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Chemistry of inorganic sulfonates and sulfates of polyvalent iodine

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Abstract. Published data on the structure, properties and methods for the synthesis of inorganic sulfonates of polyvalent iodine are surveyed. Primary attention is devoted to the reactions of these compounds with organic substrates. The bibliography includes 129 references.

I. Introduction

Derivatives of hypervalent iodine were described for the first time back in the late XIX century.[1] The unusual ability of iodine to exhibit valences of III and V in organic compounds immediately attracted the attention of chemists. The first monograph on the chemistry of polyvalent iodine containing a systematic account of the data on the synthesis of organic derivatives of iodine(III) and iodine(V) was published as early as 1914.[2] However, by the late 70s, the interest in compounds containing polyvalent iodine had markedly decreased. The data accumulated by that time have been surveyed fairly completely in two reviews.[3,4]

In the early 80s, derivatives of polyvalent iodine again attracted the attention of researchers; this was due to the wide use of these compounds in various fields of organic synthesis.[5–15]

The progress in the chemistry of polyvalent iodine derivatives is largely determined by the stability of these compounds. In particular, it is known that the high instability of aliphatic iodoso-derivatives is due to the extremely high nucleofugal properties of the iodoso-fragment, which is among the best known leaving groups.[16] The main factor influencing the stability of both organic and inorganic derivatives of polyvalent iodine is the presence of highly nucleofugal ligands or counter-ions in their molecules. The stabilising influence of nucleofugal counter-ions or ligands on compounds of polyvalent iodine is clearly illustrated by the fact that these compounds normally contain anions of strong acids, such as tetrafluoroborate (BF_4^-),[17,18] perchlorate (ClO_4^-),[17] nitrate (NO_3^-),[19] tosylate (TsO^-),[20,21] *etc*, as ligands. Compounds containing anions of sulfonic acids [tosylate, trifluoromethanesulfonate (triflate, TfO^-), or methanesulfonate (mesylate, MsO^-)] as well as sulfate or hydrogensulfate are readily available and most convenient to work with. It is the sulfonate derivatives of polyvalent iodine that are used most often in synthetic organic chemistry.[22] One of the most important applications of polyvalent iodine sulfonates is the synthesis of covalent tosylates, triflates, fluorosulfates and other compounds,[23–26] which are difficult to obtain by other methods.

Organic sulfonate derivatives of trivalent iodine, like the other representatives of this class of compound, have been referred to collectively as 'iodoso-salts',[4] which reflects the fact that these compounds have been derived from iodoso-compounds and from the corresponding acids (similarly to the interaction between acids and bases to give salts).

$$RIO + 2HX \longrightarrow RIX_2 + H_2O.$$

This analogy is made even closer by the fact that treatment of any aryliodososulfonate with an alkali affords the initial iodoso-derivative.[4]

'Iodoso-salts' are usually stable and can be easily prepared; therefore, they have found wide application in organic synthesis.

In recent years, a wide range of organic derivatives of polyvalent iodine with various sulfonate ligands at the iodine atom have been obtained, for example, phenyliodonium sulfates,[27] hydroxy(mesyloxy)iodoarenes,[28] perfluoroalkyliodoso(hydoxy)-tosylates[29–31] and μ-oxodiphenylbis(trifluoro-methanesulfonato-*O*)diiodine.[23,32] Study of the reactivities of these compounds has shown that derivatives of iodosylperfluoro-alkanes and -arenes containing nucleofugal sulfonate and sulfate groups as substituents at the iodine atoms are convenient reagents for the transformation of alkenes into vicinal disulfonates and cyclic sulfates.[27,28] At the same time, iodonium sulfates react with alkyl iodides as oxidative deiodinating agents. These reactions afford covalent monosulfates.[33]

The properties of other organic sulfonate derivatives have been studied in detail by American[21,34–38] and Japanese[39–41] researchers. The chemical properties of these compounds have been surveyed in several reviews (see, for example, Refs 7, 42, and 43). However, inorganic sulfates and sulfonates of hypervalent iodine have not been even mentioned in these reviews. This stimulated us to consider systematically studies devoted to the structure, methods for the synthesis and the chemical properties of inorganic sulfonates and sulfates of polyvalent iodine. For convenience, in the subsequent discussion, the word 'inorganic' is omitted from the expression 'inorganic sulfonates and sulfates of polyvalent iodine'.

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II. The structure of sulfonates and sulfates of polyvalent iodine

Although the chemistry of organic derivatives of polyvalent iodine has been thoroughly studied and their nomenclature has been developed, there is still no exhaustive classification for the numerous sulfonates and sulfates of iodine (both organic and inorganic). One of the most widely used classifications of organic (including sulfonate and sulfate) derivatives of trivalent iodine is based on the formal account of the number of carbon and heteroatomic ligands at the iodine atom.[4,7] According to this approach, related organic sulfonates are often considered as different structural classes. At the same time, the fact that all organic sulfonates and sulfates of polyvalent iodine [for example, $RI(HSO_4)_2$, $R_FI(OSO_2F)_2$, $PhI^+OSO_3^-$, PhI(OH)OTs, PhI(OH)OMs, $Ar_2I^+OSO_2X^-$ (X = OH, F, CF_3) and $RPhI^+TfO^-$] contain trivalent iodine is an argument for using a classification based on the valence state of iodine.

Classification of inorganic sulfonates and sulfates of polyvalent iodine takes into account the valence of the iodine atom and the types of sulfonate and sulfate ligands. The main types of known sulfonates and sulfates of polyvalent iodine are presented in Table 1. Inorganic derivatives are divided into two subgroups corresponding to I(III) and I(V).

Until the structure of iodine fluorosulfate as a derivative of I(III), $I(OSO_2F_2)I$ (**1**), had been established unambiguously by X-ray diffraction analysis, [44] the majority of researchers [45–49] had regarded this compound as a derivative of monovalent iodine. Despite the fact that no structural data have been obtained for iodine triflate, it would be legitimate to suggest (by analogy with the compound **1**) that this derivative, which is usually described by the formula $IOSO_2CF_3$, also has a 'dimeric' structure, $I(SO_2CF_3)_2I$ (**2**). A convincing argument supporting this hypothesis is that these two reagents behave similarly in reactions with halogens.[50] Therefore, in the subsequent discussion, we use the formulae **1** and **2** rather than $IOSO_2F$ and $IOSO_2CF_3$ for iodine fluorosulfate and triflate, respectively.

Analysis of the published data indicates that the nomenclature of iodine sulfonates and sulfates is also ambiguous, since for these compounds, various names are used. Table 1 presents the names that are used most frequently.

The structure of sulfonates and sulfates of polyvalent iodine has been studied using some representatives of this class as examples. In most cases, these compounds have been characterised by spectroscopic methods (^{19}F NMR, Raman, UV and IR spectroscopy), and the structure of iodine fluorosulfate **1** has been studied by X-ray diffraction analysis.[44] The most important feature of this structure is that both fluorosulfate groups are bound to one iodine atom (*i.e.* the formal oxidation state of one of the iodine atoms is +3, while that of the other atom is −1). With allowance for the two lone electron pairs present at the I(+3) atom, the geometry of its environment is a distorted trigonal bipyramid (a T-shaped structure), which is in line with the hypervalent nature of this compound. The lengths of the I–O bonds (2.26 Å) are greater than the sum of the covalent radii of I and O atoms indicating that these bonds are ionic to a certain extent. A significant feature of the geometry of the fluorosulfate **1** is the existence of an intermolecular O...I bond with a length of 3.05 Å. This bond is arranged almost across the I–I bond; this results in a distortion of the plane in which other bonds between the ligands and the 'central' iodine atom lie. The main structural parameters of the molecule **1** are shown in Fig. 1.

According to the Martin's classification of polycoordinated derivatives of Group A elements,[51] the compounds under consideration belong to the 10-I-3 type of structures. This means that the central iodine atom is surrounded by three ligands, and its valence shell contains ten electrons (including two lone pairs). The equatorial positions are occupied by the second iodine atom and by the two lone electron pairs. Fluorosulfate groups are in the axial positions. From numerous X-ray diffraction studies,[52–56] it is known that organic derivatives of trivalent iodine are built similarly. The structure of $I(SO_2F)_2I$ also resembles those of transition metal complexes.

The structures of iodine tris(fluorosulfates) and triflates have been studied by conductometry, calorimetry and spectroscopy. It was found that they behave as electrolytes in solutions of the corresponding acids. The high specific electrical conductivities of

Table 1. Types of inorganic sulfonates and sulfates of polyvalent iodine.

Ligand	Derivative of I(III)	Name of the compound	Derivative of I(V)	Name of the compound
OSO_2F	$I(OSO_2F)_2I$	Iodine fluorosulfate	$I(OSO_2F)_5$	Iodine pentafluorosulfate
	$I_2HalOSO_2F$, $IHal_2OSO_2F$, $IHal'Hal''OSO_2F$, (Hal = Cl, Br, I)	Iodine interhalogen fluorosulfates	$IF_n(OSO_2F)_{5-n}$	
	$I(OSO_2F)_3$	Iodine tris(fluorosulfate)		
	$M[I(OSO_2F)_4]$ (M = Na, K), $[I(SO_3F)]_2^+[Sn(SO_3F)_6]^{2-}$	Complex salts		
	$(OI)OSO_2F$	Iodosyl fluorosulfate	$(O_2I)OSO_2F$	Iodyl fluorosulfate
OSO_2CF_3	$I(OSO_2CF_3)_2I$	Iodine triflates		
	$IHal_2OSO_2CF_3$ (Hal = Cl, Br, I)	Iodine interhalogen triflates		
	$I(OSO_2CF_3)_3$	Iodine tris(triflate)		
	$M[I(OSO_2^{\circ}F_3)_4]$ (M = K, Rb, Cs)	Complex salts		
	$(OI)OSO_2^{\circ}F_3$	Iodosyl triflate	$(O_2I)OSO_2CF_3$	Iodyl triflate
SO_4	$I_2(SO_4)_3$	Iodine sulfate		
	$(OI)_2SO_4$	Iodosyl sulfate		
HSO_4	$I(HSO_4)_3$	Iodine hydrogensulfate		
	$(OI)HSO_4$	Iodosyl hydrogensulfate	$(O_2I)HSO_4$	Iodyl hydrogensulfate
HS_2O_7			$(O_2I)HS_2O_7$	Iodyl hydrogenpyrosulfate

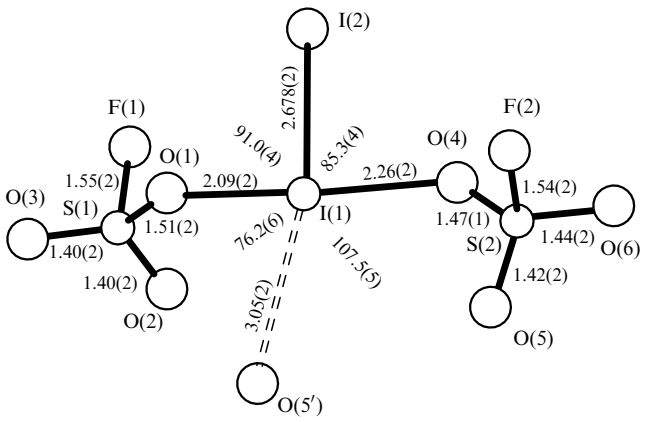


Figure 1. Molecular structure of $I(OSO_2F_2)I$ (**1**). Bond lengths (Å) and bond angles (degrees) are presented.

