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HALOACETYLENES

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CONTENTS

I. Introduction 326

II. Synthesis of the haloacetylenes and some of their derivatives 326

1. Preparative methods for haloacetylenes 326
2. Synthesis of derivatives of the haloacetylenes 328
3. Analytical determination of the haloacetylenes 328

III. Physical properties of the haloacetylenes 329

1. General characteristics 329
2. Combustibility and explosibility 329
3. Physiological activity 330
4. Structure of the molecule. Spectra 330

IV. Chemical reactions of the haloacetylenes 332

1. Reactions at the triple bond 332
2. Hydrogen exchange 334
3. Halogen exchange 334
4. Decomposition of the haloacetylenes. Oxidations 336
5. Molecular compounds of the haloacetylenes 336

I. INTRODUCTION

This review deals with the halogenated acetylenes XC≡CH and XC≡CX, where X = I, Br, Cl, or F. The chemistry of the haloacetylenes is developing rapidly and opens wide prospects for the use of these compounds in organic synthesis. Information about this class of compounds has not been systematised and it seems desirable to make the material accumulated in this field more accessible. The review covers literature published up to November 1966.

The first acquaintance of investigators with halogenated acetylenes began in 1860, when Sawitsch[1] found that the action of alcoholic solutions of sodium ethoxide (or potassium hydroxide) on tribromoethane or heating it with solid potassium hydroxide to 100° gives, in addition to dibromoethylene, a gaseous substance which ignites spontaneously in air, attacks the eyes, and gives an explosive precipitate with an ammoniacal solution of copper(I) oxide. Somewhat later Reboul[2,3] found that it was bromoacetylene but he invariably obtained it mixed with acetylene. Pure bromoacetylene was obtained only in 1885 by Sabaneev[4]. In 1865 Berend[5] first obtained di-iodoacetylene by the reaction of silver acetylide with an ethereal solution of iodine. In 1880 Wallach[6] obtained chloroacetylene on boiling barium ββ-dichloroacrylate with barium hydroxide: he characterised the product, obtained some derivatives of C_2HCl, and found that the reaction proceeds through the intermediate formation of chloropropionic acid, which is readily decarboxylated:

$$CCl_2{=}CHCOOH \rightarrow ClC{\equiv}CCOOH \rightarrow C_2HCl + CO_2.$$

Lemoult[7] obtained dibromoacetylene in 70% yield by heating an alcoholic solution of tribromoethylene with an excess of alcoholic potassium hydroxide in a stream of nitrogen and described its properties. Dichloroacetylene was discovered in 1914: Böeseken and Carrière[8] obtained it on heating the barium trichloroacrylate. Grignard and his coworkers[9], in studying the reaction of equimolecular amounts of iodine and ethynylenedimagnesium dibromide, found a little iodoacetylene among the reaction products, in addition to the main product (up to 65%), monoiododiacetylene.

In the monohalo-substituted acetylene series fluoroacetylene was the last to be discovered. It was synthesised in two different ways: by pyrolysis of fluoromaleic anhydride and by reaction of magnesium with 2-bromo-1,1-difluoroethylene. Both methods were published by Middleton and Sharkey[10] in the USA and by Yakubovich and coworkers in the Soviet Union[11].

The first information about difluoroacetylene began to appear in the literature in 1947. In an American patent[12], which describes the preparation of perfluorinated alkynes of the type $R_FC{\equiv}CR_F$, difluoroacetylene is mentioned among the products. However, the method of making it is not described there and its physicochemical characteristics are not given. In another American patent[13], which describes the synthesis of fluoropropioloyl fluoride FC≡CCOF by the pyrolysis of difluoromaleic anhydride, difluoroacetylene is mentioned as one of the products of the pyrolysis. However, it was not isolated. The author observed only the formation of a compound of composition C_4F_4, which he took to be a dimer of difluoroacetylene. In the brief information about the preparation of difluoroacetylene[14] there is also nothing about the method of preparation, purification, and properties of the substance. Slight traces of difluoroacetylene were found among the products of the photolysis of tetrafluoroethylene[15] and of the radiolysis of hexafluoroethane[16]. According to an American patent[17], the dihaloacetylenes, including difluoroacetylene, are obtained by pyrolysis of liquid or gaseous halogenated hydrocarbons at 1200–1300°C in high vacuum. Chlorofluoroacetylene was recently obtained[18] by dehydrohalogenation of 1,1-dichloro-2-fluoroethylene at 120°C in a vacuum.

The study of the halogenated acetylenes for over a century has developed rather slowly. On the one hand, the investigations, which were not stimulated by practical requirements, were theoretical and carried out on a very limited scale. On the other hand, work with haloacetylenes is accompanied by considerable difficulty and danger since these substances ignite and explode violently on contact with air. Moreover, they exhibit comparatively high toxicity. Only with the development of appropriate experimental techniques and of contemporary physical methods of investigation were significant advances made in this field. However, bromochloroacetylene, chloroiodoacetylene, bromofluoroacetylene, bromoiodoacetylene, and iodofluoroacetylene are now known.

II. SYNTHESIS OF THE HALOACETYLENES AND SOME OF THEIR DERIVATIVES

1. Preparative Methods for Haloacetylenes

The methods at present known for the production of haloacetylenes can be classified as follows, according to the reactions on which they are based.

A. The hypohalite method is based on the fact that hypohalite in alkaline medium acts on acetylene or a substance with an acetylenic hydrogen [19]:

$$CH{\equiv}CH + 2\,OX^- \rightarrow XC{\equiv}CX + 2\,OH^-.$$

Biltz and Küppers [20], having obtained di-iodoacetylene by the reaction of alkaline hypoiodite, iodine, and acetylene, ascribe to the hypoiodite the role of oxidant in the iodination. However, iodic acid, which they used as an oxidant, seemed of low activity and such oxidants, like the free hypohalogenous acids, add to the triple bond [19]:

$$RC{\equiv}CH + 2\,HOX \rightarrow [RC(OH)_2CHX_2] \rightarrow RCOCHX_2.$$

Hypoiodites are the most active; they react almost instantaneously. Hypobromites and hypochlorites are less active, especially the latter. The rate of reaction continually decreases in this sequence and a correspondingly more alkaline medium is required to effect the reaction; hypochlorite, for example, requires concentrated alkali [21,22].

Isolated authors have modified this method to obtain dihaloacetylenes (especially C_2I_2). The production of monoiodoacetylene in this way has recently been described [23,24].

The method described above [20] is the most convenient process for the preparation of *di-iodoacetylene*:

$$C_2H_2 + KOI + I_2 \rightarrow C_2I_2 + KI + H_2O.$$

The reaction proceeds rapidly and the yield of the product is close to theoretical. Dehn's method [25] is often used for the same purpose; water, NaOCl, and KI act on calcium carbide:

$$CaC_2 + 2\,H_2O + 2\,KI + 2\,NaOCl \rightarrow C_2I_2 + Ca(OH)_2 + 2KCl + 2\,NaOH + 2KCl.$$

The yield of C_2I_2 is 80–90%. An interesting variation of the hypohalogenite method for obtaining di-iodoacetylene was proposed by Dussol [26]. He electrolysed, between platinum electrodes, an aqueous solution of potassium iodide saturated with acetylene. The iodine discharged at the anode reacts with acetylene in the alkaline medium, forming di-iodoacetylene with a current efficiency of 85%.

The same method is recommended for obtaining dichloroacetylene for demonstration experiments [27]. However, in view of the low yields this method has no preparative value [28].

B. Dehydrohalogenation of polyhaloethanes or polyhaloethylenes by alcoholic or solid alkali; this method allows both dihaloacetylenes and monohaloacetylenes to be obtained:

$$CH_2XCHX_2 + 2\,MOH \rightarrow 2\,MX + 2H_2O + HC{\equiv}CX;$$

$$CHX{=}CX_2 + MOH \rightarrow MX + H_2O + XC{\equiv}CX;$$

$$CHX{=}CHX + MOH \rightarrow MX + H_2O + HC{\equiv}CX$$

where X = Cl or Br.

Dehydrogenating agents other than alkali hydroxides can also be employed, for example, catechol potassium or sodium salts [29] and catechin [30]. Dehydrohalogenation under the action of the alkali metals [31,32] has been described; it proceeds by a radical mechanism. For example, the formation of chloroacetylene from 1,2-dichloroethylene under the action of potassium can be represented as follows [32]:

$$K + C_2H_2Cl_2 \rightarrow KCl + \cdot C_2H_2Cl$$

$$\cdot C_2H_2Cl + C_2H_2Cl_2 \rightarrow C_2HCl + HCl + \cdot C_2H_2Cl.$$

Method B seemed the most promising for the preparation of *dichloroacetylene* and *dibromoacetylene* [7,33]. The method of obtaining dichloroacetylene by the dehydrohalogenation of trichloroethylene was developed by Ott and coworkers [34]. These authors passed trichloroethylene vapour at 130° over fused and uniformly ground KOH and obtained C_2Cl_2 in 65% yield. However, explosions in the reaction tube frequently occurred. Subsequently Ott and coworkers showed [35] that the addition of 1% water glass (containing 50% silicate) to pure, solid KOH makes the procedure safe. It is noted that 10% silicate completely deactivates the KOH. According to other investigators [36], the addition of even 2% sodium silicate makes the alkali inactive.

