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Oxidative Substitution of Halogen Atoms in Organic Halogeno-derivatives—a New Type of Nucleophilic Substitution Reactions at a Saturated Carbon Atom

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The review surveys and gives a systematic account of data on the oxidative substitution of halogen atoms in organic halogeno-derivatives. The stereochemistry of the reactions as well as numerous rearrangements occurring on oxidative substitution are considered. The influence of the substituted halogen (Cl, Br, or I), the substituents at the reaction centre, and the oxidant on the character of the products and the reaction mechanism is demonstrated.
The bibliography includes 97 references.

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I. INTRODUCTION

During the last decade, numerous reactions of alkyl halides with oxidising agents under mild conditions, leading to the exchange of a halogen for another nucleophilic residue and to the oxidation of the halogen eliminated to the molecular form Hal_2 or heteroatomic molecules containing the oxidised halogen, have attracted the attention of investigators:

$$RI + HNO_3 \rightarrow RONO_2 + I_2 , \quad (1)$$

$$RBr + HNO_3 \xrightarrow{HF} RF + Br_2 , \quad (2)$$

$$RI + ArCO_3H \xrightarrow{H_2O} ROH + I_2 + I_2O_5 , \quad (3)$$

$$RCl + ClOSO_2F \rightarrow ROSO_2F + Cl_2 , \quad (4)$$

$$RBr + ClF \rightarrow RF + BrCl . \quad (5)$$

Sverlakov and co-workers, who discovered such reactions in a study of the nitrolysis of halogenoalkanes with nitric acid [Eqns.(1) and (2)], who proposed an apt name, from our point of view, for reactions of this type—oxidative substitution.

Interest in these reactions has been aroused for several reasons. Thus it has been suggested that reactions of an analogous type occur in the metabolism of alkyl halides in the living organism [Eqn.3], which is the reason for the carcinogenic properties of certain halogenoalkanes. On the other hand, the introduction by this procedure into highly halogenated substrates of an oxygen-containing functional group [Eqn.(4)] or the fluorine atom [Eqn.(5)] by treatment with powerful oxidants such as chlorine fluorosulphonate, chlorine monofluoride, and related reagents is of preparative value. The third and most important stimulus which led to the investigation of these reactions has been the endeavour to understand their mechanism.

This review surveys and gives a systematic account of the available data and puts forward considerations concerning certain details of the mechanism of the oxidative substitution of the halogens at a saturated carbon atom.

II. REACTIONS OF ALKYLIODIDES AND BROMIDES WITH Cl_2, Br_2, AND ICl

In the last century, it was already known that alkyl iodides and t-alkyl bromides interact under mild conditions (at a low temperature in inert solvents) with molecular chlorine to form alkyl chlorides and I_2 or Br_2.[1-3] In the 1950's, this unusual substitution reaction at a saturated carbon atom attracted the attention of theoretical chemists.

Like aryl iodides, on chlorination alkyl iodides afford organic compounds of tervalent iodine, which, however, are unstable and readily decompose to alkyl chlorides and molecular iodine:[4,5]

$$CH_3I + Cl_2 \xrightarrow{-196^\circ C} CH_3ICl_2 \xrightarrow{-30^\circ C} CH_3Cl + ICl .$$

The first data on the mechanism of these reactions were obtained as a result of the study of the kinetics of the reactions of ICl with alkyl iodides and bromides in CCl_4 at 25 °C.[6,7] For the reaction of benzyl bromide and iodide with ICl in the presence of a large excess of the benzyl halide, the rate equation was obtained:

$$\frac{d(IX)}{dt} = k[C_6H_5CH_2X][ICl]^2 .$$

The reaction of isopropyl iodide is also of second order with respect to ICl but the rate is not directly proportional to the concentration of isopropyl iodide; analogous data have been obtained also for t-butyl bromide. The reaction of t-butyl iodide with ICl is so fast that its rate cannot be investigated even in very dilute solutions.

Under the given conditions, benzyl halides give rise to the corresponding chlorides, while in the case of isopropyl iodides mainly chloroiodopropane is formed. In the reaction with t-butyl bromide, a complex mixture of dihalogenoisobutanes is formed together with t-butyl chloride:

$$(CH_3)_3CBr \xrightarrow{ICl} (CH_3)_3CCl + C_4H_8ICl + C_4H_8Cl_2 + C_4H_8BrCl\ .$$

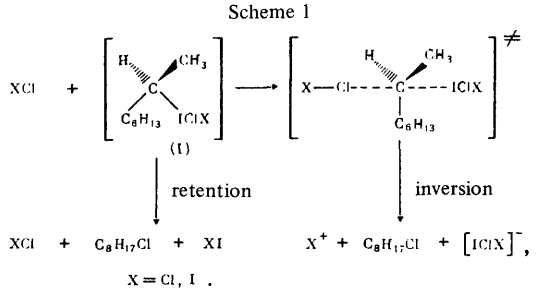
Kinetic data led to the conclusion that the rate-determining stage in the given reaction consists in the attack by the ICl molecule on the alkyl halide–iodine monochloride complex:

$$R{-}I \rightarrow I{-}Cl + ICl \rightarrow \text{products}.$$

The stereochemistry of the substitution of iodine by chlorine and bromine has been investigated in relation to the optically active 2-iodo-octane.[8,9] The reaction of 2-iodo-octane with Cl_2, ICl, and Br_2 proceeds smoothly at −78–0 °C in inert solvents (CH_2Cl_2, $CHCl_3$, CCl_4) and also in a mixture of CH_2Cl_2 with CH_3OH or pyridine, in the absence or presence of HCl, with formation of 2-chloro- and 2-bromo-octanes, preferentially with inversion of the configuration. The higher the polarity of the medium, the greater the amount of the product with inverted configuration formed. Thus the ratios c_i/c_r (c_i and c_r are the amount of products with the inverted and retained configurations respectively) in the reaction of optically active 2-iodo-octanes with an excess of Cl_2 in CH_2Cl_2 and 3:1 CH_2Cl_2–CH_3OH and [CH_2Cl_2–CH_3OH (3:1)]–HCl (4 M) mixtures are respectively 1.5, 5.8, and 10.2.[8] An analogous dependence of c_i/c_r on the polarity of the medium has been observed for the reaction of 2-iodo-octanes with ICl.

According to Corey and Wichter,[8] the results agree with a mechanism involving bimolecular nucleophilic substitution of the complex of alkyl iodide with the halogen (I) by a halogen molecule in accordance with Scheme 1:

Scheme 1



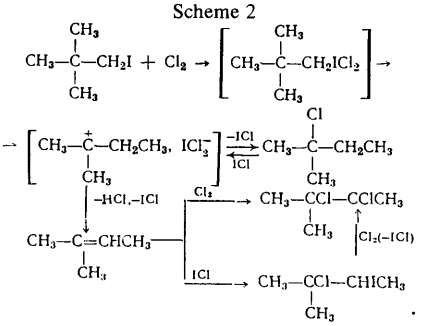
Attack on the complex (I) by the external nucleophile XCl leads to inversion of configuration, while intramolecular capture of chlorine in the complex (I) leads to the retention of configuration of the alkyl chloride. The complex (I) is in essence an intermediate—an organic compound of tervalent iodine. The mechanism presupposing the heterolysis of the complex (I) to the 2-octylcarbonium ion (II) is unlikely:

$$\underset{(I)}{[C_8H_{17}ICIX]} \rightarrow \underset{(II)}{[C_8H_{17}]^+} + [ICIX]^- \rightarrow C_8H_{17}Cl + IX\ .$$

In this mechanism, one would have to expect a higher degree of racemisation of 2-octyl chloride on increase in the polarity of the reaction medium.

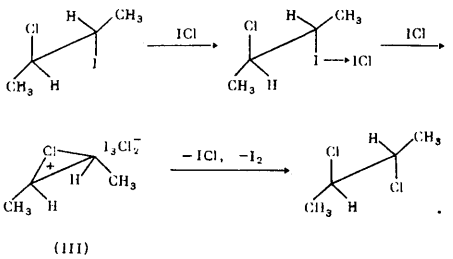
The reaction of neopentyl iodide with molecular iodine yielded t-pentyl chloride and 2,3-dichloro-2-methylbutane.[9] Special experiments showed that t-pentyl chloride also gives rise to 2,3-dichloro-2-methylbutane on treatment with a mixture of ICl and Cl_2, while the reaction with pure Cl_2 does not occur. A mechanism of the reaction of neopentyl chloride with Cl_2 has been proposed on the basis of the data obtained:[9]

Scheme 2



The kinetics and stereochemistry of the reactions of vicinal chloroiodoalkanes with ICl in CCl_4, leading to vicinal dichlorides, have been investigated in a recent study.[10] The reaction of 3-chloro-2-iodo-2,3-dimethylbutane with ICl has overall third order—first with respect to the substrate and second with respect to ICl. The substitution of iodine in *erythro*- and *threo*-3-chloro-2-iodobutanes takes place stereospecifically with retention of configuration, which can be explained by the involvement of the vicinal chlorine in retention of the configuration of the carbonium ion intermediate (III).

Scheme 3

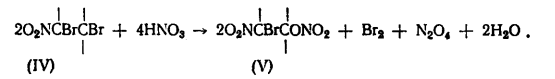


The reactions of *erythro*- and *threo*-2-chloro-1-iodo-1-phenylpropanes with ICl proceed non-stereospecifically and in each case lead to a mixture of *erythro*- and *threo*-1,2-dichloro-1-phenylpropanes. This result can be explained by the fact that the geminal phenyl substituent delocalises the positive charge on the carbonium ion intermediate and thereby prevents the involvement of the neighbouring chlorine in the formation of the bridged cation of type (III).

A single example of the use of iodine trichloride in oxidative substitution reactions has been described in the literature.[11] When n-pentyl iodide reactions with ICl_3 in CH_2Cl_2, n-pentyl chloride is formed in a high yield.

