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Chemistry of α-Halogenonitroalkanes

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Methods of preparation of α-halogenonitroalkanes and their functional derivatives are surveyed, together with the chief results obtained for the geometric parameters, electronic structure, and ultraviolet, infrared, and nuclear magnetic and quadrupole resonance spectroscopy, as well as acid - base properties. Reactions involving reduction, addition at multiple bonds, substitution of halogen atoms and the nitro-group, and interaction with diazoalkanes are analysed, and the most important mechanisms are discussed. Data are given on the toxicity, physiological activity, and practical use of these compounds. A list of 316 references is included.

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I. INTRODUCTION

The chemistry of aliphatic nitro-compounds is now a well studied field. Aspects of the preparation, structure, and chemical behaviour of nitroalkanes and their many derivatives have been quite widely discussed in several reviews[1-10] and in a monograph[11]. However, α-halogenonitro-compounds either are not discussed at all in these publications[1-3,9] or are only partly covered[4-8,10,11]. Yet their unique properties merit a separate review. This unusual class of substances has long attracted the attention of chemists and other specialists, as is indicated by the large number of original peprs in this field. The possibility of the direct use of α-halogenonitro-compounds as agricultural chemicals, and also as intermediates in the production of novel biologically active compounds, explosives, and rocket fuel components, still maintains this interest even at the present time.

α-Halogenonitroalkanes are undoubtedly also of theoretical interest. The combination of a nitro-group and a halogen attached to the same carbon atom confers on the halogen special properties differing markedly from those in ordinary halogenated aliphatic compounds. This difference is especially characteristic of α-halogenopolynitroalkanes, which exhibit the properties of compounds having a "positively" polarised halogen atom[12]. The reactions of α-halogenonitroalkanes involve either homolytic or heterolytic fission of the carbon–halogen bond depending on the nature of the halogen and the conditions: the heterolytic process may release the halogen as either a cation or an anion, so that a wide range of reactions can be accomplished. Furthermore, reactions involving the nitro-group or an α-hydrogen atom can also occur.

The present Review summarises the literature up to 1977 on methods of preparation, structure, and characteristic reactions. Since the bibliography on these compounds comprises more than 500 sources, we considered it advisable to give references to the most recent work, from which the early primary sources can usually be found. The concluding Section gives information available to us on the biological activity and practical utilisation of α-halogenonitroalkanes.

II. METHODS OF PREPARATION

1. Replacement by Halogen of an α-Hydrogen Atom in Nitroalkanes and their Derivatives

Halogenation of nitroalkanes and their functional derivatives is usually accomplished in the presence of a base, the most common method for obtaining α-halogenonitro-compounds[11]. The process is applied to a solution of the nitroalkane in aqueous alkali[13-15]; sometimes organic solvents are used[14,15].

The action of chlorine and bromine on primary mononitroalkanes may form mono- and di-halogenated derivatives, but nitromethane can also give trihalogenitromethanes, when each succeeding hydrogen atom is replaced more easily than the previous one:

$$CH_3NO_2 \xrightarrow{Br_2,NaOH} CH_2BrNO_2 \xrightarrow{Br_2,NaOH} CHBr_2NO_2 \xrightarrow{Br_2,NaOH} CBr_3NO_2 .$$

Kinetic studies have been made of the bromination of nitromethane and nitroethane[16,17]. The rate constants of the formation of mono-, di- and tri-halogenonitromethanes are in the proportions 1 : 200 : 10 000.[16] Simultaneous chlorination and bromination of salts of nitroalkanes gives bromochloronitroalkanes[18].

Hydrolysis[19] and interaction with nitroalkane salts[20-22] have been observed as side reactions accompanying the halogenation of nitroalkanes:

$$RCH{=}NOO^-Na^+ + RCH(NO_2)Cl \rightarrow RCH_2NO_2 + RC(Cl){=}NOO^-Na^+ ,$$

$$RC(Cl){=}NOO^-Na^+ \begin{cases} \xrightarrow{H_2O} RC(OH){=}NOO^-Na^+ + HCl \rightarrow RCHO + HNO_2 + NaCl , \\ \xrightarrow[RCH(NO_2)Cl]{} RCH(NO_2)CCl(NO_2)R + NaCl . \end{cases}$$

Halogenation is conducted with equimolecular quantities of reactants at low temperatures in order to suppress side reactions[23].

Halogenated 1,1-dinitroalkanes and trinitromethane are readily formed from alkali-metal salts of the nitro-compounds[25-27]:

$$RC(NO_2)_2^-M^+ + X_2 \rightarrow RC(NO_2)_2X + MX ,$$
$$R{=}NO_2, Alk;\ M{=}Na, K, NH_4;\ X{=}Cl, Br .$$

However, dinitromethane in aqueous alkali gives only dihalogenodinitromethanes[28,29]:

$$CH(NO_2)_2^-K^+ + 2X_2 + KOH \rightarrow C(NO_2)_2X_2 + 2KX + H_2O \quad X=Cl, Br .$$

Dichloro- and dibromo-dinitromethanes are easily converted by alkali into the corresponding salts of the monohalogenodinitromethanes[29,30]:

$$C(NO_2)_2X_2 + 2KOH \rightarrow XC(NO_2)_2^-K^+ + KOX + H_2O .$$

In an attempt to obtain monohalogenated derivatives of dinitromethane by acidifying their salts the dihalogenodinitromethanes were isolated[30]:

$$2XC(NO_2)_2^-K^+ + H_2SO_4 \rightarrow C(NO_2)_2X_2 + K_2SO_4 + N_2O + CO_2 + H_2O \quad X=Cl, Br, I .$$

Bromodinitromethane was reported[28] to be formed when the potassium salt of dinitromethane was treated with excess of bromine in a neutral medium.

The halogenation of nitroalkanes takes place by an ionic mechanism. The rate-determining stage is isomerisation of the true nitro-compound into the *aci*-form[16,17]. α-Halogenated polynitroalkanes are formed by halogenation of the anions of the latter, which result directly from the nitroalkane without intermediate formation of the *aci*-form[31].

Among other halogenating agents used are interhalogen compounds[28,32], sodium hypochlorite and hypobromite[33], *N*-chloro-*N*-nitroamines, *N*-bromo- and *N*-chloro-succinimide, and sodium *N*-chlorobenzenesulphonamide[34]. In several cases the selectivity is enhanced and the yield of required products increased[34]. Salts of nitro-compounds are smoothly chlorinated by chlorine fluorosulphate[35]:

$$RC(NO_2)_2^-M^+ + ClOSO_2F \rightarrow RC(NO_2)_2Cl + MOSO_2F ,$$
$$R=NO_2, CN; \quad M=Na, K .$$

Fluorination of salts of nitro-compounds is effected with elementary fluorine in water[36]. Secondary mononitroalkanes are converted into satisfactory yields of α-fluoromononitroalkanes[37], whereas the primary compounds give low (5–14%) yields of fluoro-derivatives[36]. The latter are obtained by replacing an α-hydrogen atom in the mononitroalkane by an alkoxycarbonyl group, which after fluorination is removed by alkaline hydrolysis[11]:

$$\underset{\underset{COOC_2H_5}{|}}{RC{=}NOO^-} \xrightarrow{F_2,N_2} \underset{\underset{COOC_2H_5}{|}}{RCFNO_2} \xrightarrow{C_2H_5O^-} RCF{=}NOO^- \xrightarrow{H^+} RCHFNO_2 .$$

Fluorination with elementary fluorine in water is used to obtain α-fluoropolynitroalkanes[26,36,38–40]. Solid-phase fluorination of nitroform and its salts with elementary fluorine is accompanied by fluorolysis, difluorodinitromethane being formed with fluoronitroform[41].

α-Fluoromononitroalkanes have been prepared by fluorinating salts of the mononitroalkanes with elementary fluorine in methanol at −30 to −60 °C,[42] with yields of 58–73%. Another method for obtaining α-fluoronitroalkanes consists in the action of perchloryl fluoride on the sodium salts of secondary nitroalkanes and nitrocycloalkanes[43]:

$$RR'C{=}NOO^-Na^+ + FClO_3 \rightarrow RR'CFNO_2 + NaClO_3 .$$

Alkali-metal salts of 1,1-dinitroalkanes and trinitromethane are also readily converted by perchloryl fluoride into α-fluoropolynitroalkanes[44–47]:

$$RC(NO_2)_2^-M^+ + FClO_3 \rightarrow RC(NO_2)_2F + MClO_3 ,$$
$$R=NO_2, CH_3, C_6H_5, C_6H_5CH_2; \quad M=Na, K, NH_4 .$$

Undecafluoropiperidine fluorinates smoothly the sodium salt of 2-nitropropane in methanol[48].