Haloacetylenes were also obtained from certain polyfunctional halogenated compounds. Under the action of alkali such compounds liberate haloacetylene and simultaneously undergo destructive decomposition with the formation of other products. In several studies the author discusses the mechanism of such reactions. For example, according to Wagner and Pines [37] the formation of chloroacetylene in the decomposition of ββ-dichlorovinyltrichlorosilane under the influence of aqueous KOH takes place in stages, through the intermediate formation of a carbanion, which then reacts with the solvent and forms dichloroethylene or loses a chloride ion and gives chloroacetylene:

$$OH^- + Cl_3Si{-}CH{=}CCl_2 \rightarrow (CH{=}CCl_2)^- + Cl_3Si(OH);$$

$$-CH{=}CCl_2^- + H_2O \rightarrow CH_2{=}CCl_2 + OH^-;$$

$$-CH{=}CCl_2^- \rightarrow C_2HCl + Cl^-.$$

Under the action of alcoholic alkali dimethyldihalovinylmethanols [3,4-dihalo-2-methylbut-3-en-2-ols] decompose with the formation of acetone and monohaloacetylene [38]:

$$(CH_3)_2C(OH)CX{=}CHX \xrightarrow{HX} (CH_3)_2C(OH)C{\equiv}CX \rightarrow CH_3COCH_3 + C_2HX$$

$$(CH_3)_2C(OH)CX{=}CHX \rightarrow CH_3COCH_3 + CHX{=}CHX \xrightarrow{-HX} C_2HX.$$

According to Zincke [39], the decomposition of α-dichloromethyl-β-chlorovinyldiketone[1,1,5-trichloropent-4-en-2,3-dione] on heating with an excess of alkali in a current of hydrogen takes place as follows:

$$\begin{array}{l} CHCl_2{-}CO \quad H \qquad\quad CHCl_2{-}COH \\ ClHC{=}CH{-}CO \quad OH \rightarrow \quad CHCl{=}CHCOOH \end{array}$$

$$CHCl_2{-}COH \rightleftarrows CCl_2{=}CHOH;$$

$$CCl_2{=}CHOH + NaOH \rightarrow CCl{\equiv}CH + NaClO + H_2O.$$

C. Dehalogenation of polyhaloethanes or polyhaloethylenes by a metal was used to obtain monohaloacetylenes:

$$CX_2{=}CHX + M \rightarrow MX_2 + XC{\equiv}CH \text{ (for example, X = Br, M = Zn),}$$

$$CXY{=}CHY + M \rightarrow MY_2 + CX{\equiv}CH \text{ (for example, X = F, Y = Br, M = Mg).}$$

Viehe and Franchimont [40] proposed a preparative method for obtaining *fluoroacetylene* (yield 80%) from dibromofluoroethylene with magnesium in tetrahydrofuran.

D. Reaction of metal acetylides with halogens and some of their compounds which contain a negative group (for example, with cyanogen chloride). The halogen replaces both hydrogen atoms in acetylene, irrespective of whether one or both hydrogen atoms were substituted by metal [41]:

$$MC{\equiv}CM + 2X_2 \rightarrow 2MX + XC{\equiv}CX;\ HC{\equiv}CM + 2X_2 + MOH \rightarrow H_2O + 2\,MX + XC{\equiv}CX$$

where X = Br or I. The principal use of this method is the preparation of di-iodoacetylene [5,42–44]. Evidently another example of this type of reaction must be that described [45] between sodium acetylide and epi-iodohydrin [1,2-epoxy-3-iodopropane], [45] but the yield of C_2I_2 from this is insignificant.

E. Reaction of the same reagents as in Method D with ethynylenedimagnesium dibromide, which also leads to dihaloacetylenes:

$$BrMgC{\equiv}CMgBr + 2X_2 \rightarrow MgBr_2 + MgX_2 + XC{\equiv}CX$$

where X = Br or I.

F. The decomposition of mercury monohaloacetylides is a preparative method for obtaining *bromoacetylene* and *chloroacetylene*[46]:

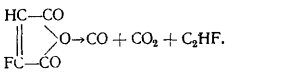
$$Hg(C{\equiv}CX)_2 + 4KCN + 2H_2O \rightarrow 2KOH + K_2Hg(CN)_4 + 2HC{\equiv}CX.$$

The initial mercury salts are readily obtained by shaking the corresponding dihaloethylenes CHX=CHX with mercury(II) cyanide in ~ 10% KOH solution:

$$2HXC{=}CXH + Hg(CN)_2 + 4KOH \rightarrow 2KCN + 2KX + 4H_2O + Hg(C{\equiv}CX)_2.$$

Fitzgibbon[47] showed that only *cis*-1,2-dichloroethylene forms a mercury bis(chloroacetylide) in this reaction. This salt liberates C_2HCl under the action of conc.HCl. *trans*-1,2-Dichloroethylene reacts with an alkaline solution of mercury(II) cyanide in another way. The author separated at least three products of the reaction, including $Hg(CCl{=}CHCl)_2$, which when boiled with conc. HCl gives dichloroethylene and $HgCl_2$.

G. The destructive decomposition of various halogen-containing compounds on heating, irradiation, etc. C_2I_2, C_2HCl, and C_2Cl_2 were obtained by heating the barium salts of iodopropiolic[48], $\beta\beta$-dichloroacrylic[6], and trichloroacrylic[8] acids respectively. The formation of C_2Cl_2 occurs in the pyrolysis of carbon tetrachloride[49]. The decomposition of dibromomuconic acid leads to the formation of C_2HBr.[50] Of the reactions of this type the most interesting from the preparative standpoint is a method of obtaining *fluoroacetylene* by the pyrolysis of fluoromaleic anhydride at 600–800°:



$$\rightarrow CO + CO_2 + C_2HF.$$

The yield of C_2HF is close to theoretical[10].

2. Synthesis of Derivatives of the Haloacetylenes

Some derivatives of haloacetylenes have been synthesised by the methods described above. Thus, Grignard and coworkers[51–53] obtained various haloacetylenes of the type RC≡CX (X = Br or I):

$$RC{\equiv}CMgX + BrCN \rightarrow MgXCN + RC{\equiv}CBr.$$

Bourguel and Truchet[54] obtained substituted chloroacetylenes by the reaction:

$$RC{\equiv}CNa + C_6H_5SO_2Cl \rightarrow C_6H_5SO_2Na + RC{\equiv}CCl.$$

Nazarov and Bergel'son[55] synthesised 4-bromo-2-methylbut-1-en-3-yne by the dehydrobromination of *cis*-1,2-dibromo-3-methylbuta-1,3-diene:

$$CH_2{=}C(CH_3){-}CBr{=}CHBr + CH_3ONa \rightarrow NaBr + CH_3OH + CH_2{=}C(CH_3)C{\equiv}CBr.$$

The reaction of 3,3,3-trifluoro-1,2-dihaloprop-1-enes with molten sodium hydroxide at elevated temperature[56] gave 1-chloro- and 1-bromo-3,3,3-trifluoroprop-1-ynes:

$$CF_3CX{=}CHX + NaOH \rightarrow H_2O + NaX + CF_3C{\equiv}CX.$$

For X = Cl the temperature of the reaction is 280–290°C and the yield 19%; for X = Br, they are 180–190°C and 27% respectively.

Eglinton and McCrae[57] obtained 1-bromoacetylenes in 80% yields by the action of bromine on organomercury compounds:

$$(RC{\equiv}C)_2Hg + 2Br_2\,(\text{in } CCl_4) \rightarrow HgBr_2 + 2RC{\equiv}CBr.$$

Various substituted haloacetylenes RC≡CX (R = Ar, $-CH_2OH$, $-CH_2OAr$, $-CH_2OCOAr$, alkenes, etc.; X = Br, I) were obtained in yields up to 50–80% by the reaction of the corresponding copper acetylides with halides (in solvents)[58–60]:

$$RC{\equiv}CCu + X_2 \rightarrow CuX + RC{\equiv}CX.$$

Chloro-, bromo-, and iodo-acetylenes were also obtained in analogous fashion[61]:

$$LiC{\equiv}C{-}C{\equiv}CH + X_2 \rightarrow XC{\equiv}C{-}C{\equiv}CH + LiX.$$

t-Butylfluoroacetylene is obtained by the dehydrohalogenation of the fluorohaloalkenes $(CH_3)_3CHC{=}CBrF$ and $(CH_3)_3CCCl{=}CHF$.[62] We note that the last is capable of spontaneous polymerisation to form interesting products. Among these are found 1,2,3-tri-(t-butyl)trifluorobenzene and other fluorinated derivatives of the valence isomers of benzene[62,63].

Tsmur and Ivanik[64] have described an interesting preparation of bromo(diethylamino)acetylene:

$$CH_2BrCON(C_2H_5)_2 \xrightarrow{PCl_5} CH_2BrCCl_2N(C_2H_5)_2 \xrightarrow{-2HCl} BrC{\equiv}C{-}N(C_2H_5)_2.$$

The lithium, sodium, and potassium salts of chloroacetylene are obtained, as Viehe[65] showed, by the reaction of a metal amide with *cis*- or *trans*-dichloroethylene in liquid ammonia:

$$ClCH{=}CHCl + 2LiNH_2 \rightarrow LiCl + LiC{\equiv}CCl + 2NH_3.$$

3. Analytical Determination of the Haloacetylenes

Little has been published on methods of analysis of the haloacetylenes. A procedure for the quantitative analysis of bromoacetylenes has been described, based on a specific method for the liberation of a halide, which is inert to ordinary hydrolysis. Chodkiewicz and coworkers[66] give two variants of this method.

