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The synthesis of organochlorine compounds from one-carbon molecules

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ABSTRACT. Studies on the synthesis of organochlorine compounds from one-carbon molecules are surveyed. The thermodynamics, kinetics, and mechanisms of the direct and oxidative chlorination of methane, the esterification of methanol by hydrogen chloride, the hydrochlorination of acetylene, the hydrodechlorination of carbon tetrachloride, and the carbonylation of chloromethanes, the catalysts employed, and the practical applications of these reactions are examined.
The bibliography includes 143 references.

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I. Introduction

The great importance of organochlorine compounds in modern chemistry and technology is determined by their extensive and rapidly growing applications. By virtue of a wide variety of physical and chemical properties, they are used in virtually all branches of industry, agriculture, and domestic technology.[1]

Poly(vinyl chloride) is "plastic number two" (after polyethylene) and chloromethanes serve as the raw materials in the manufacture of organosilicon products, fluorinated plastics, and Freons. Chloromethanes have also found extensive applications as highly effective solvents, for example, in the manufacture of cine-film and of synthetic fibre. The use of carboxylic acid chlorides for the modification of polymers is extremely promising.

Methods have now been developed for the synthesis of these organochlorine compounds from one-carbon molecules. A cheap and readily available raw material is especially necessary bearing in mind the large-scale requirements for these compounds.

We shall examine the following one-carbon substances used for the synthesis of organochlorine compounds: natural gas, methanol synthesised from carbon monoxide and hydrogen, which are in their turn obtained from natural gas, acetylene, which is a methane pyrolysis product or is obtained from calcium carbide, and carbon monoxide obtained from natural gas or coal. In fact the main starting material in all cases is natural gas or coal.

II. Direct chlorination of methane and its chloro-derivatives

The chlorination of methane and its chloro-derivatives by molecular chlorine is one of the most thoroughly investigated reactions, which has in addition found extensive practical applications.[2–4]

The chlorination of methane yields as a rule the entire range of chloromethanes:

$$CH_4 \xrightarrow[-HCl]{Cl_2} CH_3Cl \xrightarrow[-HCl]{Cl_2} CH_2Cl_2 \xrightarrow[-HCl]{Cl_2} CHCl_3 \xrightarrow[-HCl]{Cl_2} CCl_4.$$

Over a wide temperature range, the formation reactions of all chloromethanes are virtually irreversible, the heat of each successive substitution of a hydrogen atom by a chlorine atom in methane amounting to 100–102 kJ mol^{-1}.[2,3] The main advances achieved in the study of this process have been described in reviews.[2,3,5–7] Problems associated with the variation of the ratio of the products obtained towards the preferential formation of one of them, the removal of a large amount of heat of reaction at a high rate of the process, the formation of chlorohydrocarbons of the ethane–ethylene series on chlorination of methane, and the utilisation of the hydrogen chloride evolved in a large amount during the reaction are examined below.

Table 1. The ratios of the rate constants for the chlorination of methane and chloromethanes.

Catalyst	*T*, K	Relative chlorination rate constants				Refs.
		CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$	
Without catalyst	573	1	1.67	1.22	0.42	[10]
»	673	1	0.40	0.24	0.07	[10]
	673	1	3.32	1.48	1.10	[8]
Sand	573	1	2.8	1.58	0.41	[9]
»	623	1	2.60	1.50	0.50	[9]
»	673	1	2.45	1.43	0.60	[9]
»	673	1	2.00	1.00	0.50	[11]
»	623	1	1.40	0.80	0.50	[12]
Kaolin	573	1	1.83	1.23	0.35	[9]
»	673	1	1.44	0.95	0.43	[9]
Activated charcoal	573	1	5.0	10.5	9.1	[9]
ditto	648	1	5.0	7.3	6.6	[9]
»	673	1	5.0	6.6	6.0	[9]
»	648	1	0.63	1.50	2.36	[13]
$CuCl_2$.KCl on diatomite	573	1	1.92	1.27	0.66	[14]
ditto	673	1	2.17	1.47	0.50	[14]

Figs.1–3 illustrate the molar proportions of the products of the chlorination of methane as a function of the chlorine : methane ratio, obtained experimentally in the gas-phase chlorination in a hollow container[8] and in a fluidised catalyst bed.[9] Table 1 presents the ratios of the rate constants for the chlorination of methane and chloromethanes obtained by different investigators by chlorination in a hollow container and on a catalyst.

Figs. 1–3 and Table 1 show that the composition of the chloromethanes obtained can change on chlorination of methane in a fluidised bed of a solid material. Whereas the presence of quartz sand has little influence on the reactivity of methane and chloromethanes,[9,11,12] in the presence of activated charcoal the composition of chloromethanes shifts sharply towards the preferential formation of tetrachloromethane.[9,13]

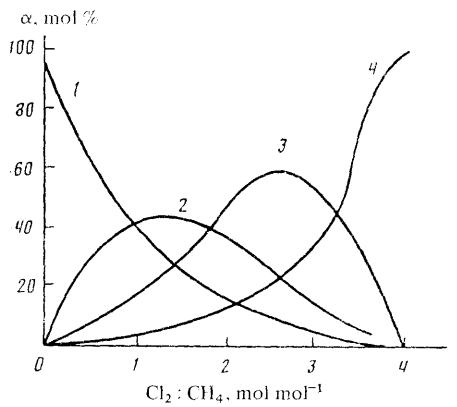


Figure 1. Free volume chlorination of methane:[8] *1*) CH_3Cl; *2*) CH_2Cl_2; *3*) $CHCl_3$; *4*) CCl_4; α—composition of reaction products.

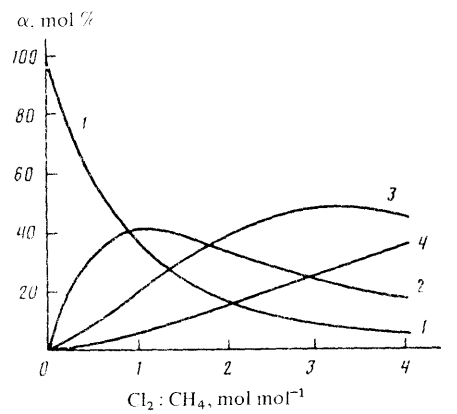


Figure 2. Chlorination of methane on quartz sand.[9]

In terms of absolute magnitude, the rate constants for the chlorination of methane and chloromethane in a fluidised quartz sand bed at 573 K are higher only by a factor of 1.5–2.6 than in a hollow container, while in the presence of activated charcoal the chlorination takes place at a much higher rate (Table 2).

Table 2. The ratios of the rate constants for chlorination in space[10] and on a catalyst[9] (the rate constants in bulk are quoted after Treger[1]).

Catalyst	*T*, K	Relative chlorination rate constants			
		CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$
Sand	573	1.5	2.6	2.0	1.5
»	673	0.6	3.4	3.4	5.0
Kaolin	573	6.3	7.2	6.8	5.5
»	573	1.7	6.5	7.2	11.6
Activated charcoal	573	6.3	18.1	55.7	142
ditto	673	0.95	11.9	26.0	83.7

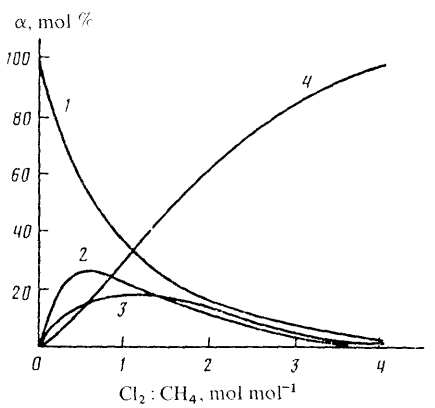


Figure 3. Chlorination of methane on activated charcoal.[9]

The heats and energies of activation for the adsorption of methane and its chloro-derivatives obtained by Belenko[15] enabled the author to put forward a mechanism for the catalytic participation of activated charcoal, kaolin, and sand in the chlorination process involving weak chemisorption of methane and chloromethanes on the surfaces of these catalysts. For activated charcoal, the activity series of methane and chloromethanes agree fully with the series based on their heats of adsorption (10.0 kJ mol^{-1} for CH_4, 29.5 kJ mol^{-1} for CH_3Cl, 43.5 kJ mol^{-1} for CH_2Cl_2, and 38.5 kJ mol^{-1} for $CHCl_3$).

It has been shown that the interaction of methane with a chlorinated carbon surface entails the substitution of chlorine atoms by CH_3 groups:[16]

$$\equiv C{-}Cl + CH_4 \rightarrow \equiv C{-}CH_3 + HCl.$$

The reaction takes place at temperatures above 470 K and at 770 K the chlorine atoms are adsorbed on the surface of technical carbon and are fully substituted, while those on the surface of activated charcoal are 78% substituted. It may be that the adsorbed CH_3 groups are rapidly chlorinated to CCl_3, which in fact explains the increased yield of tetrachloromethane when methane is chlorinated on activated charcoal.

On the other hand, one must note the fairly considerable scatter of the relative rate constants obtained by different investigators under the same chlorination conditions in a hollow container or in a fluidised catalyst bed (Table 1). The possible causes of this may be experimental difficulties [the necessity to maintain an isothermal regime under the conditions of an appreciable heat evolution and a high rate of reaction, failure to take into account the initiation of the reaction by light, different surface to volume ratios (S/V) for the reactor, and the deposition of carbon on the reactor walls or on the catalyst employed as a result of the decomposition of the chloromethanes]. It has been shown that the deposition of carbon on the catalyst increases the yield of tetrachloromethane.[17] Hence it is necessary to "condition" (coat with carbon) the walls in order to obtain reproducible results.[7]

The composition of the chloromethanes obtained on chlorination of methane can vary markedly depending on the gas flow regime in the reactor employed. Calculations have shown that on passing from the ideal displacement to the ideal mixing regime, the yield of the more chlorinated products increases.[18] Comparison of the results of the chlorination of methane in an isothermal ideal displacement reactor and in an industrial reactor showed that in the latter the yield of trichloromethane and tetrachloromethane is higher as a result of the reverse mixing.[19]

In the chlorination of methane in a hollow container,[10] the activation energy and the pre-exponential factor in the Arrhenius equation for the substitution of each successive hydrogen atom decrease steadily, since an increase in the number of chlorine atoms results in a decrease of the C–H bond energy in the chloromethane molecule but at the same time the attack by a chlorine atom on the hydrogen atom becomes more difficult. This behaviour is not observed in chlorination on catalysts.[9,14]

It is notable that the rate of chlorination both in a hollow container[10] and on a fluidised catalyst bed[9,11,12] depends on the concentrations of the initial reactants with an exponent of unity, which corresponds to the identical character of the chain termination reactions.