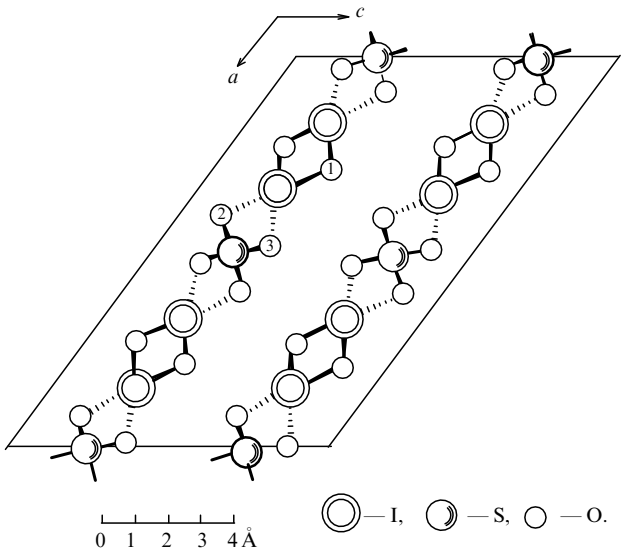


Figure 2. Projection of the polymeric chain in $(OI)_2SO_4$ along the 010 plane.

iodine tris(sulfonates) have been explained by their self-ionisation:[57, 58]

$$2I(OSO_2X)_3 \longrightarrow [I(OSO_2X)_2]^+ + [I(OSO_2X)_4]^-.$$

Iodine tris(sulfonates) have also been studied by nuclear quadrupole resonance (NQR) spectroscopy and Mössbauer spectroscopy.[59] The results of these studies together with X-ray diffraction data for a related structure, tris(acetato)iodine(III) $I(OCOCH_3)_3$, imply that these compounds, like other derivatives of trivalent iodine, have T-shaped configurations.[59]

The spectral characteristics of interhalogen fluorosulfates and interhalogen triflates, which are derivatives of trivalent iodine, make it possible to conclude that the geometries of their molecules are identical to those of other compounds of this class.[49, 60]

The tentative inferences about the structures of iodosyl and iodyl sulfonates are based on some of their physicochemical properties. The fact that iodosyl and iodyl derivatives are insoluble in the corresponding acids is strong evidence for their polymeric structures.[61, 62] The associated structure of iodosyl and iodyl sulfonates, postulated by Dasent and Wadington,[63] may be due to bridge binding of sulfonate groups or to the formation of chains consisting of $-I-O-I-$ fragments. This type of association is also supported by the Raman spectrum[63] of the iodyl fluorosulfate $(O_2I)SO_3F$ (**3**), which does not dissociate to give O_2I^+ and SO_3F^- ions. The fact that the absorption band of the O_2I group is shifted by 50 cm^{-1} to shorter wavelengths points to a polymeric structure of this compound. The vibrational spectra of iodyl and iodosyl sulfonates also point to a polymeric structure of these compounds. In particular, the presence of a vibration band at 650 cm^{-1} in the spectrum of iodosyl fluorosulfate $(OI)SO_3F$ (**4**) indicates that the OI groups are strongly associated and that $-I-O-I-$ chains are formed. In addition, the spectrum of this compound contains bands at 1350, 1150 and 1000 cm^{-1} corresponding to vibrations of the SO_3 fragment. The two former frequencies are typical of bidentate bridging SO_3 groups, while the latter frequency, which is the lowest, is characteristic of monodendate SO_3 groups.[62] Based on the spectral parameters of iodosyl trifluorosulfate and on the known structural features of other derivatives of polyvalent iodine, it can be assumed that the molecule of the compound **4** is a trigonal bipyramid, in which the base is formed by one oxygen atom and two lone electron pairs and the axial positions are occupied by the oxygen atoms of the fluorosulfate group.

Among polymeric iodine sulfates and sulfonates, only iodosyl sulfate $(OI)_2SO_4$ (**5**) has been studied by X-ray diffraction analysis.[64] The results of this study indicate that this compound has a layered structure (sandwich-like layers parallel to the 001 plane). Each layer, in turn, consists of infinite helical chains (OI) linked to one another through SO_4 tetrahedra (Fig. 2). It should be noted that the same structure for the compound **5** has been proposed[63] based on its vibrational spectra.

If the two lone electron pairs are taken into account, the overall geometry of bonds surrounding the iodine atom is a distorted trigonal bipyramid, the iodine atom being located at its centre. The four oxygen atoms lie in the equatorial plane, while the two lone pairs occupy the axial positions. The I–O bond lengths are dissimilar, namely: I–O(1) 1.97, I–O(2) 2.53 and I–O(3) 2.42 Å.

The molecular structure of the iodosyl sulfate **5** accounts for its instability with respect to water. Water molecules easily attack the SO_4 groups to give H_2SO_4, the IO group being converted into I_2O_3.[64]

Valuable information about the reactivity of inorganic sulfonates can be obtained by studying their electrolytic dissociation. Study of the electrical conductivities of solutions of fluorosulfates, triflates and sulfates in concentrated sulfuric acid has shown that the majority of sulfonate derivatives dissociate in solution.[65–67] It has also been found that in solution in trifluoromethanesulfonic acid, the fluorosulfate ligand in iodine tris(fluorosulfate) $I(OSO_2F)_3$ **6** is readily replaced by a triflate ligand.[67] Fluorosulfonic (HSO_3F) and pyrosulfuric ($H_2S_2O_7$) acids have been found to be suitable solvents for iodine(III) interhalogen fluorosulfates.[50, 60] Conductometric and spectroscopic studies of solutions of these compounds in the above acids indicate that iodine sulfates completely dissociate into ions and that dissociation is accompanied by quantitative formation of solvated cations IX_2^+(Solv) and I_2X^+(Solv). Study of the behaviour of solutions and melts of an equimolar mixture of I_3OSO_2F (**7**) and IX_2OSO_2F shows that exchange between the halide ligands occurs in these systems.

$$I_3^+(Solv) + IX_2(Solv) \longrightarrow I_2X^+(Solv)$$

X = Cl, Br.

The ionic nature of the iodine–ligand bonds has also been confirmed by X-ray diffraction data,[45, 64] which indicate that, whereas in organic sulfonates of trivalent iodine an increase in the nucleofugal capacity of the ligand results in an increase in the degree of ionicity of the bond (*i.e.* in an elongation of the I–O bond), the I–O bond (2.47 and 2.53 Å[64]) in iodosyl sulfate **5** is longer than the I–O bond in iodine fluorosulfate **1** by approximately 0.2 Å, although the fluorosulfate group exhibits supernucleofugal capacity. This seeming anomaly may be due to the fact that the iodine atom in the fluorosulfate **1** is bound to two oxygen atoms, whereas the iodine atom in the compound **5** (owing to the polymeric structure of iodosyl sulfate) is linked to four

oxygen atoms. Therefore, it may be expected that iodosyl sulfate would be a stronger electrophile than iodine fluorosulfate.

Thus, the data on the structures of inorganic sulfate and sulfonate derivatives of polyvalent iodine indicate that there is a clear-cut relationship between the nature of the ligands at the iodine atom and the structure of a particular derivative. It can be expected that the reactivity and physicochemical properties of these compounds would depend on the nature and the number of ligands and, in particular, that their electrophilicity would increase with an increase in the number and nucleofugal properties of sulfonate and sulfate residues.

III. Methods for the synthesis of sulfonates and sulfates of polyvalent iodine

The fairly intense development of the chemistry of this class of compound has resulted in the appearance of diverse methods for their synthesis most of which have been surveyed in reviews [68–70] published in 1970 and 1974. However, the progress achieved in recent years has scarcely been surveyed, and in the recent review,[71] methods for the synthesis of iodine sulfonates received little attention. We have attempted to fill this gap.

1. Iodine fluorosulfates

In most cases, various iodine sulfonates are synthesised by specific methods. Peroxydisulfuryl difluoride **8** proved to be the most convenient starting compound for the synthesis of iodine, chlorine and bromine fluorosulfates.[72] Although **8** belongs to the class of peroxides, it differs from most of the known peroxides in that it is completely non-explosive and quite stable in the isolated state.[25]

Since peroxydisulfuryl difluoride easily dissociates into relatively stable free radicals, the majority of reactions of this compound (including interaction with halogens) apparently involve fluorosulfate radicals.[73,74] The reaction of the peroxide **8** with a halogen affords various fluorosulfates of this halogen. In 1959, the first halogen fluorosulfate — fluorine fluorosulfate — was prepared in this way.[75] The first iodine fluorosulfate was obtained from another compound, namely, silver fluorosulfate.[76] However, since this starting compound is too expensive, this method has not found practical application, and later, iodine fluorosulfate has been mostly obtained using peroxydisulfuryl difluoride.[77]

The reaction of iodine with excess peroxydisulfuryl difluoride gives iodine tris(fluorosulfate) **6** in a good yield.[58]

$$\underset{}{I_2} + \underset{\mathbf{8}}{3S_2O_6F_2} \longrightarrow \underset{\mathbf{6}}{2I(OSO_2F)_3}.$$

The main advantage of this method is that the resulting product requires no purification; only excess peroxide should be removed *in vacuo*. Iodine tris(fluorosulfate) is a non-volatile solid (m.p. 32 °C), which is hydrolysed fairly readily with water.[78] It can also be obtained by the reaction of the peroxide **8** with iodine chloride.[72]

$$2ICl + \underset{\mathbf{8}}{3S_2O_6F_2} \longrightarrow \underset{\mathbf{6}}{2I(OSO_2F)_3} + Cl_2.$$

Another widely used fluorosulfate, the compound **1**, was prepared for the first time in 1965 by thermal decomposition of iodine tris(fluorosulfate).[49]

$$2\,\mathbf{6} \xrightarrow{\Delta} \underset{\mathbf{1}}{I(OSO_2F)_2I} + 2\,\mathbf{8}.$$

The compound **1** is a non-volatile diamagnetic solid.[49] An alternative and a more convenient method for the synthesis of iodine fluorosulfate **1** consists in the oxidation of iodine with an equimolar amount of peroxydisulfuryl difluoride with heating.[49]

$$I_2 + \mathbf{8} \xrightarrow{\Delta} \mathbf{1}.$$

When the reactants are taken in equimolar amounts, iodine fluorosulfate **1** is formed as the major reaction product. However, in addition to the compounds **1** and **6**, other iodine fluorosulfates of the composition I_nOSO_2F are also formed in the $I_2-S_2O_6F_2$ system; this will be discussed below.