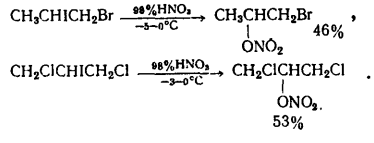
III. REACTIONS OF ALKYL HALIDES WITH NITRIC ACID AND OTHER INORGANIC OXIDANTS

It was observed in 1968 that, when αβ-dibromo-α-nitroalkanes (IV) are treated with concentrated nitric acid at 40–50 °C, the bromide atom in the β-position is replaced by the nitrate group with liberation of elemental bromine in accordance with the scheme[12]

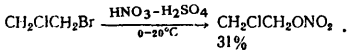


(IV) (V)

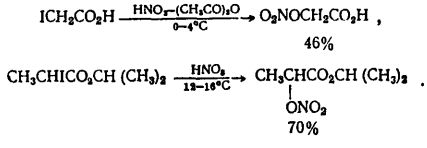
The bromine atom in the α-position is not substituted by the nitrate group. The corresponding nitric acid esters (V) have been isolated in 35–75% yields. The authors investigated this unusual reaction in detail.[13,14] It was established that alkyl iodies interact most readily (at temperature below 0 °C) with nitric acid. The reactivity of alkyl iodides varies in the sequence tertiary > secondary > primary. Under these conditions, the chlorine and bromine atoms in the molecule are not substituted, for example:



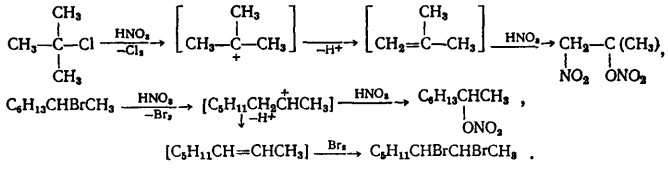
Alkyl bromides react with nitric acid with greater difficulty than alkyl iodides. The corresponding nitrates are obtained from secondary alkyl bromides at 10–15 °C in yields up to 80%. Primary alkyl bromides react with still greater difficulty and at higher temperatures. The reaction is accompanied by the oxidative decomposition of the nitrate and the yield of the nitrolysis product is therefore reduced:



Iodocarboxylic acids and their esters also react with nitric acid to form the corresponding nitrates:[14]

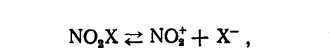


The nitrolysis of the optically active 2-iodo-, 2-bromo-, and 2-chloro-octanes with nitric acid or a mixture of nitric acid and acetic anhydride affords the optically inactive 2-octyl nitrate. On this basis, it has been concluded[13] that the reaction proceeds with formation of carbonium ion intermediates. This is confirmed by the finding that elimination products (alkenes) are formed in the nitrolysis of t-butyl chloride and 2-bromo-octane, which subsequently give rise to addition products:

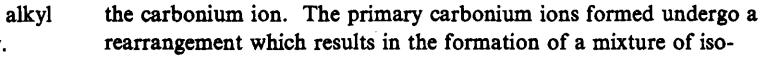


Further study of the interaction of iodo- and bromo-alkanes with nitric acid, nitrogen pentoxide, acetyl nitrate, and nitryl chloride shows that the active species inducing the heterolytic dissociation of the covalent carbon–halogen bond in the organic halogeno-derivative is the nitronium cation:[15]

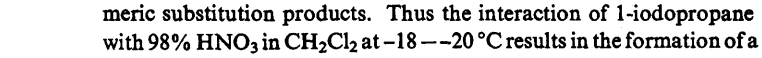
Scheme 4



(6)



(7)

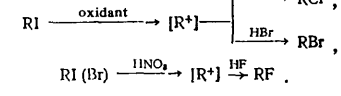


(8)

The necessary condition in the oxidative substitution of halogeno-alkanes is the oxidation of the eliminated halogen to Hal_2 [reaction (7)], which shifts the reaction equilibrium towards the formation of the carbonium ion. The primary carbonium ions formed undergo a rearrangement which results in the formation of a mixture of isomeric substitution products. Thus the interaction of 1-iodopropane with 98% HNO_3 in CH_2Cl_2 at −18 – −20 °C results in the formation of a a 48.6 : 51.4 mixture of 1-propyl and 2-propyl nitrates, while several products were obtained from 1-iodo-octane under these conditions: 1-octyl nitrate, 2-octyl nitrate, and 3(4)-octyl nitrate in proportions of 23.2 : 29.2 : 47.6. The authors note that the isomeric composition of the reaction products depends on many factors: the order in which the reactants are mixed, the concentration of nitric acid, the reaction temperature, etc. For example, when a solution of 1-iodo-butane in methylene chloride is added to nitric acid (in molar proportions of 1 : 10), the ratio of 1- and 2-butyl nitrates is 18 : 82, while for the reverse order of the addition the ratio is 96 : 4.

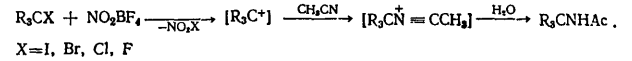
Treatment of 1-bromobutane with a mixture of concentrated nitric acid and acetic anhydride at 15–20 °C leads to the formation of 1-butyl nitrate (15.7%), 2-butyl nitrate (63.0%), 1-butyl acetate (8.1%), and 2-butyl acetate (13.2%).

Not only nitric acid but also HCl, HBr, or HF can act as nucleophiles in the oxidative substitution of the halogens in organic halogeno-derivatives.[16–18] H_2O_2, $KMnO_4$, $K_2Cr_2O_7$, $KClO_3$, $NaNO_2$, and chlorinated lime can also act as oxidants together with HNO_3:[17]



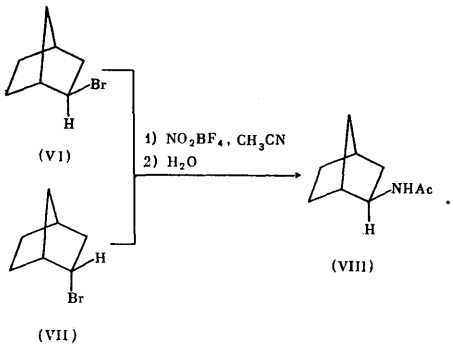
When HCl is passed into a mixture of iodoalkanes with hydrogen peroxide, the yield of the corresponding chloroalkanes reaches 88%. $KMnO_4$ and $K_2Cr_2O_7$ are active oxidants: the reactions in their presence are carried out with slight heating and the yield of chloro-alkanes exceeds 90%. When 2-iodo- or 2-bromo-alkanes are treated with a mixture of concentrated nitric acid and anhydrous hydrogen fluoride, the yield of 2-fluoroalkanes exceeds 70%.

The reactions of alkyl halides with nitronium and nitrosonium fluoroborates in acetonitrile, leading to substituted acetamides, are also a type of oxidative substitution:[19–22]

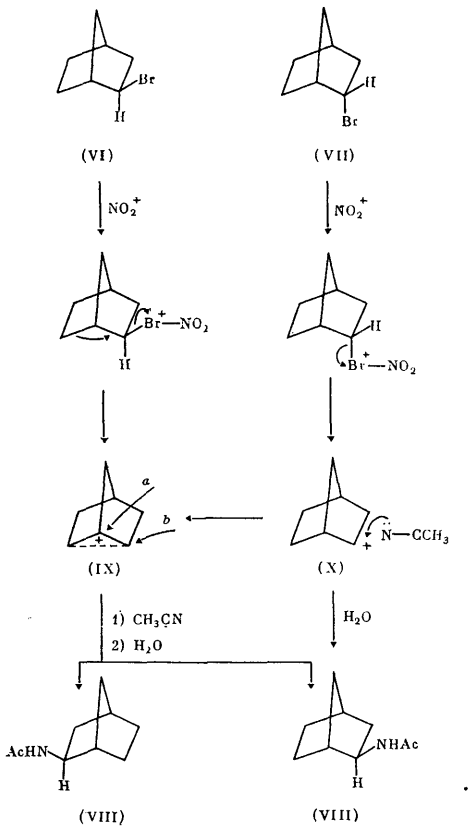


The reactivity of alkyl derivatives varies in the sequence RI > RBr ⩾ RCl > RF. In the general case, the ease of elimination of X corresponds to the stability of the carbenium ions: tertiary > secondary > primary. The relative reactivities of adamantane derivatives are AdF : AdCl : AdBr : AdI = 1 : 6.6 : 67 : 240.[21]

The oxidation of the optically active *exo*-2-norbornyl bromide (VI) under these conditions affords the optically inactive *N*-(exo-2-norbornyl)acetamide (VIII) whilst the optically active *endo*-isomer (VII) gives rise to the *exo*-acetamide (VIII) having a low optical activity (1.2–1.6%):[19]



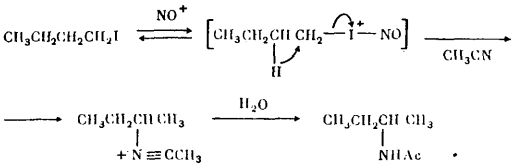
The heterolysis of the C—Br bond in *exo*-2-norbornyl bromide (VI) by the nitronium cation is accompanied by the nucleophilic attack on the C(2) atom by the electrons of the C(6)—C(1) bond, which results in the formation of the symmetrical non-classical bridged cation (IX). The capture of this cation by the solvent and the hydrolysis of the nitrylium ion afford the racemic *exo*-acetamide (VIII). In the case of the *endo*-isomer (VII), the involvement of the C(6)—C(1) bond in the heterolytic process is ruled out for geometrical reasons. The 2-norbornyl cation (X) formed is either captured by the solvent on the side opposite to that of the leaving group, or leads to the optically active *exo*-acetamide, or, to a much greater extent, rearranges to the bridge ion (IX), which gives rise to the *exo*-racemate (VIII).



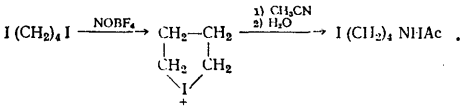
An analogous result has been obtained in the solvolysis of the optically active *exo*- and *endo*-2-norbornyl *p*-bromotoluenesulphonates.[23] In the case of the optically active *endo*-*p*-bromotoluenesulphonate, 7—8% of the optical activity was retained, while the *exo*-isomer yielded only the *exo*-racemate.

The substitution of bromine in the optically active 2-bromooctane on treatment with nitronium fluoroborate in acetonitrile takes place preferentially with inversion of configuration.[19]

Nitrosonium fluoroborate is somewhat less reactive in the oxidative substitution reaction than nitronium fluoroborate.[22] Tertiary and secondary alkyl iodides react smoothly with $NOBF_4$ in acetonitrile at 0 °C with formation of the corresponding amides. The primary iodides react more smoothly and afford a mixture of 1-alkyl- and 2-alkyl-amides:



A rearrangement is not observed for 1,4-diiodobutane owing to the involvement of iodine in the formation of a five-membered iodonium intermediate:



IV. REACTIONS OF ALKYL IODIDES WITH ORGANIC PEROXY-ACIDS

The oxidative substitution of iodine in alkyl iodides when the latter are treated with organic peroxy-acids has been thoroughly investigated[24–30] and it has been established[25] that the complete oxidation of one mole of n-heptyl iodide in methylene chloride requires about two moles of *m*-chloroperoxybenzoic acid. The products of the initial state of this reaction are O_2, I_2, and I_2O_5. The overall stoichiometry of the reaction is described by the set of equations

$$6ArCO_3H + 6RI \rightarrow 6[R\overset{+}{I}O^-] + 6ArCO_2H,$$
$$6[R\overset{+}{I}O^-] + 6H_2O \rightarrow 6ROH + 6HOI,$$
$$6HOI \rightarrow 4HI + 2HIO_3,$$
$$4HI + 2ArCO_3H \rightarrow 2ArCO_2H + 2I_2 + 2H_2O,$$
$$2HIO_3 \rightarrow I_2O_5 + H_2O,$$
$$\underline{n\,ArCO_3H \xrightarrow{[cat.]} n\,ArCO_2H + (n/2)\,O_2};$$
$$(8+n)\,ArCO_3H + 6RI + 3H_2O \rightarrow (8+n)\,ArCO_2H + 6ROH + 2I_2 + I_2O_5 + (n/2)\,O_2.$$

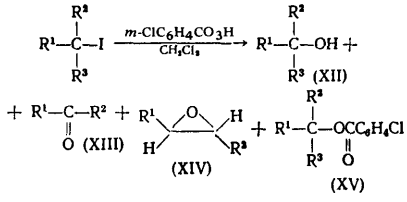
R = n-C_7H_{15}, Ar = m-ClC_6H_4, n = 4-16.