Different kinetics of the chlorination of methane in the presence of porous fillers of different nature have been obtained on a flow-circulation apparatus.[20] For the gas-phase reaction in the absence of fillers, the reaction orders with respect to the reactants were found to be unity and the activation energy was 121.3 ± 8.4 kJ mol^{-1}. The rate of reaction proved to be twice as high as in the study of Arai et al.[10] On the other hand, as will be seen in the discussion of the mechanism of the chlorination of methane, the first order reactions with respect to the reactants indicate chain termination on the wall, which should be more characteristic of the reaction in the presence of fillers.

The gas-phase chlorination of methane is initiated as a result of the effect of temperature, the catalytic effect of various solid materials or vessel walls, the effect of radiation and light, and various homogeneous catalysts. Because of its simplicity, the thermal chlorination of methane is used in virtually all industrial manufacturing processes.

The initiating influence of the surface consists in reducing the activation energy for the dissociation of the chlorine molecule by the heat of adsorption of the chlorine atom:[21]

$$\begin{array}{l} Cl_2 + 2S = 2SCl, \quad E_1 = \Delta H - 2q_{ClS}, \\ SCl = S + Cl^{\cdot}, \qquad E_2 = q_{ClS}, \\ \hline Cl_2 + S = S\,Cl + Cl^{\cdot}, E_3 = \Delta H - q_{ClS}. \end{array} \quad \begin{array}{l} (1) \\ \\ (2) \end{array}$$

The activation energy for the formation of a chlorine atom in the gas phase, based on the activation energy for the gas-phase decomposition of a chlorine molecule into atoms of 238.5 kJ mol^{-1} and the heat of adsorption of a chlorine atom on glass amounting to 67 kJ mol^{-1}, is $238.5-67 \simeq 172$ kJ mol^{-1}. Gorokhovatskii[22] proposed relations for reactions (1) and (2) linking the heat of dissociation of the adsorbed chlorine molecules ($Q_{Cl_2\,ads}$) to the heat of dissociation of chlorine in space (Q_{Cl_2}) and to the heats of adsorption of molecular (q_{Cl_2}) and atomic (q_{Cl}) chlorine, from which it is seen that Q_{Cl_2ads} must be less than Q_{Cl_2}, because q_{Cl} is always greater than q_{Cl_2}:

$$Q_{Cl_2\,ads} = Q_{Cl_2} + q_{Cl_2} - 2q_{Cl},$$
$$Q_{Cl_2\,ads} = Q_{Cl_2} + q_{Cl_2} - q_{Cl}.$$

It has been shown[23] that the heterogeneous two-stage dissociation of chlorine in the above scheme is kinetically more favourable than the heterogeneous one-stage or gas-phase dissociation for $E_3 < 170$ kJ mol^{-1} and its rate is a maximum for $E_3 \simeq 70$ kJ mol^{-1} and $E_2 \simeq 170$ kJ mol^{-1}. The rate of dissociation via the two-stage scheme is then higher by 10–11 orders of magnitude than the rate of the gas-phase dissociation. This indicates the enormous role of the wall and of the ratio of the surface area of the reactor to its volume in the study of gas-phase radical-chain reactions. In an industrial reactor, it is essential to take into account this factor for the successful performance of the process.

The experimental Arrhenius parameters for the elementary stages of the chain propagation in the chlorination of methane are available.[7,24,25] Calculated and experimental data have been published by Bell et al.[25] The energy parameters of the chain termination stages are given in Kondrat'ev's handbook;[24] the activation energies for these reactions are zero. The process kinetics vary as a function of the dominant type of chain termination.[26]

Theoretically, it is to be expected that, on chlorination, for example, in an industrial reactor, the dominant type of chain termination varies as chlorine is consumed and there is a corresponding change in the chlorine : methane ratio, from quadratic termination by chlorine atoms, through cross-termination between alkyl radicals and chlorine atoms, to quadratic termination by alkyl (or halogenoalkyl) radicals. The process kinetics should vary accordingly.

Variable reaction orders with respect to the reactants have been established experimentally, for example, in the study of the kinetics and mechanism of the vapour-phase chlorination of trichloromethane.[27,28] For the ratio of trichloromethane and chlorine concentrations $[CHCl_3]:[Cl_2] = 10:1$ and temperatures in the range 643–696 K, the rate of chlorination of trichloromethane is described by the equation

$$w = k[Cl_2] \cdot [CHCl_3]^{0.5}.$$

When trichloromethane is chlorinated in an excess of chlorine with $[CHCl_3]:[Cl_2] = 1:7$, the dependence of the rate of reaction on the reactant concentrations is described by a different equation:

$$w = \frac{k}{B^{0.5}}[Cl_2]^{0.5}\,[CHCl_3],$$

where B is the adsorption coefficient.

In studies[20,29] of the chlorination of methane in the presence of adsorbents (including adsorbents impregnated with LiCl or $K_2S_2O_4-K_2S_2O_7$), different reaction orders were also obtained depending on the ratio of the amounts of chlorine and methane in the reaction mixture. Thus, for $p_{Cl_2}/p_{CH_4} < 1$, the order with respect to chlorine was unity and that with respect to methane was 0.5, which corresponds to cross termination of the chain. For $p_{Cl_2}/p_{CH_4} > 3$, the reaction orders with respect to chlorine and methane were respectively 0.5 and 1, which indicates quadratic termination by chlorine atoms. In the transitional range of the above ratios, the reaction orders with respect to chlorine and methane had intermediate values, for example, 0.8 and 0.6 respectively.

In the chlorination of methane in a fluidised catalyst bed, the chain initiation and termination take place preferentially on the wall and a direct dependence of the reaction rates on the chlorine and methane concentration was therefore obtained.[7,10,24] Many investigators believe that the solid materials used for the chlorination of methane, other than activated charcoal, are not catalysts but constitute an "expanded wall", functioning simultaneously as a heat exchanger. Rozlovskii and Treger[30] question the catalytic function of the catalyst (with the exception of activated charcoal) in a fluidised bed reactor on the grounds that, under the conditions of the high-temperature chlorination, equilibrium in the dissociation of chlorine is always attained. It has been concluded[31] that the rates of chlorination of methane attained in a hollow container[8,10] are close to those found in a fluidised catalyst bed.[9,10] The rate proved to be higher by an order of magnitude only on activated charcoal. All these features indicate a weak non-specific catalytic effect of the majority of catalysts used for chlorination. This effect is manifested in the chain initiation and subsequent chlorination stages as a result of the stronger adsorption of chloromethanes compared with methane.

There is no unanimous view concerning the mechanism of the catalytic action of salts; the acceleration of the chlorination of methane by systems based on transition metal chlorides is sometimes attributed to their ability to generate atomic chlorine as a result of their decomposition at a lower temperature than that required for the dissociation of chlorine molecules. A mechanism including a stage in which copper chloride undergoes thermal dissociation has been adopted for the chlorination of methane by a melt of copper and zinc chlorides.[32]

Another version of the catalytic action consists in the polarisation of the adsorbed chlorine molecule and subsequent ionic chlorination. This mechanism has been considered in greater detail by Shatalov.[33] The heterogeneous mechanism is supported by the absence of an inhibiting effect by oxygen. In gas-phase chlorination, oxygen is known to inhibit the reaction as a result of the formation of the relatively inactive $\dot{R}O_2$ radicals. Depending on the thermal stability of the peroxy-radicals, inhibition is shown up to a specific temperature.

It has been established[14,29] that the presence of transition metal chlorides in the salt composition is obligatory for catalytic chlorination. On the other hand, according to the estimate by Aglulin,[14] the rate of chlorination in the presence of metal chlorides on a carrier (at temperatures below 673 K and for $p_{O_2} \to 0$) is approximately 5 times lower than on a clean carrier. Thus metal chlorides proved in this instance to be less active than the carrier, apparently as a result of the greater affinity of metal chlorides for atomic chlorine.

In contrast to lithium chloride and potassium pyrosulphate (see above), in the presence of which variable reactions orders with respect to chlorine and methane have been observed, for other salt systems ($CuCl_2-KCl$, $CuCl_2-KCl-LaCl_3$, $FeCl_3-KCl$, CsCl, LiF, and $LiCl-KCl$), the order of the methane chlorination reaction is unity with respect to methane and is close to 1/2 with respect to chlorine over the entire range of conditions investigated up to extremely low partial pressures of chlorine ($\sim 10^{-3}$ kPa),[29] which indicates the attainment of equilibrium in the chlorine dissociation stage even under these conditions. The authors[29] also concluded that the reactivities of chlorine atoms on the surface and in space are similar.

On comparing the experimental data and the results of calculations based on the known rate constants for the elementary stages in the chlorination of methyl chloride, Lebedev et al.[35] concluded that the photochemical and radiation-chemical chlorination of methane has no significant advantages as regards selectivity (with respect to individual chloromethanes) over the thermal chlorination. The use of catalysts also does not change the ratios of the chloromethanes obtained. The latter claim is insufficiently well founded especially in relation to activated charcoal as the catalyst.

The ratios of the rate constants for the consecutive-parallel reactions in the photochemical chlorination of chloromethane and dichloromethane have been determined in a bubbler apparatus at temperatures in the range 263–308 K.[36] It was shown that the selectivity of the chlorination is described satisfactorily on the assumption that the reaction is of first order with respect to the compounds chlorinated. The relative constants are almost independent of temperature, the presence of inhibitors, and the intensity of irradiation, but are influenced by the composition of the reaction medium. The last finding is interpreted by the authors as due to the influence of the polarity of the medium on the rate of the rate-limiting stage in chain propagation. In the liquid-phase initiated chlorination of trichloromethane, the order of the reaction was found to be zero with respect to trichloromethane, unity with respect to chlorine, and 0.5 with respect to the initiator (azobisisobutyronitrile). The activation energy was 157 ± 12 kJ mol^{-1}. The difference between the orders of the chlorination reaction with respect to trichloromethane when different methods are used is apparently associated with the change in the character of chain termination.

