism:

1) $Cl_2 \rightarrow Cl\cdot + Cl\cdot$,

2) $C_2H_4 + Cl\cdot \rightarrow C_2H_4Cl\cdot$,

3) $C_2H_4Cl\cdot + C_5H_{12} \rightarrow C_2H_4 + C_5H_{i1} + HCl$,

4) $C_5H_{i1} + Cl_2 \rightarrow C_5H_{11}Cl + Cl\cdot$, etc.

They introduce the concept of the so-called "induction factor", which is the ratio of chlorine reacting by substitution to chlorine reacting by addition. From their earlier work on the photochemical chlorination of paraffins and olefines, they suggest that in thermal (mainly high temperature) chlorination in the presence of olefines, the atomic chlorine formed in the chain reaction reacts by two competing processes (shown as applied to ethylene):

1a) $Cl\cdot + Cl_2 \rightarrow Cl_3$,

1b) $Cl\cdot + C_2H_4 \rightarrow C_2H_4Cl\cdot$.

Assuming that the active chlorine molecule reacts predominantly by addition and the radical $C_2H_4Cl\cdot$ mainly by substitution, they suggest that the chain mechanism of the "induced" chlorination of, for example, pentane in the presence of ethylene may be represented as follows:

2) $C_2H_4 + Cl_3 \rightarrow C_2H_4Cl_3 \rightarrow C_2H_4Cl_2 + Cl\cdot$,

3a) $C_2H_4Cl\cdot + Cl_2 \rightarrow C_2H_4Cl_3 \rightarrow C_2H_4Cl_2 + Cl\cdot$,

3b) $C_2H_4Cl\cdot + C_5H_{12} \rightarrow C_2H_4 + C_5H_{i1} + HCl$,

4) $C_5H_{i1} + Cl_2 \rightarrow C_5H_{11}Cl + Cl\cdot$,

with corresponding steps for breaking the chains.

TABLE 4.

Catalyst	Apparent energy of activation, cal/mole
None	39 000
Inert filler	17 000
Activated alumina	15 000
Silica gel	8 000
Silica gel + 20% $CuCl_2$	4 500
Iron catalyst	4 500

In more recent work, Rust and Vaughan[11] have investigated the inhibition by olefines of the substitution chlorination of paraffins and olefines at moderate temperatures (up to 200°); for example, at 135° substitution is markedly inhibited by the presence of 20% of propylene in the hydrocarbon mixture.

"Induced" chlorination and similar processes have been little studied.

Attention is drawn to papers and patents by Deanesly and his coworkers[109-111] relating to the chlorination of mixtures of paraffins and olefines.

IV. PHOTOCHEMICAL CHLORINATION

Photochemical chlorination, in which the absorption of a light quantum decomposes a molecule into two atoms or radicals, is of tremendous value in studying the theory of chain reactions.

Both liquid and gaseous hydrocarbons can be chlorinated photochemically; it is particularly convenient to chlorinate the former by passing chlorine through the liquid reaction mixture while stirring and irradiating with ultraviolet light.

Butlerov[148] chlorinated butane photochemically by mixing 10 volumes of the hydrocarbon with 9 volumes of chlorine in glass vessels in the dark, and submitting the mixture to the action of daylight; after several hours a large quantity of hydrogen chloride and a heavy oil were formed; the latter contained alkyl halides and a high proportion of higher chlorination products.

Tolloczko and Kling[149] demonstrated the influence of sunlight and light from a mercury-vapour lamp, and Bedford[150] that from an arc discharge, on the reaction between methane and chlorine.

Rollefson[151] states that the photochemical chlorination of paraffins leads to the successive substitution of two hydrogen atoms by chlorine, and is often accompanied by an explosion. However, according to Whiston[152], monochlorides can be obtained in good yields by photochlorination in diffuse sunlight or corresponding artificial light if the hydrocarbon to chlorine ratio is controlled[153].

When chlorinating gaseous hydrocarbons, it is recommended that the hydrocarbon and chlorine be introduced into a solvent inert to the action of chlorine and that the stirred solution be irradiated with ultra-violet light[44].

In spite of the large number of papers on the photochemical chlorination of paraffins, interest in this field has not decreased in recent times. Photochemical excitation is as yet little used in industry.

