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HEXACHLOROBUTADIENE

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1. INTRODUCTION

Replacement of all the hydrogen atoms in the butadiene (divinyl) molecule by chlorine atoms produces the comparatively little known compound hexachlorobuta-1,3-diene, a colourless liquid with an odour of turpentine.

Hexachlorobutadiene was first described in 1893 by Besson[1], who separated it from the thermal conversion product of chloroform. Unlike butadiene, hexachlorobutadiene is comparatively inert chemically and has a number of unexpected properties; it was these which made its identification difficult and produced several conflicting reports of its chemical properties.

There are reports[2-4] that hexachlorobutadiene is formed in the chlorination of hydrocarbons and their halogen derivatives under pressure, but Fruhwirth showed[5] that the compound so obtained is octachlorocyclopentene. The opposite mistake has also been made. In the chlorination of 1,3-dichlorobut-2-ene Akopyan *et al.*[6] isolated a substance which they could not identify, and which Jelinek and Hudlicky[7] showed to be hexachlorobuta-1,3-diene.

Hexachlorobutadiene behaves as though fully saturated[5]: it does not add chlorine in sunlight, does not react in the Diels–Alder reaction, is stable to acids and alkalis, unlike other highly chlorinated unsaturated compounds it does not give carboxylic acids with concentrated sulphuric acid, and it does not react with sulphuryl chloride in the presence of benzoyl peroxide[8]. More recent studies have only refined our knowledge of these properties of hexachlorobutadiene.

For a long period this compound had remained little known, and only recently has it begun to take on practical value[9].

2. PHYSICAL PROPERTIES

Hexachlorobutadiene is a colourless liquid with an odour of camphor[10]; it has the following physical properties: b.p. 215°/760 mmHg,[5] m.p. 18.6°,[10] n_D^{20} 1.5557,[10] d_4^{20} 1.6794,[10] molar volume at absolute zero 133 ml,[11] molar refraction (excluding the exaltation of the conjugated bonds) 48.94.[5] Its vapour pressure is 100 mmHg at 142–144°, 50 mmHg at 123°, and 20 mmHg at 101°.[12] It has zero dipole moment[13]. Its dielectric constant at 20° is 2.55,[11,13] and its breakdown potential has been reported as 194,[14] 200,[15] and 890 kV cm^{-1}.[16]. The large variation in these values is possibly due to the difference in purity of the actual samples. The molecular polarisation is 52.8 cm^3 and, as expected from the zero dipole moment, is independent of temperature.

The viscosity is 2.446 cP at 37.8° and 1.31 cP at 98.9°.[8] In the interval 50–90° the viscosity is described by the equation[11,16] $\ln\eta = A + Q/RT$, where Q is the energy of activation for the transfer of a particle of the liquid from one equilibrium position to a neighbouring equilibrium position in the same liquid. The surface tension at 20° at the interface with air is 35.9 dyn cm^{-1}.[17] The angle of contact of hexachlorobutadiene on various surfaces has been given by Zisman and coworkers[18-20].

Roedig and Kloss[12] determined the ultraviolet spectrum, Szasz and Sheppard[23] the infrared spectrum, Kohlrausch and Wittek[24] and Batuev and Matveeva[25,26] the Raman spectrum of hexachlorobutadiene; it was concluded that the hexachlorobutadiene molecule does not have the *trans*-configuration, and Kohlrausch and Wittek also excluded the possibility of a planar *cis*-configuration, since such a structure would have a distance between the extreme chlorine atoms of 1.7 Å, *i.e.* less than the bond length in the chlorine molecule (1.98 Å). It was therefore assumed that the hexachlorobutadiene molecule is non-planar, probably with one half of the molecule twisted relative to the other half so that the position of the molecule as a whole corresponds to the minimum potential energy allowing for the repulsion of the chlorine atoms.

On the basis of their investigation of hexachlorobutadiene at low temperatures, Szasz and Sheppard exclude the possibility of a mixture of non-planar rotational isomers. They suppose that two pairs of different minima on the potential energy curve for rotation about the C–C bond are possible; these minima must lie between the maxima corresponding to the unstable *cis*- and *trans*-positions and between the 90° maxima corresponding to the least favourable overlap of the π electrons of the two double bonds of the molecule. The preponderance of a single rotational isomer demonstrates that either one of these minima is considerably lower than the other, or the steric effects are so large that there is a single pair of minima near the 90° position. This last type of configuration was suggested by Kohlrausch and Wittek and confirmed by Szasz and Sheppard.

The lifetime of the phosphorescent triplet state of hexachlorobutadiene varies from 1 to 10 s.[27] The energy of the triplet state allowing for the zero point energy of the molecule is 75 kcal.

The physical properties of mixtures of hexachlorobutadiene with other compounds have been little studied. The freezing point of hexachlorobutadiene is lowered when hexachloropropylene is added to it[28].

Study has been made[11] of certain physical properties of a mixture of hexachlorobutadiene with a paraffin-base mineral oil (molecular weight 263, d_4^{20} = 0.8825): with increasing temperature the volume increases, with a maximum with an equimolar mixture, and the volume difference increases.

The molar polarisation of a mixture of hexachlorobutadiene with a mineral oil (of dielectric constant 2.215 D and molar polarisation 86 cm^3) increases linearly with the oil content of the mixture, indicating that the change of volume, referred to above, when the liquids are mixed must be considered an effect due to packing of the molecules of the two liquids.

The variation of viscosity with the composition of the mixture has been investigated (Fig. 1). The deviation of the plot $\log\eta = f(n)$, where n is the molar content of oil in the mixture, from a straight line demonstrates the existence of intermolecular interaction between the two compounds. Berger and Joerges[11] determined the difference between the experimental value of $\ln\eta$ and that calculated from the equation $\ln\eta = A + Q/RT$;[16] the difference is positive and depends on the quantity of heat ΔQ additional to the energy of activation which is liberated by the mixing of the two liquids. At low temperatures this value is within the limits of the experimental error. For 60° and 90° and an equimolecular mixture, ΔQ is 40 and 60 kcal respectively.

Ellison and Zisman[17] studied the decrease in the surface tension of a solution of the highly fluorinated nonyl

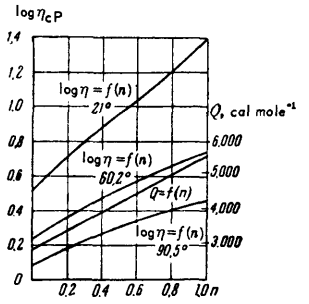


Fig.1. Logarithm of the viscosity and the energy of activation of a mixture of hexachlorobutadiene and mineral oil as functions of the composition of the mixtures. Q is the value for temperatures of 60-90°.

butyrate $H(CF_2)_3COOCH_2(CF_2)_8H$ in hexachlorobutadiene as the concentration of the solution was increased, and found the surface activity to increase exponentially with the difference between the surface tensions of the solution and the pure ester.