In the study of the kinetics of the liquid-phase chlorination of methane in the temperature range 150–293 K in dichlorodifluoromethane, the following kientic equations were obtained for 293 K:[37]

$$w_{Cl_2} = k_1 \cdot In^{0.6\pm0.1}[Cl_2] \quad \text{when } [CH_4]:[Cl_2] > 300,$$
$$w_{Cl_2} = k_2 \cdot In^{0.6\pm0.1} \cdot [CH_4] \quad \text{when } [CH_4]:[Cl_2] < 10,$$

where *In* is the intensity of the adsorbed light.

Estimation of the rate constants for the elementary stages under the conditions for the first equation showed that the rate constant for the interaction of methyl radicals with chlorine molecules is six times smaller than the value calculated from literature data, while the rate constant for the reaction of atomic chlorine with methane is smaller by two orders of magnitude compared with the literature data. Such appreciable differences are associated mainly with the decrease in the pre-exponential factor, since the activation energy obtained for this stage (12.5 ± 2.5 kJ mol^{-1}) is almost identical with the value known for the gas phase.

In our view, examination of the chemical engineering problems arising in the direct chlorination of methane and chloromethanes requires the differentiation of the following factors.

In the first place there is the problem of the removal of a large amount of heat of reaction which in the existing methane chlorination processes in hollow adiabatic reactors is solved by the recirculation of a large amount of methane. At the same time, the excess methane is used to overcome the upper limit to the susceptibility to explosion of chlorine–methane mixtures.

The above problem can be solved effectively by using a fluidised catalyst bed or by carrying out the process in the liquid phase. The presence of a liquid and a solid simultaneously prevent explosion and make it possible thereby to work with concentrated mixtures of chlorine and methane or chloromethane.

Another task is to increase the process selectivity with respect to the individual intermediates in the chlorination reaction, in the first place with respect to trichloromethane. This problem is especially acute at the present time in connection with the signing in September 1987 in Montreal of the Protocol on chlorofluorocarbons, according to which it is necessary to reduce and then stop the manufacture of Freons which decompose the ozone layer, especially Freons 11 and 12 obtained from tetrachloromethane. One of the most realistic ways of converting the Freon 11 and 12 industries is to switch them to the manufacture of Freon 22 from trichloromethane.

The increase in the yield of trichloromethane and the decrease in the yield of tetrachloromethane in chloromethane manufacturing processes is therefore at present of extremely great current interest. In the industrial manufacture of chloromethanes by the chlorination of methane at a temperature of about 773 K, with a chlorine content in the initial mixture of 20–25%, and for the recycling of the entire chloromethane formed, the trichloromethane : tetrachloromethane weight ratio in the reaction products is about 5. In the chlorination of methane on a fluidised coke bed,[17] the ratio was 3, the reaction temperature was 648 K, and the chlorine : methane molar ratio was 1.3.

A high selectivity with respect to trichloromethane ($CHCl_3 : CCl_4 = 5–7:1$) was obtained in the liquid-phase chlorination of chloromethane;[38] the reaction temperature was 333–343 K, the $CH_3Cl : Cl_2$ ratio was approximately unity, and the initiator employed was azobisisobutyronitrile.

The selectivity with respect to trichloromethane increases with decrease in the degree of conversion of chloromethane or dichloromethane during a pass, which necessitates the corresponding increase in the extent to which they are recycled. In this case, it is economical to carry out the process by combining the chlorination reaction with fractionation. Yet another problem to which little attention has been devoted in the literature but which is of interest from both theoretical and practical points of view is that of the formation of admixtures of chlorohydrocarbons of the ethane–ethylene series in the chlorination of methane. Some of these admixtures have a boiling point close to that of one of the chloromethanes (for example, 1,1-dichloroethane, *cis*-1,2-dichloroethylene, and trichloromethane), while others form an azeotrope with a boiling point close to that of the main substance (1,2-dichloroethane and tetrachloromethane). Periodic processes leading to the loss of the product, additional consumption of materials and other resources, and the formation of a large amount of waste are usually employed to remove these impurities from chloromethanes. Thus, it has been suggested that dichloromethane be purified by treatment with potassium permanganate solution; trichloromethane is nowadays purified by treatment with oleum and is then neutralised with a solution of caustic soda and dried. In view of the impossibility of separating 1,2-dichloroethane, tetrachloromethane is not isolated at all as a commercial product in the industrial manufacture of chloromethanes by the chlorination of methane. It is noteworthy that the requirements specified by the USSR state standards (GOS) as regards the contents of individual impurities are fairly stringent: the amount of 1,1-dichloroethane in trichloromethane and of 1,2-dichloroethane in tetrachloromethane must be not more than 0.002%. The concentration of the impurities formed in the industrial manufacture of chloromethanes by the chlorination of methane in a hollow reactor has been quoted by Nikitenko et al.[39]

Evidently the C_2 chloro-derivatives are formed as a result of the recombination of radicals since the initial methane is freed from homologues, including ethane. The ways which should be employed to rule out the formation of impurities are also indicated: firstly, one can attempt to prevent the quadratic termination by hydrocarbon radicals and secondly it is desirable to increase the chain length.

The influence of temperature and of the dilution of the initial mixture by an inert gas on the formation of C_2 chlorohydrocarbons in the volume chlorination of methane has been investigated.[40] A decrease in temperature alters the composition and amount of the impurities formed, one of the causes of which is apparently an increase in chain length and a decrease in the degree of decomposition of the chloromethanes. However, a significant decrease in the amount of impurities to the required level could not be achieved.

As already stated, in the chlorination of methane in a fluidised catalyst bed chain termination takes place on the surface of the solid material ("wall"). As a result, the chloromethanes obtained in this way contain virtually no impurities.[41] However, despite the evident advantages of the fluidised bed such as high productivity, the possibility of working with virtually any chlorine : methane ratio, and the excellent quality of the chloromethanes obtained, the chlorination of methane in a fluidised catalyst bed has not so far actually found application in industrial practice. Two small industrial plants of the Japanese company Asahi Glass[42] and the Indian Company Standard Alkali[43] are known.

The use of a fluidised bed is desirable for exhaustive chlorination but for the preferential yield of chlorination intermediates it has not so far been possible to use this method in industrial practice. The point is that chloromethanes decompose during the chlorination of methane and carbon is deposited on the catalyst. According to Shatalov's data,[17] under these conditions the yield of tetrachloromethane on the carbon-coated silica gel or on coke with a specific surface of 1–3 $m^2 g^{-1}$ increases to the same level as on activated charcoal with a specific surface of 1000–2000 $m^2 g^{-1}$.

The use of an inert solid (quartz sand) made it possible to increase the duration of the operation of the apparatus to 1500 h,[44] while pumice became blocked with the decomposition and charring products after 20 h. Even the use of an inert solid does not fully guarantee the absence of carbon deposition, since adiabatic heating of an equimolar mixture of chlorine and methane results in a temperature rise of more than 1000 °C and any breakdowns in the structure of the fluidised bed in the form of bubbles or thickened regions[45] can lead to local overheating and decomposition of chloromethanes. On the Asahi Glass apparatus[42] provision is made for the supply of oxygen to burn off the carbonaceous deposits. Yet another disadvantage of the fluidised bed is that, with increase in diameter on passing to industrial apparatus, an increase in the yield of tetrachloromethane is also to be expected as a result of the approach of the operating regime of the reactor to the ideal mixing model.

III. Decomposition of chloromethanes

In connection with the great influence of the decomposition of chloromethanes on the stable course of the chlorination process in a fluidised catalyst bed and also in a hollow reactor, where abrupt process terminations with an abundant release of carbon also occur, it is useful to examine the kinetics and mechanisms of these reactions. Studies by Shilov and Sabirova[46-48] have made a great contribution to the investigation of the chloromethane decomposition reactions. According to data obtained in a vacuum flow apparatus for short contact times, chloromethane decomposes at 1116 and 1147 K to hydrogen chloride, methane, acetylene, and a small amount of hydrogen, the amount of methane being three times smaller than that of HCl.[47] The activation energy for the decomposition (358 kJ mol^{-1}) is close to the bond energy. The authors suggest the following mechanism of the decomposition process:

$$CH_3Cl \rightarrow \dot{C}H_3 + Cl^{\cdot},$$
$$\dot{C}H_3 + CH_3Cl \rightarrow CH_4 + \dot{C}H_2Cl,$$
$$Cl^{\cdot} + CH_3Cl \rightarrow HCl + \dot{C}H_2Cl,$$
$$\dot{C}H_2Cl + \dot{C}H_2Cl \rightarrow CH_2Cl{-}CH_2Cl \rightarrow HCl + CH_2{=}CHCl,$$
$$CH_2{=}CHCl \rightarrow HCl + CH{\equiv}CH.$$

The thermal decomposition of tetrachloromethane[47] (827–874 K) results in the formation of chlorine, hexachloroethane, and tetrachloroethylene. The activation energy for the decomposition is 230 kJ mol^{-1}. The proposed mechanism is based on experimental data showing that hexachloroethane is an intermediate:

$$CCl_4 \rightarrow \dot{C}Cl_3 + Cl^{\cdot},$$
$$Cl^{\cdot} + CCl_4 \rightarrow Cl_2 + \dot{C}Cl_3,$$
$$\dot{C}Cl_3 + \dot{C}Cl_3 \rightarrow C_2Cl_6,$$
$$C_2Cl_6 \rightarrow C_2Cl_4 + Cl_2.$$

The thermal decomposition of tetrachloromethane to tetrachloroethylene, i.e. $2CCl_4 \rightleftarrows C_2Cl_4 + 2Cl_2$, is used in the industrial manufacture of perchlorocarbons by the exhaustive destructive chlorination of C_1–C_3 hydrocarbons and their chloroderivatives in order to obtain tetrachloroethylene and tetrachloromethane in variable proportions. The process is carried out in a hollow reactor at temperatures in the range 833–873 K or in a fluidised sand bed at 773–823 K.

Despite the fact that the C–Cl bond energy in trichloromethane is higher than in tetrachloromethane, the rate of decomposition of the latter at 832 K is 15 times smaller than that of trichloromethane.[44] This is explained[44] by the biradical decomposition of trichloromethane ($CHCl_3 \rightarrow HCl + :CCl_2$), after which the following reactions can occur:

$$:CCl_2 + CHCl_3 \rightarrow HCl + C_2Cl_4 \text{ or}$$
$$:CCl_2 + CHCl_3 \rightarrow CHCl_2CCl_3 \rightarrow HCl + C_2Cl_4,$$
$$:CCl_2 + CHCl_3 \rightarrow \dot{C}Cl_3 + \dot{C}HCl_2,$$
$$2\dot{C}Cl_3 \rightarrow C_2Cl_6.$$

The temperature dependence of the rate constant is described by the equation $k = 2.61 \times 10^{11} \exp(-197\,000/RT)$ s^{-1}.