According to the first variant 1-bromoacetylene is treated with a mixture of an acetylene compound with a trace quantity of copper(II) sulphate, a reductant (hydroxylammonium sulphate), and an organic base (for example, ethylamine) in a water–methanol medium.

According to the second variant the 1-bromoacetylene reacts with $CuSO_4$ and ethylamine in the same medium. In both variants the bromine is brought into an ionic state and determined argentometrically. The results of the analysis are reproducible with an accuracy of up to 1–2%. Both variants are also applicable to the determination of iodine in 1-iodoacetylenes, but only the second variant is applicable to the analysis of chloroacetylenes.

Widmann[67] determined the concentration of dichloroacetylene by the addition of an excess of 0.1 *N* solution of iodine in CCl_4 to an ethereal solution of the C_2Cl_2. The reaction mixture was kept for 2 h in daylight, after which the free iodine was titrated with thiosulphate. The author also found that there was a linear relation between the concentration of dichloroacetylene and the refractive index, and also the density, of ethereal solutions of C_2Cl_2.[36,38] Ott employed for analysis the ability of C_2Cl_2 to react with

certain substances with the formation of a dye. For example, an ethereal solution of C_2Cl_2 was added to a hot alcoholic solution of quinaldineiodoethylate [sic]† and the blue polymethine dye formed precipitated with perchlorate. Dyes were obtained similarly with 2-methylbenzthiazole and the corresponding selenium compound[68].

III. PHYSICAL PROPERTIES OF THE HALOACETYLENES

1. General Characteristics

With the exception of fluoroacetylenes, the halogenated acetylenes have a disgusting odour.

Under ordinary conditions C_2HBr, C_2HCl, and C_2HF are colourless gases; C_2HI, C_2Cl_2, and C_2Br_2 are liquids; and C_2I_2 is a solid.

C_2HBr condenses to a colourless liquid at room temperature and a pressure of 3 atm.[3] Aqueous and alcoholic solutions of C_2HBr and C_2HCl shine in the dark and give a strong ozone reaction[69,70]. The latent heat of vaporisation of C_2HBr is 58 cal deg^{-1} [cal g^{-1}? (Ed. of Translation)], and that for C_2HCl is 89 cal deg^{-1} [cal g^{-1}? (Ed. of Translation)].[70] The vapour pressure of C_2HBr has been measured from -58.7° (27.4 mmHg) to -1.2°C (610 mmHg) and that of C_2HCl from -68.0° (111.7 mmHg) to -35.9°C (636.9 mmHg) (see Briscoe and coworkers[71]).

The vapour pressure of C_2HF has been measured at various temperatures from -150° (26 mmHg) to -109.8°C (543 mmHg) (see Viehe and Franchimont[40]). The values of some thermodynamic quantities have been calculated for C_2HF and C_2F_2 in the temperature interval from 293.15° to 6000°K: standard free energy, entropy, change in enthalpy, and equilibrium constants for dissociation or ionisation[72]. The unusually low boiling point of fluoroacetylene shows the presence in it of only weak hydrogen bonds.

Di-iodoacetylene is readily volatile even at room-temperature[73]. The values of some thermodynamic functions have been calculated for it for temperatures from 373.16° to 1000°K: enthalpy, free energy, entropy, heat capacity[74]. The crystal lattice of solid di-iodoacetylene has been studied by X-ray diffraction[75,76].

Recently similar thermodynamic functions have been calculated for C_2HBr, C_2HCl, C_2HF, and their deuterated derivatives within the temperature limits 100–2000°K in terms of rigid rotator and harmonic oscillator models. The mean vibration amplitudes for molecules of the same compounds and the molecular polarisabilities have also been calculated[77] The calculated values of the latter for C_2HBr, C_2HCl, and C_2HF were 59.3203, 50.4078, and 31.8698 cm^3 × 10^{-25}. The values found for C_2HBr and C_2HCl were 68.1559 and 56.6645 cm^3 × 10^{-25} respectively.

Lemoult's calculated heat of combustion of dibromoacetylene is 260 kcal mole^{-1} and the heat of formation 71.4 kcal mole^{-1}. Pascal[79] gives values he found experimentally for the molecular magnetic susceptibility of dibromoacetylene and dichloroacetylene: 748 × 10^{-7} for C_2Br_2 and 526 × 10^{-7} for C_2Cl_2. The calculated values are 767.5 × 10^{-7} and 548 × 10^{-7} respectively.

Table 1 gives the most important physical constants and some physicochemical properties of haloacetylenes.

† The exact nature of this compound is not clear in Reference 68 (Ed. of Translation).

TABLE 1. Physical properties of haloacetylenes.

Haloacetylene	M.p., °C	B.p., °C	Dipole moment, D	Solubility	
				in water	in organic solvent
Bromoacetylene	—	−2[70] 4.7±0.1[71]	0[89]	soluble[3,6,70,93]	soluble in alcohol[4,93] very soluble in $C_2H_2Br_2$[3]
Chloroacetylene	—	from −32 to −30[69] −29.6±0.1[71]	0.44[89]	soluble[69]	soluble in alcohol[69]
Iodoacetylene	—	32[9]	—	—	—
Fluoroacetylene	from −165 to −160[11]	−104[11] −104.3[40] −105[87]	0.75±0.01[90] 0.73[91]	insoluble	soluble in diethyl ether
Di-iodoacetylene	74[80,81] 77–78[82,83] 78[45,73] 78.5–78.9[44] ~80[26] 81[25,43,82] 82[84–86]	98/4 mmHg (decomp. with explosion)[44]	0.33·10^{-18} e.s.u.[92]	insoluble[44]	soluble in ordinary organic solvents[45,73,80]
Dibromoacetylene	from −25 to −23[10]	76[33] 76–76.5[88] 80[7]	—	insoluble[7]	soluble in many organic solvents[7]
Dichloroacetylene	from −68 to −64[21] from −66 to −64.2[19]	32[21] 32–33/748 mmHg[5]	— —	insoluble insoluble	soluble in tetrachloroethane[24]; diethyl ether[21,24]

Note. The superscripts denote literature references.

2. Combustibility and Explosibility

Most of the halogenated acetylenes studied are capable of spontaneous ignition in air and also on heating. Often on contact with atmospheric oxygen they explode with great violence which makes it difficult and hazardous to work with them. *Bromoacetylene* burns in air with a purple smoky flame[1–3,50]. With pure oxygen it explodes with a flame and copious liberation of carbon[3]. Some authors[71] consider that C_2HBr cannot be mixed with oxygen at elevated pressure without explosion. *Chloroacetylene* also ignites and explodes on contact with air[6,46,69,94]. When insufficiently diluted with hydrogen it explodes with the formation of carbon; with insufficient air it inflames and burns with deposition of soot. The lower explosion limits with oxygen at 100°C are: for C_2HCl, 0.6–2.0 mmHg pressure, and for C_2HBr 2.5–4.5 mmHg. The presence of argon, nitrogen, and helium affect this limit for C_2HCl. The ignition of C_2HBr is inhibited by the addition of CS_2, C_2H_4, or SO_2.[71] In the gas phase fluoroacetylene is stable in air and only on setting fire to a stream of the gas does it burn, with a blue flame[10,11,40]. Viehe and Franchimont[40] reported that they did not observe explosions with C_2HF in any state of aggregation. Other investigators[10,87] showed that liquid fluoroacetylene exploded violently but the reasons are not clear. These reports are confirmed by experiments made by the authors of the present review. It has been stated[10] that solid C_2HF does not explode. *Di-iodoacetylene* decomposes to the elements with a powerful explosion on heating to 80–100°C.[87,95] According to other work, decomposition with explosion sets in between 121° and 128°C; the explosion of C_2I_2 has also been noted on vacuum distillation (4 mmHg, 98°C).[44] Jaeschke[96] reported the explosion of the dry product in work after Franzen. C_2I_2 bursts into flame sometimes even at low temperatures[44] and explodes on mechanical shock or friction. An example has been described of a violent explosion with a serious wound in an

attempt to spread crystals of C_2I_2 with a pestle[97]. *Dibromoacetylene* takes fire in air and burns with a red, smoky flame[88]; it explodes very violently on heating, decomposing with formation of carbon[7,19], and also on coming in contact with oxygen; it even explodes in an atmosphere of CO_2 or N_2 containing traces of oxygen[33]. *Dichloroacetylene* explodes violently on contact with air[19,34], and also on moderate heating[19]; diluted with nitrogen, it ignites in air[98]. Out of contact with air it decomposes with explosion at 130°C.[27]