Strigel[14] determined the impulse coefficient and other electrical properties of mixtures of hexachlorobutadiene with transformer oil, and showed that the breakdown potential of a mixture containing 3% hexachlorobutadiene is 125 kV cm^{-1}, while for pure hexachlorobutadiene and mineral oil it is 194 and 154 kV cm^{-1}.

The solubility of chlorine and carbon dioxide in hexachlorobutadiene has been studied[29].

3. CHEMICAL PROPERTIES

Reactions

Fruhwirth first studied the chemical properties of hexachlorobutadiene, and showed[5] that reduction with nascent hydrogen produces butadiene.

Zinc dust in boiling alcohol reduces hexachlorobutadiene to diacetylene in 25% yield[30].

It can be assumed that the reduction of hexachlorobutadiene proceeds in stages:

$$CCl_2{=}CCl{-}CCl{=}CCl_2 \rightarrow CH{\equiv}C{-}C{\equiv}CH \rightarrow CH_2{=}CH{-}C{\equiv}CH \rightarrow CH_2{=}CH{-}CH{=}CH_2.$$

Reduction of hexachlorobutadiene with deuterium oxide and zinc produces fully deuterated butadiene[30-32].

Prolonged bubbling of oxygen containing 1% chlorine through hexachlorobutadiene at 165-180° converts half of the reactant into various oxygen-containing compounds, of which the main product is CCl_3COCCl_2COCl.[33]

Hexachlorobutadiene does not react with chlorine when passed through an empty tube at 500°,[34] but passage of a mixture of chlorine and hexachlorobutadiene through a tube of diatomite at 450° produces decomposition of 15-20% of the initial reactant[34,35].

Hexachlorobutadiene is not chlorinated in the light but irradiation of the mixture in a sealed tube at above 25° produces hexachloroethane[8]. Somewhat later[34] prolonged action of chlorine on hexachlorobutadiene in bright sunlight at 10-20° also was found to give hexachloroethane in almost quantitative yield.

The destructive chlorination of hexachlorobutadiene in light is accelerated by ferric chloride[36]; reaction is then marked even at 0°.

It is clear that the addition of chlorine to the double bonds of hexachlorobutadiene is very difficult to accomplish, and this was confirmed by McBee and Hatton[8], who attempted unsuccessfully to carry out the reaction in a sealed tube in light at temperatures of from -70° to 75°, and by Roedig[36], who was unable to add gaseous chlorine to hexachlorobutadiene at temperatures up to 200°. However, prolonged keeping of a mixture of hexachlorobutadiene and liquid chlorine in sealed ampoules in daylight did produce addition of chlorine to the double bonds[36], the main products being octachlorobutene or decachlorobutane depending on the molar ratio of reactants used.

Fluorination of hexachlorobutadiene is accomplished comparatively readily, and this has been its most studied reaction. Different polychlorofluorobutanes and polychlorofluorobutenes are obtained by using different fluorinating agents, such as fluorine[37,39], hydrogen fluoride[39-41], chlorine trifluoride[42-44], and selenium tetrafluoride[45], with catalysts such as antimony trichloride, antimony pentafluoride, and lead peroxide, and carrying out the reaction in the liquid or gaseous phase.

The fluorination of hexachlorobutadiene with hydrogen fluoride in the presence of lead peroxide gives hexachlorodifluorobutene[41].

Krinitsky and Carhart[34] showed that hexachlorobutadiene remains stable for at least 12-15 s at 500°, but at 650° Mamedaliev and coworkers[46] observed the formation of hexachlorobenzene, in an amount which is greatly increased in the presence of carbon tetrachloride, and which is noticeable even at 550°. Although hexachlorobutadiene does not have a flash point, it ignites when sprayed into a stream of gas containing 77% oxygen[47]. The self-ignition temperature of hexachlorobutadiene is 537°.

The passage of chlorine gas through a suspension of various metal oxides in boiling hexachlorobutadiene produces a little phosgene and carbon tetrachloride[48], but unfortunately this paper gives no indication as to whether the reaction vessel was darkened or not, so that the part played by light in this reaction is not known.

Heating equal volumes of hexachlorobutadiene and dilute sodium bicarbonate solution for 4 h at 100° in the presence of iron and with vigorous stirring produced only 0.006 mg of chloride ion per gramme of initial chlorocarbon[8]. This very low degree of hydrolysis may be due to the extremely low solubility of hexachlorobutadiene in water.

Hexachlorobutadiene is stable to strong mineral acids, aqueous alkalis[49], and aqueous solutions of alkali metal hydrogen sulphides at the boiling point[40], the last two clearly also being due to its extremely low solubility in water, since in alcoholic solution hexachlorobutadiene is markedly decomposed by alkali; it has been shown[49] that this first produces 1-ethoxypentachlorobutadiene (I), which

is then converted to 2,4,4,4-tetraethoxy-1,1,3-trichlorobutene (II). An interesting set of reactions has been suggested for this process, in which the addition of alcohol takes place differently at the two ends of the molecule:

$$CCl_2{=}CCl{-}CCl{=}CCl_2 \rightarrow \underset{(I)}{CCl_2{=}CCl{-}CCl{=}CCl\,(OC_2H_5)} \rightarrow$$

$$\rightarrow CCl_2{=}CCl{-}CHCl{-}CCl\,(OC_2H_5)_2 \rightarrow CCl_2{=}CCl{-}CCl{=}C\,(OC_2H_5)_2 \rightarrow$$

$$\rightarrow CCl_2{=}CCl{-}CHCl{-}C\,(OC_2H_5)_3 \rightarrow CHCl_2{-}CCl\,(OC_2H_5){-}CHCl{-}C\,(OC_2H_5)_3 \rightarrow$$

$$\rightarrow \underset{(II)}{CHCl_2{-}C\,(OC_2H_5){=}CCl{-}C\,(OC_2H_5)_3}.$$

If sodium ethoxide is used the reaction is more vigorous.

It is interesting to compare these equations with the reaction suggested by Knunyants *et al.*[51] for the corresponding process with hexafluorobuta-1,3-diene:

$$CF_2{=}CF{-}CF{=}CF_2 \rightarrow (C_2H_5O){-}CF{=}CF{-}CF{=}CF{-}(OC_2H_5).$$

The Wurtz reaction proceeds quantitatively with hexachlorobutadiene[52]; this enables the Stepanov method for the analysis of chloro-compounds to be applied to the determination of hexachlorobutadiene.

Dye took out a patent[53] for the production of adducts of hexachlorobutadiene with compounds $P[N(Alk)_2]_3$, where Alk contains 1–4 carbon atoms; these adducts are apparently quaternary ammonium compounds, and can be used as insecticides and rodenticides.

Hexachlorobutadiene does not react with sulphuryl chloride in the presence of benzoyl peroxide[8], nor (unlike butadiene) does it form adducts with dihalogenocarbenes[54].

Fruhwirth reported[5] that hexachlorobutadiene does not react with maleic anhydride or quinone, *i. e.* it does not take part in the Diels–Alder reaction. However, Mamedaliev *et al.* have recently[55] published the results of their diene synthesis with hexachlorobutadiene as the diene component, obtaining hexachlorocyclohexane dicarboxylic acid anhydride in quantitative yield.