Fluoro-chloro-, -bromo-, and -iodo-dinitromethanes are obtained by the halogenation of bisfluorodinitromethylmercury[49]:

$$Hg[C(NO_2)_2F]_2 + 2X_2 \rightarrow 2XC(NO_2)_2F + HgX_2 ,$$
$$X=Cl, Br, I .$$

In contrast to bromo-, chloro-, and fluoro-nitroalkanes, α-iodonitroalkanes have been inadequately studied, owing to the difficulty of preparing them and their instability. The action of iodine on alkali-metal salts of mononitroalkanes led to the isolation of dimeric products, formed by reaction between the nitroalkane anion and the iodonitroalkane[20–22]:

$$2C_6H_5CH{=}NOO^-Na^+ + I_2 \rightarrow C_6H_5CH(NO_2)CH(NO_2)C_6H_5 + 2NaI .$$

α-Iodopolynitroalkanes cannot be obtained in this way, because of occurrence of the reverse reaction[24]

$$RC(NO_2)_2I + KI \rightarrow RC(NO_2)_2^-K^+ + I_2 ,$$
$$R=NO_2, Hal, Alk .$$

They are formed by the action of iodine on silver salts of polynitroalkanes in organic solvents. Iodotrinitromethane has thus been prepared with ether as solvent[27,50]. Many α-iodonitro-derivatives have been obtained by iodinating anions of mono- and poly-nitroalkanes with iodine chloride[28,32,51].

Replacement of an α-hydrogen atom in a nitro-compound by halogen in the presence of a base is a general method for obtaining functional α-halogenonitro-compounds. The reaction is selective and is not complicated by the presence of a group such as keto[52,53], amino[54], ester[55–57], nitrile[57,58], amide[59], sulphonyl[59,60], hydrazino[61] or an unsaturated bond[62].

Chlorination and fluorination of potassium salts of 2,2-dinitroethyl ethers of oximes readily yield halogeno-derivatives without affecting the C=N bond[63]:

$$RR'C{=}NOCH_2C(NO_2)_2^-K^+ \begin{cases} \xrightarrow{FClO_3} RR'C{=}NOCH_2C(NO_2)_2F , \\ \xrightarrow{Cl_2} RR'C{=}NOCH_2C(NO_2)_2Cl . \end{cases}$$

Treatment of nitroalcohols with caustic alkalis[64] or alkali-metal alkoxides[65] forms salts, whose halogenation in water or in an organic solvent yields halogenonitroalcohols:

$$RCH(OH)C(NO_2)_2^-K^+ + X_2 \rightarrow RCH(OH)C(NO_2)_2X + KX ,$$
$$(HOCH_2)_2C{=}NOO^-Na^+ + X_2 \rightarrow (HOCH_2)_2C(NO_2)X + NaX ,$$
$$X=F, Cl, Br .$$

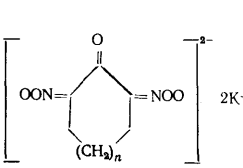
Fluoro-, chloro-, and bromo-derivatives of nitroalcohols and nitrodiols have been obtained in this way[37,39,44,65–69]. Similarly, salts of nitroalkyl ethers[70], sulphides[71], and sulphones[60] are halogenated to the corresponding halogenonitro-derivatives:

$$H_3COCH_2C(NO_2)_2^-K^+ + Br_2 \rightarrow H_3COCH_2C(NO_2)_2Br + KBr ,$$
$$RSO_2C(NO_2)_2^-Na^+ + Cl_2 \rightarrow RSO_2C(NO_2)_2Cl + NaCl .$$

Bis-1-nitroalkyl disulphides are converted by halogens into 1-halogeno-1-nitroalkylsulphenyl halides[72,73]:

$$RCH(NO_2)S{-}SCH(NO_2)R \xrightarrow{Cl_2} RCCl(NO_2)SCl .$$

Cyclic αα′-dinitro-ketones react with bromine in an alkaline medium with cleavage of the ring and formation of tetrabromodinitroalkanes[74]:



$$2K^+ + 4Br_2 + 4KOH \rightarrow O_2NCBr_2{-}(CH_2)_n{-}CBr_2NO_2 + K_2CO_3 + 4KBr \quad n=2–5 .$$

2-Nitrodimedone, 2-nitroindanedione, and analogous compounds are readily brominated and chlorinated in aqueous solution without preliminary conversion into their salts[75]. 2-Iodo-2-nitrodimedone has been obtained in 92% yield by iodinating 2-nitrodimedone with an iodine monochloride–dioxan complex in acetic acid[76].

The halogenation of mononitroalkanes, which are weak carbon–hydrogen acids, is quite rapid in acid media[16,17]. The first stage is assumed[77–79] to involve an acid-catalysed prototropic change with formation of a nitronic acid, which, passing through a stage of formation of the ion of the nitro-compound, readily adds a halogen or a hypohalic acid to form the 1-halogenonitroalkane:

$$\rangle CHNO_2 + H^+ \rightleftarrows \rangle CHNO_2H^+ \rightleftarrows \rangle C{=}NOOH + H^+$$
$$\rangle C{=}NOOH \rightleftarrows \rangle C{=}NOO^- + H^+$$
$$\rangle C{=}NOO^- + X_2 \rightarrow \rangle CXNO_2 + X^- .$$

The rate of the acid-catalysed halogenation of nitroalkanes is independent of either the nature of the concentration of the halogen, and the reaction is first order with respect to the nitro-compound[77,78].

Hydrogen can be replaced by halogen without preliminary conversion into a salt also in polynitroalkanes, which are strong carbon–hydrogen acids. This reaction was first observed by Shishkov[80], in the action of bromine on trinitromethane in sunlight:

$$CH(NO_2)_3 + Br_2 \xrightarrow{h\nu} C(NO_2)_3Br + HBr .$$

Treating polynitroalkanes with perchloryl fluoride in a solvating aprotic solvent yields the corresponding fluoro-derivatives[45]:

$$RCH(NO_2)_2 + FClO_3 \rightarrow RC(NO_2)_2F + HClO_3 ,$$
$$R{=}NO_2, F, CH_3 .$$

Fluorotrinitromethane has been prepared by the action of elementary fluorine on trinitromethane in water and in various organic solvents[26,38].

Chloro- and bromo-nitroforms are readily produced when nitroform is treated with the corresponding halogens or hydrohalic acids in a mixture of sulphuric and nitric acids[81].

2. Halogenation of Conjugated Nitroalkenes

In chloroform, tetrachloromethane, or carbon disulphide conjugated nitroalkenes readily add chlorine and bromine to form the *vic*-dihalogenated derivatives[82–85]:

$$-C{=}CNO_2 + X_2 \rightarrow -\overset{|}{\underset{X}{C}}-\overset{|}{\underset{X}{C}}-NO_2 ,$$
$$X{=}Cl, Br .$$

Bromine can be replaced by its pyridine complex to obtain dibromo-derivatives[86]. The reaction has a heterolytic mechanism, and the rate of electrophilic addition of halogen is greatly diminished by electron-accepting substituents. For example, halogens cannot be added to *vic*-dinitroalkenes under normal conditions. To obtain dichloro-derivatives a mixture of the dinitroalkene and liquid chlorine is exposed to sunlight for a long time[87]. 1,2-Dinitroethylene adds bromine in the presence of hydrobromic acid in acetic acid[88].

Addition of bromine and chlorine to nitroalkenes is hindered also by the presence of a halogen at the double bond. Trichloro- and tribromo-nitroethylenes are brominated only at high temperatures, with formation of 1,2-dibromo-1,2,2-trichloronitroethane and pentabromonitroethane respectively. Arylated 1-bromo-1-nitroalkenes are not brominated at the double bond[82].

Addition of chlorine and bromine is more difficult to 1,4-dinitrobuta-1,3-diene than to nitroalkenes: 1,2,3,4-tetrahalogeno-derivatives are formed at 56–61 °C.[85,89–91] On recrystallisation the tetrabromide is converted into 1,4-dibromo-1,4-dinitrobuta-1,3-diene[85]. Under normal conditions 2,3-dimethyl-1,4-dinitrobuta-1,3-diene reacts very slowly with bromine, forming 1,4-dibromo-2,3-dimethyl-1,4-dinitrobuta-1,3-diene. This reaction is accelerated by addition of a catalytic quantity of hydrobromic acid[85].

Phenyl substituents in dinitrobutadienes create considerable hindrance to bromination. 1,4-Dinitro-2,3-diphenylbuta-1,3-diene reacts slowly with bromine, but the 1,4-diphenyl isomer under normal conditions does not add bromine at the double bond[82].

The halogenation of conjugated nitroalkenes enables polyhalogenated nitroalkanes to be obtained that are difficult to prepare by other methods.