Not long ago, yet another method for the synthesis of the compound **1** has been proposed.[79] It involves oxidation of elemental iodine or perfluoroalkyl iodides with a milder oxidising agent, chlorine fluorosulfate $ClOSO_2F$ (**9**).

$$2I_2 + \underset{\mathbf{9}}{2ClOSO_2F} \longrightarrow \mathbf{1} + 2ICl,$$

$$2R_FI + 2\,\mathbf{9} \longrightarrow \mathbf{1} + 2R_FCl.$$

The reaction of peroxydisulfuryl difluoride **8** with excess iodine gives rise to triiodine monofluorosulfate **7**.[49]

$$\underset{}{3I_2} + \underset{\mathbf{8}}{S_2O_6F_2} \longrightarrow \underset{\mathbf{7}}{2I_3OSO_2F}.$$

A high yield of the product is achieved when iodine is taken in a slight excess with respect to its stoichiometric amount and the reaction mixture is slowly heated to 85 °C. Triiodine monofluorosulfate **7** is a hygroscopic solid; it melts at 92 °C with evolution of iodine.

Study of the magnetic, cryoscopic and spectral properties of the $I_2-S_2O_6F_2$ system has shown that, depending on the mole fraction of the peroxydisulfuryl difluoride present, several iodine fluorosulfates can be formed in the system.[80] The results of this study are presented as the dependence of the melting point of the system on the mole fraction of the compound **8** (Fig. 3). The maxima in this plot correspond to various iodine fluorosulfates. In particular, the researchers identified I_7OSO_2F, I_3OSO_2F (**7**), $I(OSO_2F)_2I$ (**1**), and $I(OSO_2F)_3$ (**6**). Molecular weights of the components were determined by cryoscopy.

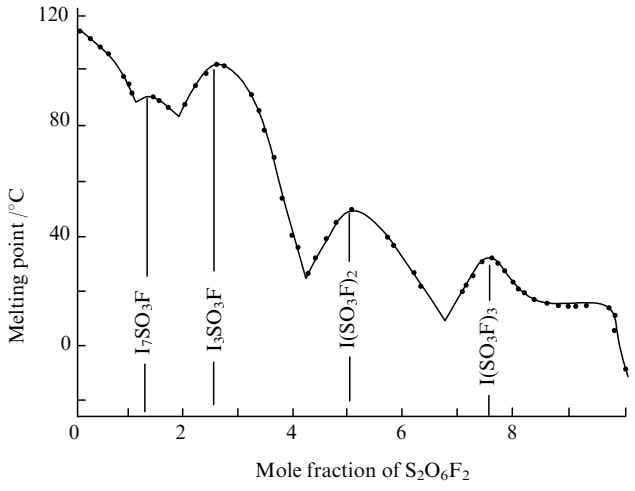


Figure 3. The $I_2-S_2O_6F_2$ system.

Another frequently encountered class of fluorosulfates of trivalent iodine comprises interhalogen fluorosulfates. These compounds can be synthesised using two approaches: direct introduction of a halogen or an interhalogen into the molecule of iodine trifluorosulfate [50] and the replacement of halide ligands at the iodine atom in a iodine interhalogen fluorosulfate or of two iodine atoms in triiodine monofluorosulfate by other halogens.[50,81]

The former method has synthetic limitations. The reaction with chlorine occurs spontaneously at room temperature, whereas the reactions with bromine and iodine are initiated by heating the mixture to 85 °C.

$$\mathbf{1} + 2Cl_2 \xrightarrow{20\ ^\circ C} 2ICl_2(OSO_2F),$$

$$\mathbf{1} + 2Hal_2 \xrightarrow{85\ ^\circ C} 2IHal_2(OSO_2F)$$

Hal = Br, I.

Solid reaction products slowly crystallise out of the melt, and excess halogen is easily distilled off upon evacuation of the mixture cooled below room temperature. However, in the case of interhalogen derivatives ICl and IBr, which act as ionising solvents, it is very difficult to isolate solid crystalline products from a viscous solution containing an excess of an interhalogen compound.

An attempt to prepare diiodobromine fluorosulfate I_2BrOSO_2F (**10**) by the addition of elementary iodine to bromine fluorosulfate failed. The reaction yielded the compounds **1** and **7**.[60] In those cases where the reaction mixture was kept at room temperature, bromine volatilised, and the excess of the reagent formed a complex with the iodine fluorosulfate **1**.

Thus, if the halogen in the Hal_2 molecule is more electron-withdrawing than the halide ligands at the iodine atom in the interhalogen compound, the reaction yields new interhalogen fluorosulfates. Otherwise, substitution of the halogen in $Hal(OSO_2F)_2Hal$ occurs.

The second approach to the synthesis of iodine(III) interhalogen fluorosulfates by the replacement of halide ligands at the iodine atom is used more frequently.[60] The compounds **7** and **10** have been used as the initial compounds for the synthesis of various interhalogen derivatives. Some examples of these reactions are given below.

$$ICl_2OSO_2F \xleftarrow{Cl_2} \underset{\mathbf{7}}{I_3OSO_2F} \xrightarrow{Br_2} \underset{\mathbf{10}}{I_2BrOSO_2F}$$

$$\uparrow \qquad\qquad\qquad\qquad \uparrow$$

$$Cl_2 \longleftarrow\!\!\!

Iodine triflate **2** is a brown hygroscopic solid, m.p. 122 °C. On heating above 170 °C, it decomposes.

Interhalogen triflates, like interhalogen fluorosulfates, are formed in the oxidative addition of halogens to the iodine triflate **2**.[50]

$$\mathbf{2} + 2X_2 \longrightarrow 2IX_2OTf$$

X = Cl, Br, I.

Despite the fact that various halogens can enter into this reaction, only the product of addition of bromine has been isolated in a pure state so far.[50] Spectroscopic studies have shown that dichloroiodine(III) triflate **17** is very unstable and readily decomposes.

$$3ICl_2OTf \longrightarrow 2ICl_3 + \mathbf{15}.$$
$$\mathbf{17}$$

Iodine adds to molten iodine triflate **2**; however, the reaction product has not been isolated;[67] apparently, this is due to the fact that triiodine triflate I_3OTf decomposes at this temperature.

3. Complex salts of iodine tris(sulfonates)

As noted above, iodine sulfonates are self-ionised in solutions of the corresponding acids. This is a rationale of the amphoteric properties of iodine sulfonates.

$$2I(SO_3F)_3 \rightleftharpoons [I(SO_3F)_2]^+ + I(SO_3F)_4]^-.$$

The basic properties of iodine tris(fluorosulfate) **6** are manifested in its reaction with tin tetrafluorosulfonate **18** in peroxydisulfuryl difluoride.[65] This reaction results in the formation of a bright yellow complex salt **19**.

$$\underset{\mathbf{6}}{2I(SO_3F)_3} + \underset{\mathbf{18}}{Sn(SO_3F)_4} \longrightarrow \underset{\mathbf{19}}{[I(SO_3F)_2]_2^+[Sn(SO_3F)_6]^{2-}}.$$

At the same time, in the reactions with alkali metal sulfonates, iodine tris(sulfonates) behave as acids.[65, 67]

$$KSO_3F + \underset{\mathbf{6}}{I(SO_3F)_3} \longrightarrow \underset{\mathbf{20}}{K[I(SO_3F)_4]},$$

$$MOTf + I(OTf)_3 \longrightarrow M[I(OTf)_4]$$

M = K, Rb, Cs.

These reactions are fairly convenient for the synthesis of iodine tetrakis(sulfonate) derivatives.

An alternative method for the preparation of the complex salt **20** and its sodium analogue **21** is the reaction of sodium (or potassium) iodide with excess peroxydisulfuryl difluoride **8** at room temperature.[84, 85] In these reactions, iodine is oxidised to the trivalent state instead of being displaced from the molecule. The researchers believe that the corresponding metal fluorosulfonates MSO_3F (M = Na, K) are formed initially, and then they are converted into the complex salts $M[I(SO_3F)_4]$ **20** and **21**.

$$MI + 2S_2O_6F_2 \longrightarrow MSO_3F + I(SO_3F)_3, \longrightarrow \underset{\mathbf{20},\ \mathbf{21}}{M[I(SO_3F)_4]}.$$

M = K (**20**), Na (**21**).

Tetracoordinated triflate iodates **22** are formed upon oxidation of alkali metal iodides with peroxydisulfuryl difluoride in trifluoromethanesulfonic acid.[67]

$$KI + 2S_2O_6F_2 + 4TfOH \longrightarrow \underset{\mathbf{22}}{K[I(OTf)_4]} + 4HSO_3F.$$

Yet another method for the synthesis of complex sulfonates is ligand exchange at a tetracoordinated iodine atom. In this case, potassium tetrachloroiodate **23** serves as the initial compound for the preparation of the salt **20**.[85]

$$\underset{\mathbf{23}}{KICl_4} + 2S_2O_6F_2 \longrightarrow \underset{\mathbf{20}}{K[I(SO_3F)_4]} + 2Cl_2.$$

A similar triflate salt **22** can be obtained by the replacement of the fluorosulfate group by a triflate group in the reaction of the salt **20** with an excess of trifluoromethanesulfonic acid **16**.[67]

$$\underset{\mathbf{20}}{K[I(SO_3F)_4]} + 4TfOH \longrightarrow \mathbf{22} + 4FSO_3H.$$

4. Iodosyl and iodyl sulfonates and sulfates

Analysis of various types of iodine sulfonates presented in Table 1 makes it possible to conclude that iodosyl and iodyl sulfonates are the most abundant type of compound among the derivatives in question. Therefore, it is expedient to consider in a separate Section the methods for synthesis of iodosyl sulfonates, which are I(III) derivatives containing an OI group, and iodyl sulfonates, which are I(V) derivatives containing an O_2I group.