The iodoso-group in the intermediate iodo-compound $R\overset{+}{I}O^-$ is substituted in this case by water, which is present in the peroxy-acid as an impurity. Careful drying of *m*-chloroperoxybenzoic acid and of the solvent reduces the amount of alcohol (60%) and increases that of n-heptyl *m*-chlorobenzoate (40%). This ratio is close to the maximum possible, because 0.5 mole of water is formed on oxidation of one mole of alkyl iodide. When the water-saturated solvent is used, the alcohol is formed exclusively.

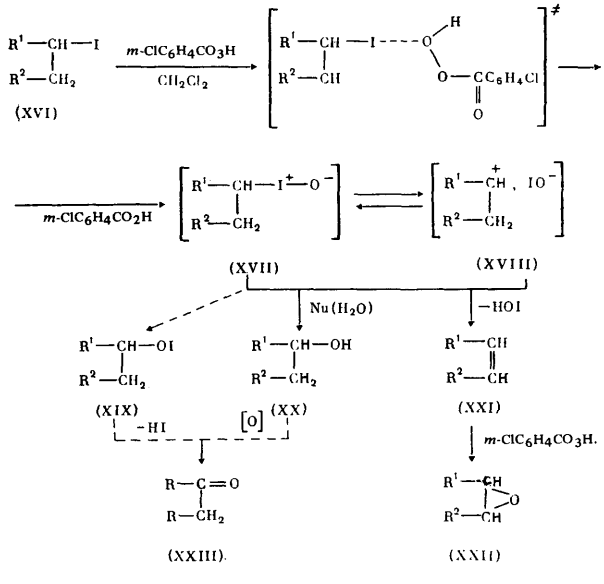
The reactivity of alkyl iodides in relation to organic peroxy-acids varies in the sequence tertiary > secondary > primary. The character of the products formed on oxidation of alkyl iodides is determined by the type of substrate and solvent. When a non-nucleophilic solvent (CH_2Cl_2, C_6H_6) or a solvent with a low nucleophilic activity [tetrahydrofuran (THF), $(C_2H_5)_2O$, C_2H_5OAc] is used, the primary alkyl iodides give rise to the corresponding alcohols and *m*-chlorobenzoates. Secondary and tertiary alkyl iodides, afford, together with substitution products, also carbonyl compounds and epoxides. By carrying out this reaction over a wide temperature range (from -80 to 80 °C), it has been shown that it leads to the same products and only their ratio depends on the temperature.

The dependence of the composition of the products on the type of substrate (in accordance with Scheme 5) is indicated in the Table.

Scheme 5

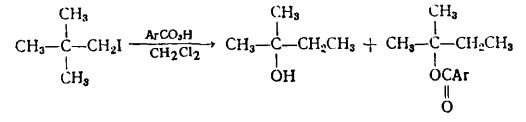


The authors explain the formation of the observed products in the following way:



The alkyl iodide (XVI) is oxidised by *m*-chloroperoxybenzoic acid to the iodoso-compound (XVII), which can dissociate to the ion pair (XVIII). The rearrangement of the iodoso-compound (XVII) to the hypoiodite (XIX) probably proceeds via the ion pair (XVIII). Nucleophilic attack on the iodoso-compound or the ion pair leads to the formation of the substitution products (XX). The elimination of HOI from the iodoso-compound (XVII) results in the formation of the alkene (XXI), which is oxidised under the reaction conditions to the epoxide (XXII). The ketone (XXIII) is formed as a result of the oxidation of the alcohol (XX) and also probably on elimination of HI from the intermediate alkyl hypoiodite (XIX).

Carbonium ion rearrangements on interaction of alkyl iodides with peroxy-acids are observed only when the substitution of iodine is sterically hindered. Thus t-pentyl alcohol and the corresponding *m*-chlorobenzoate have been obtained in the reactions involving neopentyl iodide:

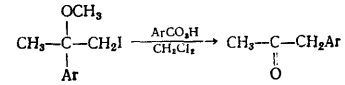


The results of the reactions of alkyl iodides $R^1R^2R^3CI$ with *m*-chloroperoxybenzoic acid.[25]

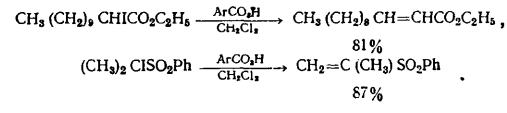
R^1	R^2	R^3	Solvent	*t*° C	Product ratios			
					(XII)	(XIII)	(XIV)	(XV)
n-C_6H_{13}	H	H	CH_2Cl_2	27	90	0	0	10
n-C_5H_{11}	CH_3	H	CH_2Cl_2	27	48	23	20	9
n-C_5H_{11}	CH_3	H	CH_2Cl_2	−80	55	18	23	4
n-C_5H_{11}	CH_3	H	C_6H_6	80	28	22	28	22
n-C_5H_{11}	CH_3	H	C_2H_5OAc	0	65	7	26	2
CH_3	CH_3	CH_3	CH_2Cl_2	27	85*	0	0	15*

*In all the experiments with the exception of the reaction with t-butyl iodide, the overall yield of the products was 80–100% for the total conversion of the initial compound: in the case of t-butyl iodide, the yield of the substitution product was 60%, the remaining 40% comprising low-boiling olefins and epoxides.

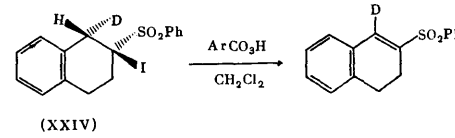
An analogous rearrangement has been observed[26] in the reaction of 2-aryl-1-iodo-2-methoxypropanes with *m*-chloroperoxybenzoic acid:



The elimination of HI can become the main reaction pathway in the presence of electronegative substituents at the α-carbon atom.[27] For example, the oxidation of ethyl 2-iododecanoate and 2-iodo-2-benzenesulphonylpropane with *m*-chloroperoxybenzoic acid leads to unsaturated compounds in a high yield:



It has been shown in relation to the bicyclic iodide (XXIV) that alkenes are formed as a result of *syn*-elimination:



(XXIV)

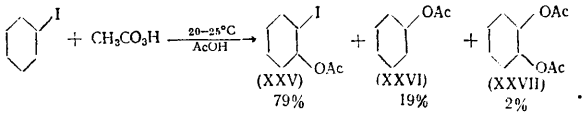
The quantitative formation of 1,2-epoxycyclohexane in the oxidation of cyclohexyl iodide by *m*-$ClC_6H_4CO_3H$ in methylene chloride has been noted.[28]

The oxidation of alkyl iodides in nucleophilic solvents (CH_3OH, CH_3COOH) gives rise mainly to products involving the solvent:[28-30]

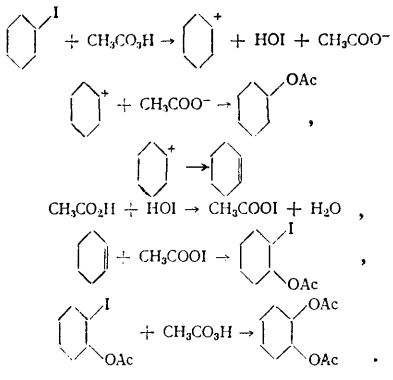
$$CH_3(CH_2)_6CH_2I \xrightarrow[CH_3OH]{ArCO_3H} \underset{91\%}{CH_3(CH_2)_6CH_2OCH_3},$$

$$CH_3(CH_2)_5CHICH_3 \xrightarrow[AcOH]{ArCO_3H} \underset{84\%}{CH_3(CH_2)_5\underset{OAc}{CH}CH_3} + \underset{15\%}{CH_3(CH_2)_5\overset{O}{\overset{\|}{C}}CH_3}.$$

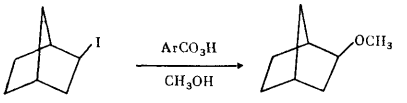
The oxidation of cyclohexyl iodide by peroxyacetic acid in acetic acid produces, in contrast to the reaction with *m*-$ClC_6H_4CO_3H$ in CH_2Cl_2, the vicinal iodoacetate (XXV) together with cyclohexyl acetate (XXVI) and diacetate (XXVII).[29] For a reactant : substrate ratio of 0.7, the following proportions of the products have been obtained:



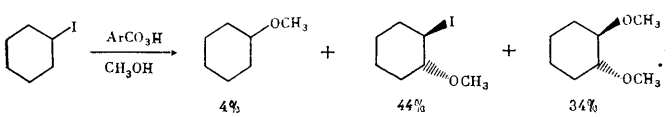
With increase in the peroxyacetic : cyclohexyl iodide ratio, the amount of iodoacetate (XXV) diminishes and that of the diacetate (XXVII) increases. The authors proposed the following reaction scheme:



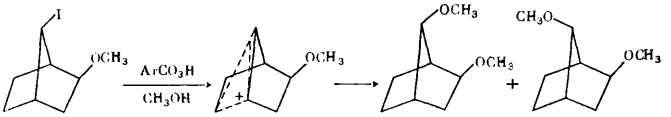
The reactions of alkyl iodides with *m*-chloroperoxybenzoic acid in methanol,[6] in which the corresponding methyl ethers have been obtained in high yield in most cases, have been studied in detail:[30]



The interaction of cyclohexyl iodide with two equivalents of *m*-chloroperoxybenzoic acid led to the isolation of products analogous to those obtained in the reaction with peroxyacetic acid in acetic acid:



Under the given conditions, it has been possible to substitute iodine in highly inert systems such as 1- and 7-bicyclo[2.2.1]heptyl iodides, but, compared with other substrates, under these conditions a (7 – 10)-fold excess of oxidant is necessary. The formation of products with the preferential retention of configuration in the oxidative substitution of iodine in the 7-*syn*-iodide (XXVIII) is explained by the fact that the intermediate species is the σ-delocalised 7-bicyclo-[2.2.1]heptyl cation (XXIX):



(XXVIII) (XXIX) 66% 15%

The influence of various lithium salts on the character of the oxidative substitution product has been investigated in relation to the reaction of n-octyl iodide with *m*-chloroperoxybenzoic acid. It was found that, in the presence of a five-fold excess of lithium chloride or bromide, the main reaction products become the corresponding chlorides and bromides, but the addition of lithium fluoride and perchlorate does not result in the formation of "participation products":

$$CH_3(CH_2)_6CH_2I \xrightarrow[CH_3OH,LiX]{ArCO_3H} \underset{70-80\%}{CH_3(CH_2)_6CH_2X} + \underset{10-15\%}{CH_3(CH_2)_6CH_2OCH_3};$$

X = Cl, Br .

