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SOME DIRECTIONS OF FLUORINE CHEMISTRY. A SERIES OF LECTURES.

COMMUNICATION 2. PART 1. FLUORINATION WITH HIGH VALENCY METAL FLUORIDES, CATION-RADICAL FLUORINATION THEORY OF AROMATIC COMPOUNDS

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Annotation: High valency metal fluorides (HVMFs) and their application for synthesis of organofluorine compounds are described. Possible fluorination mechanisms of aromatic compounds by different high valency metal fluorides are considered.

Keywords: High valency metal fluorides, cobalt trifluoride, manganese trifluoride, cerium tetrafluoride, cation-radical theory, fluorination.

Introduction

Fluorination with high valency metal fluorides (HVMFs) is one of the few methods of exhaustive fluorination of organic compounds (that is, complete replacing hydrogen by fluorine, saturation double bonds by fluorine and destroying many functional groups).

Such fluorides include cobalt trifluoride, manganese trifluoride, cerium tetrafluoride, silver difluoride and others. A number of complex fluorides are also known, such as $KCoF_4$, $CsCoF_4$ and others.

Cobalt trifluoride can be obtained from cobalt difluoride (See reaction **2**, Scheme **1**), cobalt dichloride or cobalt oxide via interaction with elemental fluorine at temperatures 200-300°C. HVMFs of manganese and cerium can be obtained similarly.

1. High valency metal fluorides and their application for synthesis of organofluorine compounds

At first HVMFs were mentioned in the paper of O. Ruff [1], who showed that these compounds are strong oxidizers.

The need for perfluorocarbons for the nuclear industry in the early 1940s led to the development of intensive research on fluorination with HVMFs. As a result, a large number of publications have appeared on the application of this method. The overwhelming number of publications describe the use of cobalt fluorides.

The basic techniques for working with HVMFs were described by R. Fowler in 1948 [2]. The main parameters of fluorination with cobalt trifluoride were determined and laboratory and industrial plant designs for carrying out the processes were described.

Besides that, R. Fowler showed, that total heat of reaction of fluorine with organic compound is distributed approximately equally between two stages – the formation of cobalt trifluoride and the reaction of the latter with organic substance (Scheme **1**):

$$1/2\ (\text{-}CH_2\text{)-} + F_2 \longrightarrow 1/2\ (\text{-}CF_2\text{)-} + HF \quad (\Delta H = \sim -435\ \text{kJ/mol})\ (\mathbf{1})$$

$$CoF_2 + 1/2\ F_2 \longrightarrow CoF_3 \quad (\Delta H = \sim -235\ \text{kJ/mol}) \quad (\mathbf{2})$$

$$1/2\ (\text{-}CH_2\text{)-} + 2CoF_3 \longrightarrow 1/2\ (\text{-}CF_2\text{)-} + HF + 2CoF_2 \quad (\mathbf{3})$$

Scheme 1.

The heat of reaction (**1**) was determined by L. Pauling [3] and was approximately -435 kJ/mol. F. Brickwedde and M. Wexler [4] conducted studies of the reaction (**2**) and showed that it is approximately -235 kJ/mol (-56 kcal/mole).

The use of HVMFs for fluorination of a wide range of organic compounds was described in considerable detail by M. Stacey and J. C. Tatlow in the book “Advances in Fluorine Chemistry” [5].

Reactions between HVMFs and organic compounds can be carried out in both liquid and vaporous phases.

In liquid-phase processes, the fluorinating agent was introduced into a stirred and heated solution or suspension of the substance being fluorinated in an inert solvent (usually a high-boiling fluorocarbons). The method was mainly used to complete the exhaustive fluorination of high-boiling compounds.

The most widely used process was fluorination, in which an organic compound reacted in the form of vapour. As a result of interaction of hydrocarbons with cobalt trifluoride under severe conditions (300-450 °C) saturated perfluorocarbons with largely unchanged carbon skeleton are obtained. By-products include fluorocarbons containing one or two hydrogen atoms, as well as degradation products. Unsaturated compounds usually do not remain.

When fluorination is carried out under milder conditions, the amount of partially fluorinated compounds increases. The result is a complex mixture of substances. For this reason, this method is considered unsuitable for producing partially fluorinated compounds.

In the initial version of this process [6], hydrocarbon vapors in a stream of nitrogen were passed at a constant rate over a thin layer of cobalt trifluoride placed in a horizontal tube. The reaction was carried out at temperature of 150-450 °C.

Later, it was found that stirring cobalt trifluoride during the reaction improves the fluorination process. This was achieved by using a horizontal cylindrical reactor equipped with a coaxial paddle stirrer for agitation. Designs of such reactors are presented in the article [7].