The first attempts to synthesise iodosyl sulfonates date back to the late XIX century. As has already been noted, the first representative of this class, iodosyl sulfate (**5**, the Chrétien reagent), was obtained as early as 1898 by thermal decomposition of iodic acid in concentrated sulfuric acid.[86]

$$2HIO_3 + H_2SO_4 \longrightarrow \underset{\mathbf{5}}{(OI)_2SO_4} + 2H_2O + O_2.$$

Later, iodosyl sulfate **5** was prepared† by heating iodine pentoxide in concentrated sulfuric acid.[87] The researchers believe that in the first stage, the oxide I_2O_5 decomposes to I_2O_3. Iodine trioxide, which possesses basic properties, reacts, in its turn, with sulfuric acid to give iodosyl sulfate **5**.

$$I_2O_5 \xrightarrow[-O_2]{215\text{ to }220\ ^\circ C} I_2O_3 \xrightarrow[-H_2O]{H_2SO_4} \underset{\mathbf{5}}{(OI)_2SO_4}.$$

More recently, iodosyl sulfate has been prepared using a redox reaction between elementary iodine and sodium (or potassium) iodate in concentrated sulfuric acid.[88]

$$2I_2 + 6MIO_3 + 11H_2SO_4 \longrightarrow \underset{\mathbf{5}}{5(OI)_2SO_4} + 6MHSO_4 + 8H_2O$$

M = Na, K.

Concentrated nitric acid was also used as the oxidising agent for the synthesis of iodosyl sulfate **5**.[88]

$$I_2 + 3HNO_3 + 8H_2SO_4 \longrightarrow (OI)_2SO_4 + 4H_3O^+ + 7HSO_4^- + 3NO^+.$$

Iodosyl sulfate **5** reacts with sulfuric acid to give iodosyl hydrogensulfate **24**.[70]

$$\mathbf{5} + H_2SO_4 \longrightarrow \underset{\mathbf{24}}{2(OI)HSO_4}.$$

The compound **24** is unstable; in the opinion of the researchers cited,[70] it polymerises. It can serve as the initial compound in the synthesis of one more derivative of trivalent iodine, namely, iodosyl hydrogenpyrosulfate **25**.

$$\underset{\mathbf{24}}{(OI)HSO_4} + H_2S_2O_7 \longrightarrow \underset{\mathbf{25}}{(OI)HS_2O_7} + H_2SO_4.$$

Based on conductometric and spectroscopic studies, it was proposed that, unlike the initial iodosyl hydrogensulfate **24**, the compound **25** is ionic.[70]

Iodosyl fluorosulfate **4** was synthesised for the first time in 1960 by the hydrolysis of iodine tris(fluorosulfate).[58]

$$\underset{\mathbf{6}}{I(SO_3F)_3} + H_2O \longrightarrow \underset{\mathbf{4}}{(OI)SO_3F} + 2\,HSO_3F.$$

Later, its structure and properties were studied.[62] This compound and related iodosyl triflate **26** were prepared by the reaction of iodine with iodine pentoxide and the corresponding acid.[62]

† In the same study,[87] the structure of iodosyl sulfate was determined for the first time.

$$2I_2 + 3I_2O_5 + 10HSO_3X \longrightarrow \underset{\mathbf{4,\ 26}}{10(OI)SO_3X} + 5H_2O$$

X = F (**4**), CF_3 (**26**).

In 1980, a new method for the preparation of iodosyl fluorosulfate **4** was proposed. The method consists in the oxidation of iodine with ozone in the corresponding acid under mild conditions.[89]

$$I_2 + O_3 + 2HSO_3F \xrightarrow{-60\ ^\circ C} \underset{\mathbf{4}}{2(OI)SO_3F} + H_2O.$$

Iodosyl sulfate **5** was also synthesised in this way.

$$I_2 + O_3 + H_2SO_4 \xrightarrow{-60\ ^\circ C} \underset{\mathbf{5}}{(OI)_2SO_4} + H_2O.$$

However, the heavy drawbacks of this method associated with the use of gaseous ozone preclude its adaptation as a preparative procedure.

Sulfonate iodosyl derivatives are also formed when HIO_3 or HI_3O_8 is used instead of iodine pentoxide.[62,87]

$$I_2 + HIO_3 + H_2SO_4 \longrightarrow \mathbf{5} + H_2O,$$

$$I_2 + 3HIO_3 + 5HSO_3X \longrightarrow 5(OI)OSO_2X + 4H_2O,$$

$$I_2 + HI_3O_8 + 5HSO_3X \longrightarrow 5(OI)OSO_2X + 3H_2O.$$

X = F, CF_3.

When the two latter reactions are carried out in trifluoromethanesulfonic acid and without iodine, they afford iodyl triflate **27** rather than iodosyl triflate **26**.[62]

$$HI_3O_8 + 5HOTf \longrightarrow \underset{\mathbf{27}}{3(O_2I)OTf} + 2H_3O^+ + 2CF_3SO_3^-,$$

$$HIO_3 + 2HOTf \longrightarrow \mathbf{27} + H_3O^+ + CF_3SO_3^-.$$

The corresponding iodyl fluorosulfate **3** can formally be regarded as the product of insertion of sulfur trioxide into the I–F bond of iodyl fluoride O_2IF. Unfortunately, the attempt to synthesise iodyl fluorosulfate in this way was unsuccessful;[90] however, this derivative can be obtained relatively easily by the reaction of peroxydisulfuryl difluoride **8** with iodine penta- and tetraoxides.[90]

$$\underset{\mathbf{8}}{I_2O_5} + S_2O_6F_2 \longrightarrow \underset{\mathbf{3}}{2(O_2I)SO_3F} + \tfrac{1}{2}O_2,$$

$$I_2O_4 + 2\ \mathbf{8} \longrightarrow 2(O_2I)SO_3F + S_2O_5F_2 + \tfrac{1}{2}O_2.$$

At the same time, the reaction of the peroxide **8** with potassium iodate gives rise to compound **29**.[61]

$$\underset{\mathbf{28}}{KIO_3} + \mathbf{8} \longrightarrow \underset{\mathbf{29}}{KIO_2(SO_3F)_2} + \tfrac{1}{2}O_2.$$

The Raman spectra of **29** indicate that this compound is a stoichiometric mixture of potassium fluorosulfate and iodyl fluorosulfate. This implies that, unlike iodine tris(fluorosulfate) which forms complex salts, iodyl fluorosulfonate does not accept the fluorosulfate group.[61]

Oxidation of iodosyl fluorosulfate **4** with the peroxide **8** affords iodyl fluorosulfate **3**.[62]

$$\underset{\mathbf{4}}{(OI)SO_3F} + \underset{\mathbf{8}}{S_2O_6F_2} \xrightarrow{25\ ^\circ C} \underset{\mathbf{3}}{(O_2I)SO_3F} + S_2O_5F_2.$$

An alternative method for the preparation of iodyl fluorosulfate is based on the interaction of potassium metaperiodate with fluorosulfonic acid.[91]

$$3KIO_4 + 9HSO_3F \longrightarrow 2(O_2I)SO_3F + HOI(O)F_4 + 4H_2SO_4 + O_2 + 3KF.$$

To the best of our knowledge, no data on the synthesis of iodyl sulfates have been reported, whereas iodyl hydrogensulfate **30** has been thoroughly studied. The latter compound has been synthesised by heating iodic acid in concentrated sulfuric acid.[92]

$$HIO_3 + 2H_2SO_4 \longrightarrow \underset{\mathbf{30}}{(O_2I)HSO_4} + H_3O^+ + HSO_4^-.$$

Like iodyl and iodosyl sulfonates, iodyl hydrogensulfate **30** is polymeric. However in a highly dilute solution in sulfuric acid, this compound exists as the solvated monomer $(O_2I)HSO_4 \cdot H_2SO_4$.[93] When the concentration of the solution increases, the solvent molecule is eliminated from the solvate, and the iodyl fragments are joined together yielding polymeric chains.[93]

Apart from iodyl hydrogensulfates, iodyl pyrosulfate **31** is also known. This derivative is readily formed upon heating of iodine pentoxide with liquid sulfur trioxide.[94]

$$I_2O_5 + 2SO_3 \xrightarrow{100\ ^\circ C} \underset{\mathbf{31}}{[O_2I]_2^+[S_2O_7]^{2-}}.$$

Iodyl pyrosulfate **31** can also be obtained by the reaction of liquid sulfur trioxide with potassium or tin iodate. However, when I_2O_4 was introduced into this reaction, it resulted in the formation of a mixed salt — iodosyl iodyl pyrosulfate **32**.[94]

$$I_2O_4 + 2SO_3 \xrightarrow{100\ ^\circ C} \underset{\mathbf{32}}{[OI]^+[O_2I]^+[S_2O_7]^{2-}}.$$

IV. Reactions of sulfonates and sulfates of polyvalent iodine

Sulfonates and sulfates of polyvalent iodine, synthesised about a century ago, have only recently attracted the attention of organic chemists as extremely reactive compounds; in some cases, the use of these reagents makes it possible to accomplish some transformations that have previously been impossible. These compounds are especially useful owing to two characteristic features of their chemical behaviour. Firstly, they are efficient oxidants and, secondly, the iodine atom in them exhibits clear-cut electrophilic properties in reactions with various organic substrates. By varying the oxidation state of the iodine atom and the nature of heteroatomic ligands, one can change substantially the particular manifestation of these properties and thus control the reactivity of sulfonates and sulfates.

Valuable information about the reactivity of iodine sulfonates could be obtained from a systematic consideration of the published data on the reactions of these compounds with alkyl halides, alkenes and aromatic compounds. Unfortunately, no systematic studies on the reactions of sulfonates with these substrates have been carried out. The available data are fairly scattered and mostly refer to the reactions of iodosyl sulfonates , iodine fluorosulfate and iodine tris(fluorosulfate). In fact, in the detailed reviews by Fokin *et al.*[25,71] devoted to synthetic applications of halogen fluorosulfates, reactions of iodine fluorosulfates are considered only cursorily.

Therefore, we attempted to classify the published data on this topic according to the type of reactions of iodine sulfonates and sulfates with unsaturated and aromatic compounds and with alkyl halides, in order to identify the common features of these reactions as functions of the nature of heteroatomic ligands at the iodine atom and its oxidation state.

1. Oxidative dehalogenation

Before we discuss the reactions of oxidative dehalogenation, we would like to emphasise that no data on this type of reaction have been reported for iodine triflates and sulfates, whereas oxidative dehalogenation of alkyl halides with iodine fluorosulfates has been studied fairly comprehensively.