3. Nitration of Halogenated Alkenes and Other Halogenated Compounds

The nitration of chloro- and bromo-alkenes with nitrogen dioxide yields a complicated mixture of products including α-halogenonitroalkanes[92–94]. Addition of nitrogen dioxide at the double bond depends in considerable measure on the nature of the halogenoalkane and the reaction conditions; dinitro-derivatives and alkyl nitrites may be formed. Furthermore, the process is complicated by substitution of a nitro-group for halogen and by formation of nitrosyl halides, which add to the halogenoalkenes to give nitroso-compounds[95–97]. The action of nitrogen dioxide on vinyl, propenyl, isopropenyl, and isobutenyl bromides and on α- and β-bromostyrenes forms dinitro-derivatives only with the last three compounds, in the respective yields 33.0%, 14.5%, and 9.7%.[92,93]

When halogenoethylenes are heated with nitrogen dioxide, the corresponding 1,2-dinitro-derivatives are formed[94,98]:

$$X_2C{=}CX_2 + 2NO_2 \rightarrow X_2C(NO_2)C(NO_2)X_2 ,$$
$$X{=}Cl, Br .$$

The yields of dinitro-derivatives are increased by the presence of anhydrous aluminium chloride[94].

In 1948 the first results were published on the nitration of fluorinated ethylenes with nitrogen dioxide[99]. Subsequently this reaction was studied in greater detail[100–104]. It was accomplished in the gas phase[100], and in non-polar solvents[101] at room or elevated temperatures and pressures[102–104]. The resulting *vic*-dinitroalkanes were accompanied by alkyl nitrites[101].

On passing from perfluoroethylene to perfluoropropene and perfluoroisobutene, the first of which reacts explosively with nitrogen dioxide in the absence of a solvent, more severe conditions are required (100 and 180 °C respectively)[101–103].

The nitration of fluoroalkenes by nitrogen dioxide is assumed to have a radical mechanism[102,103]:

$$CF_3{-}CF{=}CF_2 \xrightarrow{\dot{O}NO} CF_3{-}\dot{C}F{-}CF_2NO_2 \xrightarrow{\dot{O}NO} CF_3{-}\overset{NO_2}{\overset{|}{C}}F{-}CF_2NO_2$$
$$\downarrow \dot{O}NO$$
$$CF_3{-}\underset{ONO}{\overset{|}{C}}F{-}CF_2NO_2 \xrightarrow{H,O,H_2SO_4} CF_3{-}\overset{\overset{O}{\|}}{C}{-}CF_2NO_2 .$$

Hydrolysis of the halogenonitroalkyl nitrites yields the corresponding halogenated nitroalcohols[105–107] and nitrocarboxylic acids[100,102,107].

Nitrosyl chloride and bromide react with halogenoalkenes yielding the corresponding nitro-derivatives, which are formed by oxidation of the nitroso-derivatives by a second molecule of the nitrosyl halide. Addition of the nitrosyl halides takes place in conformity with the polarisation of the double bond[95,108,109].

Oxides of nitrogen react in hydrofluoric acid with halogenoalkenes to form the 1-halogeno-2-fluoronitroalkanes[110–112].

The nitration of halogenoalkenes by concentrated nitric acid is accompanied by degradation of the alkene molecule and yields halogenonitromethanes. Thus treatment of trichloroethylene and tetrabromoethylene leads to the isolation respectively of dichlorodinitromethane[113] and dibromodinitromethane[114]; but the main product of the degradative nitration of tetrachloroethylene is chlorodinitromethane, accompanied by small quantities of trichloronitromethane[114].

Chlorinated nitromethanes are obtained by nitrating chloroacetone with nitric acid, or by treating acetone with nitric acid saturated with chlorine[115] or in the presence of sodium chloride[116].

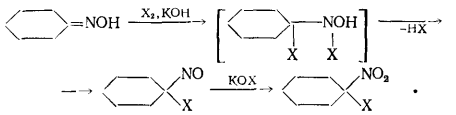
The nitration of halogenoalkenes and other halogenated compounds by nitric acid is accompanied by the oxidising action of oxides of nitrogen and halogens formed in the reaction, which results in complicated mixtures, so that this procedure is rarely used as a method of preparation.

4. α-Halogenonitro-compounds from Oximes

The halogenation of oximes in alkaline medium enables halogenated mononitroalkanes of diverse structure to be obtained[7,117,118]:

$$RR'C{=}NOH + 2X_2 + 3NaOH \rightarrow RR'C(NO_2)X + 3NaX + 2H_2O$$
$$X{=}Cl,\ Br.$$

Aliphatic and especially alicyclic ketoximes readily undergo this reaction[119,120]. It involves three stages—addition of halogen at the C=N bond in the oxime, formation of a halogenonitroso-derivative, and oxidation of the latter to the halogenonitro-derivative[117]:

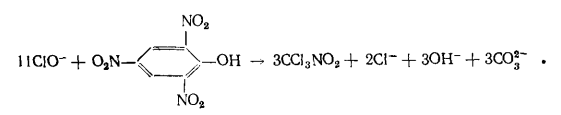


This mechanism is supported by the ease of oxidation of chloronitroso-compounds to the corresponding chloronitro-derivatives[118]. Bromonitroso-derivatives are readily formed by the action of *N*-bromosuccinimide on ketoximes[119,120]. The nitroso-group is smoothly oxidised to a nitro-group by nitric acid or its mixture with 30% hydrogen peroxide[121]. In this way 2-bromo-2-nitropropane, 2-bromo-2-nitrobutane, and 3-bromo-3-nitropentane have been obtained in yields of 18%, 46%, and 38% respectively[120], as well as other α-chloro- and α-bromo-nitroalkanes[121].

The use of oximes for the preparation of α-halogenonitro-compounds extends considerably the range of starting materials. This is important in cases in which the corresponding nitroalkanes are not available to the research worker.

5. Other Methods

When 2,4,6-trinitrophenol is treated with hypochlorite or hypobromite, the aromatic ring is cleaved to form the trihalogenonitromethanes[122]:



This method is used in industry to obtain trichloronitromethane. Picric acid, which is sparingly soluble in water, can be replaced by calcium picrate, and chlorine can be used instead of hypochlorite.

Hydrolytic cleavage of α-halogeno-α-nitro-ketones yields α-halogenonitroalkanes[123–126]:

$$CH_3\overset{\overset{O}{\|}}{C}CBr(NO_2)R \xrightarrow{H_2O} RCHBrNO_2 + CH_3COOH,$$
$$CF_3\overset{\overset{O}{\|}}{C}F_2NO_2 \xrightarrow{H_2O(NaOH)} F_2CHNO_2 + CF_3COOH.$$

Halogenonitromethanes are formed also by the hydrolysis of halogenonitroacetyl chlorides[127].

Bromopolynitroethanes are obtained from tribromonitromethane and potassium cyanide. The resulting tetrabromo-1,2-dinitroethane is easily converted into 1,2-dibromotetranitroethane[128,129].

Several α-fluorodinitroalkanes are obtained by alkylating the silver salt of fluorodinitromethane[130]:

$$CF(NO_2)_2^-Ag^+ + RX \rightarrow RC(NO_2)_2F + AgX,$$
$$R{=}CH_3,\ C_3H_7,\ C_3H_5CH_2,\ CH_2{=}CH{-}CH_2;\ X{=}Br,\ I.$$

It has recently been shown that α-halogenonitroalkanes are formed by halogenating α-nitroalkylsulphonium salts[131]:

$$(CH_3)_2\overset{+}{S}CH(NO_2)_2\ HSO_4^- \xrightarrow{X_2} CH(NO_2)_2X,$$
$$X{=}Cl,\ Br.$$

The action of nitrogen dioxide on fluoro-carboxylic acids or their silver salts yields fluoronitroalkanes[132,133].

Fluoro- and chloro-trinitromethanes have been obtained by nitrating fluoro- and chloro-dinitromethanes respectively with nitryl fluoride[134]:

$$CH(NO_2)_2X + FNO_2 \rightarrow C(NO_2)_3X,$$
$$X{=}F,\ Br.$$

Halogenotrinitromethanes are formed by reaction between tetranitromethane and chlorine, *NN*-dichlorobenzenesulphonamide[135], sodium *N*-chlorobenzenesulphonamide[136], or an alkali-metal halide[137–139].

Electrochemical methods of preparing α-halogenonitroalkanes have also been reported[140,141].

III. SPECTRAL PROPERTIES AND STRUCTURE

1. Geometrical Parameters and Electronic Structure

Structural investigations have been made only on the simplest α-halogenonitroalkanes. Gas-phase electron diffraction has been used to determine geometrical parameters for chloronitromethane[142,143], trihalogenonitromethanes[144–147], and halogenotrinitromethanes[143,148,149].

In chloronitromethane free rotation is observed about the carbon–nitrogen bond, which has the usual length for organic nitro-compounds. A conformational peculiarity of chloronitromethane is that the chlorine–carbon–nitrogen angle (114°) is considerably larger than the corresponding angle in trichloronitromethane.