The stereochemistry of the oxidative substitution of iodine by peroxy-acids has been investigated in relation to the optically active 2-iodo-octane.[28,30] The substitution of iodine in (*S*)(+)-2-iodo-octane in methylene chloride affords a mixture of products containing (*R*)(–)-octan-2-ol 56%, the corresponding *m*-chlorobenzoate (29%), octan-2-one (9%), as well as traces of octan-3-ol. Thus the chiral reaction products are formed with complete inversion of configuration, which indicates the operation of the S_N2 mechanism. However, when the reaction is carried out in methanol,[30] the corresponding methyl 2-octyl ether is formed only with the preferential inversion of configuration (c_i/c_r = 2), which indicates the partial heterolysis of the intermediate iodoso-compound on passing to a more polar solvent.

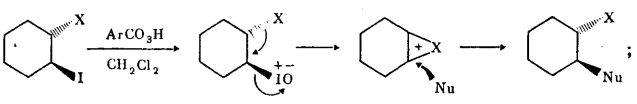
The iodoso-group is an excellent leaving group, comparable in its ability to be substituted to the diazo-group in alkanediazonium ions. It is well known that the solvolysis of the aryl ethers of β-phenylethanol in aqueous and alcoholic media proceeds without a rearrangement,[31] but the oxidation of the deuterium-labelled 1-iodo-2-phenylethane in methylene chloride results in the formation of 35% of the alcohol with migration of the phenyl group. Similarly the deamination of labelled β-phenylethylamine in aqueous solution yields 27% of the alcohol with a displaced phenyl group:[32]

$$PhCH_2CD_2I \xrightarrow[CH_2Cl_2]{ArCO_3H} \underset{65\%}{PhCH_2CD_2OH} + \underset{35\%}{PhCD_2CH_2OH},$$

$$Ph^{14}CH_2CH_2NH_2 \xrightarrow[H_2O]{HNO_2} Ph^{14}CH_2CH_2N_2^+OH^- \rightarrow$$

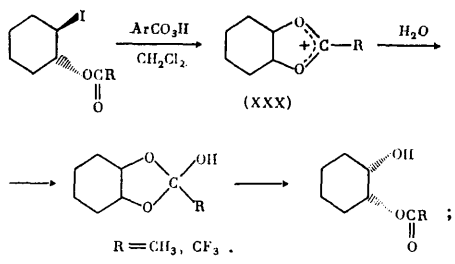
$$\rightarrow \underset{73\%}{Ph^{14}CH_2CH_2OH} + \underset{27\%}{PhCH_2^{14}CH_2OH}.$$

The substitution of iodine in *trans*-vicinally substituted iodocyclohexanes affords alcohols and the corresponding *m*-chlorobenzoates with retention of configuration also as a result of the involvement of the neighbouring group:



X = Cl, Br, OH, OCH_3, N_3 .

The formation of *cis*-hydroxyethers from *trans*-2-iodocyclohexyl acetate or trifluoroacetate is explained by the attack of water on the C(2) atom in the 2-alkyl-1,3-dioxolanolium ion (XXX).



(XXX)

R = CH_3, CF_3 .

Analogous results have been obtained in the oxidation of *trans*-vicinally substituted iodocyclohexanes by iodine trifluoroacetate (III).[33,34] The reaction with *trans*-2-bromo-1-iodocyclohexane yielded a product with retention of configuration, while in the reaction with 2-iodocyclohexyl trifluoroacetate the configuration is inverted.

V. INTERACTION OF ALKYL HALIDES WITH HYPOHALITE DERIVATIVES OF STRONG ACIDS

Hypohalite derivatives of strong acids (fluorosulphonic, trifluoromethanesulphonic, perchloric, and nitric) have been synthesised and investigated comparatively recently.[35] These compounds are very strong electrophiles capable of substituting the halogen atoms in polyhalogenoalkanes by the strong acid residue.

The hypohalite derivatives of fluorosulphonic acid, usually referred to as halogen fluorosulphates, have been most thoroughly investigated among compounds of this class.[36–48] Chlorine and bromide fluorosulphates readily interact even at temperatures below 0 °C with usually inert solvents such as CH_2Cl_2, CCl_4, and $CHCl_2CHCl_2$:[38–38]

$$CH_2Cl_2 + ClOSO_2F \xrightarrow{<0^\circ C} CH_2ClOSO_2F + Cl_2 ;$$
$$CCl_4 + n\,BrOSO_2F \xrightarrow{-22^\circ C} CCl_{4-n}(OSO_2F)_n + n\,BrCl ;$$
$$n = 1-4 .$$

Owing to the high reactivity of halogen fluorosulphates and also the low stability of the non-halogenated alkyl fluorosulphates,[38,47] these reagents have been investigated in reactions with polyfluoroalkyl halides. The reactivity of perfluoroalkyl halides in relation to chlorine fluorosulphate varies in the sequence $R_FI > R_FBr > R_FCl$.[35,39] Thus, perfluoroalkyl iodides are converted into solid white or cream coloured compounds, probably having the structure $R_FI(OSO_2F)_2$, already at tempereatures between -50° and -40 °C. With increase in temperature, these compounds decompose into perfluoroalkyl fluorosulphates and iodine fluorosulphates:[40]

$$R_FI + ClOSO_2F \xrightarrow{-50^\circ C} [R_FICIOSO_2F] \xrightarrow{ClOSO_2F} \rightarrow R_FI(OSO_2F)_2 \xrightarrow{-20^\circ C} R_FOSO_2F + IOSO_2F$$
$$R_F = CF_3,\ n\text{-}C_3F_7,\ n\text{-}C_7F_{15} .$$

Perfluoroalkyl bromides react with chlorine fluorosulphate under more severe conditions. Both primary bromine atoms in 1,2-dibromoperfluoroethane and 1,3-dibromoperfluoropropane can be substituted only at 50–60 °C:[40]

$$Br(CF_2)_3Br + ClOSO_2F \xrightarrow[48\ h]{65^\circ C} \underset{64\%}{FSO_3O(CF_2)_3OSO_2F} + \underset{31\%}{Cl(CF_2)_2OSO_2F} .$$

The secondary bromine atoms are not involved under these conditions. The chlorine atoms in chlorofluoroalkanes are substituted with even greater difficulty. The reaction is catalysed by fluorosulphonic acid.[41–43] Thus Freon 112 ($CFCl_2CFCl_2$) does not react with chlorine fluorosulphate even after prolonged heating (at 70–80 °C), but, after the addition of catalytic amounts of FSO_3H (5 mole %) an exothermic reaction begins at room temperature and is completed after 5 h at 35–45 °C:[41]

$$CFCl_2CFCl_2 + ClOSO_2F \xrightarrow{35-45^\circ C} CFCl_2CFClOSO_2F .$$

Freon 112 (CF_2Cl_2) reacts similarly but 1,2-dichlorohexafluoropropane does not react even at 100 °C.

In the presence of catalytic amounts of FSO_3H, chlorine fluorosulphate interacts with Freon 113 ($CF_2ClCFCl_2$) at 40–50 °C, but the completion of the reaction requires 8 h. The catalytic action of fluorosulphonic acid probably consists in protonating the $ClOSO_2F$ molecule, as a result of which the partial positive charge on the chlorine atom increases:[36,42]

$$ClOSO_2F + HOSO_2F \rightleftarrows \overset{+}{Cl}(H)-O-SO_2F + OSO_2F^- .$$

In fluorosulphonic acid at room temperature, chlorine fluorosulphate substitutes one chlorine atom and at 85 °C a second chlorine atom in Freon 113; all three chlorine atoms are substituted in a superacid medium (HSO_3F/SbF_5):

$$CF_2ClCFCl_2 + ClOSO_2F \xrightarrow[40-50^\circ C]{cat.\ HSO_3F} \underset{84\%}{CF_2ClCFClOSO_2F} ,$$
$$CF_2ClCFCl_2 + ClOSO_2F \xrightarrow[\sim 20^\circ C]{HSO_3F} CF_2ClCFClOSO_2F \xrightarrow{65^\circ C} \underset{65\%}{CF_2ClCF(OSO_2F)_2}$$
$$CF_2ClCFCl_2 + ClOSO_2F \xrightarrow[30^\circ C]{HSO_3F/SbF_5} FSO_2OCF_2CF(OSO_2F)_2 \rightarrow$$
$$\xrightarrow{HSO_3F/SbF_5} FSO_2OCF_2C(=O)F + S_2O_6F_2$$
$$\sim 50\% \qquad \sim 50\% .$$

With the aid of chlorine fluorosulphate in the superacid medium, it has been possible to substitute the secondary bromine atom in 2-bromohexafluoropropyl fluorosulphate (XXXI):

$$\underset{(XXXI)}{CF_3CFBrCF_2OSO_2F} + ClOSO_2F \xrightarrow[80-100^\circ C]{HSO_3F/SbF_5} \underset{\displaystyle OSO_2F}{CF_3CFCF_2OSO_2F} .$$

However, even under these conditions the secondary chlorine and tertiary bromine atom in polyfluoroalkanes cannot be substituted.[43] The reactivity of chlorine fluorosulphate increases also after the addition of bromine, which has been explained by the formation of $BrOSO_2F$ *in situ*.[40] However, in a later study[43] it was shown that bromine fluorosulphate is less reactive than chlorine fluorosulphate; in particular, it reacts with compound (XXXI) in the superacid medium even at 120–130 °C. The catalytic action of bromine in reactions involving substitution by chlorine fluorosulphate has been explained[43,44] by the formation of the compound $BrCl(OSO_2F)_2$ as a possible intermediate, whose molecule contains a tervalent bromine atom. The same workers showed that bromine tris(fluorosulphate), which readily interacts with Freon 113, is even more reactive than chlorine fluorosulphate:[45]

$$CF_2ClCFCl_2 + Br(OSO_2F)_3 \xrightarrow[2\ h]{30^\circ C} \underset{51\%}{CF_2ClCFClOSO_2F} + \underset{39\%}{CF_2ClCF(OSO_2F)_2} .$$

In the superacid medium, $Br(OSO_2F)_3$ substitutes the chlorine atom in 2,3-dichloro-2-trichloromethyl pentafluoropropane.[44]

Iodine tris(fluorosulphate)† and iodine fluorosulphate do not substitute chlorine atoms in Freons in the presence of fluorosulphonic acid even on prolonged heating.[46] $I(OSO_2F)_3$ is capable of substituting only iodine by the fluorosulphate group in perfluoroalkyl iodides:[46]

$$n\text{-}C_3F_7I + I(OSO_2F)_3 \xrightarrow[120\ h]{20^\circ C} n\text{-}C_3F_7OSO_2F + I_3SO_2F + IOSO_2F\ .$$

Nevertheless iodine tris(fluorosulphate) and iodine fluorosulphate readily interact with ethyl chloride at room temperature:[46]

$$CH_3CH_2Cl \xrightarrow[-\frac{1}{3}ICl_3,\ -ICl]{\frac{1}{3}I(OSO_2F)_3,\ IOSO_2F} CH_3CH_2OSO_2F\ (50\%)\ .$$

As regards the mechanism of the interaction of halogen fluorosulphates with alkyl halides, it has been recently suggested[48] that, in the substitution of a halogen by the fluorosulphate group, the substituted halogen is initially oxidised to the tervalent state and the resulting intermediate (XXXII) decomposes under these conditions in accordance with the scheme

$$RHal + XOSO_2F \longrightarrow \underset{\text{(XXXII)}}{R(Hal)(X)(OSO_2F)} \longrightarrow ROSO_2F + HalX\ ;$$

$Hal = Cl, Br, I$; $X = Cl, Br, I, Br(OSO_2F)_2, I(OSO_2F)_2$.