In 1965, it was found that iodine fluorosulfate **1** and iodine tris(fluorosulfate) **6** vigorously react with carbon tetrachloride at room temperature.[49] Depending on the molar ratio of the sub-

strates, CCl_4 can be oxidised stepwise to give phosgene or carbon dioxide.

$$CCl_4 + \underset{\mathbf{1}}{I(OSO_2F)_2I} \longrightarrow 2ICl + S_2O_5F_2 + COCl_2,$$

$$CCl_4 + 2\underset{\mathbf{1}}{I(OSO_2F)_2I} \longrightarrow 4ICl + 2S_2O_5F_2 + CO_2,$$

$$6CCl_4 + 4\underset{\mathbf{6}}{I(OSO_2F)_3} \longrightarrow 4ICl_3 + 6S_2O_5F_2 + 6COCl_2,$$

$$3CCl_4 + 4\underset{\mathbf{6}}{I(OSO_2F)_3} \longrightarrow 4ICl_3 + 6S_2O_5F_2 + 3CO_2.$$

Iodine fluorosulfate equally readily oxidises chloroform and trichlorofluoromethane.[49] In addition to phosgene, carbon dioxide and fluorosulfonic anhydride, these reactions yield molecular chlorine. Iodine fluorosulfate **1** was found to react efficiently with pyridine to give a yellow hygroscopic solid.[49] However, the researchers were not able to identify the unstable products of the reaction. Iodine monofluorosulfate and tris(fluorosulfate) are less reactive towards fluorinated haloalkanes than fluorosulfates of other halogens. They do not react with dichlorodifluoromethane, trichlorotrifluoroethane or with primary perfluoroalkyl bromides.[95,96]

However, iodine monofluorosulfate and iodine tris(fluorosulfate) react relatively readily with non-fluorinated alkyl halides.[96]

$$RHal \xrightarrow[-IHal]{\frac{1}{3}\,I(SO_3F)_3\ (\text{or}\ \frac{1}{2}\,I(SO_3F)_2I)} ROSO_2F$$

R = Me, Et; Hal = Cl, I.

(Triiodine monofluorosulfate has been found to be inert in all these reactions.[71])

Iodine tris(fluorosulfate) **6**, as expected, is more reactive towards alkyl halides than iodine monofluorosulfate **1**, owing to the presence of three fluorosulfate ligands at the iodine atom. Thus the reaction of iodine tris(fluorosulfate) **6** with perfluoropropyl iodide **33** resulting in the replacement of the iodine atom by a fluorosulfate group occurs at 20–45 °C, whereas the same reaction involving iodine fluorosulfate **1** can be accomplished only under conditions of superacid catalysis in fluorosulfonic acid containing 15 mol.% of SbF_5.

$$4\underset{\mathbf{6}}{I(OSO_2F)_3} + 3\underset{\mathbf{33}}{(n\text{-}C_3F_7)I} \longrightarrow$$

$$\longrightarrow \underset{\mathbf{34}}{3(n\text{-}C_3F_7)OSO_2F} + \underset{\mathbf{1}}{I(OSO_2F)_2I} + \underset{\mathbf{7}}{I_3OSO_2F}.$$

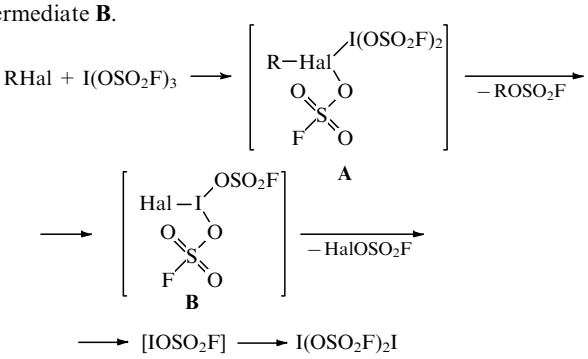
This process is accompanied by a slight exothermal effect.[71]

$$\underset{\mathbf{1}}{I(OSO_2F)_2I} + \underset{\mathbf{33}}{(n\text{-}C_3F_7)I} \xrightarrow{HSO_3F/SbF_5} \underset{\mathbf{34}}{(n\text{-}C_3F_7)OSO_2F} + \underset{\mathbf{7}}{I_3OSO_2F}.$$

Based on experimental data, the researchers cited [71] concluded that, in terms of their reactivity towards alkyl halides, iodine fluorosulfates can be arranged in the following series: $I(SO_3F)_3 > I(SO_3F)_2I > I_3SO_3F$. In other words, the activity of fluorosulfates decreases with a decrease in the number of fluorosulfate ligands.

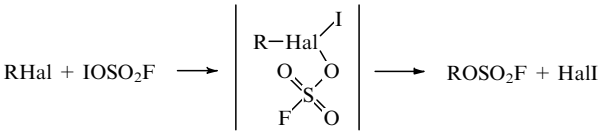
A quantitative estimate of the oxidising ability of iodine fluorosulfates (based on the standard potentials established on platinum after it has been immersed into the compound under study) has shown that these reagents are among the strongest oxidants.[97] The results obtained in this study indicate that the above series for the reactivity of fluorosulfates in the oxidative dehalogenation coincides with the order of variation of their oxidising properties. Thus, it can be assumed that it is the oxidising capacity that determines the reactivity of fluorosulfates. This hypothesis is supported by the fact that the oxidising capacity and the reactivity of iodine fluorosulfates in strongly acidic media (HSO_3F, HSO_3F/SbF_5) increase in parallel.

In the oxidative dehalogenation of RHal (Hal = Cl, I), iodine is more easily substituted by a fluorosulfate group than chlorine. An increase in the electron-withdrawing properties of groups attached to the same carbon atom as the leaving halogen atom retards the substitution of this atom by a fluorosulfate group.[71] This provided grounds for assuming that during the replacement of halogen atoms in RHal, these atoms are oxidised with fluorosulfates to the trivalent state. The intermediate **A** thus formed decomposes to give the corresponding alkyl fluorosulfate and intermediate **B**.



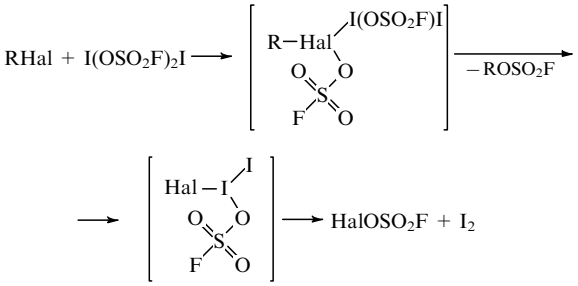
R = Me, Et; Hal = Cl, I.

Based on the wrong idea that iodine fluorosulfate is a hypoiodite derivative, Fokin *et al.*[97] proposed the following scheme for oxidative dehalogenation:



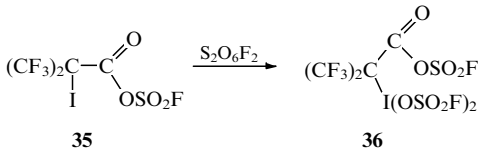
R = Me, Et; Hal = Cl, I.

However, in view of the actual structure of the iodine fluorosulfate, which is constituted as $I(SO_3F)_2I$,[44] and by analogy with iodine tris(fluorosulfate) **6**, the following reaction mechanism can be proposed:



R = Me, Et; Hal = Cl, I.

This mechanism for the substitution of a fluorosulfate group for the halogen atom in alkyl halides is supported by the data obtained by the same researchers on the interaction of iodine tris(fluorosulfate) **6** with fluoroalkenes [98] and bis(trifluoromethyl) ketene [99] (see Section IV.2) as well as by the synthesis of stable organic iodosyl fluorosulfates by oxidation of perfluoroalkyl iodides, in particular, of compound **35**.[100]



35 **36**

The adducts of type **36** formed in this reaction are syrupy yellow liquids, which are stable during storage (20 °C) and decompose on heating.[100]

Thus, analysis of the published data demonstrates that iodine fluorosulfates are convenient reagents for the preparation of esters of fluorosulfonic acid. It is noteworthy that the behaviour of other iodine sulfonates in these reactions has scarcely been studied; however, their high reactivity suggests that the use of these reagents in the processes considered above would substantially extend the potentialities of oxidative dehalogenation of alkyl halides.

2. Addition to alkenes

Electrophilic addition of iodine sulfonates has been little investigated. However, the reactions of iodine fluorosulfate **1** and iodine tris(fluorosulfate) **6** with deactivated alkenes have been studied in considerable detail.[45, 79, 101] For example, it has been shown[101] that iodine fluorosulfate **1** reacts in Freon 113 with fluoropropenes **37** and **38** and with tetrafluoroethylene **39** to give β-iodoalkyl fluorosulfates **40**–**42**.

$$\underset{\mathbf{37}}{CF_3CH=CH_2} \xrightarrow{\mathbf{1}} \underset{\mathbf{40}}{CF_3\overset{I}{C}HCH_2OSO_2F},$$

$$\underset{\mathbf{38}}{CF_3CH=CF_2} \xrightarrow{\mathbf{1}} \underset{\mathbf{41}}{CF_3\overset{I}{C}HCF_2OSO_2F},$$

$$\underset{\mathbf{39}}{CF_2=CF_2} \xrightarrow{\mathbf{1}} \underset{\mathbf{42}}{ICF_2CF_2OSO_2F}.$$

In these reactions, the addition products are formed regiospecifically, whereas in the reactions with chlorotrifluoroethylene **43** and trifluoroethylene **44**, mixtures of regioisomers have been obtained.[45]

$$\underset{\mathbf{43}}{CFCl=CF_2} \xrightarrow{\mathbf{1}} \underset{\mathbf{45}}{ICFClCF_2OSO_2F} + \underset{\mathbf{46}}{ICF_2CFClOSO_2F},$$

$$\underset{\mathbf{44}}{CFH=CF_2} \xrightarrow{\mathbf{1}} \underset{\mathbf{47}}{ICFHCF_2OSO_2F} + \underset{\mathbf{48}}{ICF_2CFHOSO_2F}.$$

The reaction with trifluoroethylene **44** gives compound **47** as the major product (85%), which has been isolated in a pure state.[46] Unfortunately, the products of addition of iodine fluorosulfate **1** to chlorotrifluoroethylene **43** have identical boiling points, which precluded separation of regioisomers **45** and **46**.[45]

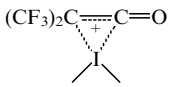
In the opinion of the researchers cited,[45] the course of the above reactions is markedly influenced by the fact that iodine fluorosulfate **1** is insoluble in Freon 113. This accounts for the relatively low reactivity of the compound **1** with respect to fluoroalkenes having less pronounced electrophilic properties. Thus the product of addition of iodine fluorosulfate **1** to octafluoroisobutene **49**, *viz.*, compound **50**, was obtained only when the reaction mixture was kept for 3 weeks at 20–25 °C.[45]

$$\underset{\mathbf{49}}{(CF_3)_2C=CF_2} + \mathbf{1} \longrightarrow \underset{\mathbf{50}\ (27\%)}{(CF_3)_2ClCF_2OSO_2F}.$$

Iodine fluorosulfate **1** adds to perfluorinated cyclobutene[45] and cyclopentene[46] and readily reacts with highly electrophilic substrates such as bis(trifluoromethyl) ketene **51**.[45]

$$\underset{\mathbf{51}}{(CF_3)_2C=C=O} + \mathbf{1} \longrightarrow \underset{\mathbf{35}}{(CF_3)_2ClC(O)OSO_2F}.$$

The ease of the reaction with the ketene **51** was attributed[45] to the tendency of iodine fluorosulfate **1** to form intermediate complexes of type **B**; this assumption implied an electrophilic mechanism of this reaction.



