Primary Toxicological Parameters of Fluorine-Containing Organic Compounds of Practical Significance

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Abstract

Primary toxicological parameters of fluorine-containing alcohols, dialkyl ethers, acetales, acrylates, esters of carboxylic and dicarboxylic aliphatic acids, epoxides and olefins used as the materials and intermediate products of organofluoric synthesis are considered. The regularities of the effect of fluorine atoms on the toxicity of the compounds are revealed. All the investigated compounds belong to the III and IV class of danger and are safe for developing fluorinated materials on their basis. Some examples of the application of these classes of compounds are discussed.

INTRODUCTION

Roles and directions of fundamental research (especially into the new classes of organic compounds) are to a great extent determined at each stage of technological progress by the requirements of the society for new materials with improved consumer characteristics suitable for performance under more rigid conditions. Fluorinated compounds meet these requirements and can play an important part in intensifying and simplifying the production of many kinds of hardware [1–4]. Fluorinated compounds form a basis on which new technologies appear, relying on the already developed technological foundations and approaches together with the available fundamental knowledge. The development of high-tech processes and satisfaction of the permanently increasing practical wants has become the main goal of investigations during the recent years.

These investigations had a substantial effect on the development of synthetic chemistry of fluorine: a number of new reagents and synthesis methods had been developed. The discovery of unique characteristics of fluorinated organic compounds and a number of the new directions of their application is of essential scientific and practical importance for the development of new highly efficient biologically active compounds and materials with unique properties [5–7].

At the first stage, the major consumers of organofluoric compounds became aerospace technology and atomic power engineering. However, as the technology of the synthesis of these compounds improved and the costs of the materials decreased, the practical attention shifted from the synthesis of multi-purpose products (fluorinated monomers, freons, dielectrics *etc.*) towards the development of synthesis methods for obtaining fluorine-containing polyfunctional compounds as the units for designing more complicated molecules, especially those possessing biological activity. Prerequisites have been created for using these

new materials in domestic equipment and medicine [8–11].

In connection with the above-indicated considerations, the works aimed at broadening of the arsenal of fluorinated materials and the development of production and technologies of a number of the key intermediate products on the basis of the industrial production of tetrafluoroethylene and hexafluoropropylene are developing in Russia. This raw material basis allows one to develop the technologies of many necessary fluorinated materials. At the same time, it is still urgent to develop a number of promising technologies of the key cheap intermediate products for use in synthetic organic chemistry of fluorinated compounds. In spite of the fact that the cost of fluorinated materials is still rather high and prevents their wide application, many specialists even do not imagine all the possibilities of the application of fluorinated compounds and the efficiency of their use.

In the present work we describe the investigation of the primary toxicity of a number of classes of fluorinated compounds that may serve as potential objects for the development of substances and materials with a set of new properties. It is necessary to stress that these classes present and depict only a small part of the possibilities of the synthetic potential of the main construction units – perfluorinated olefins; one may hope that this potential will be uncovered and realized on a large scale.

One of the goals of the present investigation was to attract the attention of chemists to this interesting and rapidly developing area of organic chemistry. The work is also intended for specialists engaged in the area of developing new preparations for medicine, agriculture, and industry.

FLUORINE-CONTAINING ALCOHOLS

Now we will consider a new raw material basis of organofluoric synthesis relying upon fluorine-containing alcohols [12–16]. The latter compounds act as intermediate products for obtaining high-temperature and highly efficient heat carriers, dielectrics [17], as efficient lubricating oils and compositions [18]. The availability of these materials broadens the areas of their application. Investigation of the acute toxicity of initial alcohols turns out to be the key and safe aspect in developing the methods of their use and transformation into useful products.

We studied the acute toxicity of partially fluorinated alcohols [14–16] for white of no breed mice under intragastric introduction in the doses 800–4000 mg/kg (Table 1). One can see that the alcohols under investigation are related to the III class of danger (moderately dangerous compounds) according to the GOST 12.1.007–76 (State Standard). Linear polyfluorinated alcohols with the carbon chain length more than 5 in the sub-toxic dose (1000 mg/kg) cause suppression of the respiratory centre in mice, disorder of coordination of movements and the central nervous system, which is expressed as a strong sedative action. Fluorinated alcohols with a short carbon chain cause anaesthesia when introduced in the dose of more than 500 mg/kg. These neurotoxic indices revert to the physiological norm after 24 h. No death cases of the mice were recorded during the experiment.