The carbon–halogen distances in trifluoro-, trichloro-, and tribromo-nitromethanes are almost the same as in other similar molecules. The bond angles of the trihalogenomethyl group are close to the tetrahedral values. A conformational peculiarity of trihalogenonitromethanes is a considerable increase in the carbon–nitrogen bond length (1.56–1.59 Å) in comparison with ordinary nitroalkanes, and the presence of a barrier to internal rotation about this bond. Trifluoronitromethane vapour contains two rotational isomers—with staggered and eclipsed forms—in the proportions 2 : 1; the CNO_2 group is non-planar, and the angle between each of the nitrogen–oxygen bonds and the plane containing the carbon–nitrogen bond is $\gamma = 9°35'$.[144] Tribromonitromethane vapour contains only the rotational isomer having the staggered form; the CNO_2 group is non-planar, and $\gamma = 8°33'$.

Electron diffraction and microwave spectroscopy give considerably different results for carbon–nitrogen bond lengths and barriers to internal rotation in trihalogenonitromethanes. The latter method indicates free rotation about the carbon–nitrogen bond in trifluoronitromethane and the usual bond length for nitroalkanes[150]. The reasons for the discrepancy have not been elucidated.

Gas-phase electron diffraction shows C_3 conformations for trinitromethane and its chloro- and bromo-derivatives, with the HCNO, etc. dihedral angles respectively 26°, 49°, and 49°.[143] According to X-ray diffraction[151] the carbon atom in iodotrinitromethane is located at the centre of an almost regular tetrahedron, with mean angles of 71° between the planes of the nitro-groups.

Increasing use has recently been made of theoretical conformational analysis to examine the structure of nitro-compounds. Angles of rotation of the nitro-group and barriers to internal rotation about the carbon–nitrogen bond in halogenated mono-, di-, and tri-nitromethanes determined by this method[152–155] agree well with experiment. The electronic structures of several α-halogenonitroalkanes have been investigated by quantum-chemical methods[153–155]. Thus calculation shows a decrease in negative charge on the halogen atom and a shift in electron density to the trinitromethyl group on passing from fluoro- to iodo-trinitromethane. The negative charge on the oxygen atoms and the carbon–nitrogen bond order diminish, while the order of the nitrogen–oxygen bonds increases, on passing from mono- to di-nitro-compounds.

Valuable information on the electronic structure of α-halogenonitroalkanes has been obtained from studies of molecular dipole moments[156–158]. Interaction of the nitro-groups with the halogen atom leads to considerable changes in the electron shell of the molecules and is responsible for differences between calculated and experimental dipole moments. Additive resolution of the dipole moment among bonds in a molecule has yielded the values

$$\mu^{+}_{C-F} = 1.0^{156};\ \mu^{+}_{C-Cl} = 0.23;\ \mu^{-}_{C-Br} = 0.15;\ \mu^{-}_{C-I} = 1.39\ D^{157}$$

for the halogenotrinitromethanes. These dipole moments differ markedly from those of the same bonds in halogenoalkanes, owing to a mesomeric effect. Quantum-chemical calculations on halogenotrinitromethanes are consistent with this view[153].

2. Vibrational Spectra

Results obtained in the numerous investigations on the vibrational spectroscopy of nitro-compounds, including α-halogenonitroalkanes, have been surveyed in reviews[6,159] and in a monograph[11]. The antisymmetric and symmetric stretching frequencies of the nitro-group are important characteristics of the vibrational spectra of α-halogenonitroalkanes. In nitroalkanes they may lie in the respective ranges 1500–1600 and 1300–1370 cm^{-1}.[6] Replacement of hydrogen by halogen atoms in nitroalkanes raises the frequency of antisymmetric and lowers that of symmetric stretching vibrations of the nitro-group, as well as lowering the carbon–nitrogen stretching frequency. A similar pattern is observed with increase in the number of nitro-groups.

The position of the absorption band of antisymmetric nitro-stretching vibrations in the infrared spectra of α-halogenonitroalkanes is determined mainly by the inductive effect of substituents[160–163], and the frequency correlates quite well with the inductive constants of the latter[162,163]:

$$\nu_{as\,(NO_2)} = 1562 + 12\sigma^{*}.$$

Furthermore, the frequency is influenced by steric factors and the conjugation effect.

The position of symmetric nitro-stretching vibrations in a series of nitroalkanes is influenced mainly by the steric factor[159], the shifts caused by different substituents being additive. The shift depends on the bulk of the substituent and is independent of its electron-acceptor or electron-donor properties. The position of these vibrations is almost uninfluenced by inductive and conjugation effects.

The solvent has an insignificant effect on the position of absorption bands corresponding to nitro-stretching vibrations in the infrared spectra and on their integral intensity[159].

The mutual influence of nitro-group and halogen is clearly evident in the vibrational spectra of halogenotrinitromethanes. Their Raman and infrared spectra show a high intensity in bands corresponding to characteristic carbon–halogen vibrations and abnormally low frequencies—366 and 344 cm^{-1} for chloro- and bromo-trinitromethanes respectively[164], compared with the range 600–700 cm^{-1} for ordinary alkyl halides—the fall in frequency being so great that it cannot be attributed solely to the inductive effect of the trinitromethyl group. It is probably due to a mesomeric effect leading to a decrease in negative charge on the halogen and a redistribution of the carbon–nitrogen and nitrogen–oxygen bond orders.

3. Electron Spectra

Two absorption bands are usually observed in the ultraviolet spectra of mono- and poly-nitroalkanes: a strong band at 200–210 nm lies in a region that is marginal for the instruments used in practical spectroscopy, and is usually disregarded; most studies are devoted to a weak band at 270 to 280 nm attributed to an $n-\pi^{*}$ transition[165,166]. The latter has no fine structure, its intensity depends on the number of nitro-groups in the molecule, and its position varies with the solvent, increase in whose polarity shifts the band to shorter wavelengths[165]. The position of this band is influenced also by substituents[6]. The introduction of halogen atoms α to the nitro-group leads to a slight bathochromic displacement and an increase in intensity, which is explained by interaction of the electron shells of nitrogen–oxygen and carbon–halogen bonds[167].

The absorption coefficent increases with the accumulation of nitro-groups in the molecule, but not in proportion to their number[165].

Anions of halogenodinitroalkanes give an intense broad band ($\varepsilon > 10\,000$) with maximum absorption at 365–380 nm.

4. Microwave Spectroscopy

The chemical shift of protons in the nuclear magnetic resonance spectra of α-halogenonitro-compounds is determined mainly by the total inductive effect of the substituents[6,11]. The presence of such electronegative substituents as nitro, fluoro, chloro, bromo greatly diminishes the shielding of α- and β-protons and produces a downfield shift of signals in the n.m.r. spectra of α-halogenonitroalkanes. The variation in the chemical shift of a 1-proton in the spectra of nitroalkanes on the introduction of electronegative substituents other than a fluorine atom parallels the variation in the acid ionisation constants of these compounds[168].

During recent years the structure of α-halogenonitroalkanes has been increasingly investigated by n.m.r. not only with hydrogen but also on nitrogen-14, carbon-13, and oxygen-17 nuclei[169–173]. Chemical shifts of the nitrogen-14

signal in n.m.r. spectra of these compounds depend linearly on the total inductive effect of the substituents[169]:

$$\delta = -25.0 + 13.8\sigma^*.$$

Increase in the electronegativity of a substituent leads to a diamagnetic shift in the signal in the spectra of mono- and poly-nitroalkanes, which indicates displacement of electron density of the nitrogen–oxygen bond from the oxygen to the nitrogen atom.

The replacement of hydrogen atoms in a nitroalkane by halogen produces a diamagnetic shift of the oxygen-17 signal in the n.m.r. spectrum. Accumulation of nitro-groups in a molecule has little influence on this chemical shift. The tendency of the latter to vary in aliphatic nitro-compounds cannot be due to inductive effects as with nitrogen-14. Perhaps it is caused by the interaction of non-bonded atoms, and also by other effects.

The introduction of halogen or a nitro-group at carbon atom 1 causes a paramagnetic shift in the carbon-13 signal, which increases in the sequence Br < CH_3 < Cl < NO_2.

Fluorine-19 n.m.r. spectroscopy has provided information on the electronic structure of the fluorine atom in α-fluoronitroalkanes[174].

Nuclear quadrupole resonance on chlorine-35, bromine-79, and iodine-127 nuclei has been used to investigate the structure of α-halogenonitro-compounds. Chloronitroalkanes have been studied in greater detail[175,176], bromo- and iodo-nitroderivatives in less detail[174,177]. The n.q.r. spectra of α-halogenonitroalkanes exhibit displacement of the halogen signal to higher frequencies than in alkyl halides, which indicates a decrease in electron density on the halogen atom in the former.