In order to intensify the process, attempts were made to carry out fluorination in a stirred fluidized bed [8]. However, judging by the lack of further publications, this idea has not been developed.

Articles [9-11] described the fluorination of organic compounds in vertical reactors filled with HVMFs. Vertical reactors did not contain stirrers, which simplified the design and increased their reliability.

A large number of examples of fluorination of various compounds with references to the original papers are given in [5, 12, 13].

The best results were obtained in the fluorination of hydrocarbons and, especially, aromatic hydrocarbons. Moreover, in the case of aromatic compounds (toluene, o-xylene, naphthalene, ethylbenzene, etc.), the yields of cyclic perfluorocarbons could reach 60-85%.

During fluorination with cobalt trifluoride of chlorine-containing compounds, hydrogen substitution and addition at the unsaturated bonds occur mainly. Chlorine atoms could remain in the compound even during fluorination at high temperatures [5].

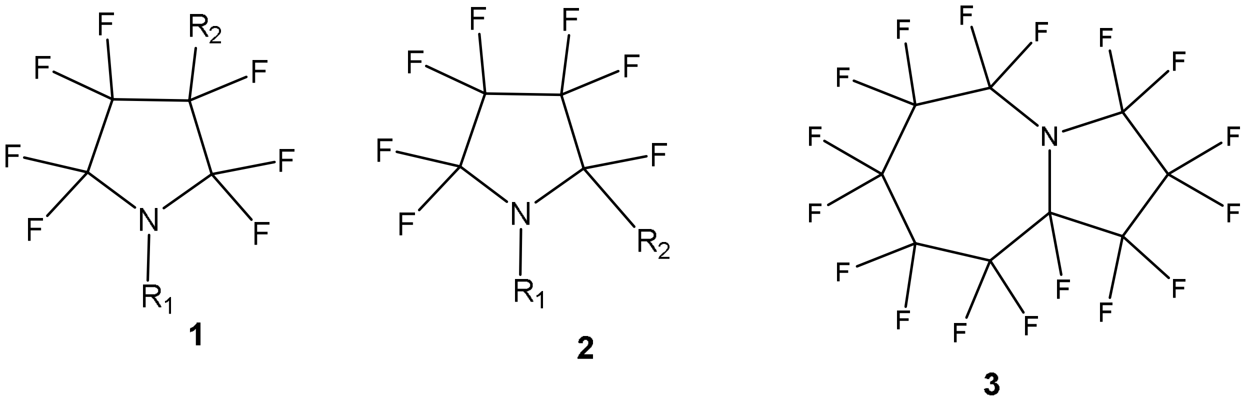
Iodine is completely displaced even from perfluoroalkyl iodides under normal fluorination conditions. Bromine occupies an intermediate position. Depending on the fluorination conditions, bromine atoms could either be retained in the reaction products or replaced by fluorine [5].

Fluorination of compounds that contain functional groups and heteroatoms in their structure (with the exception of halogens) was unsuccessful in most cases, and only destruction products were found in the reaction products.

There are a small number of examples of relatively successful attempts to fluorinate compounds with heteroatoms. These include the fluorination of methylpyridines with $CsCoF_4$, which is described in [14]. The main products were compounds with five-membered rings – pyrrolidines. (about 50%) (Scheme 2, compounds **1** and **2**) and fluorinated pyridines (about 30%). The authors explained the appearance of five-membered cycles through the skeletal rearrangement of the six-membered ring of highly fluorinated compounds, which occurred due to difficulties in forming the N-F bond.

The same authors carried out the fluorination of quinoline with cobalt trifluoride and $CsCoF_4$ [15]. The main products were perfluoroheptane and perfluoro-1-azabicyclo-[5,3,0]-decane

(Scheme 2, compound **3**), which appeared as a result of a rearrangement similar to that reported in [14] during the fluorination of methylpyridines.



1 **2** **3**

Scheme 2.

Other examples of fluorination of compounds with functional groups and heteroatoms are given in [13].