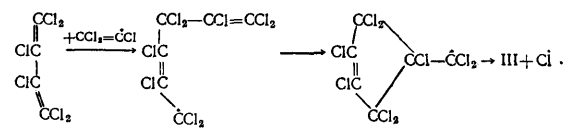
The Diels–Alder reaction of butadiene derivatives having acceptor substituents has been little studied, and in particular the influence of the increased number of chlorine atoms at the double bond of butadiene on the reactivity of polychlorobutadienes is insufficiently known. It is known that maleic anhydride participates in the Diels–Alder reaction with 2-chlorobutadiene, 2,3-dichlorobutadiene[56], and 1,4-dichlorobutadiene[57], but the reaction has not been successful with 2,4-dichlorobutadiene[58], and contacting 1,1,2-trichlorobutadiene with maleic anhydride for 8 h at 180° did not produce the desired results[59]. 1,2,3-Trichlorobutadiene appears to enter into the diene condensation[60].

The increasing difficulty and finally the loss of ability of chlorinated butadienes to act as diene component in the Diels–Alder reaction as the number of chlorine atoms in the molecule is increased may be due to the marked delocalisation of the π electron cloud of the trichlorovinyl group, which causes loss of the π–π conjugation of the double bonds. The absence of stereoisomeric forms of hexachlorobutadiene does not allow a molecular mechanism to be put forward for the Diels–Alder reaction with this compound as diene component, and the published material[55] requires careful experimental checking. Confirmation of the results obtained would provide the possibility of preparing a large number of new and interesting compounds, many of which would find application as intermediates for the production of polymers, pesticides, and other useful materials.

Hexachlorobutadiene polymerises less readily than hexafluorobuta-1,3-diene[61]. According to Fruhwirth[5] it does not polymerise at pressures up to 100 atm, but above 1870 atm it is partially converted into resinous products[62]. Gonikberg and Zhulin[63] attempted to polymerise hexachlorobutadiene by heating at 350° in a steel bomb for 6 h; the pressure attained is not given, but it apparently reached several hundred atmospheres. In addition to hexachloroethane the reaction products contained a carbon-containing residue, which unfortunately was not further investigated; because the molecular structure of the polymers is not known, the actual starting materials for the polymerisation cannot be established: these could be either hexachlorobutadiene or decomposition products thereof. Alfrey *et al.*[64] were unsuccessful in their attempt to copolymerise hexachlorobutadiene with styrene.

Under the action of an electric discharge[65] hexachlorobutadiene reacts with hydrocarbons (transformer oil) to produce hydrogen chloride, chlorine, low-molecular hydrocarbons, and phosgene.

There is no published material on the action of radiation on hexachlorobutadiene, but Henglein suggests[66] that the radiolysis of tetrachloroethylene produces $CCl_2{=}\dot{C}Cl$ radicals which combine with one another to form hexachlorobutadiene as an intermediate. According to Miller and coworkers[67] dichloromethylenehexachlorocyclopentene (III) is then produced:



Structure

Batuev and Matveeva[26] consider that the two frequencies which they observed in the double bond frequency region demonstrate interaction between the multiple bonds, *i. e.* conjugation, and they confirm this by consideration of the mean frequency of 1989 cm^{-1}, which is less than the vibrational frequency of the bond in tetrachloroethylene (1571 cm^{-1}).[68] Finally, the high vibrational frequency of the single bond in hexachlorobutadiene (1170 cm^{-1}) by comparison with that of the C–C bond in hexachloroethane (854 cm^{-1})[69] is also related by Batuev and Matveeva to the existence of conjugation. In view of other possible reasons for the appearance of these frequencies, however, the above considerations do not constitute proof of the existence of conjugation between the double bonds.

A discrepancy between the observed molecular refraction and that calculated from the atomic refractions with a correction for the double bonds appears to indicate a certain exaltation, which demonstrates that the molecule has a high polarisability and that the valency electrons are labile.

The non-polar configuration of the hexachlorobutadiene molecule shows that there is insignificant or no overlapping of the π electron clouds, and it can be assumed that the π electrons of the double bonds are to a large extent localised, and conjugation of the double bonds is absent or only minimal.

It would appear that these contradictory results are due to the particular structure of the hexachlorobutadiene molecule, the presence of the six chlorine atoms determining the behaviour of the diene, in view of the strong electric fields created by the electrons of these atoms and the large mass of their nuclei. The interaction between the π electrons of the double bonds is apparently of secondary significance compared with other effects, in particular the interaction of the electrons of the π and σ bonds with the unshared electrons of the chlorine atoms. Some confirmation of this may be found in the slight shift of the ultraviolet absorption spectrum towards longer wavelengths.

Unfortunately, the small amount of existing experimental material throws almost no light on this matter. Roedig[36] has shown that when one molecule of chlorine adds on to hexachlorobutadiene it is the symmetrical isomer which predominates in the reaction products; this may be confirmation of 1,4-addition, but unfortunately no proof was given that octachlorobut-2-ene had in fact been obtained. According to patent data, 1,4-addition accurs in the reaction of hexachlorobutadiene with hydrogen fluoride[39,40], but the products were not identified[40]. The fact that no Diels–Alder adduct has yet been prepared (if the work of Mamedaliev and coworkers[55], which requires careful checking, is discounted) is no proof of the absence of conjugation between the π bonds because of the non-planar configuration of the molecule. The lower stability of the single bond in hexachlorobutadiene in comparison with butadiene is clear from the chlorination of the two compounds. This may be due to the chlorine atoms in hexachlorobutadiene strongly attracting the σ electrons of the symmetrical molecule, so reducing the electron density around the C–C bond. Comparison of the chlorine addition reactions at the double bonds shows that this process is slower in hexachlorobutadiene than in tetrachloroethylene, the explanation of which must also be sought in the particular structure of the hexachlorobutadiene molecule. Further investigation of the physical properties and chemical reactions of hexachlorobutadiene may resolve this matter.

4. BIOLOGICAL PROPERTIES

Hexachlorobutadiene is physiologically active towards plants, insects, and animals.

An aqueous solution of concentration 1-2 mg litre^{-1} suppresses or strongly depresses the growth of the green, blue-green, and diatomic algae[62]: *Microcystis*, *Aphonizomenon*, *Scenedesmus*, *Oosyrtis*, *Navicula*, *Cyclotella*, *Pediastrum*, *Melosira*, *Coelastrum*, and others.

Hexachlorobutadiene is a herbicide for narrow-leaved weeds (grasses) growing among broad-leaved vegetables[70], and is toxic towards a number of insects[70–74] and to grape phylloxera[75]; it has shown high effectiveness against the wintering egg-laying Comstock mealybug *Pseudococcus comstocki*[76], and in concentrations of 0.05–20 mg per kg in water it produces some reaction in certain fish, but without leading to any substantial physiological changes[77].

Of its action on warm-blooded animals and man, the literature only has statements that inhalation of hexachlorobutadiene vapour causes headaches[78] and that its vapour is toxic[79]. It can be assumed that it acts on the living cell principally as a physical poison, *i.e.* it destroys its physicochemical structure, in particular its colloidal state.