A relation has been found between the ^{35}Cl n.q.r. frequencies and the induction constants of the substituents in a series of chloronitroalkanes[175]:

$$\nu^{35}_{Cl} = 34.68 + 1.63\sigma^*.$$

The frequencies $\nu_{^{35}Cl}$ for chlorodinitromethane and chlorofluorodinitromethane depart from the regression line, by 0.86 MHz to higher frequencies and 1.2 MHz to lower frequencies respectively. In the former case the departure is due to hydrogen bonding between chlorodinitromethane molecules; in the latter case it has been interpreted as resulting from conjugation of *p*-electrons of fluorine with the carbon–chlorine bond.

5. Acid–Base Properties

In polar solvents α-halogenonitroalkanes containing an α-hydrogen atom eliminate a proton and form a halogenonitroalkane anion. Deprotonation of the molecule and protonation of the anion occur by a mechanism of general acid–base catalysis[178–180]:

$$\mathrm{R{-}\underset{\mathrm{Hal}}{\underset{|}{C}}HNO_2} + B^- \rightleftarrows \mathrm{R{-}\underset{\mathrm{Hal}}{\underset{|}{C}}{=}NOO^-} + BH\ .$$

At ordinary temperatures they take place at a moderate rate, and kinetic measurements can easily be made. The rate constants correlate well with the pK_b values of the bases[179,181] and satisfactorily with the pK_a values of the α-halogenonitroalkanes[181–183].

The acid–base properties of α-halogenonitroalkanes vary over a wide range depending on the nature of the halogen and the structural parameters of the substituent. The dependence of the acidity on the total inductive effect of the substituents cannot be described by a single correlation equation[184,185]. Ionisation constants for compounds containing substituents having closely similar polar effects may differ substantially. Thus for difluoronitromethane pK_a = 12.4,[168] but the value for bromodinitromethane is 3.47.[185]

The complicated structural dependence of the acidity of α-halogenonitroalkanes is responsible for the diversity of views on this problem. Among factors determining the pK_a of nitroalkanes are inductive, steric, and mesomeric effects, $p-\pi$-electronic repulsion, solvation, and also purely formal features such as the numbers of α- and β-hydrogen atoms[186–190].

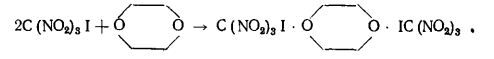
In view of the above considerations the results provided by physicochemical investigation of the structure of α-halogenonitroalkanes cannot be adequately explained in terms of the theory of the inductive effect, and most workers apply the concept of a mesomeric effect. The combination of a nitro-group and a halogen attached to the same carbon atom will obviously lead to electronic interaction between nitrogen–oxygen and carbon–halogen bonds. Such interaction affects primarily and mainly the latter bond, with the appearance of special properties in the halogen, differing substantially from the halogen in alkyl halides and constituting one reason for the peculiar chemical behaviour of α-halogenonitroalkanes.

IV. CHEMICAL PROPERTIES

1. Molecular Complexes

The specific chemical behaviour of α-halogenonitroalkanes is due primarily to the way in which the carbon–halogen bond is polarised. In ordinary alkyl halides—chlorides, bromides, and iodides—the halogen carries a strong negative charge: the dipole moments of the carbon–halogen bonds in chloro-, bromo-, and iodo-methanes lie between −1.55 and −1.17 D.[157] In the formation of complexes they usually act as *n*-donors. In α-halogenonitroalkanes the carbon–halogen bond is polarised differently: the dipole moments of such bonds in chloro-, bromo-, and iodo-trinitromethanes are resepctively −0.23, +0.15, and +1.39 D.[157] In contrast to alkyl halides these compounds act as electron-acceptors in complex formation, exhibiting the properties of pseudohalogens.

Iodo- and bromo-trinitromethanes readily form molecular complexes with various electron-donors (dioxan, *N*-, *S*-, and *P*-oxides, αα′-dioxodiazo-compounds, nitrosamines):[177,191,192]



Nuclear quadrupole resonance spectra indicate complex formation also by chlorotrinitromethane[177]. The chlorine-35, bromine-79, and iodine-127 signal frequencies in the spectra of halogenotrinitromethane complexes increase with the electron-donor power of the ligand and are higher than for these nuclei not combined in such complexes. Analogous signal shifts to higher frequencies are observed in the n.q.r. spectra of the iodine, iodine monochloride, and iodine monobromide complexes[193]. The regularity in the variation of the ^{35}Cl, ^{79}Br, and ^{127}I n.q.r. frequencies indicates an increase in the "positive" character of the halogen in the halogenotrinitromethane complexes.

Molecular complexes may play a definite part in effecting particular reactions of α-halogenonitroalkanes. A quantitative relation can apparently be expected between the frequency changes in the n.q.r. spectra of the complexes and their chemical activity in reactions involving rupture of the

carbon–halogen bond. This relation is readily seen qualitatively in the reaction with iodomethane[177]:

$$IC(NO_2)_3 + S \rightleftarrows S \cdot IC(NO_2)_3 ,$$
$$S \cdot IC(NO_2)_3 + CH_3I \rightleftarrows CH_3C(NO_2)_3 + I_2 + S ,$$

where S represents dimethyl sulphoxide, dioxan, etc. The ease of formation of 1,1,1-trinitroethane increases on passing from halogenotrinitromethanes to their complexes and with increase in the electron-donor power of the ligand[177,194–196].

2. Electrochemical Reduction

Assessment of the reactivity of α-halogenonitroalkanes can be approached by studying their electrochemical reduction. The first wave on a polarogram represents fission of the carbon–halogen bond, but subsequent waves are due to reduction of the nitro-group[197,198]. The half-wave potential $E_{1/2}$ serves as criterion of their chemical activity. These compounds are reduced at more positive potentials than are the corresponding halogenoalkanes, which indicates that the carbon–halogen bond is considerably weaker in the former.

When bromo- and chloro-nitromethanes are reduced, each gives a characteristic two-electron wave ($E_{1/2}$ = −0.05 and −0.45 V) and a wave corresponding to the reduction of nitromethane[199]:

$$CH_2(NO_2)X + 2e \rightarrow CH_2{=}NOO^- + X^- ,$$
$$CH_2{=}NOO^- + H^+ \rightarrow CH_3NO_2 ,$$
$$CH_3NO_2 + 4H^+ + 4e \rightarrow CH_3NHOH + H_2O ,$$

Polarograms obtained for dibromo- and dichloro-nitromethanes contain their own waves ($E_{1/2}$ = +0.03 and −0.12 V), waves due to CH_2NO_2Br (or CH_2NO_2Cl), and a wave due to CH_3NO_2. Trichloro- and tribromo-nitromethanes give their own waves (+0.01 and +0.02 V) and waves corresponding to the reduction of di- and mono-halogenonitromethanes, as well as a nitromethane wave. The reduction of halogenated derivatives of nitroethane[199] and 2-nitropropane[200] have been studied.

The ease of polarographic reduction of α-halogenonitroalkanes increases on passing from chloro- to iodo-derivatives and with increase in the number of nitro-groups. Chlorides are reduced with greater difficulty than are bromides, but this difference diminishes with the accumulation of nitro-groups, which facilitates also rupture of the carbon–nitrogen bond[201]. In α-fluoropolynitroalkanes the first stage of reduction corresponds to fission of this bond, not of the carbon–fluorine bond[202–204]:

$$FC(NO_2)_3 + 2H^+ + 2e \rightarrow CH(NO_2)F + HNO_2 .$$

Bromo- and iodo-trinitromethanes are reduced in the first stage to the trinitromethyl anion ($E_{1/2}$ = +0.036 and +0.42 V),[197] further reduction of which depends on the pH.[198,204] The reduction of chlorotrinitromethane takes place in two ways in the first stage—with rupture of the carbon–chlorine bond ($E_{1/2}$ = +0.248 V) and of a carbon–nitrogen bond[201].

Electron spin resonance indicates intermediate formation of radical-anions and -dianions in the electrochemical reduction of 1-halogenonitroalkanes[205–207].

3. Reactions with Nucleophilic Reagents

(a) Hydrolysis

α-Halogenonitroalkanes are slowly hydrolysed by water: the reaction goes to completion on heating in the presence of alkalis. Kinetic study of the hydrolysis of 1-chloro- and 1-bromo-1-nitroethanes showed that the reaction is preceded by a comparatively slow stage of isomerisation of the nitro- into the *aci*-form, and the latter is attacked by the solvent[180,208]:

$$CH_3CH(NO_2)Cl \xrightarrow{OH^-} CH_3C(Cl){=}NOO^- \xrightarrow[-Cl^-]{H_2O} CH_3C(OH){=}NOOH \rightarrow CH_3CHO + HNO_2 .$$

The action of bases on α-halogenopolynitroalkanes, in contrast to the mononitro-compounds, results in replacement of the halogen by the cation of the base[27,209]:

$$CH_3C(NO_2)_2X + 2KOH \rightarrow CH_3C(NO_2)_2^- K^+ + KOX + H_2O ,$$
$$3C(NO_2)_3X + 6KOH \rightarrow 3C(NO_2)_3^- K^+ + 2KX + KXO_3 + 3H_2O ,$$
$$X{=}Cl, Br, I .$$

Halogenotrinitromethanes are hydrolysed even by water[81,210]:

$$C(NO_2)_3X + H_2O \rightleftarrows HC(NO_2)_3 + HOX ,$$
$$X{=}Cl, Br, I ,$$

The equilibrium constants for the hydrolysis of chloro-, bromo-, and iodo-trinitromethanes are 8×10^{-12}, 3×10^{-11}, and 4×10^{-7} M^{-1} respectively[211].