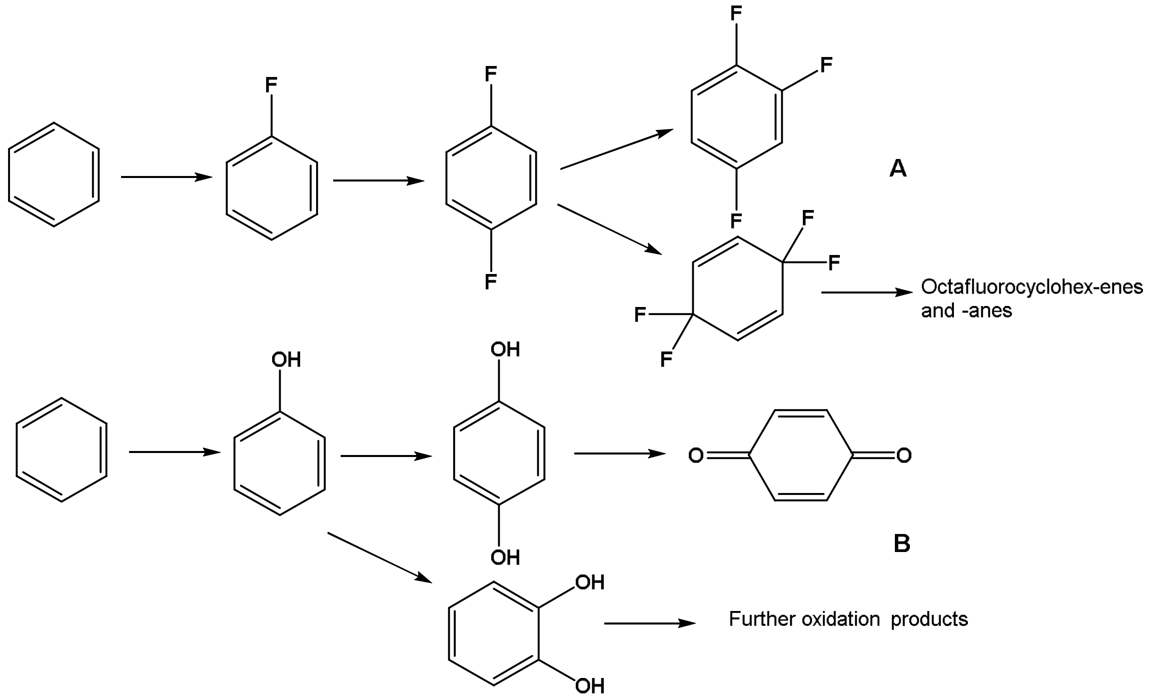
2. Possible fluorination mechanisms of aromatic compounds

The mechanism of fluorination with HVMFs differs from the mechanism of reactions with elemental fluorine. Thus, W. Miller's article [16] reported that no olefin dimerization products were found in the reaction products of halo-olefins with cobalt trifluoride, which were found in the reactions of halo-olefins with fluorine 17].

In 1960 the results of the fluorination of benzene with cobalt trifluoride at various temperatures were published in “Advances in Fluorine Chemistry” [5].

Based on these results, it was concluded that the mechanism of the process is different from the free radical one. Fluorobenzene, p-difluorobenzene, as well as exclusively 1,1,2,3,4,4,5,6-octafluorocyclohexene and 1,1,2,2,3,4,5,5,6-nonafluorocyclohexane were identified as intermediates, which is unlikely with a free radical mechanism of the process. In addition, the composition of the compounds during the fluorination of fluorobenzene and p-difluorobenzene was similar to the composition of the products during the fluorination of benzene [5].