5. METHODS OF PREPARATION

The methods for the preparation of hexachlorobutadiene can be divided into three groups: (*i*) those starting from hydrocarbons containing less than four carbon atoms, in which methane or C_2 hydrocarbons are converted into intermediates having four carbon atoms, and these are then converted into hexachlorobutadiene; (*ii*) those starting from C_5 hydrocarbons, involving splitting of the carbon skeleton; and (*iii*) those using normal C_4 compounds as starting material.

A. Preparation of Hexachlorobutadiene from C_1 and C_2 Hydrocarbons

Tolloczko and Kling[80] passed methane with an excess of chlorine at 400° through a tube containing pumice, and found a little hexachlorobutadiene in the reaction products.

As early as 1893 Besson reported[1] on the thermal conversion of chloroform into hexachlorobutadiene, and it has recently been shown[81] that despite Besson's inaccurate description of the compound, hexachlorobutadiene is in fact produced from chloroform. In a continuous process the yield of hexachlorobutadiene from chloroform is 15.6% at 550°. Decreasing the time of reaction at a higher temperature or increasing the residence time of the reactants in the reaction zone at a lower temperature reduce the yield of hexachlorobutadiene.

Most papers relate to the preparation of hexachlorobutadiene from compounds obtained from acetylene. Fruhwirth[84] proposed the production of hexachlorobutadiene from acetylene and chlorine in a single stage at 600–950°; the yield of desired product was 40%. It may be assumed that this process passes through diacetylene, hexachlorobutene, and octachlorobutane by the reactions set out below[83]. This is the shortest route for obtaining hexachlorobutadiene from a hydrocarbon, but is difficult to carry out because of the need for removing a large amount of heat and because of the recirculation of a considerable quantity of the hexachlorobutadiene. A process which follows the above mechanism has been proposed[82], starting from diacetylene[93], which is chlorinated at -30° to -25° to obtain a mixture of isomers of 1,1,2,3,4,4-hexachlorobut-2-ene in 73–80% yield; this mixture is then treated with liquid chlorine under pressure with prolonged irradiation with a quartz lamp to obtain 1,1,2,2,3,3,4,4-octachlorobutane in 76–91% yield, which on dehydrochlorination with aqueous alcoholic sodium hydroxide solution[84] produces hexachlorobutadiene in 67% yield. Since diacetylene is the main by-product in the production of acetylene from hydrocarbons, this method may be of practical interest.

Octachlorobutane can also be dehydrochlorinated by Roedig's method[85] using various metals in ether solution in the presence of aluminium chloride, or by heating at 190–200° in the presence of iron(III) chloride[84].

Keller and Keyssner[86] have proposed the production of hexachlorobutadiene from monovinylacetylene in two stages, by way of 1,2,3,3,4,4-hexachlorobutane.

The preparation of hexachlorobutadiene from butynediol has also been suggested[87]. Butynediol is reacted with thionyl chloride by Johnson's procedure[88], the resulting 1,4-dichlorobutyne is chlorinated at a temperature of -40° to -50° to give 1,2,2,3,3,4-hexachlorobutane in ~98% yield,

and this is then dehydrochlorinated with KOH in 50% yield. The 1,2,3,4-tetrachlorobutadiene is chlorinated in the presence of antimony trichloride at 30–50° to produce hexachlorobutene, which is reacted with chlorine under pressure in sealed ampoules with ultraviolet readiation to give octachlorobutane in 91% yield; this is dehydrochlorinated to hexachlorobutadiene [83].

An Austrian patent [89] describes the production of hexachlorobutadiene from chlorinated derivatives of ethane or ethylene. As gaseous mixture of 3 volumes of trichloroethane and 2 volumes of chlorine is passed rapidly through a porcelain tube at 500°, when the chlorination product contains 30% hexachlorobutadiene. Catalysts may be used. The same patent claims that polychloroethanes or polychloroethylenes can be chlorinated in a reactor as used for the production of hydrogen chloride from its elements or in an apparatus used for the high-temperature chlorination of acetylene. The reaction products contain 20% hexachlorobutadiene, corresponding to a yield of 40% based on tetrachloroethylene.

The production of hexachlorobutadiene from trichloroethylene has been described [90]. When trichloroethylene and chlorine were passed over active carbon at 350–400° the reaction product contained over 50% hexachlorobutadiene. In another case, trichloroethylene first gave 1,1,1,2,3,4-hexachlorobut-3-ene, which was passed through the catalyst at 280–300°; the yield of hexachlorobutadiene was 85%. The catalyst was activated carbon impregnated with barium chloride. The use of copper or iron chlorides or their mixtures, which may be deposited on various carriers, is also recommended.

Hexachlorobutadiene is obtained in a small amount in the continuous production of trichloroethylene by the dehydrochlorination of tetrachloroethane at 520°. [91] Wimmer [92] has shown that 1,1,2,3,4,4-hexachlorobutane and 1,2,3,4,-tetrachlorobutadiene, which are obtained in the industrial production of tri- and tetra-chloroethylene, can also be converted into hexachlorobutadiene by treating the corresponding fraction with chlorine at 70–80° in the presence of 0.1% iron(III) chloride, when 1,1,2,3,4,4-hexachlorobutane produces 1,1,1,2,3,4,4,4-octachlorobutane and 1,2,3,4-tetrachlorobutadiene produces 1,1,2,2,3,3,4,4-octachlorobutane; the resulting mixture is then heated at 100–140° to obtain hexachlorobutadiene in 90% yield. The production of hexachlorobutadiene from hexachlorobutene is similar [93].

Gonikberg and Zhulin [62,63,94,95] have also obtained hexachlorobutadiene from tri- and tetra-chloroethylene. The main product from trichloroethylene at 200–250° and pressures up to 1300 atm is 1,1,2,4,4-pentachlorobuta-1,3-diene (produced by dehydrochlorination of the trichloroethylene dimer 1,1,3,3,4,4-hexachlorobutene which is first formed); chlorination followed by dehydrochlorination then gives hexachlorobutadiene. The chlorination has been effected by Roedig's procedure [96], at 200° with irradiation by a 500 W bulb; subsequent distillation of the reaction products gave heptachlorobutene and hexachloroethane in yields of 32 and 12 wt.% respectively, and it is interesting that hexachlorobutadiene was also obtained, in 35% yield. The formation of a considerable amount of hexachlorobutadiene may be due both to dehydrochlorination of the heptachlorobutene, and to substitutive chlorination of the initial pentachlorobutadiene. The action of alcoholic alkali using Roedig's method [96] on the comparatively wide heptachlorobutene fraction gave hexachlorobutadiene in 75% yield.