Fluorotrinitromethane, unlike the other halogenotrinitromethanes, splits off a nitro-group on treatment with a base[44]. The action of alcoholic alkali breaks not only a carbon–nitrogen but also a carbon–fluorine bond[44,212].

(b) Action of reductants

Results obtained for the electrochemical reduction of α-halogenonitroalkanes provide evidence of the extraordinary ease of reduction of the halogen. In addition, the nitro-group is one of the functional groups most sensitive to reduction. Therefore reduction can occur in two directions depending on the nature of the α-halogenitroalkane and the selectivity of the reducing agent.

Chemical reduction of the halogen provides extremely interesting results. The action of reductants of basic character involves replacement of the halogen by the cation of the base with formation of a nitroalkane salt. The halogen that is eliminated behaves as an oxidant. Ease of reduction increases with the "positive" character of the halogen in the α-halogenonitroalkane, which can be explained by facilitation of nucleophilic attack by the reductant anion on the halogen atom.

More detailed research has been undertaken on the reaction with potassium iodide, which is widely used to characterise compounds having a "positively" polarised halogen atom[12]. α-Halogenopolynitroalkanes readily oxidise potassium iodide[24,210,213]:

$$RC(NO_2)_2X + 2KI \rightarrow RC(NO_2)_2^- K^+ + KX + I_2 ,$$
$$R{=}Alk, Hal, NO_2;\ X{=}Cl, Br, I, NO_2 .$$

This reaction is used for the quantitative determination of halogen in iodo- and bromo-polynitroalkanes, as well as in chlorotrinitromethane[24]; chloro-derivatives of dinitroalkanes and halogenomononitroalkanes are less reactive[214]. The "positive" polarisation of the halogen atom diminishes in the same sequence of α-halogenonitroalkanes[156,157,174].

Various views are held on the mechanism of the reaction of α-halogenonitroalkanes with the iodide ion. From general considerations on the action of bases on α-halogenopolynitroalkanes it has been suggested[10] that the first stage involves formation of the polynitroalkyl anion (nucleophilic substitution at the halogen atom):

$$C(NO_2)_3X + I^- \xrightarrow{slow} C(NO_2)_3^- + XI ,$$
$$XI + I^- \xrightarrow{rapid} I_2 + X^- .$$

This hypothesis is supported by an investigation of the mechanism of the reaction of tetranitromethane with hydrogen peroxide and alkyl peroxide anions[215]:

$$ROO^- + C(NO_2)_4 \rightarrow \left[ROO^- \cdots O{=}N^+{-}C(NO_2)_3\right] \rightarrow ROOON \rightarrow O + C(NO_2)_3^-,$$

$$ROOON \rightarrow O \xrightarrow{H_2O} ROH + O_2 + HNO_2.$$

An alternative mechanism, based on kinetic data, involves a stage of bimolecular nucleophilic substitution of halogen by the iodide ion followed by reduction of the iodopolynitroalkane by a second molecule of potassium iodide[216–219]:

$$RC(NO_2)_2X + I^- \underset{}{\overset{\text{slow}}{\rightleftharpoons}} RC(NO_2)_2I + X^-,$$

$$RC(NO_2)_2I + I^- \xrightarrow{\text{rapid}} RC(NO_2)_2^- + I_2.$$

The reaction is thus regarded as a particular case of nucleophilic substitution of the halogen attached to the carbon atom in the initial compound.

Fluorotrinitromethane undergoes denitration under the influence of the iodide or hydrogen peroxide ion[217,220]:

$$C(NO_2)_3F + 2KI \xrightarrow{H_2O} CH(NO_2)_2F + I_2 + KNO_2 + KOH.$$

Chlorotrinitromethane forms with the hydrogen peroxide ion a mixture of trinitromethane and chlorodinitromethane[10]. Tribromonitromethane reacts peculiarly with potassium iodide or cyanide in the presence of potassium nitrite[129]:

$$2CBr_3NO_2 + 6KI + 2KNO_2 \rightarrow K^+{}^-(O_2N)_2C{-}C(NO_2)_2^-K^+ + 6KBr + 3I_2.$$

The complex hydrides of alkali and alkaline-earth metals are extremely promising for the selective reduction of halogen in α-halogenonitroalkanes, because of the relative stability of nitro-groups to the action of hydride anions. A method was worked out for reducing aliphatic and alicyclic α-bromonitrocompounds with sodium tetrahydroborate in aqueous methanol to the corresponding nitroalkanes (in 15–80% yield).[119,121] This complex hydride was used also to reduce ααωω-tetrabromodinitro-compounds[74]:

$$CBr_2(NO_2)CH_2CH_2C(NO_2)Br_2 \xrightarrow{NaBH_4} CH_2(NO_2)CH_2CH_2CH_2NO_2.$$

Liquid ammonia[221] and hydrazine[222] reduce α-halogenonitroalkanes with evolution of nitrogen:

$$3C(NO_2)_2X_2 + 8NH_3 \rightarrow 3C(NO_2)_2X^-NH_4^+ + 3NH_4X + N_2,$$

$$2C(NO_2)_3X + H_2N{-}NH_2 + 4KOH \rightarrow 2C(NO_2)_3^-K^+ + 2KX + N_2 + 4H_2O.$$

Other reducing agents that are used are sodium thiosulphate, sulphide, and hydrogen sulphide[213], potassium cyanide and hexacyanoferrate(II),[223] and triphenylphosphine[224–226]. Other methods have been reported for the selective reduction of halogen in 1-halogenonitroalkanes, e.g. by the action of arsenic sesquioxide in caustic potash solution or of an aqueous–ammoniacal solution of hydrogen sulphide[227].

Still other methods reduce not only halogen but also the nitro-group. Among them are reduction with hydrogen in the presence of platinum-group metals, zinc, or iron and with tin(II) chloride in an acid medium[227].

(c) Relacement of halogen by the nucleophile

A most important property of α-halogenonitroalkanes is their ability to exchange the halogen atom for a nitro-group in the presence of alkaline potassium or sodium nitrite[11]:

$$RCH(NO_2)X + KNO_2 \xrightarrow{K_2CO_3} RC(NO_2)_2^-K^+ + KX,$$

X=Cl, Br.

This reaction, first described by ter Meer for 1-bromo-1-nitro-derivatives of ethane and propane, is now widely used to prepare *gem*-dinitroalkanes. It has been employed to obtain 1,1-dinitroethane[228–230], 1,1-dinitropropane[228,230], 1,1-dinitropentane[228], dinitromethane[231], and also ααωω-tetranitroalkanes[128].

The ter Meer reaction does not take place by the usual mechanism of nucleophilic substitution of the halogen in the *aci*-form of the α-halogenonitroalkane, as had previously been assumed[233], but is a radical-chain process[232]:

$$CH_3CH(NO_2)Cl \xrightarrow{e} CH_3\dot{C}H(NO_2)Cl^{\cdot-} \xrightarrow{-Cl^-} CH_3\dot{C}HNO_2 \xrightarrow{NO_2^-} \rightarrow CH_3CH(NO_2)_2^{\cdot-} \xrightarrow{CH_3CH(NO_2)Cl} CH_3CH(NO_2)_2 + CH_3\dot{C}H(NO_2)Cl^{\cdot-} \rightarrow \text{etc.}$$

Iodotrinitromethane is converted into tetranitromethane by the action of silver nitrite[27].

A typical reaction of 1-halogenonitroalkanes is detachment of the halogen by the anions of nitro-compounds with formation of a new carbon–carbon bond[20–22]. It has been examined in detail on salts of secondary nitroalkanes interacting with their halogeno-derivatives[234–236]:

$$(CH_3)_2C(NO_2)X + (CH_3)_2C{=}NOO^- \xrightarrow{-X^-} (CH_3)_2C(NO_2){-}C(NO_2)(CH_3)_2,$$

X=Cl, Br.

Dinitroalkenes are formed similarly[237,238]:

$$CH_3CH(NO_2)Cl + CH_3CCl{=}NOO^- \xrightarrow{-Cl^-} CH_3CH(NO_2){-}CClCH_3 \xrightarrow{-H^+} \rightarrow CH_3C(NOO^-){-}CClCH_3(NO_2) \xrightarrow{-Cl^-} CH_3C(NO_2){=}CCH_3(NO_2).$$

These reactions can occur either by normal nucleophilic substitution[239,240] or by a radical-anion mechanism[234–236].