3. Physiological Activity

Nothing has yet been published about the toxicity of iodoacetylene and fluoroacetylene. All the other mono- and di-haloacetylenes known at present are substances which exhibit comparatively high toxicity. Sabaneev[4] and Nef[93] compare bromoacetylene with phosphorus in toxicity. Ingold[69] states that inhalation of even traces of chloroacetylene produce very unpleasant sensations. Di-iodoacetylene vapour strongly attacks the eyes[43] and mucous membranes[1,73]; it is a strong poison for micro-organisms and an effective inhibitor of putrefraction, its activity to it being approached only by the extremely toxic cyanogen iodide[73], but it does not find use in the fight against putrefraction owing to its high toxicity and disgusting odour. Mebert[99] found that subcutaneous introduction of 0.2–0.3 g di-iodoacetylene into rabbits weighing 1.5–2.0 kg was lethal in two days bringing about emphysema. Loew[100] studied the toxic action of di-iodoacetylene in dilutions of 1 : 5000, 1 : 10 000, 1 : 20 000, 1 : 100 000, and 1 : 1 000 000 on bacteria (*Bac. subtillis, Bac. fluorescens liquefaciens*), fungi (spores of penicillin, *Aspergillus*), yeasts, lower algae (diatoms, *Oscillarien, Spirogyrafäden*), the infusoria *Flagellaten*, and also *Zimnaen, Copepoden, Nematoden*, and *Rotatorien*. The author found that in the presence of di-iodoacetylene, even in very great dilutions, all the micro-organisms did not develop, but either lost mobility, or usually perished. Of the vertebrate animals, they made tests on mice and porpoises. When introduced subcutaneously or *per os*, C_2I_2 acts slowly, owing to its poor solubility, but inhalation of its vapour leads to rapid destruction of the animals.

Inhalation of dibromoacetylene produces a severe, long-lasting headache[33,88], a sensation of weakness[88], difficulty in breathing, and pronounced loss of memory[33].

Dichloroacetylene shows its toxicity quite specifically[68]. On inhaling the ether addition compound of dichloroacetylene mice died from respiratory paralysis[35].

Ott and Bossaller[101] have shown, in a work devoted to the chemical reactions of dichloroacetylene, that "lower aliphatic alkylchloroacetylenes are evidently very toxic compounds, the action of which brings about prolonged disturbance of the nervous system. It appears in weakness of the legs, maintained for a week, and for some time walking is generally impossible. Temporary paralysis of the optic nerves also occurs".

4. Structure of the Molecule. Spectra

Nef[43,93] thought that the mono- and di-haloacetylenes have not a linear, but an acetylidene structure: XHC=C or X_2C=C, with a bivalent carbon atom, which also confers specific properties on these compounds. Such a view was held subsequently by Lawrie[33], and by Nekrasov[88]. Other investigators — Lemoult[102], Ward[103], Biltz[104], and Ott[34] — supported a linear structure for the haloacetylenes, chiefly on the basis of a study of their chemical properties. According to Ingold[69] the monohaloacetylenes are tautomeric compounds, since the acetylenic hydrogen atom is labile: $XC{\equiv}CH \rightleftharpoons XHC{=}C$. The properties of chloroacetylene which sharply distinguish it from acetylene, he explains by the fact that in chloroacetylene (and also in bromoacetylene) this equilibrium at ordinary temperatures is more displaced to the side of acetylenic structures than in acetylene. The dihaloacetylenes, according to Ingold, exhibit stable acetylene structures. Howell and Noyes[105] considered that the properties of di-iodoacetylene are readily explained if it is assumed that the iodine atoms in this compound are positive, and it is not necessary to resort to Nef's bivalent carbon atom.

In later work objections against the acetylidenic structures were based on the results of studies of the haloacetylenes by physical methods. Thus, Sidgwick[106] doubted the existence of acetylidenic structures on the basis that the terminal carbon in such molecules only has a valency sextet. He considers that the controversy about the structure of di-iodoacetylene was settled in favour of the linear structure of its molecule since the dipole moment of this compound was found to be 0.33 D, that is, closer to zero. Glockler and Morrel[107] initially favoured the linear structure on the basis of a study of the Raman spectrum of di-iodoacetylene in alcoholic solution, but in later work[108] supported a non-linear structure for this compound. However, Cleveland and Meister[109], on comparing their results from an investigation of the vibrational spectrum of di-iodoacetylene with data of other authors, again supported the linear, symmetrical structure for this compound. There have been other investigations of the spectra of di-iodoacetylene[110-112]. Table 2 gives some of the results obtained in these investigations.

de Laszlo[119] studied the structure of C_2I_2, C_2Br_2, and C_2Cl_2 by electron diffraction in the gas phase and concluded that the first two compounds had linear structures. However, he thought that the experimental results agreed with the acetylidene structure for dichloroacetylene. An investigation of the radial distribution curve led him to the conclusion that dichloroacetylene is a mixture with $\geq 20\%$ molecules with a linear structure. de Laszlo thought that a difference in the structure of C_2Cl_2 may also appear in some of its chemical properties. For example, C_2Cl_2, unlike di-iodo- and dibromo-acetylene, invariably explodes on contact with air, forms carbonyl chloride on oxidation, etc.

The results of other authors who investigated dichloroacetylene by the same method completely disagree with those of de Laszlo. Thus Hassel and Viervoll[123] found de Laszlo's conclusion about the C_2Cl_2 structure erroneous, and on the basis of an analysis of the experimental data they concluded that its molecule is linear, symmetrical, and corresponds to the formula Cl–C≡C–Cl. Hassel and Taarland[120] came to the same conclusion, and also Finbak and Hassel[121], who also studied the molecular structure of C_2Cl_2 by electron diffraction.

The linear structure of bromoacetylene and chloroacetylene was demonstrated by electron diffraction[23]. Microwave spectroscopy confirmed the linearity of the molecules of chloroacetylene[115] and showed an analogous structure of fluoroacetylene[23].

The structure of iodoacetylene has not yet been studied.

The infrared spectra of all the monohaloacetylenes are now known. The infrared spectra of gaseous C_2HF, C_2HBr, C_2HCl, and their deuterated derivatives have been studied and published in the detailed review of Hunt and Wilson[23] and more recently also by Nagarajan and Hariharan[77]. Brown and Tyler[24] investigated the infrared spectra of C_2HF, C_2DF, and C_2HI. Other authors[10,11,40] have also considered the infrared spectrum of fluoroacetylene.

Displacement of the bond frequencies to longer wavelengths is observed in the infrared spectra of deuterated monohaloacetylenes. The force constants of the C–halogen bonds in these molecules are considerably greater than in the corresponding haloethanes and are essentially the same as in the cyanogen halides, but the C–halogen bond length is much (~ 10%) shorter than in the corresponding haloethanes and a little greater than the same bonds in the cyanogen halides[23].

White observed the $J = 1 \rightarrow 2$ transition taking place in the microwave spectrum of DC≡CCl obtained with the aid of a spectrometer of high resolution, and found a hyperfine structure, due to the quadrupole moment of the deuterium. He measured the constants of quadrupole interaction of deuterium, 175 ± 20 kHz, calculated the field gradient at the deuterium nucleus, $q = (8.85 \pm 0.9) \times 10^{-14}$ e.s.u., and discussed the results obtained[124,125].

The bond lengths in the haloacetylene molecules were calculated from the results of microwave spectroscopy[91], but chiefly from the investigation of these substances by electron diffraction. Table 2 gives the vibration frequencies found in the infrared spectra of halogenated acetylenes and also the calculated values of the lengths and force constants of the bonds in these molecules according to the work of various authors. The Stark effect which can be observed in the microwave spectrum of C_2HCl was close to that calculated[115].

Bykov[126] proposed a scheme for calculating the electronic charges of the bonds, starting from the values of the electronegativities of the atoms and calculated the σ- and π-electron charges of the bonds in the chloroacetylene molecule; such a calculation gives:

$$H \overset{1.91}{\underset{0.91}{}} C^{2\pi} \overset{2.00}{\underset{2.00}{}} C^{2\pi} \overset{2.09}{\underset{1.09}{}} Cl$$

(the lower row is for π-electrons).

Anno and Sado[127] found that the relation between the length and order of the C–Cl bond in the chloroacetylene molecule is expressed by a relation similar to that given earlier by Coulson for C–C bonds[127].

Analysis of the infrared and microwave spectra for chloroacetylene led some investigators to conclude that the C–Cl bond has some degree of double-bond character, which explains the resonance of the

$$H-C\equiv C-C \quad \text{and} \quad H-\overset{-}{C}=C=\overset{+}{Cl}$$

structures[113,115]. Comparison of chloroacetylene with methyl chloride shows that on going to chloroacetylene the length of the C–Cl bond decreases from 1.786 Å (in CH_3Cl) to 1.632 Å (in C_2HCl). During this the force constant of this bond rises sharply, by approximately 45%. In analysing this fact, Duchesne[118] finds that the concept of resonance is here insufficient, since it can explain the increase in the force constant of the bond to the extent of only ~ 15%. The author assumes that this phenomenon is explained by the large value of the overlap integral of the chlorine and carbon orbitals.

An analogous tendency also appears in the C–F bond in fluoroacetylene[23,24,40]. See Moreau[128] for the electronic structure of C_2HF and C_2HCl.

TABLE 2.