Heating tetrachloroethylene at 350° and pressures up to 1870 atm produces hexachlorobutadiene and hexachloroethane [63], the amount of the former decreasing as the pressure is increased because of the accelerating effect of pressure on the thermal conversion of hexachlorobutadiene into resinous products. The formation of hexachlorobutadiene is thought to be a chain reaction:

$$2C_2Cl_4 \rightarrow \dot{C}_2Cl_3 + \dot{C}_2Cl_5,$$

$$\dot{C}_2Cl_3 + C_2Cl_4 \rightarrow CCl_2{=}CCl{-}CCl_2{-}\dot{C}Cl_2,$$

$$CCl_2{=}CCl{-}CCl_2{-}\dot{C}Cl_2 + C_2Cl_4 \rightarrow CCl_2{=}CCl{-}CCl{=}CCl_2 + \dot{C}_2Cl_5,$$

$$\dot{C}_2Cl_5 + C_2Cl_4 \rightarrow C_2Cl_6 + \dot{C}_2Cl_3,$$

with termination by the reaction:

$$2\dot{C}_2Cl_3 \rightarrow C_4Cl_6.$$

A defect of both methods of obtained hexachlorobutadiene is the use of high pressure, and also the fact that they are multistage processes, since the production of tri- or tetra-chloroethylene from hydrocarbons is itself an independent process.

Trichloroethylene can also be dimerised without the use of pressure. Frank and Blackham [97] used azodiisobutyronitrile (Porofor N) and obtained 1,1,3,3,4,4-hexachlorobut-1-ene in 61.5% yield; the same product is obtained with benzoyl peroxide [98]. Boiling trichloroethylene in the presence of aluminium chloride causes dimerisation and dehydrochlorination with the formation of 1,1,2,4,4-pentachlorobutadiene in 12% yield [99]. The conversion of these two compounds into hexachlorobutadiene can also be effected without pressure [100], but the described methods for obtaining hexachlorobutadiene from trichloroethylene suffer from being multistage processes.

The production of hexachlorobutadiene in 75% yield by chlorinating 1,3-dichlorobut-2-ene at 475° has been described [7,101,102], and might be of practical interest where dichlorobutene, a by-product in chloroprene manufacture, is readily available, but a special synthesis of dichlorobutene from acetylene would make this method cumbersome.

Fig. 2 shows the methods for the production of hexachlorobutadiene from acetylene. With methods starting from methane or chlorinated methanes the yield of hexachlorobutadiene is low; starting from acetylene a multistage process is necessary.

B. Production of Hexachlorobutadiene from C_5 Hydrocarbons

In most of these methods the hexachlorobutadiene is formed as a by-product in 10–25% yields in the production of hexachlorocyclopentadiene from polychloropentanes, the carbon chain being broken [103-105].

A higher yield, up to 60%, is attained in the chlorinolysis of octachloropenta-1,3-diene [11]. Since the formation of hexachlorocyclopentadiene from pentane or polychloropentanes proceeds by way of octachloropenta-1,3-diene and octachlorocyclopentene [106], the formation of hexachlorobutadiene in the process is apparently due to decomposition of the intermediately formed octachloropenta-1,3-diene. The yield of octachloropenta-1,3-diene in the chlorination of polychloropentanes has been raised to 30% by recycling

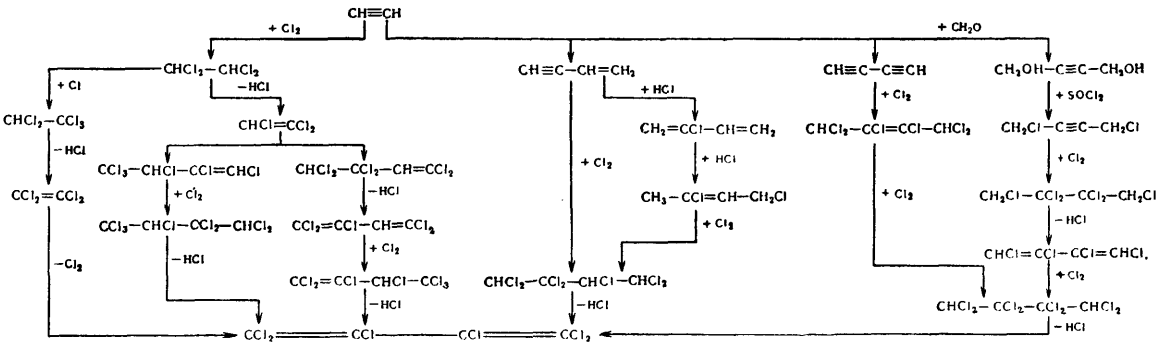


Fig.2. Reaction schemes for the conversion of acetylene into hexachlorobutadiene.

the octachlorocyclopentene[107]; the overall yield of hexachlorobutadiene from pentane or polychloropentanes is thus 15–20%.

These methods for the production of hexachlorobutadiene are of secondary importance, since the main product of the extensive chlorination of C_5 hydrocarbons is hexachlorocyclopentadiene.

C. Production of Hexachlorobutadiene from C_4 Hydrocarbons

This group of methods has the most pratical interest, since it provides the shortest route from hydrocarbon to product. The starting material may be n-butane, the isomeric straight-chain butylenes, or butadiene; isobutane and isobutylene are unsuitable, since under the conditions studied these or their polychloro-derivatives do not isomerise to straight-chain compounds, but are decomposed.

The methods for obtaining hexachlorobutadiene from C_4 hydrocarbons can be divided into two groups[108]. One includes two-stage processes involving the production of polychlorobutanes which are then converted into the desired product, and the other embraces single-stage conversions of the hydrocarbons into hexachlorobutadiene.

Nearly all published work on the chlorination of butane has related to the production of monochlorides, so that polychlorides are obtained in small amounts and are generally dichlorides containing only small amounts of trichlorobutanes. Light[8] and chemical initiation[109-111] have generally been employed for chlorinating butane or its polychloro-derivatives to obtain polychlorobutanes having a considerable chlorine content.

In their article on the production of hexachlorobutadiene, McBee and Hatton[8] report the use as starting materials of the polychlorobutanes obtained by chlorinating butane at 80–90° in the presence of light; the butane was completely converted into a mixture of chlorobutanes, of average composition $C_4H_4Cl_6$. A mixture of polychlorobutanes of about the same composition was also obtained by another method.

Another procedure[109] used as starting material the mixture of trichlorobutanes obtained in small amount in the thermal chlorination of butane; this was subjected to liquid-phase chlorination in the dark, with Porofor as initiator.

Kogan and Ignatova have made a detailed investigation of the chlorination of butane[110,111], using carbon tetrachloride, hexachlorobutadiene, and the chlorination products as reaction medium and Porofor as initiator. They studied the influence of the reaction conditions on the extent of the reaction between butane and chlorine and on the extent of the chlorination.

In addition to chemically irreversible reactions, physical equilibrium processes (dissolution of gases), which determine the mass transfer, also play a significant part, and their influence on all processes must be taken into account when considering the results of any study. Thus increase of temperature should increase the rate of dissolution of gases, their diffusion in the liquid, and the rate of chlorination reactions, but at the same time the solubility of butane and chlorine in the liquid will decrease. Increasing the molar ratio of chlorine to butane creates favourable conditions for the dissolution of butane, because of its decreased partial pressure in the gas mixture. Different conditions will arise in the solution in respect of the chlorination of butane and polychlorobutanes, because of the low concentration of butane in the reaction mixture in comparison with the polychlorobutane content. The difference in these concentrations is apparently not compensated by the presence in the butane molecule of the more reactive hydrogen atoms of the methylene groups, these being absent or present to a lesser extent in the polychlorobutanes.