Kornblum et al. have shown[241] that the reaction with alkali-metal sulphinates has the latter mechanism:

$$(CH_3)_2C(NO_2)I + PhSO_2^- \rightarrow (CH_3)_2C(NO_2)I^{\cdot-} + PhSO_2^{\cdot},$$

$$(CH_3)_2C(NO_2)I^{\cdot-} \rightarrow (CH_3)_2C\dot{N}O_2 + I^-,$$

$$(CH_3)_2C\dot{N}O_2 + PhSO_2^- \rightarrow [(CH_3)_2C(NO_2)SO_2Ph]^{\cdot-},$$

$$[(CH_3)_2C(NO_2)SO_2Ph]^{\cdot-} + (CH_3)_2C(NO_2)I \rightarrow (CH_3)_2C(NO_2)SO_2Ph + (CH_3)_2C(NO_2)I^{\cdot-}.$$

The action on halogenotrinitromethanes of aryl derivatives of magnesium, mercury, and tin involves a stage of electron transfer from the organometallic compound with formation of a radical-anion of the halogenotrinitromethane[242–244]:

$$PhMgCl + BrC(NO_2)_3 \rightarrow \left[\begin{matrix}BrC(NO_2)_3^{\cdot-}\\ PhMgCl^+\end{matrix}\right] \rightarrow Ph^{\cdot} + {}^1/_2Mg[C(NO_2)_3]_2 + {}^1/_2MgCl_2 + Br^{\cdot}.$$

The appearance of radical-anions in the action of nucleophilic reagents on difluorodinitromethane and fluorotrinitromethane has been confirmed by electron spin resonance[245–247]:

$$CF_2(NO_2)_2 + ArO^- \rightarrow CF_2(NO_2)_2^{\cdot-} + ArO^{\cdot}$$

The radical-anions can break down with fission of either a carbon–nitrogen or a carbon–halogen bond[248]:

$$C(NO_2)_3X^{\cdot-} \rightarrow \begin{cases} C(NO_2)_3^- + X^{\cdot} & (X{=}Cl, Br, NO_2), \\ C(NO_2)_2X^- + NO_2^{\cdot} & (X{=}F, Cl, Br, NO_2). \end{cases}$$

It has recently been established[138,139,249] that fluorotrinitromethane and tetranitromethane, under the influence of alkali-metal halides in anhydrous polar solvents, form products in which a nitro-group has been replaced by a halide ion; under these conditions chlorotrinitromethane forms both nitro-substitution and halogen-substitution products:

$$XC(NO_2)_3 + MY \rightarrow \begin{cases} XC(NO_2)_2Y & (X{=}F, NO_2), \\ XC(NO_2)_2Y + YC(NO_2)_3 & (X{=}Cl), \\ YC(NO_2)_3 & (X{=}Br), \end{cases}$$

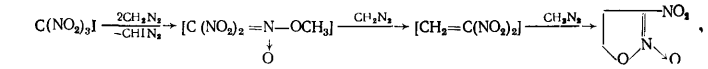
M=K, Li, Rb, Cs; Y=F, Cl, Br.

It is supposed that bimolecular nucleophilic substitution at the carbon atom is involved[216]. In electron-donor polar solvents intermolecular halogen exchange occurs in halogenated derivatives of di- and tri-nitromethanes[250]:

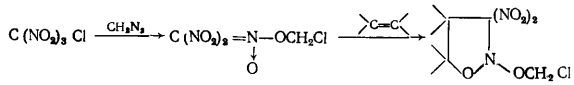
$$C(NO_2)_3Cl + C(NO_2)_2Br_2 \rightleftarrows C(NO_2)_3Br + BrC(NO_2)_2Cl\ ,$$
$$2BrC(NO_2)_2Cl \rightleftarrows C(NO_2)_2Br_2 + C(NO_2)_2Cl_2\ .$$

(d) Reaction with diazoalkanes

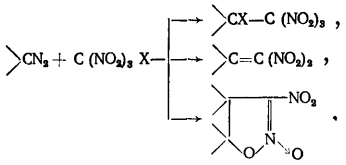
The action of diazomethane on chloro-, bromo-, and iodotrinitromethanes is accompanied by detachment of a nitro-group and of halogen, and yields 3-nitroisoxazoline *N*-oxide[251,252] with intermediate formation of *O*-alkyl esters of trinitromethane followed by 1,1-dinitroethylene[252]:



In the case of chlorotrinitromethane the *O*-chloromethyl ester of trinitromethane is formed as intermediate[252]:



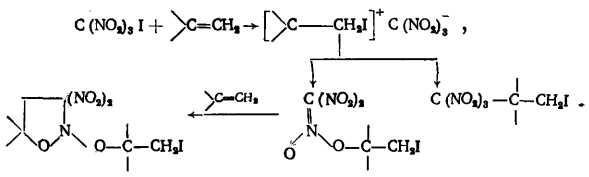
When halogenotrinitromethanes are treated with diazomethane derivatives—9-diazofluorene, diazoanthrone, diazoacetic ester—derivatives of 1-halogeno-2,2,2-trinitroethane, *gem*-dinitroalkenes, and 3-nitroisoxazoline *N*-oxide can be isolated depending on the nature of the reagents and the conditions[251]



(e) Reaction with alkenes

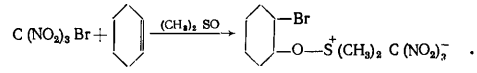
Electrophilic addition at the double bond occurs with iodo- and bromo-trinitromethanes, which is explained by the considerable "positive" character of the halogen. Chlorotrinitromethane does not undergo this reaction.

Iodotrinitromethane reacts exceptionally with alkenes[253–255], forming with ethylene *N*-2′-iodoethoxy-3,3-dinitroisoxazoline and 1-iodo-3,3,3-trinitropropane. Electrophilic attack at the double bond gives the corresponding carbocation and the ambident trinitromethyl anion, which is able to react with either the carbon or the oxygen centre depending on the cation and the solvent[253]:



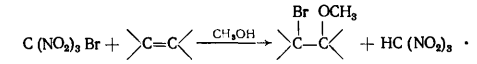
Only *O*-alkylated products are formed with cyclohexene[254] and with trimethylsilylethylene[255].

The reaction between bromonitroform and alkenes has been studied in detail[256–259]. Hardly any reaction occurs in non-polar or weakly polar solvents (benzene, chloroform), but in dimethyl sulphoxide it takes place even at room temperature. However, the products are not nitronic esters of trinitromethane, as had been supposed earlier[256,257], but sulphonium derivatives[258]:



Addition of bromonitroform is slowed down by the presence of electron-accepting substituents at the double bond: cinnamic acid, acrylic esters, and 2,3-dibromopropene do not form adducts even after an hour[256]. Addition of bromotrinitromethane to methyl vinyl ketone and to isopropyl vinyl ether gives *C*-alkylated products[260,261].

In alcoholic solution the reaction of bromotrinitromethane involves intermediate formation of an alkyl hypobromite, which with the alkene gives the final product[262]:



Aromatic hydrocarbons are brominated in the ring by bromotrinitromethane[259].

4. Nucleophilic Addition at Multiple Bonds

(a) Michaelis reaction

Primary α-halogenonitroalkanes are added at an activated double bond[263–266]. The activating influence of substituents diminishes in the sequence[267]

$$CHO > COR > CN > COOR > NO_2.$$

The reactivity of these compounds is determined by their acidity, with fluoro- and chloro-dinitromethanes reacting especially readily[53,263,265,266]:

$$CH(NO_2)_2X + CH_2{=}CHR \rightarrow XC(NO_2)_2CH_2CH_2R\ ,$$
$$R{=}CHO,\ COR',\ COOCH_3,\ CN,\ NO_2;\ X{=}F,\ Cl,\ Br\ .$$

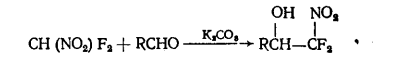
(b) Condensation with aldehydes and ketones (Henry's reaction)

1-Halogenonitroalkanes resemble other compounds containing a mobile hydrogen atom in undergoing condensation with aldehydes:

$$RCH(NO_2)X + R'CHO \rightarrow \underset{\displaystyle X}{\underset{|}{RC(NO_2)}}\underset{\displaystyle OH}{\underset{|}{CHR'}}\ ,$$
$$R{=}H,\ Alk;\ R'{=}H,\ CH_3;\ X{=}F,\ Cl,\ Br\ .$$

The reaction goes especially smoothly between the lower homologues[268–271]. It is assumed that an aldol-type condensation is involved. The rate depends on the nature of the reactants, the catalyst, the ionising power of the solvent, and other factors.