The proposed scheme is hardly applicable to the substitution of chlorine atoms in alkyl halides by bromine and iodine fluorosulphates. In particular, it is unlikely that the electropositive iodine should oxidise the chlorine atom in C_2H_5Cl to the tervalent state in the above reaction of ethyl chloride with $I(OSO_2F)_3$ or $IOSO_2F$.

Chlorine and bromine trifluoromethanesulphonates are also capable of substituting the Cl and Br atoms in perfluorohalogenoalkanes by the trifluoromethanesulphonate group. In contrast to the analogous fluorosulphates, chlorine and bromine trifluoromethanesulphonates are unstable at temperatures above 0 °C and the reactions with them have therefore been carried at low temperatures (down to −160 °C).[49] Comparison of the reactivities of chlorine and bromine trifluoromethanesulphonates and fluorosulphates shows readily that the corresponding trifluoromethanesulphonates are significantly more vigorous reagents. For example, the reaction of $ClOSO_2CF_3$ with Freon 12 takes place readily at −60 °C,[50,51] while in the case of chlorine fluorosulphate heating to 80 °C is necessary:[41]

$$CF_2Cl_2 + ClOSO_2CF_3 \xrightarrow{-60^\circ C} CF_2ClOSO_2CF_3\ ,$$
$$CF_2Cl_2 + ClOSO_2F \xrightarrow{80^\circ C} CF_2ClOSO_2F\ .$$

As for chlorine and bromine fluorosulphates, the reactivity of $ClOSO_2CF_3$ is higher than that of $BrOSO_2CF_3$, which can be seen especially well in the reactions with perfluoroalkyl bromides:[50]

† Bromine tris(fluorosulphate) and iodine tris(fluorosulphate) are considered in this Section as compounds related to the hydrophalite derivatives of fluorosulphonic acid.

$$CF_3Br + ClOSO_2CF_3 \xrightarrow[1\ h]{-111^\circ C} \underset{95\%}{CF_3OSOCF_3}\ ,$$
$$CF_3Br + BrOSO_2CF_3 \xrightarrow[15\ h]{-111\div-10^\circ C} \underset{58\%}{CF_3OSO_2CF_3}\ .$$

In relation to $ClOSO_2CF_3$, the reactivity of alkyl chlorides decreases in the sequence

$$CCl_4 > CCl_3F > CCl_2F_2 > CF_3Cl\ .$$

Chlorotrifluoromethane does not react with $ClOSO_2CF_3$ in the course of 24 h at temperatures in the range −111 − 22 °C. The reactivity series obtained can be accounted for by the decrease in the negative charge on the chlorine atom with increase in the number of fluorine atoms, which should hinder the interaction with the electropositive halogen in $ClOSO_2CF_3$. Under the conditions indicated, the secondary bromine atoms in perfluoroalkanes are not substituted, which the authors explain by the increasing steric hindrance.[50]

The stereochemistry of the substitution of the chlorine atom in *erythro*- and *threo*-$CF_3CO_2CHFCHFCl$ has been investigated.[50] For each diastereoisomer, one diastereoisomer of trifluoromethanesulphonate (XXXIII) was obtained:

$$CF_3CO_2CHFCHFCl + ClOSO_2CF_3 \xrightarrow{-111\div22^\circ C} \underset{\text{(XXXIII)}}{CF_3CO_2CHFCHFOSO_2CF_3}\ .$$

Careful examination of the ^{19}F NMR spectra of the diastereoisomers obtained enabled the authors to conclude that the substitution takes place with retention of configuration. On the basis of the data obtained, a synchronous cyclic mechanism of the type S_Ei was proposed:

Scheme 6

$$\text{—C—Cl} + ClOSO_2CF_3 \longrightarrow \text{—C—Cl}\cdots O(SO_2CF_3) \longrightarrow \text{—C—}OSO_2CF_3 + Cl_2\ .$$

The hypochlorite derivative of perchloric acid (chlorine perchlorate) and virtually all covalent perchlorates are explosive substances sensitive to impact. Chlorine perchlorate is itself stable at room temperature.[52] Perfluoroalkyl and perfluoroaryl iodides interact vigorously with chlorine perchlorate. As for the majority of the reactions of alkyl iodides with oxidants described above, here organic compounds of tervalent iodine (XXXIV) are formed initially and are then converted into the corresponding alkyl perchlorates (XXXV):[53]

$$2R_FI + 4ClOClO_3 \rightarrow \underset{\text{(XXXIV)}}{(R_F)_2I^+I(OClO_3)_4^-} \rightarrow \underset{\text{(XXXV)}}{2R_FOClO_3} + 2[IOClO_3]\ .$$

The intermediates (XXXIV) have been isolated and characterised for R_F = n-C_7F_{15}, iso-C_3F_7, or C_6F_5. The covalent perchlorates (XXXV) cannot always be obtained on heating the intermediates (XXXIV). Thus explosions occurred in the cases of the perfluorophenyl and perfluoroisopropyl derivatives.

Perfluoroalkyl bromides interact just as readily with chlorine perchlorate and afford covalent perchlorates in satisfactory yields. Molecular chlorine and bromine perchlorates are then produced:

$$R_FCFBrCF_2Br + ClOClO_3 \xrightarrow{-25\div0^\circ C} \underset{40-90\%}{R_FCFBrCF_2OClO_3} + BrOClO_3 + Cl_2\ .$$

Primary and secondary perfluoroalkyl chlorides do not enter into this reaction. In the less fluorinated chlorofluorohydrocarbons, the chlorine atoms can also be substituted:[53]

$$\begin{array}{l}CF_2{-}CCl_2\\ |\quad\ |\\ CF_2{-}CCl_2\end{array} + 2ClOClO_3 \rightarrow \begin{array}{l}CF_2{-}CClOClO_3\\ |\quad\ \ |\\ CF_2{-}CClOClO_3\end{array}.$$

Bromine perchlorate is formed in the reactions of $ClOClO_3$ with perfluoroalkyl bromides probably as a result of the oxidation of the elemental bromine formed as an intermediate; owing to the lower reactivity, $BrOClO_3$ accumulates in the reaction products:

$$R_FBr + ClOClO_3 \xrightarrow{k_1} R_FOClO_3 + BrCl,$$
$$BrCl \rightleftarrows {}^1/_2Br_2 + {}^1/_2Cl_2,$$
$${}^1/_2Br_2 + ClOClO_3 \xrightarrow{k_2} BrOClO_3 + {}^1/_2Cl_2.$$

The absence of appreciable amounts of elemental bromine may be evidence that Br_2 is oxidised more readily than the bromine atom in the perfluoroalkyl bromide, i.e. in the reaction schemes presented we have $k_2 > k_1$. Bearing in mind that chlorine trifluoromethanesulphonate[51] and chlorine fluorosulphate[54] readily oxidise Br_2 to the corresponding hypobromites, presumably an analogous picture obtains also in the substitution by these reagents of the bromine atoms in the relatively unreactive perfluoroalkyl bromides.

Yet another representative of reagents of this type, namely chlorine nitrate, is stable at low temperatures (–40 °C), decomposing gradually at 20–25 °C.[55] Trifluoromethyl iodide is readily oxidised at low temperatures by chlorine nitrate, but covalent alkyl nitrates have not been isolated, in contrast to the perchlorates:[56,57]

$$CF_3I + ClONO_2 \xrightarrow{-45^\circ C} [CF_3IClONO_2] \xrightarrow{-20^\circ C} CF_3I(ONO_2)_2 + Cl_2.$$

Trifluoromethyl iodosodinitrate decomposes at room temperature in accordance with the scheme[57]

$$10CF_3I(ONO_2)_2 \xrightarrow{20^\circ C} 5CF_3I + 5COF_2 + 10N_2O_4 + I_2 + IF_5 + I_2O_5.$$

VI. THE INTERACTION OF ALKYL HALIDES WITH HALOGEN FLUORIDES

The most readily available halogen fluorides, namely IF_5, BrF_3, ClF, and ClF_3, were tested as early as the 1930's–1950's as fluorinating agents in the substitutional fluorination reactions of polyhalogenohydrocarbons, mainly halogenomethanes:[58–61]

$$CHI_3 + IF_5 \rightarrow CHF_3 + I_2,$$
$$CBr_4 + BrF_3 \rightarrow CBrF_3 + Br_2,$$
$$CCl_4 + BrF_3 \rightarrow CCl_2F_2 + BrCl.$$

It was then already noted that, as the geminal halogen atoms (I, Br, Cl) are substituted by fluorine, further fluorination is hindered.

Bromine and chlorine trifluorides effectively substitute the iodine atoms by fluorine in perfluoroalkyl iodides, the corresponding perfluoroalkanes being then formed in high yields.[62] Later it was shown that at low temperatures the interaction of ClF_3 and BrF_3 with perfluoroalkyl iodides leads to the formation of the corresponding derivatives of tervalent and quinquevalent iodine:[63]

$$R_FI + 2ClF_3(BrF_3) \rightarrow R_FIF_2,$$
$$R_FI + 4ClF_3 \rightarrow R_FIF_4,$$
$$R_F = C_2F_5,\ C_4F_9,\ \text{etc.}$$

Overall, the early data surveyed in a number of reviews[59–61] led to the conclusion that halogen fluorides are relatively unselective reagents and that their application in organic chemistry would be restricted to reactions with highly halogenated substrates. Nevertheless, subsequent investigations demonstrated that highly reactive compounds such as ClF and BrF_3 can be used successfully for the selective substitution of bromine and chlorine atoms by fluorine in hydrogen-containing halogenoalkanes.[64–70] Thus the use of a solution of bromine trifluoride in bromine for the selective fluorination of bromofluoroethanes has been described:[64]

$$CF_3CHBr_2 \xrightarrow[25-35^\circ C]{BrF_3/Br_2} \underset{92\%}{CF_3CHBrF} + \underset{5\%}{CF_3CHF_2},$$
$$CF_2BrCH_2Br \xrightarrow{BrF_3/Br_2} \underset{77\%}{CF_3CH_2Br}.$$

A possible reaction mechanism taking into account the tendency of BrF_3 to undergo self-ionisation has been proposed:

$$2BrF_3 \rightleftarrows BrF_2BrF_4 \rightleftarrows BrF_2^+ + BrF_4^-,$$
$$-\overset{|}{\underset{|}{C}}-Br + BrF_2^+ \rightarrow [-\overset{|}{\underset{|}{C}}\overset{\delta+}{\cdots}Br\cdots Br^{\delta-}F_2] \rightarrow [-\overset{|}{\underset{|}{C^+}}] + [Br_2F_2],$$
$$[-\overset{|}{\underset{|}{C^+}}] + BrF_4^- \rightarrow -\overset{|}{\underset{|}{C}}-F + BrF_3,$$
$$[Br_2F_2] \rightarrow 2BrF \rightleftarrows {}^2/_3Br_2 + {}^2/_3BrF_3.$$

