

THE FLUOROSULPHONIC ACID INFLUENCE ON INTERACTION OF COVALENT FLUOROSULPHONATES WITH SULFOREPLACED AMINODERIVATIVES

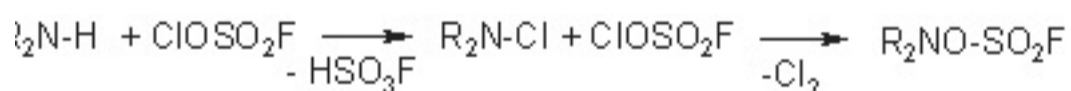
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Many reactions of covalent fluorosulphonates with organic compounds of different structure are described in literature. It was stated, that the catalytic influence of fluorosulphonic acid on mentioned above reactions exists because of covalent fluorosulphonate protonation and thereafter increasing of its reaction capacity. As for non-organic compounds their interaction with covalent fluorosulphates is studied much less.

We have studied the interaction of chlorine fluorosulphonate, peroxydisulphurylfluoride, peroxydisulphuryldifluoride and sulphoderivatives of ammonia, hydroxylamine, their salts and halogen derivatives, such as difluorosulphonylamine and others.

As we have supposed, the most active compound among covalent fluorosulphonates in the studied reactions was chlorine fluorosulphonate. Thus, the use of liquid fluorosulphonate resulted in intensive interaction with vigorous heating and decomposition of reaction mass even at low temperatures and dilution of aminoderivatives in all cases.

At mild conditions chlorine fluorosulphonate in the form of vapour, diluted with inert gas, even at room temperature smoothly chlorinates *bis*-fluorosulphonilamine and potassium imidodisulphonate with formation of fluorosulphonic acid and corresponding chloroamine, which at more severe conditions (heating above 110 ° C, UV-radiation etc) reacts with the second molecule of chlorine fluorosulphonate, at that isolating the elemental chlorine and thereafter forming *tris*-(fluorosulphonyl)-hydroxylamine or *o*-(fluorosulphonyl)hydroxylaminedisulphonate of potassium .



where R = SO₂F, SO₃K

An unexpected thing about this reaction is that the chlorination of aminoderivatives' potassium salts instead of aminoderivatives themselves at the first stage passes more smoothly and with higher yield. (up to 88-90%).

Peroxydisulphuryldifluoride is less reactive. The reactions with peroxydisulphuryldifluoride can be carried out even in liquid phase variant, though it is necessary to take into account great induction period at start phase, which also can lead to uncontrolled process of reaction with overheating and reaction mass blowout out of reactor. To eliminate these effects the addition of bromine catalytic quantities is necessary, or peroxydisulphuryldifluoride should contain low admixtures of chlorine fluorosulphonate (~ 0,5%).

The interaction of peroxydisulphuryldifluoride with *bis*-fluorosulphonylamine, *bis*-fluorosulphonylchloroamine, potassium salts of *bis*-fluorosulphonylamine and imidodisulphonate steadily results in formation of corresponding *o*-fluorosulphonylhydroxylamines. As in the case

of chlorine fluorosulphonate the reaction becomes more effective at using potassium salts, at that the yield of *tris*-(fluorosulphonyl)hydroxylamine at interaction of *bis*-fluorosulphonylchloroamine and peroxydisulphuryldifluoride at analogous conditions is higher, than at reaction with chlorine fluorosulphonate. The last mentioned circumstance indicates the fact, that interaction of chloroamines and covalent fluorosulphonates most probably passes according to the radical mechanism, because the changing of such an active electrophilic reagent as chlorine fluorosulfonate for the less reactive peroxydisulphuryldifluoride, relating to reagents of classic radical type, not only doesn't decrease the yield of target product *o*-fluorosulphonylhydroxylamine but also increases it at conditions, which are more mild.

Though the potassium hydroxylaminedisulphonate structure differs from the aminoderivatives analyzed above, its reactions with peroxydisulphuryldifluoride also lead to binding of movable hydrogen atom in the form of fluorosulphonic acid and formation of potassium *o*-fluorosulphonyl-hydroxylamindisulphonate:



As in reactions with peroxydisulphuryldifluoride the yield greatly increases at binding of resulting fluorosulphonic acid.

The obtained experimental data testifies, that in reactions with sulpho-replaced aminoderivatives the unknown before inhibiting action of extracting during reaction fluorosulphonic acid is observed, which explains rather low yield (up to 55 .. 60%) in reactions studied.

This effect can be explained by forming of fluorosulphonic acid and starting amine complexes, which are more inert to action of fluorosulphonates.

Physical and chemical research of *bis*-fluorosulphonylamine solutions in fluorosulphonic acid indicated, that amine molecule bound up to 3 molecules of acid. In the NMR ^{19}F spectra of amine and acid mixture the signal (41,42 ; trichlorofluoromethane standard) is detected, which is referred to the supposed complex, while there is no signal corresponding to fluorosulphonic acid (41,97).

The formation of complexes also explains the fact, that the use of salts of corresponding amines, which excludes the fluorosulphonic acid forming, greatly increases the reaction yield.

We have used different salts for fluorosulphonic acid binding. Potassium sulphate appeared to be the most effective reagent, which on the one hand fully binds the fluorosulphonic acid and on the other hand, after thorough dehydration and drying doesn't interact with peroxydisulfuryldifluoride and pyrosulphuryldifluoride. This allows to measure it out (in doses) immediately with source amine. As for reaction with chlorine sulphonate, it is reasonable to enter the reaction mixture by portions according to the fluorosulphonate dosage, if you wish to get maximum effect.

The high yields of *o*- fluorosulphonylhydroxylamines, simplicity of their isolation and ease of necessary compounds extraction using filtration allow to recommend the studied reactions as perspective obtaining methods of sulpho-replaced hydroxylamines.