The formation of two molecules from two radicals thermodynamically provides the possibility of the reverse reaction, the production of two radicals from two valency-saturated molecules[112].

The energy of activation of the reaction

$$CH_3{=}CH_3{+}Cl_2 \rightarrow CH_3Cl{-}CH_2{+}Cl$$

is 41 kcal, *i.e.* considerably less than 57 kcal which is the energy of activation for the dissociation of chlorine molecules into atoms. The transition to butylene and butadiene leads to a decrease in the energy of activation for the formation of the corresponding radical. This opens up the possibility of using this method of initiating the

reaction of butane with chlorine not only for the preparation of monochlorobutane[113], but also for the production of more highly chlorinated products. This was the basis of experiments[111,114] in which butane was highly chlorinated in the presence of butylene and butadiene instead of the known initiators. The addition of 15–20% of butylene to the butane under the reaction conditions previously used[110] produces tetrachlorobutanes, and if butadiene is used instead of butylene, pentachlorobutanes are obtained. When butylene or butadiene is chlorinated, the addition of chlorine to the double bonds is accompanied by substitutive chlorination[115].

The production of polychlorobutanes in these reactions can be represented as follows:

from butylene

$$CH_3-CH=CH-CH_3 \xrightarrow{+Cl_2} CH_3-CHCl-\dot{C}H-CH_3+\dot{C}l \rightarrow CH_3CHClCHCl-CH_3 \xrightarrow[-HCl]{+Cl^\cdot} \longrightarrow \dot{C}_4H_7Cl_3 \xrightarrow{+Cl_2} C_4H_7Cl_3+Cl^\cdot \xrightarrow[-HCl]{} \dot{C}_4H_6Cl_3 \xrightarrow{+Cl_2} C_4H_6Cl_4+\dot{C}l \text{ etc.},$$

and from butadiene

$$CH_2=CH-CH=CH_2 \xrightarrow{+Cl_2} CH_2Cl-CH=CH-\dot{C}H_2+Cl^\cdot \rightarrow$$
$$\rightarrow CH_2Cl-CH=CH-CH_2Cl \xrightarrow{+Cl_2} CH_2Cl-CHCl-\dot{C}H-CH_2Cl+\dot{C}l \rightarrow$$
$$\rightarrow CH_2Cl-CHCl-CHCl-CH_2Cl \xrightarrow[-HCl]{+Cl_2} C_4H_5Cl_4 \xrightarrow{+Cl_2} C_4H_5Cl_5+\dot{C}l \text{ etc.}$$

The use of these unsaturated compounds instead of Porofor, benzoyl peroxide, or other such initiators avoids the use of expensive and explosive substances and simplifies the production of polychlorobutanes.

When butane is chlorinated the hydrogen atoms on the secondary carbon atoms are first replaced, because of the smaller energy required in forming the corresponding free radical. The tendency after this is to produce symmetrical molecules, so that if the final products are hexachlorobutanes the predominant isomer will be 1,2,2,3,3,4-hexachlorobutane.

The chlorination of polychlorobutanes to produce hexachlorobutadiene, which takes place in the gas phase either without[8,35,116,117] or with a catalyst[34,109,118], has already been reviewed[9], and we shall consider here only work published since 1959.

The production of hexachlorobutadiene from trichlorobutanes over diatomite[109] has been confirmed by Nekrasova and Shuikin[119], who used as catalyst specially treated Crimean coquina and a mixture of chromium, aluminium, and magnesium oxides, and obtained hexachlorobutadiene in yields of 57 and 37% respectively. Dilution of the chlorine with an equal volume of nitrogen increased the yield to 66–68%, but it did not reach 76% as in the previous method[109].

Kogan and Burmakin[35] made thermodynamic calculations and carried out a comparative investigation of the chlorination of polychlorobutanes in the absence of a catalyst and in the presence of diatomite, using the following reactions:

$$CH_2Cl-CCl_2-CCl_2-CH_2Cl+Cl_2 \rightarrow CHCl_2-CCl_2-CCl_2-CH_2Cl+HCl, \quad (a)$$
$$CHCl_2-CCl_2-CCl_2-CH_2Cl+Cl_2 \rightarrow CHCl_2-CCl_2-CCl_2-CHCl_2+HCl, \quad (b)$$
$$CHCl_2-CCl_2-CCl_2-CHCl_2 \rightarrow CCl_2=CCl-CCl_2-CHCl+HCl, \quad (c)$$
$$CCl_2=CCl-CCl_2-CHCl_2 \rightarrow CCl_2=CCl-CCl-CCl_2+HCl, \quad (d)$$

Fig. 3 shows the results of the thermodynamic calculations.

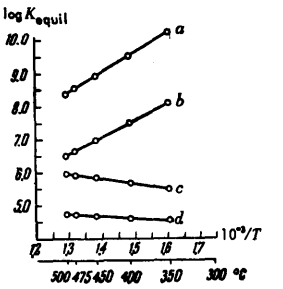


Fig. 3. Variation of the equilibrium constant with the reaction temperature in the chlorination of hexachlorobutane to hexachlorobutadiene.

All the reactions are irreversible over a wide temperature range; reaction (d) is the limiting stage. The equilibrium constant for reaction (c) decreases with the temperature considerably more rapidly than the equilibrium constant for reaction (d).

One of the interesting questions which arise in the study of hexachlorobutadiene production is the influence of the chlorine content of polychlorobutanes when they are reacted with chlorine at elevated temperatures (Fig. 4). Figs. 5, 6, and 7 show the influence of other factors on the process.

Polychlorobutanes react with chlorine to produce hexachlorobutadiene, decomposition products, and resins. The decomposition products apparently arise because of cracking of the higher polychlorobutanes. Lower polychlorobutanes mainly undergo further chlorination, while hexachlorobutadiene is stable under the reaction conditions in

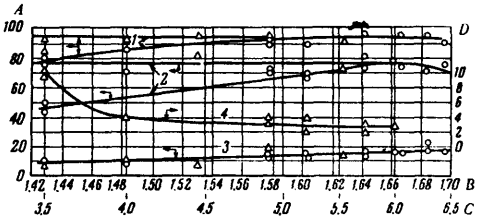


Fig. 4. Influence of the degree of chlorination of butane on the reaction of polychlorobutanes with chlorine. In the absence of catalyst: excess of chlorine 40–50%, t_1 = 350°, l_1 = 120 mm, t_2 = 475°, l_2 = 750 mm, rate of feed of polychlorobutanes (PCB) 0.35–0.40 g-mole h^{-1}. Over diatomite: excess of chlorine 40–50%, t_1 = 350°, l_1 = 120 mm, t_2 = 425°, l_2 = 750 mm, rate of feed of PCB 0.33–0.35 g-mole h^{-1}. *A* is yield in %, *B* is the specific gravity of the PCB, *C* is the number of chlorine atoms in the PCB molecule, and *D* is the amount of involatile residue in wt.%; 1) conversion of the PCB; 2) yield of C_4Cl_6; 3) yield of decomposition products; 4) amount of involatile residue. Circles represent absence of catalyst, triangles represent use of diatomite.