The BrF formed in the above scheme is extremely unstable and readily disproportionates to Br_2 and BrF_3.[58] Ultimately 1/3 of a mole of BrF_3 is consumed in the substitution of a single bromine atom in the bromoalkane:

$$RBr + {}^1/_3BrF_3 \xrightarrow{Br_2} RF + {}^2/_3Br_2.$$

In a recently published series of studies, it has been shown that ClF and BrF_3 smoothly substitute a bromine atom by fluorine in bromine-containing alkanes and esters.[66–70] The process is carried out at room temperature by the gradual addition of pure BrF_3 to a solution of the bromo-derivative in Freon (5–30 vol.%).[69] In the case of chlorine monofluoride, the gaseous reagent is passed through the liquid bromoalkane or its solution in an inert solvent ($CHCl_3$, CCl_4, $CF_2ClCFCl_2$) at temperatures between –50° and 50 °C.[66]

Fluorination with chlorine monofluoride and bromine trifluoride produces virtually identical results both as regards the yield and the character of the reaction products, for example:

$$CH_2ClCHBrCH_2Br \xrightarrow{ClF \text{ or } 1/3BrF_3} \underset{60\%}{CH_2ClCHFCH_2Br} + \underset{20\%}{CH_2ClCHBrCH_2F}.$$

Bearing in mind that the reactions of ClF with bromo-derivatives result in the formation of elemental bromine, which is capable of reacting with ClF to form BrF_3,[58] one may assume that ClF reacts only initially with the bromoalkanes and that subsequently the fluorination is effected by BrF_3:

$$RBr + ClF \rightarrow RF + BrCl,$$
$$2BrCl \rightleftarrows Br_2 + Cl_2,$$
$$Br_2 + 6ClF \rightarrow 2BrF_3 + 3Cl_2,$$
$$RBr + 1/3BrF_3 \rightarrow RF + 2/3Br_2.$$

However, special experiments have shown that chlorine monofluoride reacts with hydrogen-containing bromoalkanes as a rule much faster than with bromine.[69]

As already mentioned previously, the opposite ratio of the rates of reaction with the organic substrate and elemental bromine (see Section V) is observed in the reactions of chlorine perchlorate with perfluoroalkyl bromides. This difference is apparently associated

with the fact that the electron density of the bromine atom of the perfluoroalkyl bromide is greatly reduced under the influence of the powerful $-I$ effect of the perfluoroalkyl group and not with the character of the oxidant (ClF and $ClOClO_3$). For this reason, substitution of bromine in perfluoroalkyl bromides is slower than the oxidation of the elemental bromine (formed as a result of the reaction) to $BrOClO_3$. On the other hand, the organic bromides used in the reactions with ClF do not as a rule have such poweful electron-accepting substituents at their reaction centre.[66,69] For this reason, in the interaction of ClF with hydrogen-containing alkyl bromides, Br_2 does not enter into a competing reaction and BrF_3 is not formed as an intermediate.[69] Virtually identical results of the substitutional fluorination with chlorine monofluoride and bromine trifluoride indicate a common mechanism of fluorination by these reagents.

The interaction of alkyl bromides with chlorine monofluoride and bromine trifluoride probably proceeds with formation of linear bromonium ions in the first stage of the reaction, which is followed by the substitution of the Br—X group by the fluoride anion or an internal nucleophile:

$$R{-}Br + ClF \rightarrow R{-}\overset{+}{Br}{-}Cl, F^- \rightarrow RF + BrCl\ ,$$

$$R{-}Br + BrF_3 \rightarrow R{-}\overset{+}{Br}{-}BrF_2, F^- \rightarrow RF + Br_2F_2\ ,$$

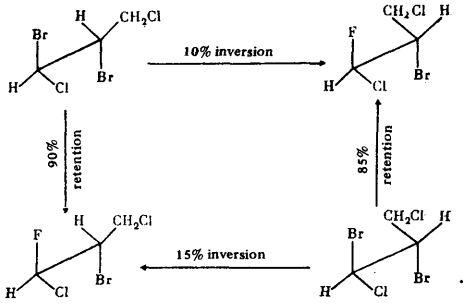
$$Br_2F_2 \rightarrow 2BrF \rightleftarrows {}^2/_3Br_2 + {}^2/_3BrF_3\ .$$

A characteristic feature of the reactions involving the oxidative substitution of bromine by ClF and BrF_3 is that rearrangement products are formed exclusively from primary alkyl bromides in a non-polar medium:[66,68,69]

$$CH_3(CH_2)_3CH_2Br \xrightarrow{ClF \text{ or } 1/3BrF_3} CH_3(CH_2)_2CHFCH_3\ ,$$

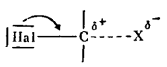
$$\underset{CH_3}{\overset{|}{CH_3CHCH_2Br}} \xrightarrow{ClF} \underset{CH_3}{\overset{|}{CH_3CFCH_3}} + CH_3CHFCH_2CH_3\ ,$$

$$\underset{CH_3}{\overset{|}{CH_2ClCFCH_2Br}} \xrightarrow[90\%]{{}^1/_3BrF_3} CH_2ClCF_2CH_2CH_3 + \underset{CH_3}{\overset{|}{CH_2ClCFCH_2F}}\ .$$
$$\qquad\qquad\qquad



The fluorination of *erythro*- and *threo*-1-bromo-1,2-dichloro-2-fluoroethanes by chlorine monofluoride or bromine trifluoride proceeds non-stereospecifically.[66,69]

The influence of geminal and vicinal halogen atoms on the rate of the oxidative substitution of bromine by chlorine monofluoride in a non-polar medium has been investigated recently[68] by the method of competing reactions. It has been shown that the vicinal halogens greatly retard the rate of fluorination ($CH_3CHBrCH_3 \gg CH_3CH.BrCH_2Cl \gg CH_2ClCHBrCH_2Cl$). The geminal halogen atoms (Br, Cl) have only a weak influence on the rate of substitution. Thus the halogenoethanes CH_3CH_2Br and $CH_3CHClBr$ react with the monofluoride at approximately the same rates, while the accumulation of the halogens at the substituted bromine atom only slightly reduces the rate of the oxidative substitution ($CH_2BrCH_2Br : CH_2BrCHClBr : CH_2BrCCl_2Br = 10:3:1$). It is of interest to compare the results with data for the influence of the geminal and vicinal halogen atoms on the rates of solvolytic reactions proceeding via carbonium ion transition states. According to the results of Winstein and Grunwald,[74] the vicinal chlorine atom decreases the rate of solvolysis by a factor of 1000 compared with the hydrogen atom. On the other hand, geminal halogens increase the rate of reaction by stabilising the transition state:



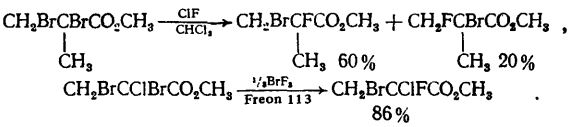
In particular, the ratios of the rate constants for the hydrolysis of benzyl bromide, 1-bromo-1-chloromethylbenzene, and 1-bromo-1,1-dichloromethylbenzene in 50% aqueous acetone are 1:6:70.[75] The geminal chlorine atom increases the rate of reaction more than does the bromine atom as a result of the powerful "back donation" effect ($C_6H_5CBr_3$‡ : $C_6H_5CClBr_2 : C_6H_5CCl_2Br = 1.0:2.4:5.6$). Analogous results have been obtained also for the hydrolysis of 2,2-dihalogenopropanes[76] ($CH_3CHBrCH_3 : CH_3CBr_2$‡$CH_3 : CH_3CClBrCH_3 = 1:6:47$). Thus vicinal halogen atoms significantly reduce the rate of both solvolysis and oxidative substitution. By increasing the rate of solvolysis, geminal halogens lower the rate of oxidative substitution. The observed difference is probably associated with the fact that the geminal halogens exert a dual influence on the rate of reaction in substitutional fluorination reactions. As a consequence of the significant inductive effect, they diminish the electron density on the substituted bromine atoms, as a result of which the rate of reaction should decrease as the geminal halogen atoms accumulate. However, the significant decrease in the rate of reaction compared with the influence of the vicinal halogens shows that the geminal halogens stabilise the transition state by diminishing the positive charge on the α-carbon atom:

‡ The rate of hydrolysis calculated per bromine atom.

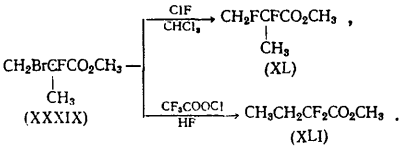


Nevertheless, the deactivating inductive effect proves stronger than the activating mesomeric effect.

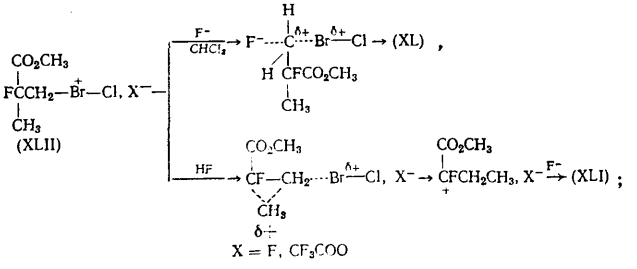
Compounds containing a functional group—esters of halogenated carboxylic acids—can be used as substrates in reactions involving substitutional fluorination by chlorine monofluoride or bromine trifluoride:[66,69]



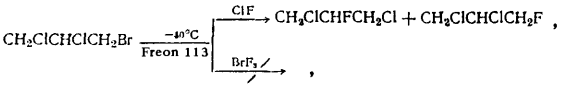
Interesting data have been obtained for the interaction of methyl 3-bromo-2-fluoro-2-methylpropanoate (XXXIX) with ClF in chloroform[66] and for the oxidative substitution of the ester (XXXIX) by the trifluoroacetyl hypochlorite–anhydrous HF system (the stoichiometric equivalent of ClF).[77] The vicinal difluoride, namely methyl 2,3-difluoro-2-methylpropanoate (XL), was obtained in a high yield in a non-polar medium, while in HF the product was methyl 2,2-difluorobutyrate (XLI), formed as a result of the 1,2-migration of the methyl group:



The result obtained can be explained by the fact that the Br–Cl group in the ion pair (XLII) formed is substituted in a non-polar medium by the fluoride ion, while hydrogen fluoride, which is a highly polar weakly nucleophilic solvent, promotes the splitting off of Br–Cl with the simultaneous migration of the methyl group:



Chlorine monofluoride is a more vigorous reagent than BrF_3. For example, whereas ClF readily substitutes the bromine atom in 1-bromo-2,3-dichloropropane at –40 °C, BrF_3 does not react under the conditions indicated:[69]



The chlorine atoms present in the substrate molecule are not as a rule involved in the reactions of ClF and BrF_3 with organic bromo-derivatives. Nevertheless, depending on the electronic properties of the substitutents in the α- and β-positions with respect to the chlorine atom to be substituted, the substitution of the latter by fluorine can

take place in a non-polar medium or in anhydrous HF.[67] In order to predict the influence of substituents on the ease of substitution of chlorine atoms in alkyl chlorides, one can undoubtedly use the result obtained in a study of the relative rates of reaction of ClF with alkyl bromides.[68] Chlorine atoms are most readily substituted when electron-donating substituents are present at the reaction centre. For this reason, the interaction of t-butyl chloride and 1,2-dichloropropane in an inert solvent (Freon 113, CCl_4) at temperatures between -30° and -50°C with an equimolar amount of ClF affords the corresponding fluorides. In the case of 1,2,3-trichloropropane and chloroform, the completion of the reaction requires an excess of the reagent:

$$(CH_3)_3CCl \xrightarrow[CCl_4,\ -60\text{—}-30^\circ C]{ClF} (CH_3)_3CF\ ,$$
$$CH_3CHClCH_2Cl \xrightarrow[-30^\circ C]{ClF} CH_3CHFCH_2Cl\ ,$$
$$CHCl_3 \xrightarrow[-50\text{—}-40^\circ C]{ClF} CHCl_2F\ .$$

Low temperatures promote the reactions by increasing the solubility and hence the concentration of chlorine monofluoride in the substrate.