Another expression has been quoted[49] for the trichloromethane decomposition rate constant: $k = 6.3 \times 10^8 \exp(-157\,000/RT)$ s^{-1}, but the values of the constant at temperatures in the range 750–850 K differ little from those of Shilov and Sabirova.[48] A radical mechanism has been proposed for the decomposition process: $CHCl_3 \rightarrow \dot{C}HCl_2 + Cl^{\cdot}$. The main decomposition products are HCl and C_2Cl_4, as well as C_2Cl_6, C_2HCl_5, etc.

The study of the thermal decomposition of trichloromethane with the aid of shock waves[50] has confirmed the formation of the $:CCl_2$ biradicals and hydrogen chloride.

In the thermal decomposition of dichloromethane (806 K), CH_3Cl, $CHCl{=}CCl_2$, C_2Cl_4, $CHCl_3$, CCl_4, and *cis*- and *trans*-$CHCl{=}CHCl$ were detected.[51] The activation energy for the decomposition is 184 kJ mol^{-1}. The authors[51] propose a degenerate-branched mechanism involving the formation of an intermediate (dichloroethylene), chain propagation with the aid of $Cl^{\cdot}$ atoms and the radicals $\dot{C}H_2Cl$, and the chain branching reaction $CHCl{=}CHCl \rightarrow \dot{C}_2H_2Cl + Cl^{\cdot}$.

It must be recognised that the biradical decomposition of dichloromethane is nevertheless more probable. The formation of biradicals (or carbenes) in the decomposition of dichloromethane and trichloromethane was demonstrated in an early study by Semenov.[26]

The decomposition of dichloromethane was not observed in the temperature range 673–753 K in a gradient-free quartz reactor with a stirrer which had been coated with carbon beforehand.[52]

The heterogeneous thermal decomposition of tetrachloromethane[53] as well as trichloromethane and dichloromethane[54] has been studied at temperatures in the range 773–873 K on a quartz fibre (S_{sp} = 0.26 m^2 g^{-1}) and on carbon black (S_{sp} = 100 m^2 g^{-1}) both of which had been coated beforehand with a layer of pyrolytic carbon obtained as a result of the decomposition of toluene.

The ratios of the rate constants (in g cm^{-2} s^{-1} Pa^{-1}) for the pyrolysis of tetrachloromethane, trichloromethane, and dichloromethane at 773 K are 1:80.6:15.7. The rate of formation of pyrolytic carbon on quartz in the decomposition of dichloromethane is given by the equation $w = 7.7 \times 10^{-4} p \exp(-163\,000/RT)$, while in the decomposition of trichloromethane the equation is $w = 2.1 \times 10^{-3} p \exp(-159\,000/RT)$.

The decomposition of chloromethanes on the surface of pyrolytic carbon at a low pressure in the temperature range 850–1280 K has been investigated.[55] While CH_3Cl is stable under the conditions investigated, the decomposition of CH_2Cl_2 and CCl_4 over clean silicon dioxide surface takes place initially with appreciable self-acceleration as a result of the formation of soot on the reactor walls and then the rate of the decomposition reaction remains constant but twice as high as the rate of the homogeneous pyrolysis under the same conditions.

An analogous increase in the rate of reaction during the initial period in the decomposition of dichloromethane on alumina (S_{sp} = 10 m^2 g^{-1}) was noted by Kovaleva et al.[56] The rate of decomposition then begins to fall. Simultaneously with the change in the degree of deposition of carbon, the specific surface of the decomposition catalyst initially increases and then falls.

The rate of the catalytic decomposition of dichloromethane depends on its concentration (with an exponent of unity) and has an activation energy of 105 kJ mol^{-1}.[57] Only carbon and hydrogen chloride were detected among the catalytic decomposition products[57] in accordance with the proposed reaction mechanism:

$$CH_2Cl_2 \rightarrow CHCl_{ads} + HCl,$$
$$CHCl_{ads} \rightarrow C + HCl$$

The study of the decomposition of chloromethanes in a fluidised activated charcoal bed was undertaken by Shatalov et al.[58] The qualitative results obtained agree with the decomposition reaction mechanisms proposed by Shilov and Sabirova.[46-48] The decomposition of mixtures of various chloromethanes and mixtures of methane with chloromethanes has also been studied.[58] For example, it has been noted that, in the presence of CH_4, the degree

of decomposition of tetrachloromethane increases, apparently as a result of the binding of chlorine.

A thermodynamic analysis of the reversible reactions in the formation of chloromethane has been carried out:[59]

$$CH_4 + CCl_4 \rightleftarrows CH_3Cl + CHCl_3,$$
$$CH_4 + CHCl_3 \rightleftarrows CH_3Cl + CH_2Cl_2,$$
$$CH_3Cl + CCl_4 \rightleftarrows CH_2Cl_2 + CHCl_3.$$

The highest equilibrium constant was obtained for the first reaction.

The study of the interaction of tetrachloromethane and methane showed that the experimental data are in satisfactory agreement with calculations based on the known constants for the elementary stages.[60] The exchange reaction has an order of 1.5 (0.5 with respect to CCl_4 and 1 with respect to CH_4) and the effective calculated rate constant given by

$$k = 10^{14.94} \exp(-205\,600/RT)\ \text{cm}^{1.5}\ \text{mol}^{-0.5}\ \text{s}^{-1}.$$

Thus the thermal stabilities of chloromethanes increase in the sequence $CHCl_3 < CH_2Cl_2 < CCl_4 < CH_3Cl$, and the pyrolytic carbon formed in the decomposition process can accelerate further decomposition. Apparently a proportion of the C_2 chlorohydrocarbon impurities are obtained from the radicals and biradicals formed on decomposition of chloromethanes.

IV. Benson's process

It is of interest that "undesirable" (in the synthesis of chloromethanes) reactions involving the decomposition of chloromethanes and the recombination of radicals have been used by Benson to develop a process for the preparation of hydrocarbons by the high-temperature interaction of chlorine with methane.[61] The process is carried out at atmospheric pressure, high temperatures (973–1983 K), methane : chlorine ratios ranging from 1:1 to 10:1, and short contact times counted in milliseconds. The combustion of a mixture of methane with chlorine results in the formation of ethane at temperatures of about 1000 K or of ethylene and hydrogen at temperatures of about 2000 K.

The method consists in chlorinating methane to chloromethane, the pyrolysis of chloromethane, and the formation of C_2 hydrocarbons as a result of the recombination of hydrocarbon radicals.[62]

The thermal reaction of a mixture of chlorine and methane has been investigated[63,64] at temperatures in the range 1081–1273 K, at pressures in the range 150–577 mm Hg, for a chlorine content in the mixture with methane of 0.42–1.2%, and for contact times of 0.8–1.6 s. The carbon-containing products are CH_3Cl, C_2H_4, C_2H_6, C_2H_2, and C_3H_6. The fraction of the non-chlorinated unsaturated hydrocarbons increases with increase in temperature and reaches 77% at 1273 K. The following radical process mechanism, divided into several stages, has been proposed:

I. Initial ethane

Initiation:

$$CH_4 \rightarrow \dot{C}H_3 + H^{\cdot},$$
$$Cl_2 + M \rightarrow 2\,Cl^{\cdot} + M.$$

Chain transfer:

$$H^{\cdot} + CH_4 \rightarrow H_2 + \dot{C}H_3,$$
$$H^{\cdot} + Cl_2 \rightarrow HCl + Cl^{\cdot}.$$

Chain propagation:

$$\dot{C}H_3 + Cl_2 \rightarrow CH_3Cl + Cl^{\cdot},$$
$$Cl^{\cdot} + CH_4 \rightarrow HCl + \dot{C}H_3.$$

Chain termination:

$$2\,\dot{C}H_3 \rightarrow C_2H_6. \qquad (3)$$

Chain termination is also possible (to a lesser extent) via the reaction:

$$\dot{C}H_3 + Cl^{\cdot} \rightarrow CH_3Cl,$$
$$\dot{C}H_3 + H^{\cdot} \rightarrow CH_4. \qquad (4)$$

The first stage can be characterised by the overall equations:

$$2\,CH_4 + Cl_2 \rightarrow C_2H_6 + 2HCl,$$
$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl.$$

II. Second stage

$$\dot{C}H_2Cl + RH \rightleftarrows CH_3Cl + R^{\cdot},$$
$$\dot{C}H_2Cl + Cl_2 \rightarrow CH_2Cl_2 + Cl^{\cdot},$$
$$\dot{C}_2H_5 \rightarrow C_2H_4 + H^{\cdot},$$
$$\dot{C}_2H_5 + RH \rightleftarrows C_2H_6 + R^{\cdot},$$
$$\dot{C}_2H_5 + Cl_2 \rightarrow C_2H_5Cl + Cl^{\cdot},$$
$$\dot{C}H_3 + \dot{C}H_2Cl \rightarrow C_2H_5Cl, \qquad (5)$$
$$2\,\dot{C}H_2Cl \rightarrow CH_2Cl{-}CH_2Cl. \qquad (6)$$

The concentration of the $CH_2Cl^{\cdot}$ radicals is negligible compared with the $\dot{C}H_3$ concentration so that the chain termination via reactions (5) and (6) is insignificant compared with the termination via reaction (3).