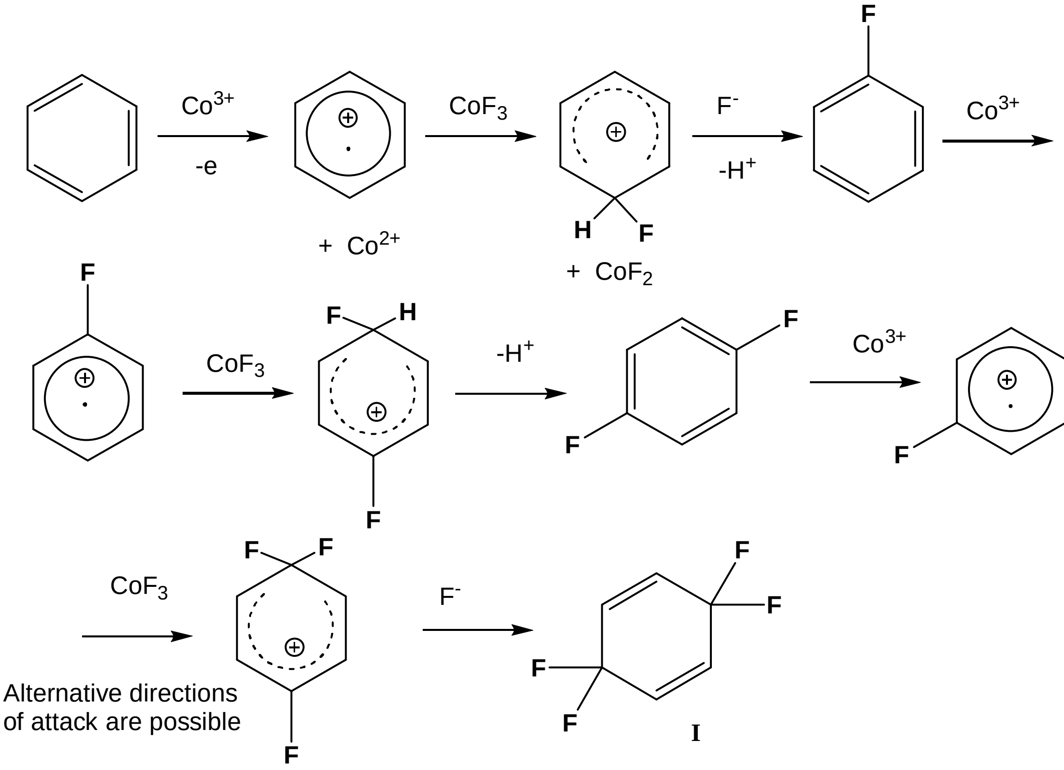
In 1972, J. Burdon, I. W. Parsons and J. C. Tatlow proposed a mechanism for the fluorination of benzene with cobalt trifluoride, which in the initial steps is similar to the mechanism of the aqueous oxidation of benzene by cations Co^{3+} (Scheme 3) [18].



Scheme 3. *The initial steps of the processes of benzene fluorination (A) with cobalt trifluoride and benzene oxidation in an aqueous medium (B) in the presence of cations [18].*

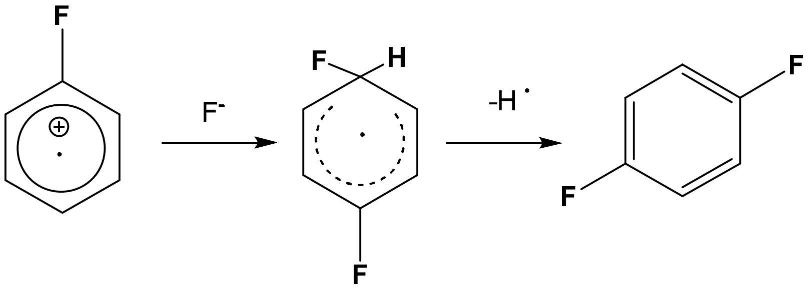
A hypothesis was developed, that each process had two steps:

1) removal of an electron from the aromatic by the metal ion (shown as Co^{3+}, but it could be Ag^{2+}, Ce^{4+}, Mn^{3+}, Pb^{4+}, etc.) to give a radical-cation.
2) the quenching of the radical-cation by a fluorine atom derived from cobalt trifluoride or by an OH radical from some $Co(OH)^{2+}$ species (Scheme 4).



Scheme 4. *Possible mechanism of fluorination [18].*

At the same time, the authors of the proposed mechanism allowed for the possibility of parallel processes occurring during the fluorination of aromatic compounds with the quenching of the radical cation not by fluorine atoms (Scheme 4), but by the fluorine anion (Scheme 5) [18].



Scheme 5. *The quenching of the radical cation by the fluorine anion.*

By analogy with the oxidation processes, the dependence of the fluorinating power of higher fluoride on the oxidizing potential of the metal cation was proposed. According to the fluorination power, HVMFs were arranged according to the oxidation potential in the following order [18]:

$$\mathbf{AgF_2 > CoF_3 > MnF_3 > CeF_4}.$$

Houben-Weyl provides a more extended range of HVMFs that includes nickel fluorides [13].