Haloacetylene	Bond frequencies found in the infrared and Raman spectra, cm^{-1}			Lengths of the bonds in the molecule, Å			Force constants of the bonds in the molecule, 10^{-5} dyn cm^{-1}		
	C–H	C≡C	C–X	C–H	C≡C	C–X	C–H	C≡C	C–X
Bromoacetylene	3325 [23]	2085 [23]	618 [23]	1.0587 [23,114]	1.20±0.04 [89]	1.80±0.03 [89]	5.85 [23,122]	15.7 [23]	4.6 [23]
Chloroacetylene	3340 [23] 3319 [113]	2110 [23] 2109 [113]	756 [23,113]	1.0587 [23,114] 1.052±0.001 [115]	1.211±0.001 [23] 1.21±0.04 [99] 1.211 [115,117,118]	1.632±0.001 [115] 1.68±0.04 [89] 1.630 [118]	5.85 [23,122]	15.8 [23] >15.0 [118]	5.4 [23] 5.0 [118]
Iodoacetylene	3320 [24]	2075 [24]	about 629 [24]	1.055 [116]	1.203 [116]	1.988 [116]			
Fluoroacetylene	3330 [10,11] 3333 [40]	2210 [10,11] 2255 [23]	1000—1100 [10,11]	1.0587 [23,114]	1.2054 [23]	1.275 [23]		15.85 [23,114]	8.8 [23]
		2245 [24]	1055 [23]		1.198 [90]	1.279 [90]	5.85 [23,122]	15.8 [24]	
	3355 [23]	2092	1064 [24]	1.053 [90]		1.280 [40]	6.06 [24]		8.64 [21]
	3370 [24]	2118 2247 2222 } [40]	1052,1077 [40]		1.20 [23]				
Di-iodoacetylene	—	2109 [107]	627 [107]	—	1.18 [74,119]	2.03 [74,119]	—	—	—
Dibromoacetylene	—	—	—	—	1.18 [119]	1.84 [119]	—	—	—
Dichloroacetylene	—	—	—	—	1.195 [120,121] 1.18 [119]	1.64 [120] 1.640 [121] 1.75 [119]	—	—	—

Note: The superscripts denote literature references.

IV. CHEMICAL REACTIONS OF THE HALOACETYLENES

All the haloacetylenes are very reactive substances. They vigorously add halogens and various nucleophilic reagents, and polymerise. Monohaloacetylenes enter into reactions which depend on the presence of a labile acetylenic hydrogen atom. Thanks to the displacement of electrons towards the electronegative halogen atoms, the hydrogen in such compounds is more protonic than in acetylene. For this reason it readily reacts with substances of basic character.

As already mentioned, Howell and Noyes [105], in objecting to the acetylidenic structure of Nef, expressed an opinion about the positive nature of the halogen in the haloacetylene molecules. Although the conclusions advanced by the authors on this basis are quite controversial and on the whole do not constitute a sufficiently weighty argument, such a standpoint is firmly based, bearing in mind the strong *I*-effect of the C≡C group. The latter can be shown as follows.

Petro [129] considered the problem of the influence of hybridisation of the carbon atom on bond polarity. On going from sp^3-hybridisation to sp^2- and sp- the electronegativity of the carbon atom rises appreciably. This leads to a corresponding rise in the dipole moment of the H–C bond:

$$\text{H—C}\,(sp^3) = 0.31$$
$$\text{H—C}\,(sp^2) = 0.63$$
$$\text{H—C}\,(sp) = 1.05.$$

The prediction of the direction of polarisation of the C–halogen bond in haloacetylene molecules (sp-hybridisation) is especially interesting. Let us consider, for example, chloroacetylene. The dipole moment of the chloroacetylene molecule is 0.44 D. The dipole moment of the H–C bond in C_2HCl is 1.05 D. Since the dipole moment of the molecule is significantly lower than the dipole moment of the H–C bond, then starting from the fact that the dipole moment of a molecule is the vector sum of the ≡C–H and ≡CCl moments, it can be concluded that in the chloroacetylene molecule, which has a linear structure, the direction of the Cl–C vector is opposite to the H–C vector, that is, the bond has the character $\equiv\bar{C}-\dot{C}l$. Analogous discussions are evidently also correct for C_2HBr and C_2HF.

It is known that compounds with positively charged halogen atoms exhibit certain specific physical and chemical properties [130,131], which are also encountered in the haloacetylenes. Thus, the haloacetylenes are of low stability and readily decompose with explosion. Di-iodoacetylene displaces iodine from a solution of potassium iodide, the iodine atom is replaced by hydrogen on hydrolysis, and oxidises phenylhydrazine with release of nitrogen. Some other reactions of haloacetylenes [132,133] can also be explained from the standpoint of the concept of the positive nature of the halogen atom.

We considered it desirable to classify the reactions of haloacetylenes as follows: (1) reactions at the triple bond; (2) reactions with replacement of hydrogen; (3) reactions with replacement of halogen; (4) decomposition of the haloacetylenes, and oxidations; (5) molecular compounds of haloacetylenes.

1. Reactions at the Triple Bond

a. Reactions with halogen and hydrogen halides. Bromoacetylene [2,3], chloroacetylene [6,19,39], and fluoroacetylene [10,11] react vigorously with bromine, adding two molecules of the latter:

$$CH \equiv CX + 2Br_2 \rightarrow CHBr_2 - CXBr_2.$$

Bromoacetylene adds HI and HBr, the latter forming *trans*-dibromoethylene [134]. An American patent [135] stated the possibility of obtaining fluoro-compounds by the reaction of chloroacetylene with HF in the presence of BF_3 at 70–250°C, but the composition of the products formed was not given.

Di-iodoacetylene, on adding on free chlorine and bromine at the triple bond, also exchanges both iodine atoms during this. For example, hexachloroethane is obtained in good yield in the reaction of chlorine with solid di-iodoacetylene [44,105] or on passing dry chlorine into a chloroform solution of this substance [73]. On standing for many days with bromine in a sealed glass vessel, C_2I_2 is converted into hexabromoethane [73]. In chloroform solution at ~ 0°C, bromine is added immediately. The product is a mixture of ICBr=ClBr (80%), CI_2=ClBr (10%), and CBr_2=CBrI (10%).[43] On treatment with an ethereal solution of iodine, di-iodoacetylene is smoothly converted into periodoethylene [43]. The solvent and temperature play an important part in this. For example, in benzene the reaction takes place on heating for 1 h; [44] in boiling toluene the addition of two atoms of iodine is instantaneous [20,73]. However, equivalent quantities of iodine and di-iodoacetylene in carbon disulphide combine (in the absence of light) only after several days [73,136]. The reagent is greatly inhibited by oxygen [137].

Under the action of bromine (without a solvent or in ether) dibromoacetylene is converted into tetrabromoethylene in 89% yield [19,88]. One molecule of iodine is also added, being converted into symmetrical dibromodi-iodoethylene in 82.5% yield [19]. Hydriodic acid gives both dibromoiodoethylene CBrI=CHBr and dibromodi-iodoethylene. If the HI is not purified from free iodine, then only the latter of these products is obtained in practice [33].

Dichloroacetylene adds elemental chlorine to form hexachloroethane. With bromine water, tetrabromodichloroethane is obtained [19]. With elemental bromine, without a solvent or in carbon tetrachloride medium, dichloroacetylene gives *sym*-dibromodichloroethylene [34]. It slowly reacts with a dilute ethereal solution of iodine, adding on one molecule of iodine and forming dichlorodi-iodoethylene [34,35]. The same reaction proceeds rapidly in carbon tetrachloride [35].

b. Reactions with ammonia and amines. Chloroacetylene does not react with ammonia. With diethylamine in diethyl ether it slowly forms diethylformamide and diethylammonium chloride. It reacts with aniline only at 150–160°C, forming anilinium chloride and indole [138]. Fluoroacetylene reacts with liquid ammonia forming ammonium fluoride and acetonitrile. According to Viehe and Franchimont [40] the mechanism of the reaction is the nucleophilic addition of amide ions at the triple bond with subsequent elimination of a fluoride anion: the intermediate formation of aminoacetylene is proposed:

$$FC\equiv CH \xrightarrow{NH_3} H_2N\!-\!C(F)=C^{-}\!-\!H \longrightarrow NH_2C\equiv CH \longrightarrow CH_3CN.$$

Dichloroacetylene in ethereal solution reacts with gaseous ammonia, forming ammonium chloride and chloroacetonitrile in good yield. The intermediate formation of chloroaminoacetylene is proposed [139]:

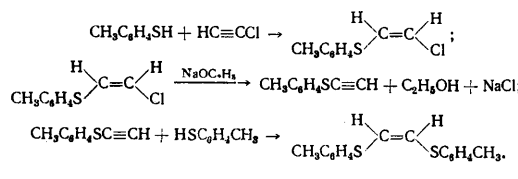
$$ClC\equiv CCl + NH_3 \rightarrow ClCH=C(NH_2)Cl \xrightarrow{-HCl} ClC\equiv CNH_2 \rightarrow CH_2ClC\equiv N.$$

With primary amines dichloroacetylene forms, in addition to the hydrochloride of the base, aminoamidines in good yield[139], analogous to those obtained earlier by other authors from tetrabromoethane or trichloroethylene with aniline and other aromatic amines[140,141]. With diethylamine the asymmetric 2-chloro-1,1-bis(diethylamino)-ethylene is formed[138]:

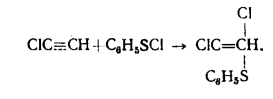
$$(C_2H_5)_2NH + ClC{\equiv}CCl \rightarrow (C_2H_5)_2NCCl{=}CHCl;$$
$$(C_2H_5)_2NCCl{=}CHCl + (C_2H_5)_2NH \rightarrow HCl + [(C_2H_5)_2N]_2C{=}CHCl.$$

The passage of dichloroacetylene into an excess of triethylamine gave a quaternary ammonium salt which was converted into the perchlorate and the hexachloroplatinate(IV); a compound with gold(III) chloride was also characterised[139].

c. Reactions with sulphur-containing, mercury-containing, and other reagents. In the presence of the $C_2H_5O^-$ ion chloroacetylene adds *p*-tolylthiol to form *cis*-1,2-bis-(*p*-tolylthio)ethylene (77.4%) and *cis*-1-chloro-2-(*p*-tolylthio)ethylene (20.3%). Traces of *p*-tolylthioacetylene are also formed[142]. The initial addition product *cis*-1-chloro-2-(*p*-tolylthio)ethylene is converted, as a result of dehydrohalogenation, into *p*-tolylthioacetylene, which then also reacts with the *p*-tolylthiol. During this there is trans-nucleophilic addition of the latter at the triple bond with formation of *cis*-1,2-bis-(*p*-tolylthio)ethylene[143]:



Such a reaction mechanism is confirmed by the fact that treatment of *cis*-1-chloro-2-(*p*-tolylthio)ethylene with sodium ethoxide in alcohol gives *cis*-1-ethoxy-2-(*p*-tolylthio)ethylene[144]. The reaction of chloroacetylene with benzenesulphenyl chloride[145] in ether gave *trans*-1,2-dichloro-2-phenylthioethylene in 38% yield:



The reaction of fluoroacetylene with thiophenol proceeds by nucleophilic addition of the latter with formation of 1-fluoro-1-phenylthioethylene[146]. The addition of thiophenol to dichloroacetylene in alcoholic–ethereal solution gave *cis*-1,2-dichloro-2-phenylthioethylene, in addition to *cis*-1,2-dichloro-2-ethoxyethylene as a side-product[145]. In the presence of alkoxides, dichloroacetylene adds alcohols without loss of halogen, forming $\alpha\beta$-dichlorovinyl esters[139]:

$$ClC{\equiv}CCl + ROH \rightarrow HCCl{=}CClOR.$$

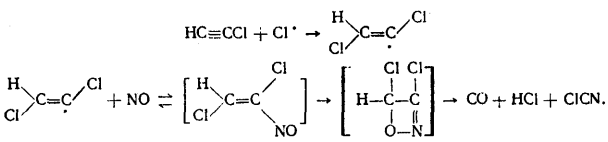
Chloroacetylene, on reacting with an aqueous solution of mercury(II) chloride, gives tris(chloromercury)acetic acid $(ClHg)_3CCO_2H$.[46] The following mechanism for the reaction is proposed:

$$HC{\equiv}CCl + 2\,ClHg^+ + 2\,Cl^- = (ClHg)_2CHCCl_3 \xrightarrow[+ClHg^+ + Cl^-]{-HCl} (ClHg)_3CCl_3 \xrightarrow{H_2O} (ClHg)_3COOH.$$

Sherwood and Gunning[147] described an interesting reaction of chloroacetylene with nitrogen monoxide, induced by a chlorine radical, leading to the breaking of the triple carbon bond:

$$HC{\equiv}CCl + NO \xrightarrow{Cl^\cdot} ClCN + CO + HCl.$$

The authors irradiated a rarefied mixture of C_2HCl, NO, and $COCl_2$ (a source of chlorine radicals) with radiation from a quartz mercury lamp at room temperature through a filter which cuts off the short waves. They give a reaction mechanism with hypothetical formation of an intermediate product of cyclic structure:



When chloroacetylene served as the source of radicals diacetylene was also found in the products:

$$C_2HCl \xrightarrow{+h\nu} C_2H^\cdot + Cl^\cdot$$
$$C_2H^\cdot + C_2HCl \rightarrow C_4H_2 + Cl^\cdot.$$

On passing fluoroacetylene into a neutral solution of potassium tetraiodomercurate(II) HgI_2 adds at the triple bond and forms, in over 90% yield, bis-(2-fluoro-2-iodovinyl)-mercury — white, well-formed crystals, m.p. 97°C:[148]

$$FC{\equiv}CH + HgI_2 = (FIC{=}CH)_2Hg.$$

Dichloroacetylene reacts vigorously with sodium ethyl malonate. A solution of dichloroacetylene in diethyl ether is used for the reaction. The reaction mixture contains chloroethylenebismalonic ester [sic] plus a variable amount of its hydrogenation product. In an analogous reaction with the sodium derivative of diethyl ethylmalonate the main reaction product was diethyl (chloroethynyl)ethylmalonate $ClC{\equiv}C.C(C_2H_5)(CO_2C_2H_5)_2$ (~ 55%). About 33% tetraethyl chlorovinylenebis(ethylmalonate) $(C_2H_5OCO)_2C(C_2H_5).CH{=}CCl.C(C_2H_5)(CO_2C_2H_5)_2$ was also obtained; the residue (12%) was a mixture of the ester of α-methylbutyric acid (80%) and the ester of α-chlorovinylbutyric acid (20%).[139] Dichloroacetylene reacts sluggishly with diazoacetic ester; the product isolated corresponded to the empirical formula $C_{10}H_{12}N_4Cl$, but was not studied further[101]. 1,2-Dichloro-1-nitroethylene was obtained in good yield by the addition of NO_2 to dichloroacetylene[101]; the mechanism of this reaction has not been studied. The action of NO_2Cl (in ether) leads to 1,1,2-trichloro-2-nitroethylene[149]. The reaction of dichloroacetylene with thiocyanate in ether gave 1,4-bis-thiocyanatobut-2-ene in 80% yield; the mechanism of this reaction also has not been explained[150].

d. Polymerisation. Monohaloacetylenes are trimerised into symmetrical trihalobenzenes, but the yields are usually low. The main mass of the product consists of polymers whose structure has not been investigated.

Gaseous bromoacetylene does not polymerise but the liquid does. The polymerisation is catalysed by light and a molecular compound of composition $[(C_6H_5)_3P]_2NiBr_2.n\text{-}C_4H_9Br$.[151] In the liquid phase under the action of light it yellows and becomes turbid in a few hours, but after a month it has become almost completely converted into turmeric-coloured powder, only partly soluble in organic solvents. Tribromobenzene amounts to ~ 10% of the polymerisation products[4].

The copolymerisation of C_2HBr with vinyl acetate was effected in sealed glass ampoules, the reaction mixture

being kept in bright sunlight for 11 days [152]. The product was a brown amorphous substance soluble in chloroform and acetone. The copolymer decomposes at 101–102°C and by analysis it corresponds to the composition $[(CH_3COOCHCH_2)(CHCBr)]_n$. Copolymerisation with styrene was carried out similarly. The reaction products isolated were coloured solids, which by analysis and molecular weight corresponded to copolymers of composition $[(C_6H_5CHCH_2)(CHCBr)]_2$; $[(C_6H_5CHCH_2).(CHCBr)]_2$; $[(C_6H_5CHCH_2)_4(CHCBr)]_3$. [152] The reaction of C_2HBr with octacarbonylcobalt gave a solid infusible substance corresponding to the empirical formula $C_3H_3BrCoO_6$. [151]

On illumination and heating with a 100 W lamp, chloroacetylene polymerises even in the gaseous state. It gives, together with 1,3,5-trichlorobenzene, a polymer which decomposes at 290°C. [69,153]

Fluoroacetylene polymerises spontaneously at room temperature in the absence of polymerisation initiators, whether in the light or whether in the dark [11], forming a brown powder [10,11] soluble with difficulty in organic solvents. The solubility of the polymer shows its linearity, and the colour its polyene, conjugated structure [11]. A little *sym*-trifluorobenzene is also formed [10]. Dichloroacetylene is converted into resinous products and hexachlorobenzene at a temperature below 130°C. [27] Hexachlorobenzene is also formed, together with other products, in diethyl ether under the action of light or in heating the solution on the water-bath under pressure [139]. Other authors [19] maintain that dichloroacetylene is insensitive to light.