B

When iodine fluorosulfate **1** reacts with perfluorinated methyl vinyl ether **52**, compound **53** resulting from the atypical addition of the fluorosulfate at the multiple bond is formed as the major product, whereas only traces of the normal addition product **54** have been isolated.[102]

$$\underset{\mathbf{52}}{CF_3OCF=CF_2} + \mathbf{1} \longrightarrow \underset{\mathbf{53}}{CF_2I-\overset{OSO_2F}{C}FOCF_3} + \underset{\mathbf{54}}{F_2C-\overset{OSO_2F}{C}FIOCF_3}.$$

Adducts of iodine fluorosulfate with perfluoroalkenes are readily converted into acid fluorides.[102] Recently, β-iodoperfluoropropyl fluorosulfate **55** has been converted into α-iodoperfluoropropionyl chloride **56**, which is a convenient intermediate for the manufacture of ion-exchange membranes.[47]

$$\underset{}{CF_3CF=CF_2} \xrightarrow{\mathbf{1}} \underset{\mathbf{55}}{CF_3CFICF_2OSO_2F} \xrightarrow[-SO_2F_2]{KF} \underset{\mathbf{56}}{CF_3CFIC(=O)F}$$

Although the electrophilic properties of iodine tris(fluorosulfate) have been little studied, the available data indicate that it is more reactive than iodine fluorosulfate.[95] Iodine tris(fluorosulfate) **6** reacts with fluorinated derivatives of ethylene and propylene with heat evolution.[98] Its reactions with tetrafluoroethylene, 1,2-dichlorodifluoroethylene, chlorotrifluoroethylene and perfluoropropylene give rise to β-iodoalkyl fluorosulfates and perfluoroalkane-1,2-diyl bis(fluorosulfates), *i.e.* the products of formal addition of iodine fluorosulfate and peroxydisulfuryl difluoride at the double bond.[98, 100]

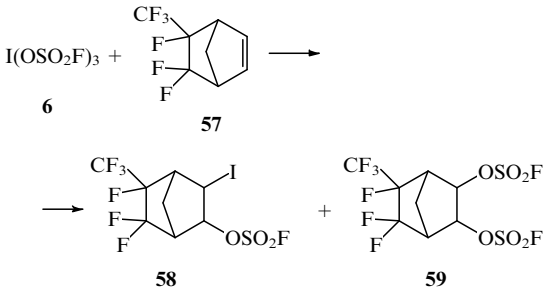
$$CF_2=CF_2 \xrightarrow{\mathbf{6}} ICF_2CF_2OSO_2F + FO_2SOCF_2CF_2OSO_2F,$$

$$CFCl=CFCl \xrightarrow{\mathbf{6}} ICFClCFClOSO_2F + FO_2SOCFClCFClOSO_2F,$$

$$CF_2=CFCl \xrightarrow{\mathbf{6}} ICF_2CFClOSO_2F + FO_2SOCF_2CFClOSO_2F,$$

$$CF_3CF=CF_2 \xrightarrow{\mathbf{6}} CF_3CFICF_2OSO_2F + CF_3\overset{OSO_2F}{C}FCF_2OSO_2F.$$

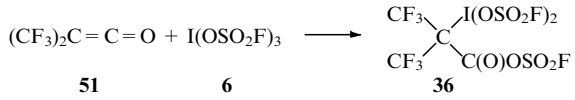
In order to elucidate the nature of the multiple bond in fluorine-containing bicycloheptenes, the reaction of iodine tris(fluorosulfate) **6** with the adduct formed by hexafluoropropene and cyclopentadiene **57** has been studied.[103] Despite the fact that the compound **6** is highly electrophilic, it adds at the double bond in bicycloheptene **57** without rearrangement to give 1,2-addition products. As in the case of acyclic perfluoroalkenes, the reaction affords iodofluorosulfate **58** and bis(fluorosulfate) **59**.



6 **57** **58** **59**

Important conclusions concerning the mechanism of this reaction could be drawn from the configurations of substituents in the reaction products. Unfortunately, the stereochemistry of the reaction was not studied.

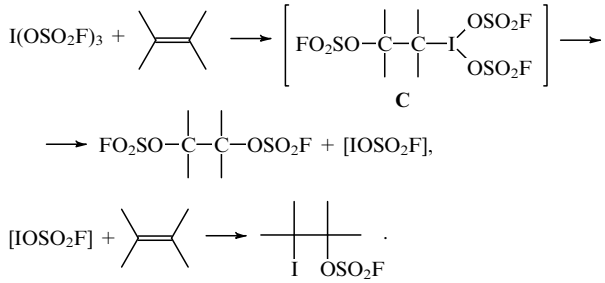
The reaction of iodine tris(fluorosulfate) **6** with bis(trifluoromethyl)ketene **51** is of considerable interest. This reaction has permitted the synthesis of a stable organic iodosyl fluorosulfate **36**.[99]



51 **6** **36**

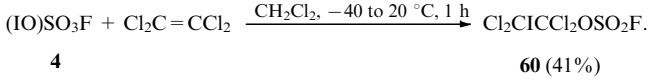
The stability of the compound **36** is due to the strong electron-withdrawing influence of the perfluoroalkyl and ester groups, which markedly hamper processes of nucleophilic substitution in this molecule.

The latter reaction also seems to be of prime importance from the theoretical viewpoint. The fact that a stable product of 1,2-addition is formed in this reaction makes it possible to rationalise the formation of bis(fluorosulfates) and β-iodofluorosulfates in the reactions of iodine tris(fluorosulfate) **6** with alkenes.[99,100] It was assumed that these reactions involve type **C** intermediates, which are unstable and decompose to give a bis(fluorosulfonyloxy)alkane and iodine fluorosulfate. The latter adds to the excess of the alkene giving rise to β-iodo-fluorosulfate.[99]



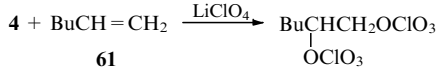
C

The authors of the present review have studied electrophilic addition of iodosyl fluorosulfate **4** to various alkenes.[104–106] In the case of simple alkenes, these reactions occur vigorously and are accompanied by strong resinification. Normal addition products were obtained only for deactivated alkenes. For example, tetrachloroethylene reacts with iodosyl fluorosulfate **4** to give β-iodofluorosulfate **60**.[104]



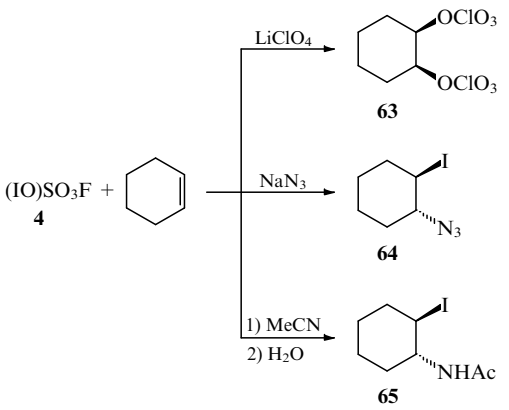
4 **60** (41%)

One of the possible ways of controlling the reactivity of iodosyl fluorosulfate **4** is to conduct the reactions with activated acyclic and cyclic alkenes in the presence of external nucleophiles. Thus the reaction of **4** with hex-1-ene **61** in the presence of lithium perchlorate results in the formation of bis(perchlorate) **62**.[104]



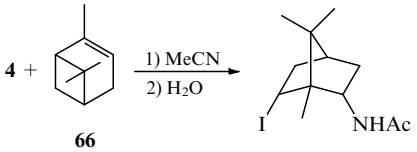
61 **62** (65%)

Stereochemical features of the addition of the reagent **4** to double bonds with the participation of external nucleophiles have been studied for the reactions with cyclohexene. If perchlorate anion is added as the nucleophile, the reaction affords 1,2-*cis*-diperchloryloxycyclohexane **63** in 61% yield;[104] if sodium azide is used instead of the perchlorate, 2-iodocyclohexyl azide **64** having the *trans*-configuration is formed.[104] When this reaction was carried out in acetonitrile, the product of conjugate addition, *trans*-iodoacetamide **65**, was obtained in a yield of 46%. In the presence of lithium perchlorate, in addition to the substituted acetamide **65** the yield of which increased under these conditions to 61%, diperchlorate **63** (15%) resulting from the competing addition of the nucleofugal perchlorate anion was isolated in a relatively low yield (15%).