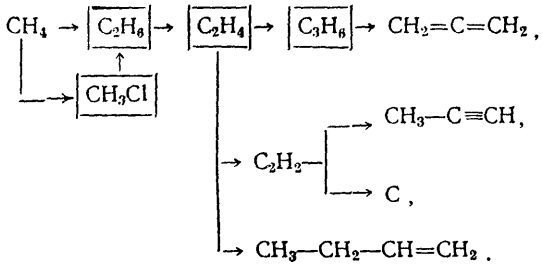
III. Third stage

$$\dot{C}H_3 + C_2H_4 \rightleftarrows CH_3{-}CH_2{-}\dot{C}H_2,$$
$$\dot{C}_2H_5 + C_2H_4 \rightarrow CH_3{-}CH_2{-}CH_2{-}\dot{C}H_2,$$
$$CH_3{-}CH_2{-}\dot{C}H_2 \rightarrow CH_3{-}CH{=}CH_2 + H^{\cdot},$$
$$CH_3{-}CH_2{-}CH_2{-}\dot{C}H_2 \rightarrow CH_3{-}CH_2{-}CH{=}CH_2 + H^{\cdot},$$
$$R^{\cdot} + C_2H_4 \rightarrow RH + \dot{C}_2H_3,$$
$$\dot{C}_2H_3 \rightarrow C_2H_2 + H^{\cdot}.$$

IV. Fourth stage

$$\dot{C}H_3 + C_2H_2 \rightleftarrows CH_3{-}CH{=}\dot{C}H,$$
$$R^{\cdot} + CH_3{-}CH{=}CH_2 \rightarrow RH + \dot{C}H_2{-}CH{=}CH,$$
$$R^{\cdot} + C_2H_2 \rightarrow RH + CH{\equiv}C^{\cdot},$$
$$CH_3{-}CH{=}\dot{C}H \rightarrow CH_3{-}C{\equiv}CH + H^{\cdot},$$
$$CH{\equiv}C^{\cdot} \rightarrow 2C + H^{\cdot},$$
$$\dot{C}H_2{-}CH{=}CH_2 \rightarrow CH_2{=}C{=}CH_2 + H^{\cdot}.$$

Under the conditions indicated, Benson's process can be summarised by means of the scheme presented below, the main products being ethane, ethylene, chloromethane, and propene, while the rest are present as impurities:



In our view, in the scheme for the initial stage it is necessary to make provision for the decomposition of methyl chloride, i. e. the reaction which is the reverse of reaction (4), as a result of which the $\dot{C}H_3$ and $Cl^{\cdot}$ radicals are returned to the reaction sphere and virtually the only possible termination involves the recombination of the $\dot{C}H_3$ radicals. Benson's process is based on the ease of dissociation of chlorine and the lower thermal stability of methyl chloride compared with methane.

V. Oxidative chlorination of methane and its chloro-derivatives

One of the deficiencies of the processes involving the direct chlorination of methane and its chloro-derivatives, not mentioned above, is the conversion of half of the chlorine used into hydrogen chloride. The necessity to utilise increasing amounts of the latter has been the cause of the development of a method for the oxidative chlorination of methane, where the chlorinating agent is a mixture of hydrogen chloride and oxygen.

The oxidative chlorination of methane is based on the oxidation of hydrogen chloride by oxygen to chlorine, which is usually carried out in the gas phase copper chloride-containing catalysts.

From the results of kinetic studies of the oxidative chlorination of methane, it has been concluded[14,23,65] that the oxidation of hydrogen chloride (also called the Deacon reaction) takes place at the same rate both in the presence and absence of methane, i.e. regardless of its subsequent chlorination. The oxidation of hydrogen chloride to chlorine is a reversible reaction, which usually occurs at temperatures in the range 623–723 K, the equilibrium constant K_e decreasing appreciably with increase in temperature. When the Deacon reaction and the methane chlorination reaction take place simultaneously, the equilibrium in the first reaction is displaced as a result of the consumption of chlorine, as can be seen from the data presented below:[2]

$$2n\,HCl + n/2O_2 \rightleftarrows n\,Cl_2 + n\,H_2O,\quad K_e(700\ K)\,8.3,$$
$$CH_4 + n\,Cl_2 \rightarrow CH_{4-n}Cl_n + n\,HCl$$
$$CH_4 + n\,HCl + n/2\,O_2 \rightarrow CH_{4-n}Cl_n + n\,H_2O,$$
$$K_e(700\ K)\,9.1\cdot10^{8} - 9.8\cdot10^{33}.$$

A number of recent publications have been devoted to the gas-phase heterogeneous-catalytic oxidative chlorination of hydrocarbons and their chloro-derivatives.[2,23,66]† The problem of the oxidative chlorination of methane will therefore be considered here in a more concise form.

Since, as can be seen from the above, the methane chlorination reaction at temperatures at which the Deacon reaction is carried out can proceed without the participation of a catalyst, the main task in the development of a process for the oxidative chlorination of methane is the selection of a catalytic system for the first stage.

Despite a number of advances achieved on these lines, copper(II) chloride, proposed as the catalyst for the oxidation of hydrogen chloride already in the past century, still remains the main component of catalysts for the Deacon and oxidative chlorination reactions.[67] Catalytic systems based on palladium, chromium, and iron chlorides proved to be less active.[68] Platinum(II)–platinum(IV) chloride complexes have been recently proposed as well as the complex $K_4Ru_2OCl_{10}$; being deposited on alumina or silicon dioxide, they catalyse the oxidative chlorination of methane in aqueous solutions or in the gas phase.[69,70] The catalysts obtained proved to be more active than catalysts based on copper and potassium chlorides. Our studies on catalysts which Tret'yakov et al.[69,70] prepared by adding a ruthenium complex to copper and potassium chlorides on α-alumina confirmed the higher activity of the ruthenium-containing catalyst. However, the addition of a lanthanide chloride[71] proved to be more effective.

It is noteworthy that catalysts for the oxidative chlorination of methane based on copper, alkali metal, and alkaline earth metal chlorides on a porous carrier constitute an extremely unusual system; apart from the traditional questions of activity, selectivity, and stability, problems associated with the volatility of copper chlorides in the formation of a melt of catalytically active salts under the reaction conditions arise here.

The addition of alkali metal chlorides to copper chloride diminishes the volatility of the latter.[72] The greatest decrease in volatility is observed when rubidium chloride is added, but, as regards the combination of efficiency with availability, preference was given to potassium chloride. The dependence of the volatility of copper chlorides and of the activity of the catalyst on the ratio $KCl:CuCl_2$ is illustrated in Fig.4. The equimolar ratio has been recognised as optimal in terms of the combination of activity and stability. The influence of the nature of the alkali metal (lithium, sodium, potassium, and caesium) and of the potassium : copper ratio in catalytic systems on the kinetic parameters of the hydrogen chloride oxidation reaction has been examined in detail.[23] The changes in these parameters are attributed to the formation of copper and alkali metal chlorides. It is most likely that this is also the cause of the decrease in the volatility of copper chlorides.

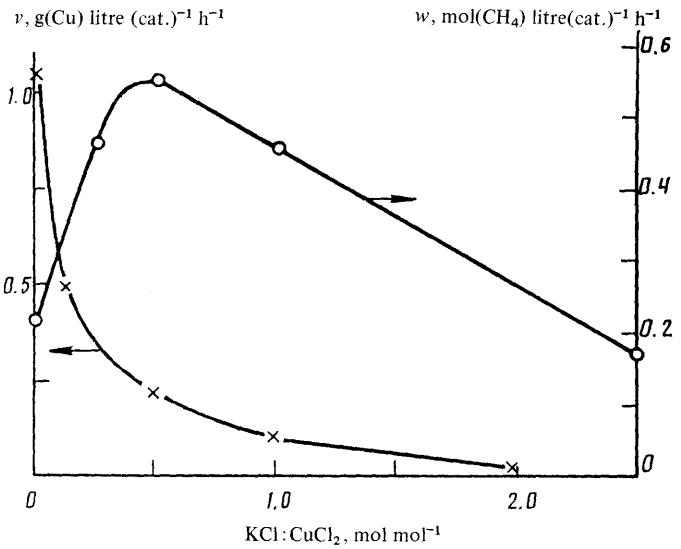


Figure 4. Dependence of the activity and stability of the catalysts for the oxidative chlorination of methane on the $KCl:CuCl_2$ ratio;[14,72] *w*—rate of overall conversion of methane at 648 K; *r*—rate of volatilisation of copper chlorides at 723 K.

†Yu A Treger, V N Rozanov, M R Flid, L M Kartashov, *Uspekhi Khim.*, 1988, **57** 577 [*Russ. Chem. Rev.*, 1988(4)]

The influence of potassium chloride on the activity of the catalyst based on copper chloride in the oxidative chlorination of methane has been investigated in detail in a recently published study.[73] The maximum activity was observed for the ratio potassium : copper = 1, the composition of the chloromethanes obtained varying as a function of the presence or absence of potassium chloride.

The attempts to bind copper in the spinel structure ($CuAl_2O_4$, $CuCr_2O_4$) in order to eliminate the volatility were unsuccessful, since, under the conditions of an excess of hydrogen chloride at an elevated temperature, these compounds gradually decompose with segregation of copper chloride as the active component of the catalyst.[68,74]

A melt of the active mass of the copper and potassium chlorides, on carriers of different chemical nature and with different specific surfaces, forms in the extensive pore system of the carrier isolated inclusions with a thickness equivalent to 10–200 molecular layers.[75,76]

The interaction of the salts with the carrier, the surface migration of the salt phases, and the change in the structure and surface area of the salt clusters have been demonstrated by electron microscopy and also by studying adsorption in conjunction with X-ray diffraction and differential thermal analysis.[77]

Porous substances with a wide range of specific surfaces are used as carriers for the catalysts of the oxidative chlorination of methane.[66] However, the choice of the carrier is fairly specific. For example, when the process is carried out in a fluidised catalyst bed, the use of carriers with a large specific surface proved preferable, since this ensures excellent fluidisation without bubbles and lumps.[78] However, on these catalysts the process selectivity, characterised by the degree of conversion of methane into chloromethanes relative to the overall conversion into chloromethanes and carbon oxides, is lower than in the case where inert carriers with a limited specific surface are used. At the same time, the catalysts on carriers with a limited specific surface in a fluidised bed form lumps probably owing to the partial emergence of the melt onto the surface. As a result, carriers with an average specific surface of 10–60 $m^2\ g^{-1}$ proved optimal.[78]

In the stationary catalyst bed, one can use carriers with a specific surface less than 10 $m^2\ g^{-1}$, but when it is reduced to 1 $m^2\ g^{-1}$ and less, the corrosion of the metallic walls of the reactor at the sites of contact intensifies sharply, which is also most probably associated with the presence of the melt.[79] Under these conditions, iron chloride, a corrosion product, enters the catalyst and increases the rate of the extensive oxidation of methane and chloromethanes to carbon oxides, while nickel and chromium chlorides hardly affect the activity and selectivity of the catalyst.[80]

Communications have been published recently concerning the possibility of carrying out the oxidative chlorination of methane at relatively low temperatures (less than 473 K) by using colloidal silicon dioxide as the carrier.[81]

The kinetics and mechanism of the oxidative chlorination of methane on traditional catalysts with copper chlorides have been described in greatest detail in Refs. 14, 23, 65, and 82. It was shown that the oxidation of HCl proceeds throughout the bulk of the salt melt with participation of copper chloride. The rate of the Deacon reaction is independent of the partial pressure of hydrogen chloride when it is above 0.04 atm, its observed reaction order with respect to oxygen is 0.5, and, when account is taken of the inhibiting effect of chlorine, it is unity. The observed activation energy on the catalyst containing an equimolar mixture of copper and potassium chlorides is 129 kJ mol^{-1}.