McBee and Pierse[154] chlorinated methane at 150°–450° under the influence of ultra-violet radiation with a contact time of 5 min, and obtained tetrachloroethylene (35% conversion) and carbon tetrachloride. In the industrial process methane is 80–90% converted into chlorinated products at 340°–370°; by adjusting the reaction conditions it is possible to obtain the final products in any desired proportions. The reaction of methane with chlorine at 315° in a tube filled with Fuller's earth produces 46% C_2Cl_4, 45% CCl_4, and 9% C_6Cl_6 and C_2Cl_6; the conversion is 67% (based on chlorine). The chlorination of ethane at 400° with a contact time of 0.19 sec produces 4% C_2H_3Cl, 60.2% C_2H_5Cl, 29.2% $CHCl_2CH_3$, 6.4% CH_2ClCH_2Cl, and 0.2% $CHCl_2CH_2Cl$; the overall conversion, based on ethane, is 81.2%. The chlorination of hexane at 97° with a contact time of 0.2–0.3 sec produces 67% of a mixture of primary and secondary chlorides. The chlorination of heptane at 157° gives 57% of secondary and 19% of primary chlorides; of octane at 177°, 66% and 32% respectively; of nonane at 187°, 65% and 3%; and of decane at 197°, 61% and 3%. It may be concluded that increasing the molecular weight of the hydrocarbon leads to a reduced selectivity and the formation of a larger amount of dichlorides.

Henning and Pessel[155] prepared CCl_4 by chlorinating $CHCl_3$, heated to nearly 61°, in the liquid phase in the presence of PCl_3 as catalyst under illumination. Chlorine was passed into the solution through a porous glass plate while illuminating the apparatus with two 100 W bulbs; the yield of CCl_4 was 90–95%, based on reacted $CHCl_3$, or 90% based on chlorine, with recycling of unreacted chlorine.

An autocatalytic photochlorination process has been described. A mixture of chlorine and hydrogen was burnt in a concentric tube at 250°–300°, and a 1 : 4 methane–chlorine mixture (20 g CH_4 + 80 g Cl_2 per hour) was simultaneously passed into the tube; in addition to hydrogen chloride 0.06 parts of a mixture of $CHCl_3$ and CCl_4 were obtained[156].

Skuters and Cooper[157] also prepared CCl_4 by the photochemical chlorination of methane by continuously introducing Cl_2 into a stream of liquid CH_4.

McBee, Hass, Burt, and Neher[158] chlorinated (by the photochemical method) ethane, saturated at 0° with lead tetraethyl, with a mixture of chlorine and nitrogen at 132°. The chlorine utilisation was 95%, and the product contained 80 mole % of ethyl chloride and 20 mole % of higher chlorides, mainly 1,1-dichloroethane. The products of the photochemical chlorination of ethane at 125°–150°, using a substantially equimolar proportion of chlorine, contained ethyl chloride and dichloroethane[159–161].

Governale, Huguet, and Neher[162] have also chlorinated alkanes to alkyl chlorides photochemically.

Brow and Panis[163] chlorinated propane photochemically at 50° in a liquid medium consisting of polychloropropanes. The product contained 79.7% of chlorine, and was passed together with more chlorine into a salt bath containing equimolar amounts of potassium and zinc chlorides heated to 428°; the reaction product contained carbon tetrachloride, tetrachloroethylene, hexachloropropane, and hexachlorobenzene.

The productivity per unit volume of reaction mixture is considerably greater in the photochemical chlorination of ethane and propane than in the thermal chlorination; this fact merits particular attention.

Pritchard, Pyke, and Trotman-Dickenson[164] studied the rates of the light-induced reaction of chlorine with methane, ethane, propane, isobutane, neopentane, cyclopentane, methyl chloride, and ethyl chloride. They found that methyl chloride is more easily chlorinated than methane, but ethyl chloride less easily than ethane. The rate of reaction of chlorine atoms with hydrogen-containing compounds is very sensitive to the presence of traces of impurities, the surface condition of the reaction vessel, and, in photochemical processes, the intensity of the absorbed light. Tamura[165] found the upper limit of the energy of activation of the reaction

$$Cl\cdot + CH_4 \rightarrow CH_3 + HCl$$

to be 6 kcal/mole.

La Mare and Vaughan[166] also showed that ethyl chloride is less easily chlorinated than ethane, and that at elevated temperatures (above 280°) large amounts of ethylene and 1,1-dichloroethane are formed. Schumacher and Wolf[167] found the energy of activation for the reaction of Cl_2 with chloroform to be less than 4.3 kcal/mole.