The synthetic possibilities of the substitutional fluorination of organochlorine compounds increase significantly when anhydrous HF is used as the solvent.[67] Hydrogen fluoride does not then play solely the role of a highly polar solvent but also increases the reactivity of ClF as a result of the formation of the complex $Cl^{\delta+}-F-H-F^{\delta-}$.[78] The esters of chlorine-containing carboxylic acids, forming homogeneous mixtures with HF, are convenient substrates in this case:

$$CH_3CClFCHClCO_2C_2H_5 \xrightarrow[HF]{ClF} \underset{90\%}{CH_3CF_2CHClCO_2C_2H_5}\ .$$

The reactions of chloroalkanes are performed by passing ClF through a cooled stirred emulsion of the corresponding chloroalkane in anhydrous HF. Under these conditions, the oxidative substitution of the primary chlorine atom in 1,3-dichloro-2-fluoropropane is accompanied by the 1,2-hydride shift and the formation of a geminal difluoride:

$$CH_2ClCHFCH_2Cl \xrightarrow[HF]{ClF} CH_2ClCF_2CH_3\ .$$

An even greater increase in the fluorinating capacity of chlorine monofluoride is observed as a result of the use of catalytic amounts (1—5%) of antimony halides in a non-polar medium.[67] ClF then becomes so reactive that at -40 °C it substitutes the chlorine atoms in Freon 113:

$$CF_2ClCFCl_2 + ClF \xrightarrow[-10^\circ C]{SbF_5} CF_2ClCF_2Cl\ .$$

Antimony pentafluoride does not react under these conditions with Freon 113. Probably in the presence of antimony halides the fluorinating agent is the intermediate fluorodichloronium hexafluoroantimonate $Cl_2F^+SbF_6^-$—a compound analogous to $Cl_2F^+AsF_6^-$ and $Cl_2F^+BF_4^-$ described in the literature.[79]

The fluorinating capacity of BrF_3 also increases sharply in the presence of antimony halides. Tin halides can be used as effective catalysts of the fluorination of alkyl halides by bromine trifluorides.[80] Evidently, other Lewis acids, capable of producing salt-like compounds containing the BrF_2^+ cation on reaction with BrF_3, are also suitable for this purpose. The fact that the oxidising capacity of such compounds is much higher than that of the initial halogen fluorides has been demonstrated for the reactions of $BrF_2^+SbF_6^-$, $ClF_2^+BF_4^-$, $BrF_4^+SbF_6^-$, $IF_4^+SbF_6^-$, and $BrF_4^+Sb_2F_{11}^-$ with aromatic perfluoro-compounds.[81,82] The reactions proceed via a mechanism involving the one-electron oxidation of the aromatic perfluoro-substituted nucleus.[82] There is every reason to believe that such compounds should be the most powerful reagents for the substitutional fluorination of relatively unreactive alkyl halides.

Alkyl iodides react very vigorously with ClF and BrF_3 but they are not suitable substrates for fluorination by these reagents—the reactions result in complex mixtures of products, among which alkyl fluoride as well as alkyl chlorides or alkyl bromides respectively have been found.

When the *N*-bromosuccinimide—anhydrous HF system (the stoichiometric equivalent of BrF) is used as the reagent,[65] it is possible to achieve successfully the oxidative substitution of the iodine atom by fluorine in primary alkyl halides, for example, in 2,3-dichloro-1-iodopropane:

$$CH_2ClCHClCH_2I \xrightarrow[HF]{>N-Br} \underset{56\%}{CH_2ClCHFCH_2Cl} + \underset{14\%}{CH_2ClCHClCH_2F}\ .$$

The oxidative substitution of bromine atoms in tertiary and secondary alkyl bromides takes place on treatment with stoichiometrically equivalent amounts of ClF (the *N*-chloramine—HF system):[77]

$$CH_2BrCBrCH_2Cl \xrightarrow[HF]{>N-Cl} \underset{CH_3}{\overset{|}{CH_2BrCFCH_2Cl}}\ .$$

In the reactions presented, *N*-chloramine (*N*-bromamine) acts as the oxidant and HF acts as a highly polar ionising solvent and a source of fluoride anions.

VII. THE MECHANISM OF THE OXIDATIVE SUBSTITUTION

Critical examination of the original communications devoted to the reactions of alkyl halides with oxidants makes it possible to propose, in our view, the following general reaction mechanism:

$$R—Hal + X^{\delta+}—Y^{\delta-} \rightarrow \underset{(XLII)}{R—\overset{+}{Hal}—X,\ Y^-}\ ,$$
$$R—\overset{+}{Hal}—X,\ Y^- \rightarrow \text{products}.$$

The first rate-determining reaction state consists in the electrophilic attack by the reagent on the unshared electron pairs of the halogen atom with formation of the ion pair (XLII). The subsequent reaction of the ion pair can take place via several competing pathways: the first involves the substitution of the Hal—X group by the internal or external nucleophile, the second involves the addition of the anion Y^- with formation of compounds of the tervalent halogen $R-Hal\begin{matrix}X\\ \diagup\\ \diagdown\\ Y\end{matrix}$, the third involves elimination with formation of an olefin, and in the fourth Hal—X is split off with formation of a carbonium ion. The preferential occurrence of one of these reactions depends both on the halogen substituted itself and on the oxidant, the structure of the hydrocarbon group, and the reaction conditions.

The possibility of the formation of a linear halogenonium ion ($R-\overset{+}{Hal}-X$) as an intermediate species follows from the fact that halogenonium ions of analogous structure are well known.[83—85] Thus, as early as the middle of the 1950's, diarylhalogenonium salts having the general formula $Ar-\overset{+}{Hal}-ArX^-$ (Hal = I, Br, or Cl X = BF_4

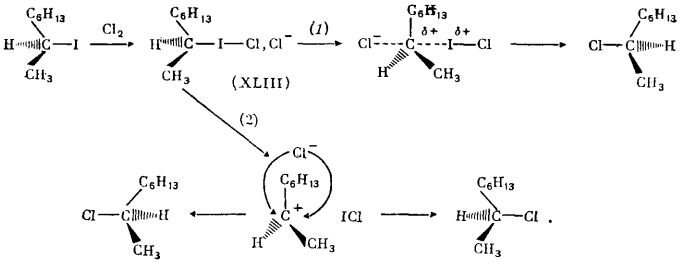
etc.) were obtained.[83] Olah and Demember[85] detected spectroscopically the formation of dialkylhalogenonium ions following the addition of a solution of antimony pentafluoride in SO_2 to an excess of the corresponding alkyl halide:

$$2R{-}Hal \xrightarrow[-60°C]{SbF_5,SO_2} R{-}\overset{+}{H}al{-}R,\ SbF_5Hal^- ;$$
$$Hal = I,\ Br,\ Cl,\quad R = CH_3,\ C_2H_5,\ iso\text{-}C_3H_7.$$

Alkylmethylhalogenonium ions are formed when an alkyl halide is treated with the complex of antimony pentafluoride and methyl fluoride:

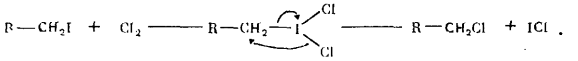
$$R{-}Hal + (CH_3F + SbF_5) \rightarrow R{-}\overset{+}{H}al{-}CH_3\,SbF_6^- .$$

The general mechanism of the reactions of alkyl halides with oxidants discussed above makes it possible to explain satisfactorily also the majority of experimental data. Thus the formation of products with the preferential inversion of configuration on interaction of the optically active 2-iodo-octane with Cl_2, ICl, and Br_2 in methylene chloride probably takes place as follows:

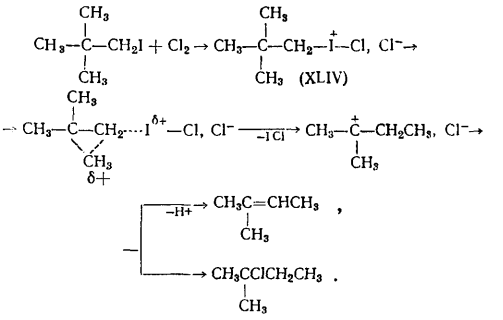


When 2-iodo-octane interacts with molecular chlorine, the ion pair (XLIII) is formed and is converted into the reaction product via two competing pathways. The main pathway (1)—the substitution of I—Cl by the chloride anion—is a usual S_N2 process which takes place with inversion of configuration. However, the I—Cl elimination reaction with formation of a carbonium ion takes place simultaneously. This is pathway (2), which in fact affords a racemic product. The increase in the yield of the products having inverted configuration following an increase in the nucleophilicity of the medium (as a result of the addition of pyridine, methanol, or diethyl ether) can be explained by the solvation of the halogenonium ion, as a result of which attack from the front becomes increasingly difficult.