The process mechanism put forward by Slama and Kodajs[83] in connection with the observed second order of the oxygen absorption reaction with respect to Cu^+ assumes the following form:

$$2\,CuCl_2 \overset{\text{fast}}{\rightleftarrows} 2CuCl + Cl_2,$$
$$2\,CuCl + O_2 \xrightarrow{\text{slow}} Cu_2O_2Cl_2,$$
$$Cu_2O_2Cl_2 + 4HCl \xrightarrow{\text{fast}} 2CuCl_2 + Cl_2 + 2\,H_2O.$$

The following kinetic equation corresponds to this mechanism:

$$w = 4kK\,[CuCl_2]^2\ p_{O_2}/p_{Cl_2} = k' p_{O_2}/p_{Cl_2},$$

where k is the rate constant, K the equilibrium constant, and $k' = 4kK[CuCl_2]^2$.

The above mechanism may serve as an illustration of one of the first theories of catalysis, which explains the mechanism of the catalytic reaction by the formation of intermediate compounds which are then converted into the reaction products with regeneration of the initial catalysts. All the stages of the mechanism have been investigated separately and can proceed as independent reactions.[84,85]

On the basis of the results of the study of the adsorption of oxygen, Ruthven and Kenney[86] believe that the rate of the Deacon reaction is determined by the rate of oxidation of CuCl to $CuCl_2$ and is described by the equation

$$w = 4k\gamma^2K^2a^2p_{O_2}\{\gamma K + (p_{Cl_2})^{1/2}\}^2,$$

where K is the equilibrium constant of the thermal dissociation of copper chloride, a the mole fraction of copper in the melt, γ the ratio of the activity coefficients of Cu^{2+} and Cu^+, and k the rate constant for the absorption of oxygen.

When $(p_{Cl_2})^{1/2} \gg \gamma/K$, the familiar equation

$$w = k'' p_{O_2}/p_{Cl_2}, \text{ where } k'' = 4k\gamma^2K^2a^2,$$

holds. Two probable mechanisms of the HCl oxidation reaction have been examined.[23] The author took into account primarily data (including his own) concerning the complex-forming properties of copper, which influence both the stage involving the formation of the active form of the catalyst and the stage in which the reactants are activated in the oxidation-reduction reaction. It is notable that the formation of complexes between copper and potassium chlorides, namely $KCuCl_3$, K_2CuCl_4, K_2CuCl_3, and $K_2Cu_2Cl_6$, has been noted by many investigators.[83–87]

The first mechanism is based on the fact that chlorine is formed in the copper(II) chloride decomposition stage, the copper(II) chloride being regenerated by reaction with oxygen and then with hydrogen chloride. In the second mechanism, chlorine is evolved in the stage involving the interaction of oxygen with copper(II) chloride which is promoted by the formation of complexes with HCl and KCl.

Subject to certain assumptions, the equations corresponding to both mechanisms simplify and are converted into

$$w = k'''(p_{O_2}/p_{Cl_2}).$$

Gel'bshtein[23] gave preference to the first mechanism.

The kinetics of the formation of chloromethanes proved to be the same both in the oxidative chlorination reaction and in the direct chlorination reaction in the presence of the $CuCl_2$–KCl system.[14,65,82] Both reactions are characterised by the first kinetic order with respect to methane, a fractional order with respect to

chlorine, and virtually identical activation energies (113 kJ mol^{-1}). The rates of the oxidative chlorination and chlorination can be described with the same accuracy by an equation of the fractional-rational type:

$$w = \frac{kp_{CH_4} \cdot p_{Cl_2}}{1 + ap_{Cl_2} + bp_{O_2}},$$

where a and b are adsorption coefficients. Or they can be described by the equation

$$w = kp_{CH_4}\, p_{Cl_2}^{0.6}\, p_{O_2}^{-n},$$

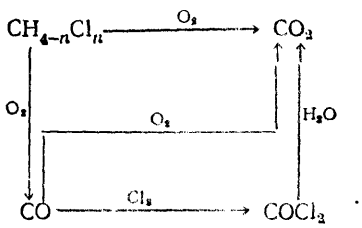
where n varies from 0.25 to 0 as the temperature increases.

It is of interest that the rate of chlorination is independent of the presence of copper in the salt composition, i.e. the presence of variable-valence metal cations in the centres on which chlorination takes place is not obligatory. It has been suggested[14,65,82] that the chlorination of methane at temperatures below 425 °C takes place on the surface of the melt preferentially as a result of the interaction with a polyhalide complex of the type ZCl_3 formed when molecular chlorine is chemisorbed by metal chlorides. An increase in temperature increases the contribution of the reaction involving the thermal volume chlorination by free chlorine.

Subsequently, evidence in support of the catalytic or heterogeneous-homogeneous chain mechanism of the chlorination of methane in the presence of oxidative chlorination catalysts was re-examined by Aglulin.[29] It was established that in a flow-circulation apparatus there is a possibility of additional chlorination in the free volume as a result of the contamination of the glass surface by volatile catalytic compounds (copper and iron chlorides) and also under the influence of light. The reduction of the distorting factors to a minimum enabled the authors[29] to support the heterogeneous-homogeneous mechanism of chlorination under the conditions of the oxidative methane chlorination reaction.

The use of semiconductor detectors, mass-spectrometric and molecular beam methods made it possible to develop these ideas.[88] On interaction with molecular chlorine, the carrier or catalyst generates atomic chlorine in space and subsequent chlorination proceeds via the usual chain mechanism.

The kinetics of the side reactions in the oxidation of methane and its chloro-derivatives have been established.[82] The mechanism of the formation of carbon oxides assumes the following form:



The rates of formation of carbon oxides are described by the following equations at $p_{Cl_2} > 0.01$ atm:

$$w_{CO} = \frac{k_i^{CO}\, p_i\, p_{O_2}\, p_{HCl}}{1 + Kp_{HCl}},$$

$$w_{CO_2} = \frac{k_i^{CO_2} p_i p_{O_2}}{1 + Kp_{HCl}},$$

where k_i and p_i are the rate constants and partial pressures of methane and chloromethanes respectively and K is the equilibrium constant for the absorption of hydrogen chloride.

At $p_{Cl_2} < 0.01$ atm, the rates of formation of carbon oxides depend also on $p_{Cl_2}^{0.5}$. The ratios of the rates of oxidation of methane and chloromethanes are $CH_3Cl:CH_2Cl_2:CHCl_3:CH_4:CCl_4 = 1:0.5:0.33:0.18:0.033$.

The mechanism of the extensive oxidation reactions has been hardly investigated. It is believed[89] that the oxidation reactions of hydrogen chloride and the reactions leading to the extensive oxidation of methane and chloromethanes are catalytic and that chlorination takes place mainly as a homogeneous process.

The view has been expressed[90] that the chlorination of methane occurs on the surface of the melt of copper chlorides. This is justified by the different selectivities in the formation of chloromethanes in catalytic and thermal chlorination processes and by the considerable difference between the rate of evolution of chlorine from the melt and the rate of chlorination. However, the activation energies obtained for the catalytic chlorination of methane (176 kJ mol^{-1}) and the oxidative chlorination of methane (172 kJ mol^{-1}) do not agree with the known values for the energy barriers in the gas-phase chlorination of methane (139 kJ mol^{-1}) and the oxidation of hydrogen chloride (126 kJ mol^{-1}), which can be associated with the change in the activity of the catalyst.

In conclusion one should note that the oxidative chlorination of methane has not been achieved on an industrial scale anywhere in the world. By virtue of the large amount of experimental and design studies, a balanced (with respect to chlorine) industrial manufacture of chloromethanes has been planned and is being established in the USSR, where the entire hydrogen chloride formed in the direct methane chlorination stage is processed in the oxidation chlorination stage. The report[91] concerning the construction of a plant for the preparation of chloromethanes by the oxidative chlorination of methane in fused salts was not confirmed—apparently technological difficulties arose.

VI. Interaction of methanol with hydrogen chloride

The heat of the reaction

$$CH_3OH + HCl \rightarrow CH_3Cl + H_2O$$

is low (32.9 kJ mol^{-1}). Dimethyl ether is formed as a side product:

$$2\,CH_3OH \rightarrow (CH_3)_2O + H_2O.$$

Dimethyl ether also interacts with hydrogen chloride:

$$(CH_3)_2O + 2HCl \rightarrow 2\,CH_3Cl + H_2O.$$

As a result, the selectivity in the formation of chloromethane is usually high and amounts to more than 99%.

Chloromethane can be synthesised from methanol and hydrogen chloride in both liquid and gas phases. Under laboratory conditions, chloromethane is obtained by refluxing methanol with hydrochloric acid without a catalyst. The kinetics of the reaction of hydrogen chloride with methanol at 363 K have been investigated.[92] When the initial hydrogen chloride concentration is varied from 0.115 to 1.623 M, the relative equilibrium degree of conversion of methanol changes only slightly—from 96.5 to 96.1%. The same method of synthesis has been proposed also for use in industry.[93,94] The process temperature is 343–423 K. Zinc chloride is usually employed as the catalyst of the liquid-phase process and a quaternary ammonium halide has been proposed for this purpose recently.[95]

However the majority of companies prefer to carry out the reaction of methanol with hydrogen chloride in the gas phase in the presence of a catalyst in the industrial manufacturing process.[4] Chloromethane is obtained in the USSR by the same method. The reaction is usually carried out in an excess of hydrogen chloride (about 30%), which suppresses the formation of dimethyl ether as the side product; the degree of conversion of methanol under these conditions is about 99%.

A comparative study of the catalytic activities of various salts (zinc, magnesium, calcium, strontium, barium, manganese, cobalt, nickel, copper, cadmium, bismuth, and mercury chlorides) in the reaction of methanol with hydrogen chloride has been carried out in a study for a dissertation.[96] It was shown that zinc chloride exhibits the highest catalytic activity. Comparative tests of various carriers (alumina, activated charcoal, silica gel) for the catalytically active zinc chloride mass led to the selection of activated alumina. The catalytic activity of pure alumina has also been studied.