Topchiev and Krentsel'[168] chlorinated *n*-butane photochemically in the annulus between two concentric glass tubes 44 and 40 mm in diameter and 600 mm long. The experimental results show that, in contrast to the thermal chlorination of butane, increasing the excess of hydrocarbon in the reaction mixture, even to a 10-fold proportion, does not lead to the formation of monochlorobutanes alone; under all conditions products boiling higher than the monochlorobutanes were obtained in considerable amounts; analysis showed that these were all dichlorobutanes. The formation of dichlorobutanes is apparently due to the action of light, which causes more extensive chlorination of the hydrocarbon. The monochlorobutane mixture has the same composition as the product obtained in the thermal chlorination of butane. In photochemical and catalytic chlorination, the reduction of the reaction temperature (because of the catalyst or photochemical effect) always leads to a much greater production of dichloro derivatives.

According to published data[169] the photochemical chlorination of isobutane takes place to a considerable extent on the surface of the reaction vessel.

TABLE 5.

Chlorination products	Initiator					
	benzoyl peroxide		azodiisobutyronitrile		dimethyl percarbonate	
	g	wt.%	g	wt.%	g	wt.%
Ethyl chloride	68.73	34.8	51.27	26.3	36.12	24.9
Polychloroethanes	128.51	65.2	143.48	73.7	109.00	75.1
Totals	197.24	100	194.75	100	145.12	100

Cantzler, Krekeler, and Leutner[170] prepared monochloro derivatives by the liquid-phase chlorination of hydrocarbons which are gaseous or highly volatile under normal conditions, using catalysts or irradiation to accelerate the reaction. Vajta, Toperczer, and Lengyel[171] used X-rays to accelerate the chlorination of paraffins.

Highly chlorinated products are obtained by chlorinating the higher paraffins in the liquid phase while irradiating with a mercury lamp; for example, with hydrocarbons having 10–16 carbon atoms, commencing the chlorination at 75° and gradually raising the temperature to 160° gives products containing 60% of chlorine[172]. In this connection it is interesting to note a new method now being developed for the extensive chlorination of high-molecular-weight hydrocarbons, in which chlorination is effected in liquid chlorine as solvent[173,174].

V. INITIATED CHLORINATION

At the present time great interest is being shown in initiated chlorination. The introduction into the reaction zone of substances which can form radicals in considerable quantities facilitates the decomposition of chlorine molecules into atoms and enables the chlorination to be effected at lower temperatures.

The use of organic peroxides for the chlorination of paraffins is suggested in the American patent literature[106]. The chlorination of hexane and other saturated hydrocarbons is accelerated at temperatures below 200° in the presence of organic peroxides such as ascaridole (Δ^2-*p*-menthene-1,4-dioxide).

Vaughan and Rust[10] described the chlorination of lower paraffins using lead tetraethyl as initiator. It has long been known that lead tetraethyl may be used as a source of ethyl radicals, which are easily formed by thermal decomposition above 200°. For example, ethane and chlorine react in the presence of lead tetraethyl at 132°, i.e. at a temperature 150°–250° lower than that of the purely thermal chlorination. It is remarkable that propane is chlorinated even at 0° in the presence of lead tetraethyl. In both cases about 95% of the chlorine reacts, and the chlorination of *n*-pentane in the liquid phase with $Pb(C_2H_5)_4$ as initiator takes place to the same extent.

Kharasch and his coworkers[107] studied the chlorination of paraffins with sulphuryl chloride in the presence of very small quantities (0.05%) of various organic peroxides; the most effective were benzoyl and lauroyl peroxides. In his review, Hass[7] considers in detail the combined action of SO_2 and Cl_2 on paraffins. He does not think it surprising that sulphur dioxide "initiates" the substitution of hydrogen by chlorine; in this he is in complete agreement with Deanesly's work[110] on the "induced" chlorination of paraffins in the presence of olefines, which is in accord with the theory of chain reactions.

Franck[176], Terenin[177], and Kondrat'ev[178] detected and discussed theoretically the decomposition of molecules into atoms or free radicals by the action of light quanta of sufficiently short wave length. Thus acetone decomposes to form CH_3 with light of wave length 2540 Å. This method of initiating a chain reaction is notable in that definite quantities of primary radicals can be produced.