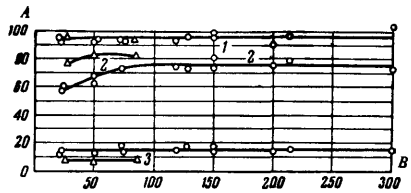


Fig.5. Influence of the excess of chlorine on the gas-phase chlorination of polychlorobutanes. In the absence of catalyst: PCB d_{20}^{20} = 1.6423, n_D^{20} = 1.5290, rate of feed 1.6–1.7 g min^{-1}, t_1 = 350°, l_1 = 120 mm, t_2 = 475°, l_2 = 750 mm. Over diatomite: PCB d_{20}^{20} = = 1.4344, n_D^{20} = 1.5010, rate of feed 0.5 g min^{-1}, t_1 = = 350°, l_1 = 120 mm, t_2 = 450°, l_2 = 750 mm. *A* is yield, %, *B* is excess of chlorine, %; 1) conversion of the PCB; 2) yield of C_4Cl_6; 3) yield of decomposition products. Circles and triangles as in Fig.4.

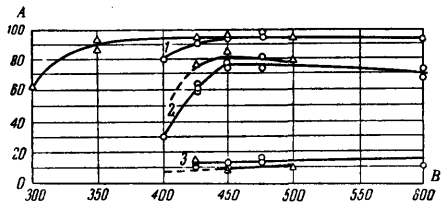


Fig.6. Influence of temperature on the chlorination of polychlorobutanes. In the absence of catalyst: d_{20}^{20} = 1.6423, n_D^{20} = 1.5290, excess of chlorine 150%, t = 350°, l_1 = 120 mm, l_2 = 750 mm, rate of feed of PCB 1.6–1.7 g min^{-1}. Over diatomite: excess of chlorine 45–55%, t_1 = 350°, l_1 = 120 mm, l_2 = 750 mm, rate of feed of PCB (d_{20}^{20} = 1.4344, n_D^{20} = 1.5010) 0.5 g min^{-1}. *A* is the yield, %, *B* is the temperature, °C; 1) conversion of PCB; 2) yield of hexachlorobutadiene; 3) yield of decomposition products. Circles and triangles as in Fig.4.

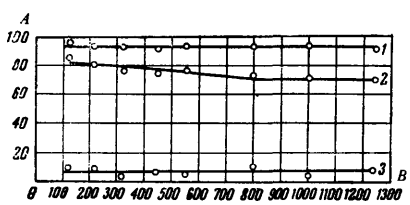


Fig.7. Influence of loading rate of the polychlorobutanes on their overall conversion and on the yield of hexachlorobutadiene and decomposition products over diatomite. PCB d_{20}^{20} = 1.4344, n_D^{20} = 1.5010, t_1 = 350°, excess of chlorine 45–55%, l_1 = 120 mm, t_2 = 450°, l_2 = 750 mm. *A* is the yield, %; *B* is the loading rate of the PCB, kg m^{-3} h^{-1}; 1) conversion of the PCB; 2) yield of C_4Cl_6; 3) yield of decomposition products.

the absence of a catalyst. The greater degree of chlorination of polychlorobutanes of the same chlorine content when the reaction is effected over diatomite, as compared with reaction in the absence of a catalyst, demonstrates the increased rate of the process in the former case, *i.e.* the catalytic action of the diatomite; this is also seen in the lower temperature required when diatomite is used. The presence of diatomite (or other porous material) in the reaction zone has a number of technological advantages. Packing the reactor favours mixing, and the retention of the chlorine in the pores of the contact mass enables the amount of chlorine feed to be reduced.

Hexachlorobutadiene can be produced from C_4 hydrocarbons in a single step in the absence [120] or presence of a catalyst [92,120], including a fluidised-bed catalyst [105,121,122], or in an orifice burner [104]. The single-stage methods require the use of a large excess of chlorine, which raises the difficulty of extracting chlorine from the exit gases and recycling it; this can be met by using hexachlorobutadiene (see below).

6. SOME MATTERS CONCERNING THE INDUSTRIAL PREPARATION

A number of problems arise in the production of hexachlorobutadiene on a commercial scale; we shall consider only three: the choice of material for the high-temperature chlorination reactor, the separation of the reaction products, and the purification of the hexchlorobutadiene.

For chlorination under industrial conditions, only nickel is suitable for the reactor, if porcelain [120], which is not suitable for construction purposes, and graphite [120], which is not very convenient and will apparently react with the chlorine, are not taken into account. Carbon steel, various iron alloys, including EZh-17† and EYa1T‡, cast iron, and many metals (aluminium, copper, lead, magnesium, silver, gold, and platinum) are unsuitable because of their corrosion [123,124]; moreover certain metal chlorides, *e.g.* of iron, cause polymerisation of the unsaturated intermediates and so produce resinification.

The rate of corrosion of nickel by chlorine at 500° is 0.5 g m^{-2} h^{-1}; raising the temperature by only 40° increases the rate of corrosion to 2.1 g m^{-2} h^{-1}, and the use of a maximum temperature of ~500° is therefore recommended [123,124]. It is important to note that with prolonged working of the reactor the actual temperature must apparently be lower, because of the gradual evaporation of the protective film of nickel chloride and the formation of a new film, *i.e.* corrosion of the nickel. A large excess of chlorine aids the evaporation of the nickel chloride.

When chlorination has been properly carried out, the liquid reaction products have considerably different boiling points and can be readily separated. With incomplete chlorination of the starting materials, the reaction product will contain, in addition to chlorocarbons, highly chlorinated polychlorobutanes, polychlorobutenes, and polychlorobutadienes, and these impurities are very difficult to remove because they have boiling points close to

† Cr 16.0–18.0, Ni ≯ 0.60, C ≯ 0.12, Si ≯ 0.80, Mn ≯ 0.70, S ≯ 0.030, P ≯ 0.035% (Ed. of Translation).

‡ Cr 17.0–20.0, Ni 8.0–11.0, C ≯ 0.12, Si ≯ 0.80, Mn ≯ 2.0, S ≯ 0.030, P ≯ 0.035%, stabilised with Ti from (C–0.03)× 5 to 0.08% (Ed. of Translation).

that of hexachlorobutadiene. The presence of these impurities in commercial hexachlorobutadiene renders the latter unstable on storage and in certain of its uses; in particular the physical properties of the liquid (especially its electrical properties) deteriorate and it gives off hydrogen chloride, etc. Chemical methods have been suggested for purifying the hexachlorobutadiene; one[50] is based on its stability towards aqueous solutions of alkali metal hydrogen sulphides, the chlorine atoms in polychlorobutanes being replaced by the thiol group; according to another[125] the impure hexachlorobutadiene is treated with non-alkaline substances which can take up hydrogen chloride: carbohydrates (*e.g.* sucrose), sawdust, paper, or cotton.