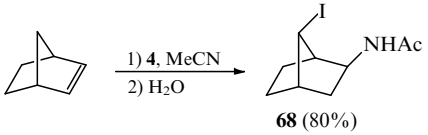
4 **63** **64** **65**

The addition of the reagent **4** to α-pinene **66** in acetonitrile occurs regioselectively and gives the rearranged acetamide **67**.[107]

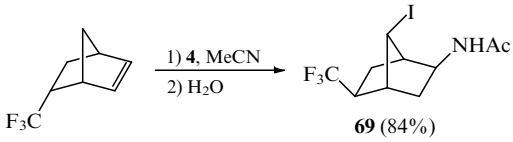


66 **67** (47%)

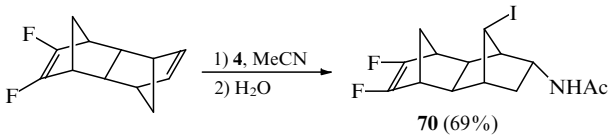
Other rearranged products, namely, compounds **68**–**71**, have been obtained by the reactions of iodosyl fluorosulfate **4** with alkenes of the norbornane series.[104,105,108–110]



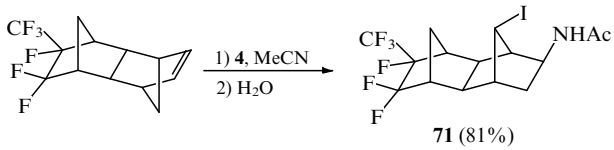
68 (80%)



69 (84%)

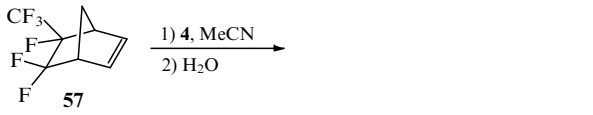


70 (69%)

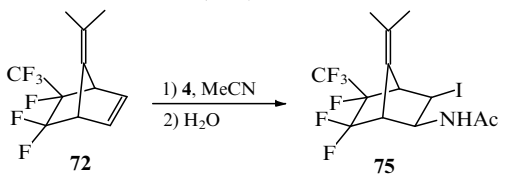


71 (81%)

However, the reactions with the most deactivated fluoro-containing bicyclo[2.2.1]heptenes **57** and **72** afford 1,2-adducts **73**–**75** as the only products.[105,109,110]

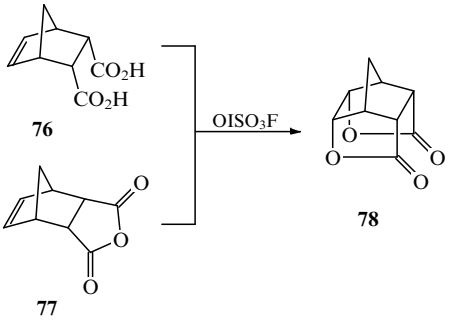


57 **73** (39%) **74** (30%)

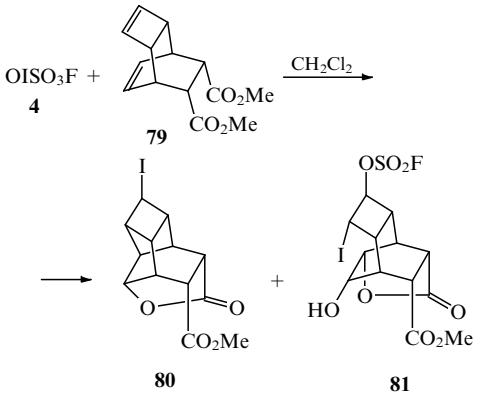


72 **75**

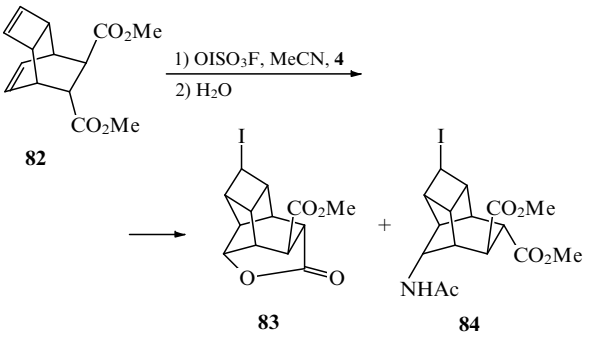
The reactions in which the addition of iodosyl fluorosulfate **4** to an unsaturated molecule is accompanied by ring closure are of particular interest.[104, 111, 112] For example, norbornenedicarboxylic acid **76** and its anhydride **77** react with **4** to give bis-γ-lactone **78**. When the reaction with the acid **76** is carried out in acetonitrile, the yield of the lactone **78** is nearly quantitative.[104]



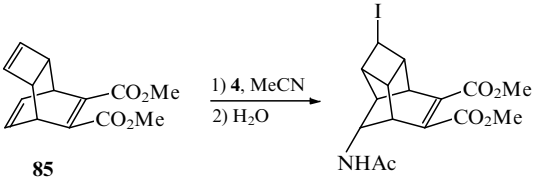
The reaction of the compound **4** with the cage diene **79** containing *cis*-arranged methoxycarbonyl groups in dichloromethane affords a mixture of two products, δ-lactone **80** and γ-lactone **81**.[111] When more polar acetonitrile is used as the solvent, δ-lactone **80** becomes the only reaction product.[104]

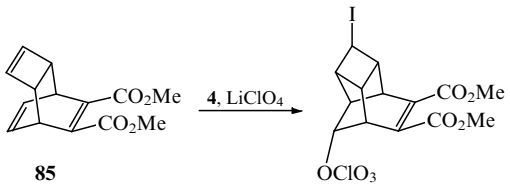


The reaction of iodosyl fluorosulfate with diene **82** containing *trans*-methoxycarbonyl groups in acetonitrile gives rise to δ-lactone **83** and amide **84**.[104]

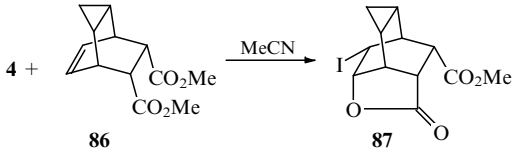


A similar reaction involving triene **85** the geometry of which precludes its lactonisation yields products of addition formed with the participation of external nucleophiles.

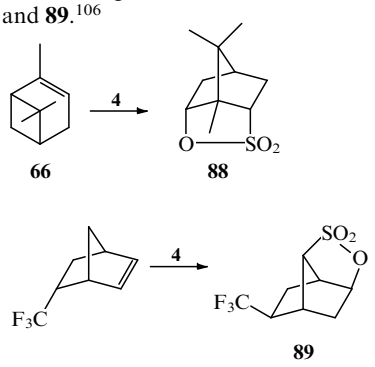




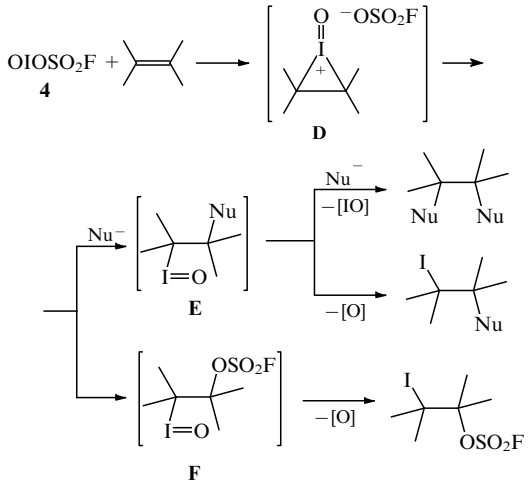
It is of interest that in the case of unsaturated cage ester **86** containing a cyclopropyl fragment, the attack is directed at the double bond, the three-membered ring being retained in the final product **87**.[112]



An alternative route for the transformations of iodosyl fluorosulfate, in particular, the transfer of its SO_3 fragment onto a double bond, was discovered when this reagent was made to react with α-pinene **66** and 5-*endo*-trifluoromethylnorbornene in ether without any additional nucleophiles. These reactions, which are accompanied by skeletal rearrangements and are highly stereo- and regio-selective, result in the formation of γ-sultones **88** and **89**.[106]

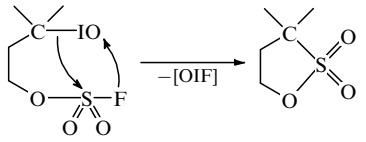


Based on these results, all the characteristic features of the reactions of iodosyl fluorosulfate **4** with alkenes can be interpreted in terms of a single mechanism. According to this mechanism, in the first step the double bond in the substrate is attacked by the iodosyl cation (the reagent **4**).[104] The subsequent opening of intermediate **D** can occur under the action of either the anion of **4** or an external nucleophile.



The formation of products of skeletal rearrangements in the case of bi- and polycyclic alkenes indicates that intermediate **D** is highly ionic and, hence, that iodosyl fluorosulfate is a strong electrophile. A distinctive feature of these processes is that most of the products contain an iodine atom rather than an iodosyl group. The elimination of oxygen from the intermediate iodosyl compounds of type **E** and **F** is due to the influence of excess alkene. This type of behaviour of iodosyl compounds has been established reliably for aromatic iodosyl derivatives.[113–115] It can be assumed that aliphatic iodosyl compounds would behave similarly. The regioselectivity of reactions in the series of fluorine-containing norbornenes and α-pinene is controlled by electronic effects of the substituents.

In the case where sultones are formed, the reaction occurs *via* compound **G**, which eliminates iodosyl fluoride. The formation of the OI–F bond is the driving force of this process.



G

Thus, the reactions of iodosyl fluorosulfate with alkenes considered above indicate that this reagent, like iodine mono- and tris(fluorosulfates), is highly electrophilic. By varying the conditions of the reactions involving iodosyl fluorosulfate, one can control its reactivity, which makes its possible to transform alkenes into diverse derivatives.

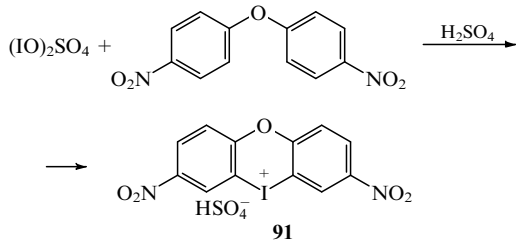
3. Aromatic electrophilic substitution

The ionic nature of the majority of sulfonate derivatives of polyvalent iodine accounts for their possible participation in aromatic nucleophilic substitution reactions. These reactions yield iodosylarenes, which are traditionally used in the synthesis of diaryliodonium salts.[116–119] Therefore, the high reactivity of iodine sulfonates permits them to be used as convenient initial compounds for the preparation of diaryliodonium salts, which are efficient arylating reagents.[120–122] In particular, treatment of chlorobenzene with iodosyl sulfate gives rise to diaryliodonium salt **90**.[88]

$$(OI)_2SO_4 + 2PhCl \xrightarrow{H_2SO_4} (p\text{-}ClC_6H_4)_2I^+HSO_4^-.$$

90 (60%)

At the same time, when di(4-nitrophenyl) ether is introduced in this reaction, cyclic product **91** is formed.[121]



91

The formation of diaryliodonium hydrogensulfates has been explained[83] in the following way. Electrophilic attack by the iodosyl cation $^+I{=}O$ on the aromatic ring yields an intermediate iodosylarene derivative the condensation of which with a second molecule of the aromatic compound gives rise to the diaryliodonium salt.

$$ArH + {}^+I{=}O \rightleftharpoons ArIO + H^+ \rightleftharpoons$$

$$\rightleftharpoons ArI^+{-}OH \xrightarrow{ArH} Ar_2I^+ + H_2O.$$

Diaryliodonium hydrogensulfates can also be obtained by using iodosyl hydrogensulfate **24**.[92]

$$2PhX + \underset{\mathbf{24}}{OIHSO_4} \longrightarrow (p\text{-}XC_6H_4)_2I^+HSO_4^-$$

X = Alk, Hal.