The present authors[179,180] have studied the low-temperature chlorination of ethane in the presence of initiators (benzoyl peroxides, azodiisobutyronitrile, and dimethyl percarbonate), using an ethane fraction containing 0.2 vol.% of ethylene and 1% of oxygen, with carbon tetrachloride as solvent. The experiments were carried out on a continuous basis in a glass column fitted with a jacket, a glass atomiser, a thermometer, and a reflux condenser. The column contained about 0.7 litre of CCl_4 with 1 mole % of initiator. Table 5 gives the results of a series of chlorinations with a chlorine to ethane ratio of 1 : 2.5 and a methane feed-rate of 45 h^{-1} [volumes per hour? Original reference not available for checking (Ed. of Translation)].

25–35% of ethyl chloride and 65–75% of polychloroethanes are formed. The polychloro fraction contains ~11% of trichloroethane, 27% of tetrachloroethane, and 12% of pentachloroethane. With chlorine to ethane ratios of 1 : 2.5 and 1 : 1.7, the ethane conversions are ~30% and ~60% respectively. It was shown that complete utilisation of chlorine is attained at 60°–70°, with a contact time of 36 sec, a benzoyl peroxide concentration of ~0.25 mole %, and $Cl_2 : C_2H_6 = 1 : 1$. The efficiency of the initiators falls off with time in the order benzoyl peroxide, azodiisobutyronitrile, dimethyl percarbonate.

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THE HYDRIDES OF THE RARE-EARTH METALS

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INTRODUCTION

Whilst developing methods of physicochemical analysis, Kurnakov has paid particular attention to one of the fundamental questions of inorganic chemistry — the definition of the concept of a chemical compound and its relation to the concept of a solution[1,2].

The concept of "berthollide" phases, with no singular points, was put forward by Kurnakov in his study of metallic alloys and has since proved applicable to other classes of inorganic compound. In particular, Kurnakov has pointed out[1] that hydrides of the transition metals form interesting examples of phases of variable composition. Kurnakov considered that berthollide phases are based on compounds present in a dissociated state. Deeper study of the properties of metallic berthollide compounds[3,4] led to the theory that the metals were exhibiting variable valency, the dissociation being regarded as a mobile equilibrium between different valency states of one of the components. In the study of metallic phases, however, such a conclusion can only be reached from a study of the composition–property diagrams constructed both experimentally and on the basis of the law of mass action. It is impossible to prove the existence of different compounds within a range of metallic berthollide phases either by preparative methods or by X-ray structural analysis.

Work in recent years has shown that the chemistry of the hydrides reveals greater possibilities for understanding the nature of phases of variable composition than the chemistry of metals, since in the study of the former the construction of the composition–property diagrams can be supplemented by synthesis of the hydrides and their derivatives by reaction between the metal salts and various reducing agents in non-aqueous media. The unique position of hydrogen relative to the other elements leads to great variety in its compounds. The fact that hydrogen reacts with almost all the elements in the Periodic Table to form many types of chemical bond makes it possible to clarify the chemical character of other elements from the properties of their compounds with hydrogen.

In recent years considerable attention has been paid to the hydrides of the rare-earth metals, because of their chemical nature and the possibility of their practical application in metallurgy, vacuum technology, inorganic synthesis, etc.

In spite of the fact that rare-earth metal hydrides have been known for a considerable time, they had not until recently been studied in sufficient detail to enable any conclusions to be drawn regarding the nature of the chemical bonding of the hydrogen in these compounds.

An increasing amount of work devoted to their preparation, composition, and properties has appeared in the past few years. The aim of the present article is to summarise the published material in this field.

I. Reaction of the Rare-Earth Metals with Hydrogen

A general method for the preparation of the rare-earth metal hydrides is by the direct reaction between the metal and hydrogen. Sometimes the reaction proceeds fairly vigorously even at room temperature, but in other cases direct hydrogenation by molecular hydrogen at low temperatures is fairly slow. When this is so, for example with cerium, the metal is given a preliminary thermal treatment by heating in vacuo[5]. Several workers have related the resultant activation to the formation of microscopic cracks which facilitate the penetration of hydrogen into the metal[6]. It has also been suggested that the activation is related to the dissolution, at the high temperature, of cerium oxides blocking the metal surface. Dialer[7,8] has shown that the