Sometimes the reaction products contain a considerable quantity of hexachloroethane (b.p. 187°); to prevent this crystallising on the walls of the condenser, injection of water has been suggested[92], which prevents adhesion of the hexachloroethane particles to the walls, or the addition to the initial mixture of a substance whose boiling point is near that of hexachloroethane.

7. FIELDS OF USE

The uses of hexachlorobutadiene are based on its comparative chemical stability, especially its non-inflammability, and its particular combination of physical properties. It has been proposed for use in hydraulic[126-131] and electrically insulating[11,33,118,126,127,131] liquids, as a lubricant[126] and solvent[118], and, to a lesser extent, as a chemical reagent and pesticide.

One of the most interesting uses of hexachlorobutadiene is as a dispersion medium in the determination of the infrared spectra of various substances[132,133]. The paraffin oil used for this purpose has strong absorption bands at 3.4, 6.85, and 7.26 μm and weaker bands at 2.4, 3.8, and 13.8 μm, which considerably limit its range of applicability. Hexachlorobutadiene can be used over practically the whole range of infrared spectra, except for the regions of frequency 1640–1510, 1200–1140, and 1010–760 cm^{-1}, where the absorption exceeds 25%.[134] Hexachlorobutadiene is widely used in spectroscopy[135-142].

An important problem in the production of chlorinated organic compounds is the purification of the hydrogen chloride given off in the chlorination from unreacted chlorine and volatile organic compounds. Until recently this had been achieved by absorbing the hydrogen chloride in hydrochloric acid followed by desorption, but this method has many disadvantages. In 1958 a patent was taken out[143,144] for obtaining pure hydrogen chloride by washing the chlorination gases first with carbon tetrachloride and then with hexachlorobutadiene (Fig. 8). The first wash dissolves chlorine and the organic compounds, which are separated by rectification and recycled to the chlorination; the second wash dissolves the volatile CCl_4 entrained by the hydrogen chloride in the first wash. Both washing columns are operated at 35°. After a further wash with hexachlorobutadiene under pressure at -15° the hydrogen chloride is almost free of carbon tetrachloride and contains less than 0.01% by weight of hexachlorobutadiene and less than 0.001% of chlorine. The initial cost using this method is half that using the hydrochloric acid method[145], and it is in use in the USA.[146]

Hexachlorobutadiene has been used as a solvent for chemical reactions; of most interest is its use as a chlorination medium, and indeed it is difficult to find another compound

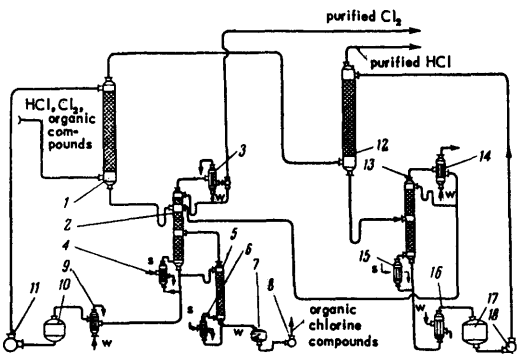


Fig. 8. Principle scheme for the purification of hydrogen chloride with carbon tetrachloride and hexachlorobutadiene:
1) absorber for Cl_2 and organic compounds; 2) chlorine desorber; 3) dephlegmator; 4) boiler; 5) column for the separation of the organic compounds; 6) boiler; 7) receiver for organic compounds; 8) pump for organic compounds; 9) CCl_4 condenser; 10) CCl_4 receiver; 11) pump for CCl_4; 12) CCl_4 absorber; 13) column for separating CCl_4; 14) dephlegmator; 15) boiler; 16) C_4Cl_6 condenser; 17) C_4Cl_6 receiver; 18) pump for C_4Cl_6; w = water, s = steam.

which is so inert towards chlorine up to 215°. A patent[147] recommends the chlorination of paraffin and rubber in hexachlorobutadiene.

A recent paper[48] describes the selective chlorination of metal oxides in boiling hexachlorobutadiene to separate metals of similar properties. A metal chloride is produced quantitatively and dissolves in the boiling chlorocarbon, separating out when the solution is cooled to room temperature; $MoCl_4$, $NbCl_5$, and $FeCl_3$ can be obtained in this way from the corresponding oxides. Other oxides, in particular MoO_3, Cr_2O_3, and Ta_2O_5, react little or not at all under these conditions.

Hexachlorobutadiene is recommended as a solvent for obtaining hexachlorocyclopentadiene dimer[148,149], and also for the investigation of the mechanism[150] and kinetics[151] of reactions.

Hexachlorobutadiene has been used as an additive for high-pressure lubricating oils[152]. It can be added to motor fuel with tetraethyl lead, which has the same vapour pressure as hexachlorobutadiene[153]; the addition of the latter apparently acts to remove the lead from the engine as lead chloride. Studies of the vulcanisation of RGS rubber with hexachlorobutadiene[154] have shown it to be inactive or only weakly active in the reaction.

An extremely important use of hexachlorobutadiene is as a biologically active material. It has been suggested[155-157] that the physical and chemical properties of some highly effective pesticides, which determine the duration of their retention at the site of the biological objective, are of greater significance than their toxicity. This may happen when the living organisms inhabit media (water, soil) which are comparatively active towards the chemicals added; thus in selecting pesticides for organisms in such media the aim should be to find compounds which are

stable over a period of time. These considerations have led to the investigation of hexachlorobutadiene for use against lower aquatic plants and certain soil pests.

Hexachlorobutadiene has been proposed for the suppression of the growth of algae in fresh water[69,158].

The addition of small doses of hexachlorobutadiene to vineyard soil successfully combats the most serious grape disease, phylloxera[75,159]. This work led to considerable investigation of the proposed use of a fumigant for this purpose[76,160-171]. The particular features of hexachlorobutadiene in comparison with known phylloxerocides (carbon disulphide, dichloroethane, and other polychloroethanes and propanes) are the manifestation of activity only 3-4 months after its introduction into the soil, its penetration throughout the whole depth of the root system, its lasting action (at least 3-4 years), and its application in smaller doses. Hexachlorobutadiene is added to the soil in amounts of 15 to 25 g m^{-2}, depending on the local conditions. At such doses there is practically complete mortality of the phylloxera, with no effect on the biochemical indices of the fruit (sugar content, acidity), and, in some cases, stimulation of growth of the plant. Larger doses have an adverse effect on the plant. A procedure is being developed for using hexachlorobutadiene in separate soil climatic zones in viniculture. Thus the reflections given above on the choice of pesticides have led to the use of hexachlorobutadiene, which is not outstandingly toxic among chlorine compounds, as a highly effective pesticide against certain organisms in media where such other compounds would be considerably less effective.

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ADVANCES IN THE CHEMISTRY OF THIAMINE

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