Diaryliodonium salts also arise in the reaction of potassium iodate **28** with aromatic substrates in the H_2SO_4–AcOH–Ac_2O system.[88] This method is especially significant for the synthesis of salts containing electron-withdrawing substituents.

$$2ArH + \underset{\mathbf{28}}{KIO_3} \xrightarrow{H_2SO_4-Ac_2O-AcOH} Ar_2I^+HSO_4^- + <O>$$

Although potassium iodate acts as an initial compound in this reaction, it was assumed[88] that diaryliodonium salts are formed by a mechanism that includes the *in situ* generation of iodyl hydrogensulfate **30**.

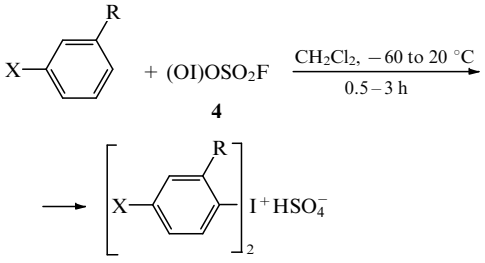
$$IO_3^- + H_2SO_4 \rightleftharpoons HOIO_2 + HSO_4^-,$$

$$HOIO_2 + H_2SO_4 \rightleftharpoons H_2O + \underset{\mathbf{30}}{(O_2I)HSO_4},$$

$$ArH + \mathbf{30} \rightleftharpoons ArIO_2 + H_2SO_4,$$

$$H_2SO_4 + ArIO_2 + ArH \longrightarrow Ar_2I^+HSO_4^- + <O>.$$

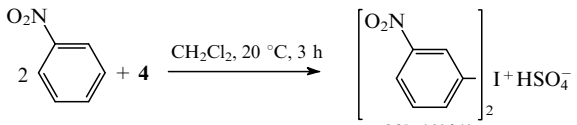
The participation of iodine fluorosulfates in aromatic electrophilic substitution has been studied only for iodosyl fluorosulfate **4**. Recently, it has been found that this compound reacts efficiently under mild conditions with benzene and its derivatives containing *ortho*- and *para*-orienting substituents to give diaryliodonium hydrogensulfates **92** with a *para*-substituted aromatic ring.[123]



92a–g (53%–95%)

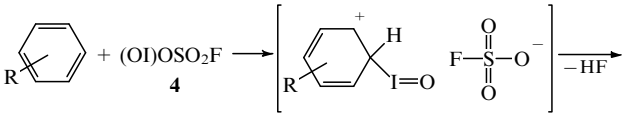
R = H: X = H (**a**), Me (**b**), Bu^t (**c**), F (**d**), Cl (**e**), Br (**f**);
R = X = Me (**g**).

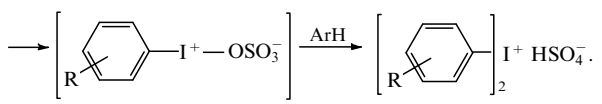
The fact that this reaction is regioselective confirms the ionic structure and, hence, the high electrophilicity of iodosyl fluorosulfate. Moreover, this compound is highly reactive towards deactivated substrates such as halobenzenes and nitrobenzene. The latter reaction occurs at room temperature and yields 3,3'-bis(nitrophenyl)iodonium salt **92h** as the only product.



92h (60%)

In all cases, iodonium hydrogensulfates were isolated instead of the expected fluorosulfates. This can be due to the intermediate formation of aryliodonium sulfates.





The formation of iodonium hydrogensulfates **93** in the reaction of phenyliodonium sulfate **94**, generated from iodosyl benzene and sulfur trioxide,[124] with aromatic compounds [120] can serve as experimental evidence supporting this mechanism.

$$\underset{\mathbf{94}}{PhI^+-OSO_3^-} + ArH \xrightarrow[1-3.5\ h]{CH_2Cl_2,\ -50\ to\ 20\ ^\circ C} \underset{\mathbf{93}\ (54\%-84\%)}{PhArI^+HSO_4^-}$$

Ar = Ph, 4-MeC_6H_4, 4-FC_6H_4, 4-IC_6H_4, 4-$Bu^tC_6H_4$, 2,4-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, 3-$NO_2C_6H_4$.

Unlike the above reactions involving sulfates and hydrogensulfates, which occur in sulfuric acid as a solvent and give products in low yields, the reactions with iodosyl fluorosulfate proceed under mild conditions even with aromatic compounds deactivated with respect to electrophilic attack, for example, with fluorobenzene and nitrobenzene. Since this procedure readily gives diaryliodonium salts in high yields directly from aromatic compounds, and the target products can be easily isolated, this method can find wide use in organic synthesis.

An important feature of the reactions of iodosyl fluorosulfate **4** is that they enable the preparation of diaryliodonium hydrogensulfates, which are convenient synthons that can be further converted into other iodonium salts with non-nucleophilic anions (BF_4^-, SbF_6^- or PF_6^-). In recent years, these salts have been finding increasing application as catalysts of radiation-induced cationic polymerisation.[125] In order to prepare these salts, the diaryliodonium hydrogensulfates were treated, without isolation, with aqueous solutions of inorganic salts containing the anions listed above. Thus, diaryliodonium salts with the desired non-nucleophilic anions can be obtained in one stage.[88, 120]

It may be expected that not only iodosyl sulfates, hydrogensulfates and fluorosulfates, but also other sulfonates of polyvalent iodine would be highly reactive towards aromatic compounds. In fact, recently it has been found that iodosyl triflate **26** is a convenient reagent for the synthesis of diaryliodonium triflate **95** from trimethylsilylarenes.[126]

$$\underset{\mathbf{26}}{(OI)OTf} + ArSiMe_3 \xrightarrow[-(Me_3Si)_2O]{CH_2Cl_2,\ -78\ to\ 20\ ^\circ C,\ 0.5\ h} \underset{\mathbf{95}}{Ar_2I^+TfO^-}.$$

The versatility of this method was demonstrated for a wide range of alkyl- and halogen-substituted benzene derivatives. The yields of products reached 57%–93%.

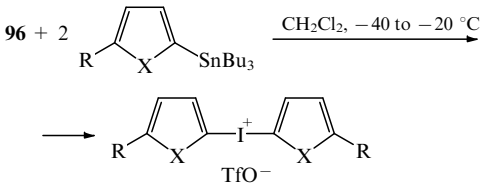
It should be noted that no information about the reactions of other iodine sulfonates with aromatic compounds can be found in the literature.

4. The reactions of iodosyl triflate with trimethylsilyl cyanide and trimethylsilylacetylenes

Apart from aromatic electrophilic substitution typical of all iodosyl sulfonates, the interaction of iodosyl triflate **26** with trimethylsilyl cyanide is also of particular interest.[127] This reaction gives rise to bis(cyano)iodonium triflate **96**.[127]

$$\underset{\mathbf{26}}{(OI)OTf} + 2NCSiMe_3 \xrightarrow{CH_2Cl_2,\ -78\ to\ -20\ ^\circ C} \underset{\mathbf{96}\ (60\%)}{(NC)_2I^+TfO^-}.$$

Crystalline bis-cyanide **96** is unstable. At room temperature, it entirely decomposes over a period of 3–5 min. Nevertheless, despite its instability, the bis-cyanide **96** obtained *in situ* is efficiently used in the synthesis of diaryl- and bis(hetaryl)-iodonium salts.[128] Bis(hetaryl)iodonium triflates **97** were prepared for the first time in this way, the reaction being carried out under mild conditions (in dichloromethane, at a low temperature).[128]



97 (66%–76%)

X = O, S; R = H, Br.

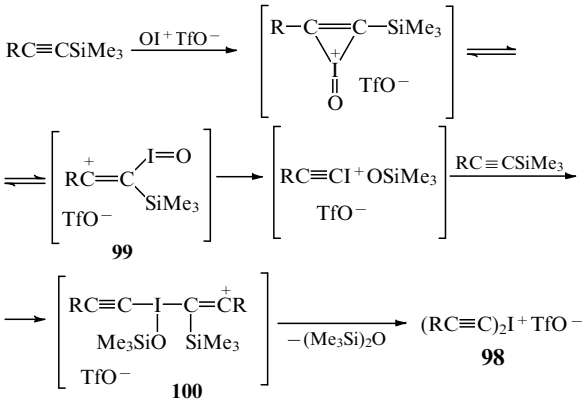
A similar reaction of iodosyl triflate **26** with trimethylsilylacetylenes results in the formation of bis(alkynyl)iodonium salts **98**.[129]

$$\underset{\mathbf{26}}{} + RC{\equiv}CSiMe_3 \xrightarrow[-(Me_3Si)_2O]{CH_2Cl_2,\ -78\ to\ -20\ ^\circ C} \underset{\mathbf{98}}{(RC{\equiv}C)_2I^+TfO^-}$$

R = Bu^t, Me_3Si, Pr^i_3Si.

The stability of the iodonium salts **98** was found to decrease in the following series of substituents: Pr^i_3Si > Me_3Si > Bu^t.

It can be seen from the presented examples that the synthetic strategy based on the use of iodosyl triflate is determined by its ability to react under extremely mild conditions with organic substrates containing readily leaving trimethylsilyl groups to give a highly reactive iodonium intermediate (for example, salt **100**), which subsequently decomposes with evolution of $(Me_3Si)_2O$.



This mechanism is supported by the fact that the vinyl cations **99** are stabilised by bulky substituents with positive inductive effects.[129]

In conclusion, it should be noted that iodosyl triflate still remains the only reagent used for the synthesis of bis(cyano)- and bis(alkynyl)-iodonium salts.

V. Conclusion

The published data indicate that methods for the synthesis, the physical properties and mutual transformations of inorganic sulfonates of polyvalent iodine have been studied much more thoroughly than their reactions with organic substrates; this is confirmed by the number of relevant publicatons. There are only few studies devoted to electrophilic addition reactions involving certain iodine fluorosulfates and to electrophilic substitution for iodosyl sulfonates. Publications dealing with the electrophilic addition of sulfates and triflates of polyvalent iodine to alkenes are totally missing.

Nevertheless, the existing material indicates that these compounds possess unique reactivity, which permits them to be regarded as promising reagents in organic synthesis.

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