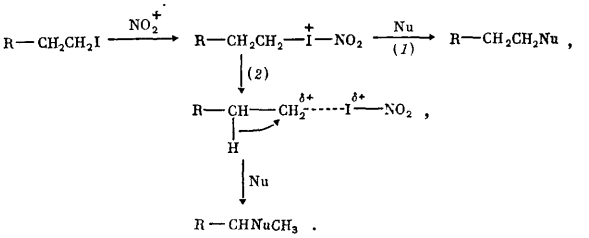
The absence of rearranged products in the interaction of chlorine and bromine with primary alkyl iodides shows that the reaction takes place exclusively via the S_N2 pathway. On the other hand, bearing in mind the fact that the interaction of alkyl iodides with Cl_2 at a low temperature leads to the formation of alkyliodine(III) dichlorides, the following alternative mechanism can be put forward:



The non-rearranged products are formed as a result of intramolecular substitution. However, the reaction of neopentyl iodide with Cl_2, which results in the formation of only a tertiary chloride and of the products of the further reaction of trimethylethylene, shows that the intramolecular substitution in alkyliodine(III) dichloride is unlikely. The interaction of neopentyl iodide with Cl_2 is consistent with the following mechanism:

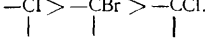


For the halogenonium ion (XLIV) formed, the presence of the bulky t-butyl group in the α-position relative to the reaction centre precludes the nucleophilic attack from the rear and this is why the methyl group behaves as the internal nucleophile, i.e. the splitting off of I—Cl and the migration of the methyl group take place simultaneously. The tertiary carbonium ion formed actually affords the reaction products. An analogous picture has been observed also in the solvolysis of neopentyl derivatives[86] and it has been shown with the aid of kinetic isotope effects that the methyl group migrates in the rate-determining stage and that the successive conversion of the primary carbonium ion into the more stable tertiary carbonium ion does not occur. The reactions of primary alkyl iodides with nitrous acid and other nitrogen-containing oxidants are always accompanied by hydride shifts. This can probably be explained by the occurrence of the reaction via two competing pathways:



Depending on the reaction conditions, one of the two possible pathways can operate. Thus in the reaction in the weakly polar methylene chloride, the iodonium ion is more stable than the secondary carbonium ion formed as a result of the rearrangement and the reaction therefore takes place fully via pathway (1) (see Section III). In nitric acid, which is highly ionising weakly nucleophilic solvent, pathway (2), leading to a secondary carbonium ion, begins to predominate.

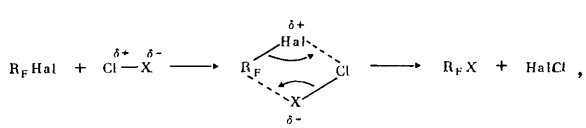
In the light of the mechanism which we propose, the general features of the oxidative substitution reactions can also be explained. Since the halogenonium ion formation stage is rate determining, it follows that the more readily is the electron pair of the halogen atom oxidised and the higher the electron density on it, the higher should be the rate of the reaction. Indeed, the reactivity of alkyl halides in reactions with any oxidant decreases in the sequence



The dependence of the reactivity on the structure of the hydrocarbon group, namely tertiary > secondary > primary, is also general. This sequence is inverted for perfluoroalkyl halides: primary > secondary > tertiary, because perfluoroalkyl substituents reduce the electron density

on the halogen atom. A characteristic feature of the reaction considered is that the structures of the products of the oxidative substitution of alkyl iodides, on the one hand, and alkyl bromides and chlorides, on the other, differ significantly. Thus the reactions of primary alkyl iodides with various oxidants (Cl_2, ICl, ICl_3, RCO_3H, HNO_3) in a non-polar medium result in the preferential formation of non-rearranged products, in contrast to the reactions of alkyl bromides with ClF and BrF_3. This is probably associated with the fact that the iodonium ion $R-\overset{+}{I}-X$, formed on oxidation of alkyl ioides, is fairly stable and that substitution takes place only on treatment with a nucleophile. It is noteworthy that the I—X group is an excellent leaving group, which is indicated by the significant involvement of the aryl substituent in the reaction of β-phenylethyl iodide with *m*-chloroperoxybenzoic acid and also by the fact that, together with the usual products, the corresponding covalent tosylates, perchlorates, triflates, etc. were isolated in the oxidative iodine substitution reactions on treatment with Cl_2, $ArCO_3H$, and NO_2BF_4 in the presence of nucleofugitive anions (TsO^-, ClO_4^-, $CF_3SO_3^-$, etc.).[87,88] However, we have observed that iodine pentafluoride in Freon 113 readily substitutes the iodine atom in 1-iodohexane with formation of 2-fluorohexane. An analogous result was obtained in the reactions of 1-bromopentane with ClF and BrF_3. Therefore the nature of the oxidant and hence the structure of the cationic intermediate probably has a decisive influence on the structure of the oxidative substitution products.

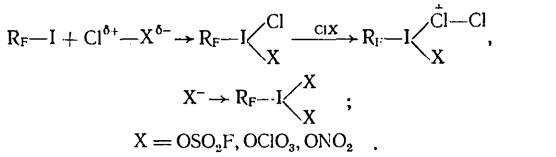
The oxidative substitution of bromine and chlorine atoms is possible only on treatment with vigorous reagents such as the hypohalite derivatives of strong acids and halogen fluorides. As a consequence of the high electronegativity of bromine and chlorine, it is inconvenient for the latter to acquire a positive charge and for this reason the halogenonium ion $R-\overset{+}{Hal}-X$, formed in the oxidation of alkyl chlorides and bromides, is extrememly unstable. The Hal—X group is readily eliminated, generating a considerable positive charge on the carbon atom, which in fact accounts for all the wide variety of rearrangements observed in the reactions with halogen fluorides. Analogous rearrangements are probably to be expected in the reactions of alkyl bromides and chlorides with the hypohalite derivatives of strong acids. However, in the substitution of chlorine and bromine atoms in perfluoroalkyl halides the accumulation of a significant positive charge on the halogen or carbon atom on oxidation is unlikely and the reaction mechanism probably therefore acquires the features of the synchronous mechanism proposed by Katsahara and Des Marteau:[50]



Hal = Br, Cl X = OSO_2F, OSO_2CF_3, $OClO_3$.

It is noteworthy that *erythro*- and *threo*-2-chloro-1,2-difluoroethyltrifluoroacetates, selected to demonstrate this mechanism, are not very suitable for this purpose, because the molecule contains the trifluoroacetate group, which can act as an internal nucleophile (see Section III). For this reason, the retention of configuration may be due to the involvement of the trifluoroacetate group and not the operation of a cyclic mechanism.

The formation of organic derivatives of tervalent iodine in reactions of perfluoroalkyl iodide with the hypohalite derivatives of strong acids can be described by the scheme

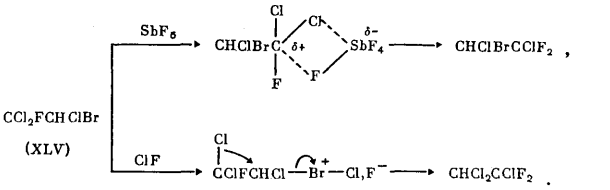


It is of interest to compare the reactions of alkyl halides with oxidants and Lewis acids such as mercury and antimony halides, silver salts, etc. The action of these reagents reduces to the conversion of the substituted halogen into a more readily eliminated group:

$$R—Hal + X^{\delta+}—Y^{\delta-} \rightarrow R—\overset{+}{Hal}—X,\ Y^- \rightarrow R—Y + HalX\ ,$$
$$R—Hal + MHal_n' \rightarrow R^{\delta+}\text{--}Hal\text{--}MHal_n'^{\delta-} \rightarrow R—Hal' + MHal_{n-1}'Hal\ .$$

In the classical solvolytic reactions, the protic solvent plays an analogous role.

However, whereas the substituted halogen atom is split off in the form of a negatively charged species in the interaction of alkyl halides with Lewis acids, on treatment with oxidants it is split off in an oxidised form. Therefore, in the interaction of polyhalogenoalkanes, the Lewis acid attacks the halogen atom whose elimination gives rise to the more stable carbonium ion, whereas the attack by the oxidant is always directed to the more readily oxidised halogen atom. Thus the interaction of 1,2-dibromo-2-chloropropane with mercury fluoride leads to the formation of 1-bromo-2,2-difluoropropane.[89] In the Swarts fluorination of 1-bromo-1,2,2,-trichloro-2-fluoroethane (XLV), only the chlorine atoms of the CCl_2F group are substituted by fluorine,[90] while on treatment of compound (XLV) with chlorine monofluoride the bromine atom is substituted with accompanying 1,2-migration of the chlorine atom:



Yet another feature of the oxidative substitution reaction consists in the fact that the halogen atom is as a rule substituted by a more electronegative atom or group. Bearing this in mind, one may say that ultimately not only the halogen atom but also the carbon atom at the reaction centre is oxidised.

The term "halogenophilic reaction" has been recently applied[91] to reactions involving the substitution of halogens on treatment with chlorine and bromine fluorosulphates. In our view, this term is inapplicable to the reactions discussed, since halogenophilic reactions are usually understood as reactions in which a halogen atom in an organic substrate is attacked by nucleophiles and the intermediate is a carbanion.[92] In oxidative substitution reactions, the halogen atom is attacked by an electrophilic species, which is followed by the nucleophilic substitution of the oxidised halogen.

Thus the reactions discussed are nucleophilic substitution reactions at a saturated carbon atom. The principal role of the oxidant consists in converting the substituted halogen into a readily eliminated group.

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During the preparation of the manuscript for the press, a study was published[93] in which the authors estimated quantitatively the oxidising capacity of a series of halogeno fluorosulphates as well as

peroxysulphuryl difluorides [$(FSO_2O)_2$] and showed that the reactivity of these compounds changes on the whole in parallel with their oxidising capacity. It was also shown that the increase in the reactivity of these compounds in a mixture with HSO_3F and HSO_3F-SbF_5 is consistent with the increasing strength of oxidants in strongly acid media.[93,94] The results obtained[93] and the proposed reaction schemes are of undoubted interest for the understanding of the mechanism of the oxidative substitution of the halogens in alkyl halides. Nevertheless, one cannot agree with the treatment of these reactions as oxidative electrophilic substitution at a carbon atom, since in electrophilic substitution at an sp^3-carbon atom the attack by the electrophile is directed to the carbon atom with which the entering electrophile subsequently forms a σ-bond. Taking this into account, the term "electrophilic substitution at a halogen atom" proposed by Katsahara and Des Marteau[50] (see Scheme 6) may be regarded as more apt. However, this definition can also be hardly regarded as acceptable for organic reactions where the carbon-containing fragment of the substrate is considered in the first place. Furthermore, in such a case the numerous nucleophilic substitution reactions occurring in electrophilic catalysis by Brønsted or Lewis acids would have to be classified as electrophilic substitutents at a heteroatom.

According to Fokin and co-workers,[93,95] the substitution of the nitroso-group in CF_3NO by chlorine fluorosulphate takes place analogously to the substitution of the halogens. One cannot rule out the possibility that the heterolytic substitution of the hydrogen atom in the C–H bond by oxidants[45,46,97] can also be interpreted as oxidative nucleophilic substitution. However, thse reactions are not numerous and are not as important as the substitution of the halogens.

In conclusion of this review, we should like to note that the reactions involving the oxidative substitution of the halogens in alkyl halides, which initially appeared to be unusual to chemists working with various oxidants and substrates, have been explained within the framework of the classical ideas of theoretical organic chemistry and have been defined as a new type of nucleophilic substitution at an sp^3-carbon atom. Many reactions of this type can be regarded as constituting yet another method for the generation of various cationoid species in polar and, what is particularly important, in non-polar media. Interesting results can apparently be obtained by using as reagents compounds such as PtF_6, $O_2^+SbF_6^-$, $XeF^+SbF_6^-$, and other "superoxidants", with an extremely high electron affinity. One may expect that further studies will make it possible to extend the synthetic possibilities of these interesting reactions and also to achieve a deeper understanding of their mechanism.

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