Alcohols and glycols can be obtained from monohalogenonitromethanes depending on the proportions of the reactants[271,272]. Difluoronitromethane condenses with aldehydes when heated (100–120 °C) in the presence of potassium carbonate[103,268]:



The condensation of α-halogenonitroalkanes with aldehydes may be accompanied by dehydration with formation of alkenes[273].

The action of formaldehyde on halogenodinitromethanes yields the corresponding halogenodinitroethanols[44,53,68], which readily break down to give the original α-halogenonitroalkane[185]:

$$XC(NO_2)_2CH_2OH + H_2O \rightleftarrows XCH(NO_2)_2 + CH_2(OH)_2 ,$$
$$X=F, Cl, Br .$$

Fluorodinitromethane condenses with acetaldehyde[270] and with glycollaldehyde[68] in the absence of a catalyst at room temperature. With dialdehydes fluorodinitromethane forms the corresponding tetranitro-diols[270]. With glyoxal at 45 °C it forms also β-fluoro-α-hydroxy-ββ-dinitropropionic acid[68]:

$$\begin{matrix}CHO\\|\\CHO\end{matrix} + FCH(NO_2)_2 \rightarrow FC(NO_2)_2-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-C(NO_2)_2F + FC(NO_2)_2\underset{\underset{OH}{|}}{CHCOOH} .$$

The reaction with pyruvaldehyde involves only the formyl group[68].

Less detailed study has been made of the condensation of α-halogenonitroalkanes with ketones[263,266,274,275]. With the lower ketones in the presence of potassium carbonate difluoronitromethane gives nitroalkanols[268,274]:

$$R-\underset{\underset{O}{\|}}{C}-R + F_2CHNO_2 \rightarrow RRCC(NO_2)F_2 .$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad \underset{\underset{OH}{|}}{}$$

With unsaturated aldehydes and ketones the reaction involves primarily the carbon–carbon double bond, and only then is the carbonyl group affected[263,266].

An unusual method of obtaining *gem*-dinitro-alcohols is to boil 1-bromo-1,1-dinitro-compounds with aqueous formaldehyde[209,276]; the process is analogous to Henry's reaction:

$$RC(NO_2)_2Br + CH_2O \xrightarrow{H_2O} RC(NO_2)_2CH_2OH ,$$
$$R=CH_3, CH_2CH_2COOH .$$

Under these conditions dibromidinitromethane is converted into 2,2-dinitropropane-1,3-diol[277]. ββ-Dinitro- and βββ-trinitro-alcohols are formed by the action of formalin on halogenotrinitromethanes, when the course of the reaction varies[277–279]:

$$C(NO_2)_3X + CH_2O + H_2O \begin{cases} \rightarrow C(NO_2)_3CH_2OH \quad (X=Br, I) , \\ \rightarrow XC(NO_2)_2CH_2OH \quad (X=Cl) , \\ \rightarrow XC(NO_2)_2CH_2OH + (HOCH_2)_2C(NO_2)_2 \quad (X=F, NO_2) . \end{cases}$$

5. Radical Reactions

(*a*) Thermolysis

The gas-phase thermolysis of α-halogenopolynitroalkanes involves as first stage rupture of a carbon–nitrogen bond[280–284]:

$$RC(NO_2)_2X \rightarrow R\dot{C}(NO_2)X + NO_2^{\cdot} ,$$
$$R=CH_3, C_2H_5, NO_2, F, C(NO_2)_2F, C(NO_2)_3;$$
$$X=F, Cl, Br, I.$$

In all cases the reaction is predominantly homogeneous and unimolecular. Only 1-chloro-1,1-dinitroethane shows a surface effect, which is due to loss of resulting chlorine atoms on the walls of the reaction vessel[281]. Loss of the halogenonitroalkyl radical in systems containing nitric oxide and nitrogen dioxide occurs broadly similarly in all the α-halogenonitroalkanes investigated, and can be represented by the scheme

$$CH_3\dot{C}(NO_2)X- \begin{cases} \xrightarrow{NO_2} CH_3-\underset{\underset{NO_2}{|}}{\overset{\overset{X}{|}}{C}}-ONO \rightarrow CH_3C\overset{O}{\underset{X}{<}} + NO + NO_2 , \\ \xrightarrow{NO} CH_3-\underset{\underset{NO_2}{|}}{\overset{\overset{X}{|}}{C}}-NO \rightarrow CH_3\dot{C}(NO)X + NO_2 \rightarrow CH_3CN + XO^{\cdot} . \end{cases}$$

The rate of the gas-phase thermal decomposition of trichloronitromethane depends on the initial pressure and on additions of inhibitors (toluene, formaldehyde)[285].

The dependence of the carbon–nitrogen bond dissociation energy on α-substituents has been established. Chlorine, bromine, and iodine atoms lower this energy in α-halogenonitroalkanes, but a fluorine atom has an insignificant effect comparable with that of hydrogen. The rate of decomposition increases in the sequence of substituents from nitro through chloro and bromo to iodo[281–284]. This dissociation energy is closely similar in magnitude to the activation energy of thermolysis, which is evidence of a radical mechanism of decomposition with initial rupture of a carbon–nitrogen bond in α-halogenonitroalkanes.

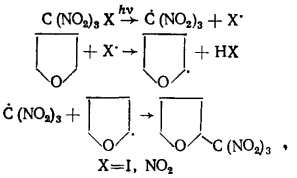
Products of the thermal breakdown of the potassium salts of chloro- and bromo-dinitromethanes in aprotic solvents have been studied[286,287]. The reaction probably involves intermediate formation of dinitro- and halogenonitro-carbenes[287].

(*b*) Other reactions

The possibility of homolytic fission of a carbon–halogen bond in an α-halogenonitroalkane was first shown in the oxidation of tetralin catalysed by bromo- and chloro-trinitromethanes[288], and was later demonstrated in the polymerisation of methyl acrylate in the presence of an α-halogenonitroalkane[289].

It has recently been found that iodotrinitromethane and tetranitromethane react with cyclic ethers (oxolan, oxan) by a non-chain radical mechanism with intermediate formation of the trinitromethyl radical[290–294]:

$$C(NO_2)_3X \xrightarrow{h\nu} \dot{C}(NO_2)_3 + X^{\cdot}$$



$$\dot{C}(NO_2)_3 +$$

$$C(NO_2)_3 ,$$
$$X=I, NO_2$$

However, the photolysis of tetranitromethane and of fluoro- and chloro-trinitromethanes in dimethylformamide and in hydroxylated solvents involves decomposition of the polynitroalkanes to give only anions of the latter[295].

Radical addition of tribromonitromethane at a double bond has been reported[296].

V. PHYSIOLOGICAL ACTIVITY AND PRACTICAL USE

Halogenonitro-compounds are of interest as a consequence of their great physiological activity. Accumulation of nitro-groups at the same carbon atom in α-halogenonitroalkanes leads to an increase in acute toxicity, and a similar effect is observed with increase in the number of halogen atoms. Dihalogenodinitromethanes are the most toxic. Bromonitroalkanes are usually more toxic than their chlorinated analogues[297]. The majority of α-halogenonitroalkanes (but not 1,1-dichloro-1-nitroethane) have a lachrymatory action, which diminishes with increase in molecular weight[298,299].

The antibacterial activity of α-halogenonitroalkanes has been studied[297,300]. Derivatives of nitroethane are more active than those of nitromethane towards *Escherichia coli* and *Staphylococcus aureus pyogenes*[297]. The accumulation of bromine atoms in nitroalkanes leads to an increase in antibacterial activity. The bactericidal activity of α-halogenonitroalkanes is usually attributed to their oxidising power[300].

α-Halogenonitroalkanes exhibit a broad spectrum of activity and possess insecticidal[298–301], fungicidal[302–306], herbicidal[307], bactericidal[308], and nematocidal[302,308,309] properties. Trichloronitromethane and 1,1-dichloro-1-nitroethane are used as insecticides and fungicides either alone or mixed with other compounds[305,310]. "Mixed" α-halogenonitroalkanes, which possess greater activity, have been proposed as fumigants. Thus it is recommended that bromodifluoronitromethane should be used in amounts of 0.15–0.30 g m^{-3} to combat granary pests, and at doses below 448 kg per hectare to treat soil against nematodes[302]. Bromochloronitroalkanes containing 1–5 carbon atoms possess insecticidal and fungicidal activity[302,303].

α-Halogenonitroalkanes can be used also an antibacterial additives in diesel fuels, lubricating oils, and hydraulic fluids[311,312]. They have been recommended for combination with tetraethyl-lead in antiknock compositions, for the thinning and dispersion of oils[313], and for the deparaffination of diesel fuels and oils[314].

1-Chloro-1-nitroethane is an excellent agent for preventing the gelling of rubber additives[315].

α-Halogenonitroalkanes are used also as intermediates in the production of biologically active compounds[316], explosives, and rocket fuel components[137,224].

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