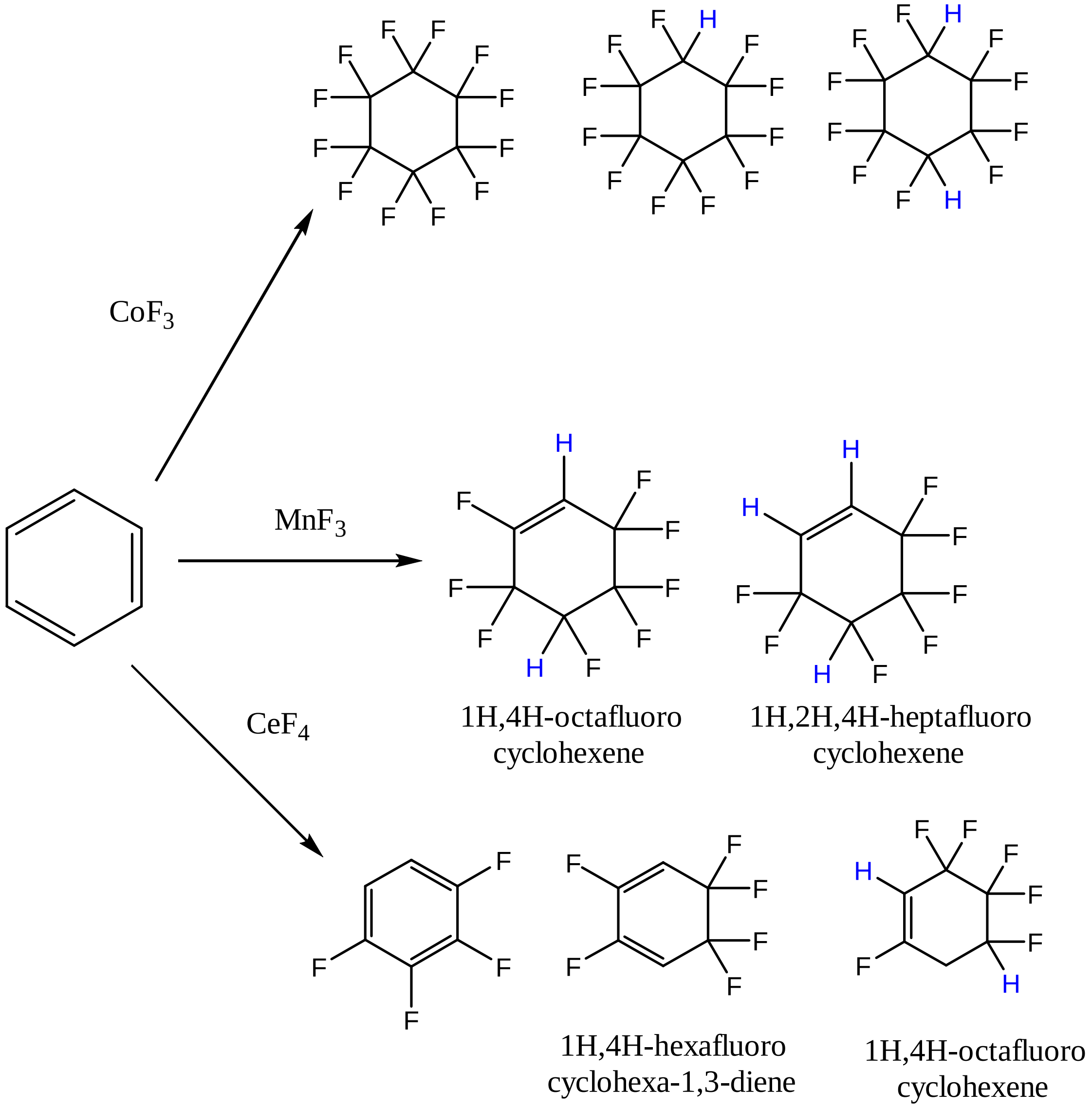
$$\mathbf{NiF_4 > NiF_3 > AgF_2 > CoF_3 > MnF_3 > CeF_4}.$$

It has been noted that complex fluorides are always weaker than simple fluorides at the same oxidation state of the metal [13].

$CoF_3 > KCoF_4 > K_3CoF_6$ (all Co^{3+}); $NiF_4 > K_2NiF_6$ (both Ni^{4+})

The assumptions about the dependence of the fluorinating power of HVMFs on the oxidation potential of the metal have certain experimental confirmation.

As an example, one can cite the results of fluorination of benzene with higher fluorides of cobalt, manganese and cerium. If the main products of the reactions of benzene with cobalt trifluoride were polyfluorocyclohexanes [5], then with manganese trifluoride - polyfluorocyclohexenes [19], and with cerium tetrafluoride - polyfluorocyclohexadienes and polyfluorinated aromatic compounds [20] (Scheme **6**).



Scheme 6.

Cation-radical theory of fluorination of aromatic compounds received its further development in 1974 in the paper of R. Chambers et al. [21]. The fluorination of hexafluorobenzene and a number of chlorofluoropyridines with a mixture of cobalt trifluoride and calcium difluoride (ratio 1:1) was studied. An assumption was made about the coordination of the electron transfer to the metal cation with the subsequent “quenching” of the intermediate cation-radical by a fluorine atom or ion. Such a transition could occur when the aromatic compound molecule is positioned parallel to the surface of the cobalt trifluoride crystal (which has an octahedron shape) at a distance corresponding to the Co-F distance.