2. Hydrogen Exchange

Bromoacetylene and chloroacetylene form copper salts with solutions of copper(I) oxide in ammonia. Copper bromoacetylide is evidently unstable and is converted into copper acetylide [13,50]. Copper chloroacetylide is more stable although it changes rapidly in air: the concentration of copper in it is 9% in excess of theoretical. Under the action of HCl or KCN the substance liberates chloroacetylene, which shows the structure to be ClC≡CCu. [6,46] Silver chloroacetylide is obtained similarly [6,32,39,46,69], and also releases C_2HCl under the action of HCl and KCN. The copper and silver salts of chloroacetylene explode more violently than the corresponding salts of acetylenes, especially the silver salt, which explodes even under water [69]. The lithium salt of chloroacetylene is obtained by the reaction of *cis*- or *trans*-1,2-dichloroethylene with lithium amide, and also with organolithium compounds, for example, with n-butyl-lithium in absolute ether [154,155]:

$$CHCl{=}CHCl + LiC_4H_9 \rightarrow C_4H_{10} + CCl{\equiv}CH + LiCl;$$
$$CCl{\equiv}CH + LiC_4H_9 \rightarrow C_4H_{10} + CCl{\equiv}CLi.$$

The mercury salts of bromoacetylene and chloroacetylene $(BrC{\equiv}C)_2Hg$ and $(ClC{\equiv}C)_2Hg$, in distinction from the chlorovinyl compounds, do not exhibit the properties of quasicomplexes. They are indifferent to the action of triphenylphosphine; aqueous and alcoholic solutions of potassium cyanide or potassium iodide bring about only hydrolysis (alcoholysis) of these substances with release of the haloacetylene:

$$(BrC{\equiv}C)_2Hg + 2H_2O + 4I^- \rightarrow 2\,BrC{\equiv}CH + HgI_4^{2-} + 2\,OH^-$$

but do not lead to the liberation of elemental carbon [156]. With an aqueous solution of silver nitrate, fluoroacetylene forms only a yellow salt, also extremely explosive on heating or friction [10,11].

Deuterated derivatives of monohaloacetylenes BrC≡CD, ClC≡CD, and FC≡CD were obtained by repeatedly passing C_2HBr, C_2HCl, and C_2HF through weakly alkaline D_2O and were purified by distillation. The exchange of hydrogen by deuterium reached 70%. [23,90]

3. Halogen Exchange

The bromine atom in bromoacetylene is replaced by copper on reaction with an ammoniacal solution of copper(I) oxide. The formation of copper acetylide is proved by the production of pure acetylene when this precipitate is treated with HCl. [50] Reboul describes the decomposition of bromoacetylene in the initial stage of this reaction by the equation:

$$C_2HBr + 3\,Cu_2O \rightarrow C_2HCu_3 + CuBr + 3\,CuO.$$

Zavgorodnii and Petrov assume that in the reaction of bromoacetylene with sodium trialkyltin in liquid ammonia the lability of the hydrogen atom in the C_2HBr molecule exceeds the lability of the bromine atom. As a result of the reaction the authors obtained trialkyl(bromoethynyl)-tin(IV), together with μ-ethynylbis(trialkyltin): [157]

$$HC{\equiv}CBr \xrightarrow{R_3SnNa} R_3SnC{\equiv}CBr \xrightarrow{R_3SnNa} R_3SnC{\equiv}CSnR_3$$

where R = CH_3, C_2H_5.

Study of the reactions of dichloroacetylene showed that the first chlorine atom undergoes various reactions very readily. Its activity in reactions with ammonia and amines is comparable with the activity of chlorine in acid chlorides [139], and Viehe [154] speaks of them as "positive, capable of being replaced by metal". Under the action of alcoholic potassium hydroxide dichloroacetylene is partly converted into chloroacetylene and potassium hypochlorite. Arens [132] presents this reaction as a nucleophilic substitution of a hydroxide ion for the chloroacetylide ion at the chlorine:

$$ClC{\equiv}CCl + OH^- \rightleftarrows ClC{\equiv}C^- + OHCl;$$
$$ClC{\equiv}C^- + H_2O \rightleftarrows ClC{\equiv}CH + OH^-.$$

With organolithium compounds dichloroacetylene almost quantitatively exchanges the chlorine atom for lithium with the formation of a lithium salt of chloroacetylene [65]:

$$RLi + ClC{\equiv}CCl \rightarrow RCl + LiC{\equiv}CCl.$$

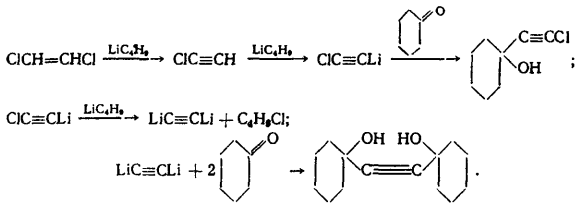
With the aid of such salts a chloroethynyl group has been introduced into the molecules of various organic compounds [65], for example:

$$LiC{\equiv}CCl + CH_3CH_2CHO \rightarrow CH_3CH_2CH(OH){-}C{\equiv}CCl;$$
$$2\,NaC{\equiv}CCl + Br(CH_2)_6Br \rightarrow 2\,NaBr + ClC{\equiv}C(CH_2)_6{-}C{\equiv}CCl;$$
$$NaC{\equiv}CCl + (C_6H_5)_3SnCl \rightarrow NaCl + (C_6H_5)_3Sn{-}C{\equiv}CCl.$$

In the decomposition of LiC≡CCl by water chloroacetylene is formed in 85% yield [154]; by the carbonisation of this salt chloropropiolic acid is obtained; reaction with orthocarbonic ester gives the ethyl ester of this acid, and with aliphatic acid anhydrides chloroethynylketones [155] are formed:

$$ClC{\equiv}CLi + (C_2H_5CO)_2O \rightarrow ClC{\equiv}CCOC_2H_5 + C_2H_5COOLi.$$

Reactions between cyclohexane and LiC≡CCl show that both chlorine atoms in dichloroacetylene can be successively replaced by lithium[155]:



With silver nitrate in water or alcohol, dichloroacetylene forms a precipitate sensitive to light, apparently consisting of C_2Ag_2 and AgCl.[19] Dichloroacetylene and also di-iodoacetylene replace both halogen atoms on reaction with Ilosvay solution. The first gives Cu_2C_2,[19] the second a mixture of Cu_2I_2 and Cu_2C_2.[42]

Exchange of the halogen atoms in reactions with organometallic compounds is characteristic for all the haloacetylenes.

With ethylmagnesium iodide bromoacetylene forms ethynylenedimagnesium dibromide[132]:

$$HC{\equiv}CBr + 2\,C_2H_5MgBr \rightarrow BrMgC{\equiv}CMgBr + C_2H_5Br + C_2H_6.$$

Fluoroacetylene reacts to form alk-1-ynes[87]:

$$2\,FC{\equiv}CH + 2\,RMgBr \rightarrow MgBr_2 + MgF_2 + 2\,RC{\equiv}CH$$
$$FC{\equiv}CH + RLi \rightarrow LiF + RC{\equiv}CH.$$

With butyl-lithium and phenyl-lithium, hex-1-yne and phenylacetylene are obtained respectively[40]; alkynes are also obtained with many other alkyl-lithiums or Grignard compounds (R = CH_3, n-C_5H_{11}, n-C_6H_{13}, n-C_7H_{15}, $CH_2C_6H_5$).

Dichloroacetylene reacts readily with organomagnesium compounds with the formation of 1-alkyl- or 1-aryl-2-chloroacetylenes of the general formula ClC≡CR. In this way 2-chloro-1-phenylacetylene was obtained in yields of 70% and other 2-choroacetylenes in yields of 40–52% (R = *p*-tolyl, *p*-anisyl, cyclohexyl, dodecyl)[101], and also various unsaturated compounds, including chloro(phenyl)diacetylene[154]:

$$C_6H_5C{\equiv}CMgCl + ClC{\equiv}CCl \rightarrow MgCl_2 + C_6H_5C{\equiv}C{-}C{\equiv}CCl.$$

The reaction of ClC≡CR, in which R is an unsaturated radical, with organolithium compounds, gives highly unsaturated compounds, for example, diphenyloctatetrayne and *cis*,*cis*-deca-2,8-diene-4,6-diyne.

The haloacetylenes RC≡CX (mainly with X= Br) readily undergo the Arbuzov rearrangement under ordinary conditions with the formation of the esters of alk-1-ynylphosphonic acids:

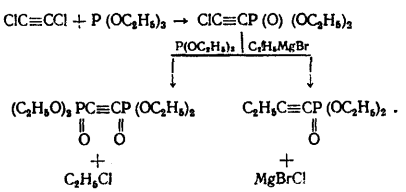
$$R'C{\equiv}CX + (RO)_3P \rightarrow R'C{\equiv}C{-}\underset{\underset{O}{\|}}{P}(OR)_2 + RX.$$

The yields are 67% for R′ = C_6H_5 and 48% for R′ = $-CH{=}CH_2$.[158] Analogous products were obtained also by the reaction of 1-bromoacetylenes with sodium dialkyl phosphites[133]:

$$(C_2H_5O)_2P(O)Na + BrC{\equiv}CR \rightarrow (C_2H_5O)_2P(O)C{\equiv}CR + NaBr$$

where R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}, C_6H_5; yields 37–72%.