The rate of reaction of methanol with hydrogen chloride is described by the equation

$$w_1 = k_1\, p_{CH_3OH}\, p_{HCl}.$$

The activation energy for the reaction in the presence of the catalyst containing 60% of zinc chloride on alumina is 36.5 kJ mol^{-1} and that on pure alumina is 51.5 kJ mol^{-1}, the pre-exponential factors being respectively 2.2×10^8 and 1.5×10^8 litre litre(cat.)$^{-1}$ h^{-1} atom^{-2}.

The kinetic equation for the side reaction involving the formation of dimethyl ether is

$$w_2 = k_2\, p^2_{CH_3OH}.$$

The activation energies for the side reactions in the presence of the same catalysts (60% $ZnCl_2/Al_2O_3$ and Al_2O_3) are 192 and 96 kJ mol^{-1} and the pre-exponential factors at 10^{19} and 2.5×10^{12} litre litre(cat.)$^{-1}$ h^{-1} atm^{-2} respectively.

The kinetics of the reaction of dimethyl ether with hydrogen chloride have also been studied.[96] It was found that the rate of reaction depends on the partial pressures of dimethyl ether and hydrogen chloride with an exponent of unity. It is suggested that the last reaction takes place consecutively—via a stage involving the interaction of dimethyl ether with one hydrogen chloride molecule:

$$w_0 = k\, p^0_{HCl}\, p^0_{CH_3OH}/\{1 + (K_{HCl}\, p^0_{HCl})^{1/4}\}^2,$$

and the methanol formed then reacts with another HCl molecule. Here we have $k_3 < k_1$.

Various possible mechanisms of the main reaction have been examined.[96] It has been suggested that a ternary complex of the metal chloride with methanol and HCl is formed as an intermediate[97] and then decomposes into the reaction products.

A correlation-regression analysis has been carried out[98-100] for the heterogeneous-catalytic reaction involving the synthesis of chloromethane from methanol and hydrogen chloride. Out of the 16 kinetic equations for the initial rate of reaction at temperatures in the range 423–473 K, the following equation was selected after resorting to IR spectroscopic data:

$$w_0 = k\ p^0_{HCl}\ p^0_{CH_3OH}/\{1 + (K_{HCl}\ p^0_{HCl})^{1/2}\}^2,$$

where p^0_{HCl} and $p^0_{CH_3OH}$ are the initial partial pressures of hydrogen chloride in methanol and K_{HCl} is the adsorption constant for hydrogen chloride.[99] It is suggested that the reaction takes place on the surface between the hydrogen chloride dissociatively adsorbed on activated charcoal and methanol from the gas phase.[100]

In a study of the kinetics of the reaction of hydrogen chloride with methanol over alumina,[101] it was found that the rate of reaction depends on the partial pressure of HCl with an exponent of unity and is independent of the partial pressure of methanol. The differential rate constant is proportional to the specific surface of the catalyst and is independent of its crystalline modification. Ageing of the catalyst takes place as a result of the deposition of carbon, its activity diminishing exponentially as a function of time.

Studies by Svetlanov[96] made it possible to develop and apply in an industrial process a stronger and more stable catalyst containing 35–38 wt.% of zinc chloride on active γ-alumina instead of the previously employed catalyst (zinc chloride on activated charcoal). The reaction kinetics were revised for the recommended catalyst and a mathematical model of the process was set up, which made it possible to design and recommend a two-compartment adiabatic reactor instead of the tubular reactor currently used.

An analogous catalyst ($ZnCl_2/Al_2O_3$) has been proposed in a patent.[102]

Nevertheless, even this improved catalyst, used nowadays in the industrial manufacture in the USSR,[103] has an appreciably shorter useful life (approximately half a year) compared with the useful life of catalysts of the best foreign companies (1–2 years). This stimulated further research into factors influencing the stability of the catalyst of the synthesis of chloromethane. One of the causes of the decrease in the activity of the catalyst with time is the volatilisation of its active component—zinc chloride.[104] It has been established that the carrier greatly retards the desorption of zinc chloride and that a limiting degree of desorption of zinc chloride corresponds to each temperature. The thermal desorption of zinc chloride from the carrier surface increases by a factor of 3–4 in the presence of reactants, in the first place methanol. Modifying additives have made it possible to reduce by a factor of 2–3 the loss of the active component.[104]

The gradual decrease in the rate of sublimation of zinc chloride as a function of time occurs, according to Grinberg et al.,[105] initially as a result of the slow establishment of the capillary equilibrium within the carrier pores and then as a result of the strengthening of the bond between the salt and the carrier surface.

In contrast to the above view,[105] according to which the surface of the catalyst working above the melting point of zinc chloride is the surface of melt menisci, fusion structures were not discovered in the study of Glazunova et al.[106] Apart from $ZnCl_2$, variable-composition zinc hydroxide chlorides as well as the structures resulting from the insertion of zinc into the spinel-type aluminium oxide lattice were detected by X-ray diffraction and thermal analyses.

Another factor influencing the stability of the operation of the catalyst of the synthesis of chloromethane is the deposition of carbon on its surface during the reaction. It has been observed[107] that the decrease in the specific surface of catalyst on deposition of carbon is associated with the reduction of the fraction of pores with effective dimensions less that 20 Å. A relation between the degree of deposition of carbon, on the one hand, and the surface acidity and the irreversible adsorption of methanol, on the other, has been demonstrated.

It is noteworthy that γ-alumina without salts is normally employed abroad in the manufacture of chloromethane from methanol and hydrogen chloride. Salt-free catalysts are used at a somewhat higher temperature, apparently in order to block the highly acid centres which are responsible for the deposition of carbon on the

catalyst and it is recommended that a small amout (0.05–2.0 wt.%) of an alkali metal oxide be introduced into the γ-alumina.[108]

It has been suggested that the reaction of methanol with hydrogen chloride be carried out in the presence of a natural or synthetic ion-exchange zeolite.[109] Chlorine-containing hydrogen chloride reacts with methanol in the gas phase and in the presence of alumina containing <0.5 wt.% of iron (as iron oxide).[110] A mixture obtained by chlorinating methane and containing methane, chloromethanes, nitrogen, and a small amount of chlorine is used in certain cases.[95,102]

In view of the difficulty of applying the oxidative chlorination of methane on an industrial scale, the reaction of methanol with hydrogen chloride has found extensive application abroad, as an HCl-consuming stage, in the industrial manufacture of chloromethanes from methanol and chlorine.[4] Chloromethane is chlorinated in the gas or liquid phase to di-, tri-, and tetrachloromethanes and the hydrogen chloride formed is used to synthesise chloromethanes from methanol. Although methanol is in fact more expensive than methane, the solution of the problem of the utilisation of hydrogen chloride by a relatively simple procedure compensates for the increased cost of the raw material.

VII. Hydrodechlorination of tetrachloromethane

The hydrodechlorination of tetrachloromethane has assumed major importance recently in connection with the positive imbalance which has arisen in the manufacture and consumption of tetrachloromethane. The large excess of tetrachloromethane is caused, firstly, by the cessation of its use as the raw material for the manufacture of Freons 11 and 12, which decompose the ozone layer; secondly, there has been a continuous growth of the processing of waste from organochlorine industries by exhaustive chlorination to perchlorocarbons (CCl_4 and C_2Cl_4). The presence of the stage involving the selective hydrodechlorination of tetrachloromethane to $CHCl_3$, CH_2Cl_2, and CH_3Cl combined with the direct chlorination of methane makes it possible to obtain chloromethanes in any required proportions.

Various methods are known for the reduction of tetrachloromethanes. For example, chloroform can be obtained by the slow (3–4 days) reduction of CCl_4 with iron and hydrochloric acid at 288 K or by treatment with zinc dust and a 50% NH_4Cl solution at 323–333 K and also by treatment with water, zinc, and nickel.[111]

Various methods for the reduction of organochlorine compounds have been examined in reviews.[112,113] In the electrochemical reduction,[114] two electrons are consumed in the dissociation of the carbon–chlorine bond, the half-wave potential being independent of the pH of the medium and the reactions being reversible overall. There is a linear relation between the half-wave potentials for the reactions

$$RCl + 2e + H^+ \rightarrow RH + Cl^-$$

and the R–Cl bond dissociation energies. With an increase in the number of chlorine atoms in the molecule, the reduction is facilitated as a result of the shift of the half-wave potential in the positive direction. Thus the half-wave potentials (relative to the saturated calomel electrode) for chloromethanes are respectively −3.23, −2.33, −1.67, and −0.78 V. The reduction of tetrachloromethane yields mainly di- and tri-chloromethanes. A publication[115] has also been devoted to the study of the adsorption and dehalogenation of chloromethanes on a platinised platinum electrode.

In a number of studies, the CCl_3 group has been reduced to $CHCl_2$ with the aid of hydrogen donors. Thus it has been shown[116] that the reduction by treatment with $(CH_3)_2C_6H_4$ or $(C_2H_5)SiH$ with participation of $Fe(CO)_5$ takes place selectively as far as the $CHCl_2$ group. Mercaptans, n- and t-C_4H_9SH, and $C_6H_5CH_2SH$ have been used[117] to reduce the CCl_3 group in the presence of the metal carbonyls $Mo(CO)_6$, $W(CO)_6$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $Fe(CO)_5$. The $Re_2(CO)_{10}-(C_2H_5)_3SiH$ system has been used for the same purposes.[118] The reduction of CCl_4 by isopropyl alcohol initiated with iron, molybdenum, and manganese carbonyls has been described.[119] The reaction of tetrachloromethane with alcohols, catalysed by metal complexes,[120,121] in particular dichlorotris-(triphenylphosphine)ruthenium(II) $RuCl_2(PPh_3)_3$ and also by rhodium, ruthenium, and iridium complexes immobilised on polystyrene,[122] has been investigated:

$$R^1R^2CHOH + CCl_4 \rightarrow R^1R^2CO + CHCl_3 + HCl$$

Strunkina and Brainina[123] used the zirconium and hafnium hydride complexes Cp_3ZrH, Cp_3HfH, and Cp_2ZrClH for the reduction of CCl_4. A review has been devoted[124] to new redox catalysts for the homolytic reduction of trichloromethyl compounds to dichloromethyl compounds.

However, the hydrodechlorination of tetrachloromethane with the aid of hydrogen donors is relatively unpromising from the practical point of view; in the industrial process, it is necessary to use hydrogen as the reductant. Few studies have been carried out on these lines.