According to the calculations of the authors, the resulting electrostatic interaction of the radical cation with neighboring ions is preferable by 50 kcal/mol. Based on calculations of the spin density, charge density distribution of possible intermediates, and experimental results, it was assumed that radical cation is most likely "quenched" by ions rather than fluorine atoms. At the same time, it was noted that neither anions nor fluorine atoms exist as free particles in the cobalt trifluoride layer.

In 1975, J. Burdon and I.W. Parsons compared experimental results on the fluorination of a number of aromatic compounds with various possible scenarios for the processes arising from the cation-radical theory [22]. Using calculated data on the charge distribution and spin density of the initial and possible intermediates, the authors attempted to establish a fluorination mechanism for benzene, benzotrifluoride, naphthalene, phenanthrene, and anthraquinone. The CNDO/2 (Complete Neglect of Differential Overlap) and INDO (Intermediate Neglect of Differential Overlap) methods were used for the calculations.

The fluorinating agents were: CoF_3, $KCoF_4$, $LiCoF_4$, $CsCoF_4$.

Based on the research, the following conclusions were made:

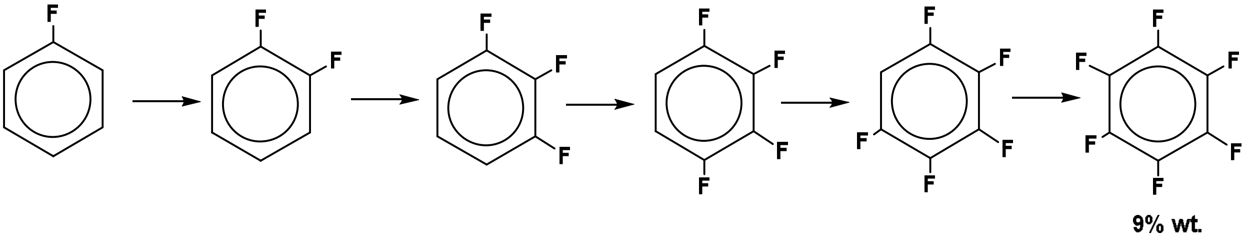
1. There is no single mechanism for fluorination by various HVMFs; the direction of the reaction was determined by the nature of the fluoride used.
2. The cation-radical theory agrees well with experimental data on the fluorination of monocyclic aromatic compounds using CoF_3, $KCoF_4$, and $LiCoF_4$. When using $CsCoF_4$ as a fluorinating reagent, there was no unambiguous reaction direction.
3. The results of fluorination of condensed arenes cannot be explained based on calculations of charge distribution and spin density.

As a hypothesis, it was suggested to use data on the stability of intermediates to explain the reaction mechanism.

These ideas were developed further in the following article by the same authors [23], which attempted to explain the different results of fluorination with different HVMFs. The fluorination processes of pyridine and benzofuran with $CsCoF_4$ and benzene with $CsTlF_4$ were studied.

It was found that the reaction products of benzene with $CsTlF_4$ and pyridine with $CsCoF_4$ contained a significant amount of fluorinated aromatic compounds.

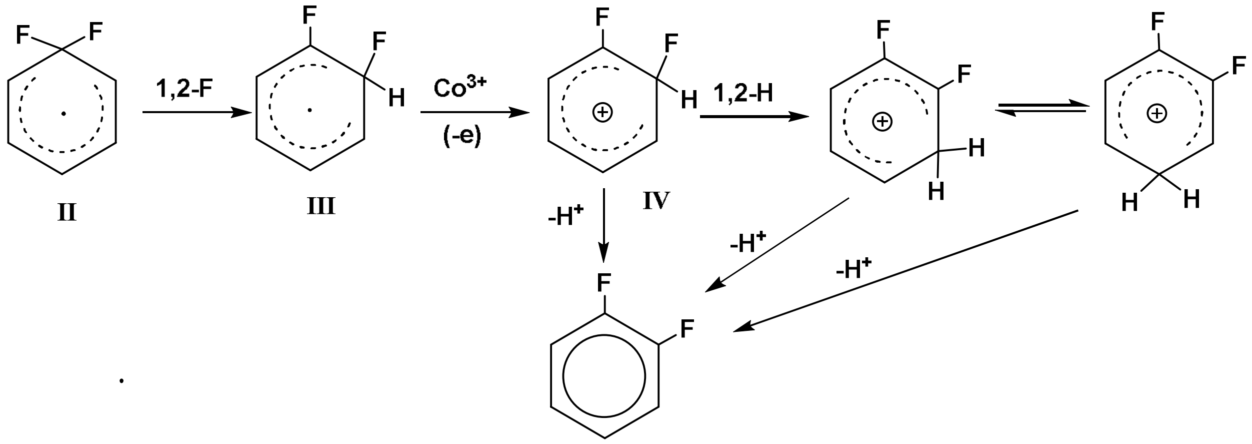
In the case of benzene with $CsTlF_4$, almost all polyfluorobenzenes were obtained as a result of sequential substitution of a hydrogen atom with fluorine, which was in an ortho position to the already introduced fluorine (Scheme **7**). This contrasted strongly with the reactions of benzene with cobalt trifluoride, where the main intermediate was 3,3,6,6-tetrafluorocyclohexa-1,4-diene (Compound **I**, Scheme 4).