Ionin and Petrov showed[159] that dichloroacetylene also reacts readily with trialkyl phosphite. The chlorine atom in the diethyl chloroethynylphosphonate is labile. For example, it is replaced in the action of a second molecule of triphenylphosphine, organomagnesium compounds, etc.:



Di-iodoacetylene reacts with phenylhydrazine, exchanging one iodine atom by a phenyl radical[25]:

$$C_2I_2 + 2\,C_6H_5NHNH_2 \rightarrow C_6H_5NHNH_2 \cdot HI + N_2 + H_2 + C_6H_5C{\equiv}CI.$$

In reactions with organomagnesium compounds, both iodine atoms are exchanged by the residue MgX:

$$2\,RMgX + IC{\equiv}CI \rightarrow XMgC{\equiv}CMgX + 2\,RI.$$

Hence di-iodoacetylene can be used as an iodinating agent. The reaction is effected by simple addition of an ethereal solution of di-iodoacetylene to an ethereal solution of a Grignard compound with stirring at 0°C. The conversion proceeds without difficulty and with almost quantitative yield[86,97]. Therefore di-iodoacetylene is becoming a useful auxiliary medium for preparative organic chemistry. By this method, for example, iodobenzene is obtained from phenylmagnesium bromide and di-iodoacetylene in 95–97% yield. In a similar reaction phenylethynylmagnesium bromide with 2-iodo-1-phenylacetylene in the presence of cobalt(II) chloride gave diphenyldiacetylene with a yield of 75%. However, phenylethynylmagnesium bromide and di-iodoacetylene in this way did not give diphenyltriacetylene[160]. The reaction proceeds just as with other organomagnesium compounds:

$$2C_6H_5C{\equiv}CMgBr + IC{\equiv}CI \rightarrow 2\,C_6H_5C{\equiv}CI + BrMgC{\equiv}CMgBr.$$

Both iodine atoms in di-iodoacetylene can be replaced by hydrogen. Such exchange proceeds during reaction with potassium iodide in neutral or weakly acid aqueous solution:

$$IC{\equiv}CI + 2H_2O + 2\,KI \rightleftarrows H{-}C{\equiv}C{-}H + 2\,KOH + 2\,I_2.$$

C_2I_2 in alcoholic solution is also converted into acetylene under the action of zinc dust in dilute H_2SO_4 or by sodium amalgam. Also both iodine atoms are replaced by hydrogen in the electrochemical reduction of C_2I_2 at a mercury cathode. The reaction is[161]:

$$I{-}C{\equiv}C{-}I + 4e + 2\,H^+ \rightarrow H{-}C{\equiv}C{-}H + 2I^-.$$

The synthesis of bis(trimethylsilyl)acetylene by the reaction of tetrabromoethylene with trimethylchlorosilane and metallic magnesium in tetrahydrofuran[162] should be expected to lead to the conversions being considered, since the reaction undoubtedly proceeds through the intermediate formation of dibromoacetylene with subsequent replacement of both bromine atoms by the trimethylsilyl radical:

$$CBr_2{=}CBr_2 + 3\,Mg + 2\,(CH_3)_3SiCl \rightarrow 2\,MgBr_2 + MgCl_2 + (CH_3)_3SiC{\equiv}CSi(CH_3)_3.$$

Exchange of halogen atoms can be effected by the action of halogens on haloacetylenes. Information has been given above about the formation of hexachloro- and hexabromo-ethane from di-iodoacetylene. Ingold[69] observed the formation of di-iodoacetylene on passing chloroacetylene into a benzene solution of iodine. However, that conversion is accompanied by other reactions; therefore it has no preparative value.

4. Decomposition of the Haloacetylenes. Oxidations

Various authors[73,163,164] have observed the decomposition of di-iodoacetylene in light or on heating in solvents, proceeding by the equation:

$$2\,C_2I_2 = C_2I_4 + 2\,C.$$

Study of the kinetics in various solvents (benzene, chloroform, alcohol, etc.) at 100°C and 138°C showed that this is a first-order reaction. The mean temperature coefficient of its rate has been determined and it has also been found that the influence of the solvent on the rate constant is not great. The reaction is brought about by the violet part of the solar spectrum[80] and is catalysed by HgI_2.

The explosive decomposition of the haloacetylenes on heating without solvent proceeds with the release of carbon. Bromoacetylene and chloroacetylene decompose according to the equation[6,39]:

$$C_2HX \rightarrow HX + 2\,C$$

the dihaloacetylenes decompose to the elements. Bromoacetylene burns in air to give CO, CO_2, and HBr.[93] Lawrie[33] found that on oxidation in absolute alcohol by dry oxygen dibromoacetylene is 78.4% converted into C_2Br_4 by the reaction:

$$2C_2Br_2 + O_2 = C_2Br_4 + 2CO;$$

~15.6% of it is oxidised to oxalyl bromide, and ~6.1% forms ethyl dibromoacetate. Biltz[104] also found the formation of oxalyl bromide in the oxidation of C_2Br_2 by atmospheric oxygen, quoting this fact in support of the acetylenic structure of the substance. However, later work did not confirm Lawrie's results. Hauptmann writes that the oxidation of dibromoacetylene by oxygen in absolute alcohol either does not occur at all, or proceeds extremely slowly and does not go far. Straus and coworkers[163] assume that the reasons for the violent explosions of C_2Cl_2 and C_2Br_2 with traces of oxygen must be sought in the nature of the products of the addition of oxygen and not in the decomposition or oxidation itself. Other authors[71] state that the oxidation of chloroacetylene and bromoacetylene proceeds by a chain mechanism and the difference in the oxidation of acetylene and haloacetylenes C_2HX may be ascribed to the different relative stabilities of the intermediate peroxide compounds formed in the oxidation. Dichloroacetylene burns with the formation of carbonyl chloride[98].

In its careful oxidation, greatly diluted with carbon dioxide, CO and CO_2 are obtained, as well as carbonyl chloride, and the reaction can be expressed by the equation[35]:

$$2\,C_2Cl_2 + 5O \rightarrow 2\,COCl_2 + CO + CO_2.$$

A substance of general formula $(COCl)_x$ is formed simultaneously, which gives an anilide with aniline. However, its structure has not been found precisely. On passing oxygen into a 5–10% ethereal solution of dichloroacetylene the same substance was obtained as the main reaction products; formation of oxalyl chloride was not observed[34]. Di-iodoacetylene in neutral solutions is slowly oxidised in the air[42,43,73]:

$$2\,C_2I_2 + O_2 \rightarrow C_2I_4 + 2\,CO.$$

Ingold[69] oxidised chloroacetylene with hypochlorous acid and isolated chloroacetic acid, chloral hydrate, and dichloroacetaldehyde hydrate. The oxidation of di-iodoacetylene with cold conc. HNO_3 (d = 1.4) or chromic acid (in acetic acid) gives CO_2 and C_2I_4, but cold fuming HNO_3 gives CO_2, iodine, and tri-iodovinyl nitrate $I_2C{=}C(I)ONO_2$.[43]

5. Molecular Compounds of the Haloacetylenes

Such compounds are described for dichloroacetylene and di-iodoacetylene. Ott and Packendorff[35] found that with diethyl ether dichloroacetylene forms even under ordinary conditions a compound with b.p. 32.5°C at 743 mmHg. Ether depresses the autoxidation of dichloroacetylene and the compound does not ignite in a stream of pure oxygen, and also shows great resistance to bromine and ozone. It contains 62% C_2Cl_2, which corresponds to a molar ratio of the components, and decomposes water — in this, owing to the partial solubility of ether in water the dichloroacetylene released ignites. Ott[68] showed the importance of this compound: the C_2Cl_2 content in it is readily determined by volumetric analysis, and it allows various experiments with dichloroacetylene to be carried out without danger even in lectures. Recent investigators in working with dichloroacetylene have usually employed a solution of it in ether. Under other conditions the reaction of C_2Cl_2 with ether is more complex. In a boiling solution under the action of sunlight or ultraviolet radiation in the presence of catalysts (t-butyl peroxide, azo-bisisobutyronitrile) the reaction leads to the formation of several products, chiefly[150]:

$$CHCl{=}CClCH(CH_3){-}O{-}C_2H_5 \text{ and } [CHCl{=}CClCH(CH_3)]_2O.$$

Analogous products (each in the form of *cis*- and *trans*-isomers) were obtained with chlorofluoroacetylene[18].

Other authors state that C_2Cl_2 reacts with ether at room temperature to form 1,2-dichloro-1-ethoxybut-1-ene and other similar compounds which have not been studied[27].

With secondary and tertiary amines di-iodoacetylene forms the compounds $(C_3H_7)_2NH.(C_2I_2)_2$, $(C_2H_5)_3N.(C_2I_2)_2$, and $C_5H_{11}N.(C_2I_2)_2$.[25] Furthermore, a compound of it with 1,4-dioxan is known[165], of composition $C_4H_8O_2.C_2I_2$.

Prévost states[166] that iodoacetylene forms various vinyl iodobenzoates with the complex $[(C_6H_5CO_2)_2Ag]^-I^+$. The same author observed an interesting reaction — the formation of C_2I_2 by the action of acetylene on the above complex — taking place, he thought, according to the equation:

$$2\,[(C_6H_5CO_2)_2Ag]^-I^+ + HC{\equiv}CH \rightarrow 2\,[(C_6H_5CO_2)_2Ag]^-H^+ + IC{\equiv}CI.$$

A reaction described by Nieuwland and Vogt[44,167] is also of interest. The authors showed that iodine is capable of replacing both hydrogen atoms in acetylene in a medium of liquid ammonia, and in this way C_2I_2 can be obtained in good yield:

$$C_2H_2 + 2I_2 + 2NH_3 \rightarrow C_2I_2 + 2\,NH_4I.$$

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THE MECHANISM OF THE FISCHER–TROPSCH REACTION AND THE INITIATED HYDROPOLYMERISATION OF ALKENES, FROM RADIOCHEMICAL AND KINETIC DATA

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CONTENTS

I. Introduction 339

II. The theory of intermediate formation of alcohols in the Fischer–Tropsch reaction 339