The gas-phase hydrodechlorination of tetrachloromethane on the Pt/Al_2O_3 catalyst has been investigated at temperatures in the range 285–396 K.[125] The reaction products are methane, trichloromethane, and hydrogen chloride, trichloromethane being inactive in the hydrogenation reaction even when it is added to the initial mixture. The authors proposed a radical reaction mechanism in which hydrogen and tetrachloromethane dissociate on platinum and then two parallel reactions take place: CCl_3 interacts with H_2 or absorbs atomic hydrogen, affording tri-chloromethane. In the alternative reaction, CCl_3 is readsorbed on platinum and is not desorbed until it is converted into CH_3 and three molecules of hydrogen chloride. The reaction of the CH_3 radical with hydrogen gives rise to methane.

The hydrodechlorination of CCl_4 by hydrogen has been investigated[126] at 643 K over the nickel-containing zeolites NiNaY, NiCuNaY, NiCrNaY, NiCoNaY, and CuNaY. The amount of nickel was 30 wt.%.

In the reaction of tetrachloromethane with hydrogen on palladium membrane catalysts, the formation of tetrachloroethylene and hexachlorobuta-1,3-diene has been observed.[127]

A study of the interaction of tetrachloromethane with hydrogen by the pulse compression method in a free-piston apparatus with characteristic process times of 10^{-3} s showed that the reaction occurs in two regions.[128] At 1150 K (degree of conversion up to 20%), the process is relatively slow. By regulating the composition of the initial mixture and the process temperature, it is possible to obtain a 16% yield of trichloromethane with a selectivity close to 100%. In a certain temperature range, under the conditions corresponding to the self-inflammation of the mixture, the reaction can be directed to the preferential formation of tetrachloroethylene.

The gas-phase hydrodechlorination of tetrachloromethane over the palladium catalyst has two characteristic features according to Zanaveskin:[129] firstly, the reaction does not stop at an intermediate stage but proceeds as far as the formation of methane and, secondly, the catalyst is rapidly deactivated.

In order to maintain the stable operation of the catalyst (platinum on alumina) in the hydrodechlorination of trichloromethane to dichloromethane, it has been recommended[130] that water, which according to the authors promotes the removal of chlorine from alumina, preventing excess acidity and the associated rapid deposition of carbon, be added to the initial mixture. The addition of a small amount of H_2S lowers the initial activity of the catalyst but increases its stability.

The hydrodechlorination of tetrachloromethane has been studied[131] on palladium catalysts in the liquid phase at temperatures in the range 313–343 K. On palladium acetates with added acetic acid and using C_7–C_{12} paraffins, ethyl methyl ketone dimethylformamide, dioxan, and benzyl alcohol as the solvents, the only reaction product proved to be methane. By carrying out the reaction in isopropyl and t-butyl alcohols as solvents, it was possible to obtain trichloromethane and chloromethane as the main products, the yield of methane varying from trace amounts to 5%. The catalyst containing 4% of palladium on charcoal proved to be more active (approximately by a factor of 20). However, the activities of both catalysts fall appreciably during the experiment (5 h). Only the catalyst containing 0.1% of palladium and 1% of KOH on γ-alumina retains its activity during the experiment.

It has been found[132] that the palladium–cobalt catalysts on activated graphite are more active in the reactions involving liquid-phase hydrogenation with hydrogen than any non-prefused metals.

By passing the vapours of chloromethanes over metals (Ni, Co, Cu, Fe, Rh, Pd) or alloys (Ni–Cu, Ni–Pd), either in a pure form or in a mixture with hydrogen or H_2 + CO, it has been observed[133] that metals which are active in the Fischer–Tropsch reactions afford higher hydrocarbons both in the absence and in the presence of carbon monoxide.

VIII. Carbonylation of chlorohydrocarbons

The method of synthesis of carboxylic acid chlorides by carbonylating chlorohydrocarbons has been known for a long time.[134] It is best to use nickel carbonyl as the catalyst, but cobalt, iron, palladium, and rhodium compounds can also be used.[135] The following reaction mechanism has been proposed:

$$RX + Ni(CO)_4 \rightarrow RNi(CO)_2X + 2CO,$$
$$RNi(CO)_2X + CO \rightarrow RCONi(CO)_2X,$$
$$RCONi(CO)_2X + 2CO \rightarrow RCOX + Ni(CO)_4.$$

The process takes place at temperatures in the range 200–300 °C and pressures in the range 600–1000 atm; in the presence of tertiary amines or alkoxides in amounts equimolecular with the initial halide in the presence of the $NaCo(CO)_4$ catalyst, it is possible to attain a yield of 80% at 0–100 °C without using high pressure.[135]

The development of metal complex catalysis permitted the creation of catalytic systems, with the aid of which it is possible to obtain acetyl chloride by carbonylating methyl chloride:

$$CH_3Cl + CO \rightarrow CH_3COCl.$$

Table 3 presents examples illustrating the conditions in this reaction.

In the vapour-phase carbonylation of methyl chloride in the presence of catalysts—transition metal compounds deposited on activated charcoal—acetic acid with an admixture of methyl acetate is formed on treatment with water.[141]

The authors of a patent[142] describe a process leading to the formation of halogenoacetic acid halides from polyhalogenomethanes by a reaction with carbon monoxide in the presence of platinum and palladium catalysts. Most attention has been devoted to the synthesis of chloroacetyl chlorides by the reaction of polychloromethanes with carbon monoxide in the presence of palladium chloride at 20–250 °C and a carbon monoxide pressure of 30–300 atm:

$$CX_nH_{4-n} + CO \xrightarrow{PdCl} CX_{n-1}H_{4-n}C(=O)X$$
X=F, Cl, Br; $n = 2 - 4$.

The process is applicable to any polychloromethane having two or more halogen atoms of the same or different types.

Table 3. Carbonylation of methyl chloride with formation of acetyl chloride.

Catalytic system	Solvent	T, °C	Patm	t^*_{CO}, min	Yield, %	Refs.
$RhCl_3$, CH_3I, Bu_3P, Bu_3PO	toluene	150	20	120	45.5	[136]
$RhCl(CO)(PPh_3)_2$, CH_3I, Bu_3P	»	130	20	30	25	[137]
$RhCl_3$, $CrCl_3$, CH_3I, $(C_6H_5)_3PO$, $(C_6H_5)_3PCH_3I$	n-heptane	180	82.5	35	56	[138]
Ditto	»	180	75	60	54	[138]
$RhCl_3$, $[Re(CO)_5]_2$, $(C_4H_9)_3PCH_3I$, $(C_6H_5)_3PCH_3I$, CH_3I	»	180	75	35	62.8	[139]
$RhCl_3$, Li (CH_3COO), CH_3I, CH_3COOH, $(CH_3CO)_2O$	—	180	82.5	60	51.6	[140]

* t_{CO} is the time during which CO is passed through the system.

Any platinum or palladium group metals (Ru, Rh, Os, Ir, Pt, and Pd) or their compounds such as salts (nitrates, chlorides, bromides, benzoates, or acetates), oxides, or complexes with organic compounds for example, acetylacetonates) can be used as catalysts. Palladium halides ($PdCl_2$ or $PdBr_2$), which are relatively cheap and entirely effective, are preferred. It is recommended that other transition metal halides (Cu, Ni, Fe, and Co) be used as promoting agents. Inert organic solvents (hexane, octane, decane, benzene, toluene, etc.), are employed in the reaction, anhydrous solvents being preferred.

The use of phase transfer catalysts increases the activity of the catalytic system in reactions involving the cabonylation of organic halides.[143]

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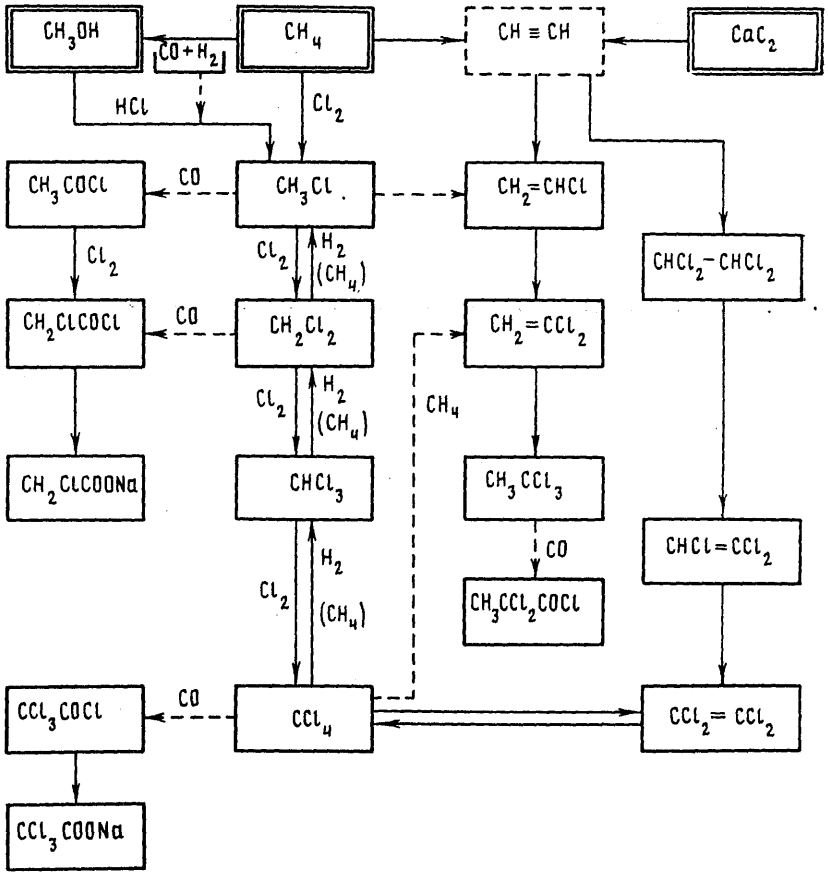


Figure 5. Schematic illustration of the synthesis of organochlorine compounds from one-carbon molecules.

The employment of one-carbon compounds such as methane, methanol, and carbon monoxide as starting material makes it possible to manufacture organochlorine compounds on an industrial scale both at the present time and probably in the future. The scheme presented in Fig. 5 illustrates the conversion of the one-carbon compounds into organochlorine compounds, the continuous lines indicating the reactions achieved in industry and the dashed lines the reactions so far attained only in the laboratory. The time when the latter will also become industrial processes is apparently not distant either.

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