Scheme 7.

Furthermore, the almost complete absence of hydrogen-containing compounds in the reaction products of $CsCoF_4$ with naphthalene, anthracene, and other condensed arenes required an explanation. At the same time, significant amounts of hydrogen-containing compounds remained in the reaction products of these arenes with the apparently stronger fluorinating agent, cobalt trifluoride.

The authors suggested that, besides being oxidized, the radical (**II**) can rearrange by 1,2-migration of fluorine followed by oxidation and loss of a proton, either before or after further proton migrations, to give 1,2-difluorobenzene (Scheme 8).



Scheme 8.

Further attack of F^- on a F-bearing carbon in the cation-radical of 1,2-o-difluorobenzene, followed by 1.2-F migration - would lead to 1,2,3-triifluorobenxene and so on (Scheme 7).

Based on calculations of the thermodynamic stability of intermediate radicals and cations, it was concluded that 1,2-migration (**II→III**, Scheme 8) almost always leads to thermodynamically more favorable intermediates.

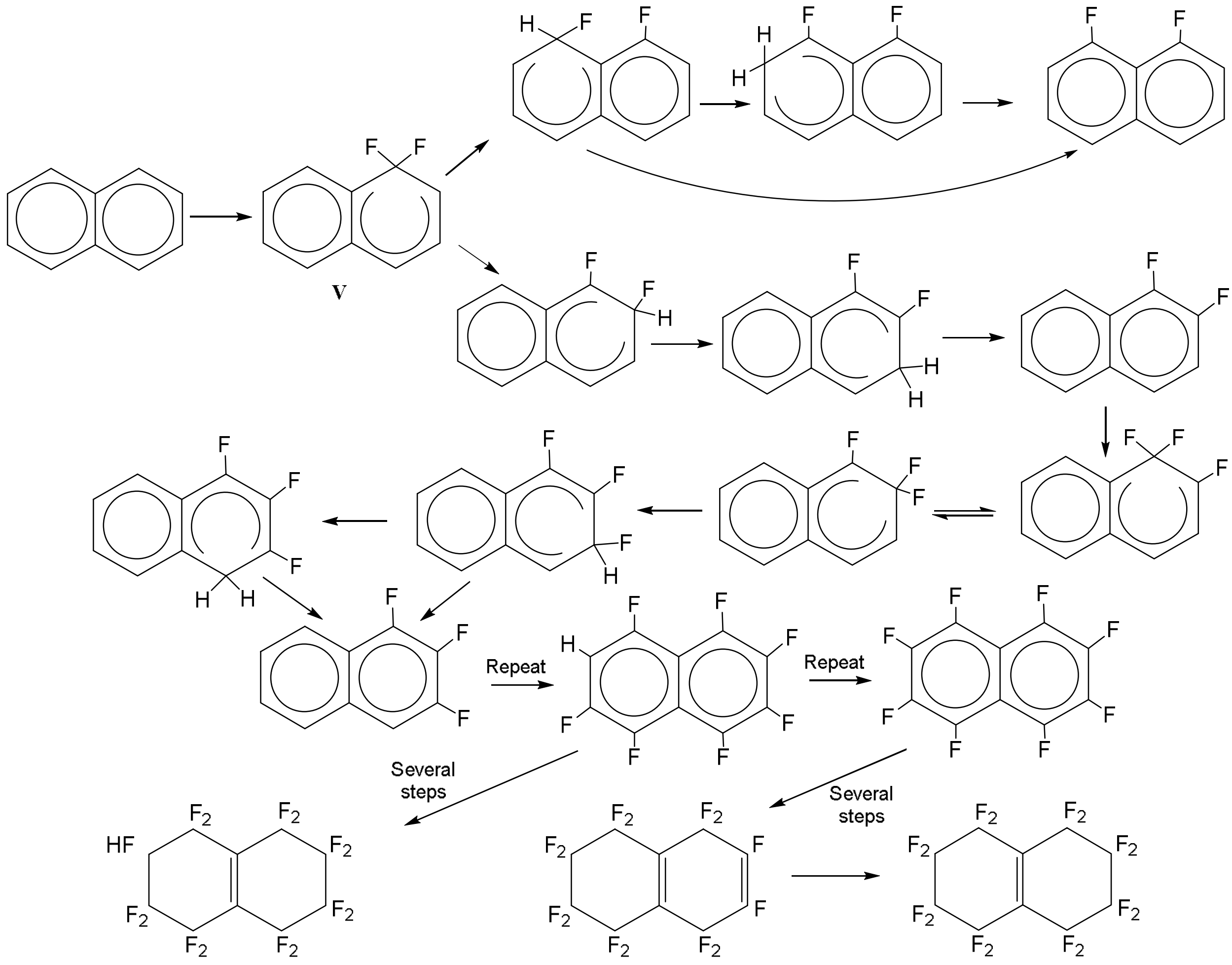
Different mechanisms of reactions for considered HVMFs (Schemes 4 and 8) were explained by different structure of crystal lattice of fluorides, and also by stability of intermediate radicals (ions).

The authors suggested that after electron abstraction with a metal ion (or via F atom bridge between Co^{3+} ion and the organic radical), for further "quenching" of the organic derivative (Scheme 4**)** a fluorine species (ion or atom) must be available on the surface of the HVMF. And this may not always be so. Since the fluorine in the surface layer was gradually exhausted (one atom per HVMFs molecule), some sort of movement will have to occur within the HVMF lattice to bring fluorine to the surface.

The key assumption was that the time required to bring a fluorine to the surface is different for the different fluorides. If this process is slow, radicals of type **II** (Scheme **8)** or the corresponding cation would have longer lifetimes and hence a greater opportunity to undergo the 1,2-migrations described above.

This is precisely what explained the results of the fluorination of benzenes with $CsTlF_4$ and pyridines with $CsCoF_4$, where a significant amount of aromatic compounds was observed in the reaction products.

In reactions with polycyclic arenes (naphthalene, anthracene, phenanthrene), intermediate radicals or ions (e.g., **V**, Scheme 9) will be more stable relative to monocyclic aromatic compounds due to greater delocalization. Therefore, the lifetime of such radicals (ions) will be quite long even under conditions of relative availability of fluorine atoms (ions).



Scheme 9. *Major routes for the fluorination of naphthalene over* $CsCoF_4$ *and* $KCoF_4$ *[23].*

The type of atom movements through the crystal lattices of different HVMFs was left open for further discussion.

It has been suggested that once the surface CoF_3 has been converted into, formally, CoF_2 the small Co^{2+} ions would migrate through the fluoride lattice into vacancies in the interior and so leave an effective layer of CoF_3 on the surface again. This can happen over a short period of time, so the "quenching" occurred much faster than the 1,2-migration process.

In the cases of $KCoF_4$ and especially $CsCoF_4$, the introduction of K^+ (or Cs^+, respectively) ions into crystals caused additional spatial difficulties in delivering fluorine to the surface, which created opportunities for 1,2-migration.

These compounds have layered structures (two-dimensional layers having the empirical formula CoF_4^-, with the potassium or caesium ions placed between them). Therefore, the mechanism of fluorine delivery to the particle surface at some point could involve the movement of fluorine atoms (or ions) between the layers through the gaps occupied by the K or Cs ions. For information on the structure of the $KCoF_4$ crystal lattice, see [24].

Due to the structural features of the crystal lattices, the transportation of fluorine through $CsCoF_4$ is even slower, so there is more time for 1,2-migration.

Based on their research [22,23], J. Burdon and I.W. Parsons made the following conclusions:

- Two reaction sequences can occur during fluorination of an aromatic compound, the predominant of which is determined by the presence of fluorine on the surface of HVMF and the stability of radical **II** (or the corresponding cation) in the case of fluorination of benzene (Scheme 8) or similar radicals (cations) during fluorination of other arenes.
- Radicals of type **II** have two ways of further transformation - either oxidation followed by quenching with fluorine ions, or 1,2-migration of fluorine. None of them is the only way until the entire fluorination process of the aromatic compound is completed.
- The stability of certain types of radicals or cations may well vary depending on the degree of fluorination, and therefore it is possible that during fluorination, the process may shift from predominantly 1,2-migration to quenching, or vice versa.

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