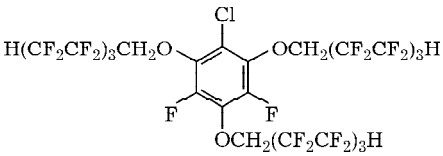
We suppose that this investigation will promote substantial broadening of the areas of application of fluorinated alcohols and the possibilities of their use as the key products in organofluoric synthesis.

POLYFLUORINATED DIALKYL ETHERS

Another class of compounds investigated by us is partially fluorinated dialkyl ethers. The latter compounds are sued first of all as solvents, liquid dielectrics, heat carriers *etc*. Freon HFE 7110 ($CH_3OCF_2CF_2CF_2CF_3$) was developed by 3M Co. (the USA) for use as a solvent. Tetrafluoroethyldifluoromethyl ether ($CHF_2CF_2OCHF_2$) can replace Freon 11 which is used as a frothing in the production of foam plastics, and also perfluorocarbons in dry etching processes in microelectronics [19]. Ethers like $C_4F_9OCH_3$ (m. p. 61 °C), $(CF_3)_2CFCF_2OC_2H_5$ *etc*. were used to extract essential oil from lavender and demonstrated good results both in the quality of the extracted substance and in the purity of the oil [20]. They are efficient as the solvents carrying surfactants, coatings, agents

TABLE 1

Some toxicological characteristics of fluorinated alcohols and dialkyl ethers

Compound	LD_{50}, mg/kg	LD_{100}, mg/kg	Class of danger
$HCF_2CF_2CH_2OH$	2320	3000	III
$HCF_2CF_2CH(CH_3)OH$	692	1000	III
$CF_3CHFCF_2CH_2OH$	640	1000	III
$HCF_2CF_2CF_2CF_2CH_2OH$	1180	2000	III
$H(CF_2CF_2)_3CH_2OH$	3375	5500	III
$CF_3(CF_2)_5CH_2OH$	2320	4000	III
$HCF_2CF_2CH_2OCHF_2$	5000		IV
$HCF_2CF_2CH_2OCH_2CH_3$	3420	6000	III
$CF_3CHFCF_2OCH_2CF_2CHF_2$	5000		IV
	5000		IV

for form release, and water-oil repellents [21]. These ethers were used as solvents to carry out chemical reactions, in particular for the synthesis of amides of fluoropolyalkyl ethers used for magnetic reproducing media [22] and oxidation of tetrafluoroethylene [23]; the products of the interaction of hexafluoropropylene and polyoxaalkyleneglycols were used as compression, motor and vacuum oil [24], with polyatomic alcohols – as dielectric heat carriers of the broad range of application (liquids with freezing points −20 °C and boiling points 330−350 °C). Fully fluorinated dialkyl ethers, for example $(CF_3)_2CFCF_2OC_nF_{2n+1}$, are used as solvents to clean electronic circuits, freons, foamers, media for polymerisation *etc.* [25−28].

The results of investigation of the acute toxicity of fluorinated dialkyl ethers and fatty-aromatic esters synthesized by us [29, 30] are listed in Table 1. It was established that the latter have no local effect on skin and mucous coat of eyes. The alcohols under investigation belong to the III or IV group of danger (moderately or low toxic substances).

FLUORINE-CONTAINING ACRYLATES AND METACRYLATES

One of the most important places among fluorinated polymers [31] is occupied by a separate and intensively developing class of polymers and copolymers: fluorine-modified acrylates, metacrylates [32] and maleinates [33, 34]. These polymers are composed of polyacrylic or polymetacrylic acid in which the carboxylic groups are transformed into ester groups with fluorocarbon chains (C8−C10) [35−38]. The area of their application is diverse. As an example, we may mention the preparations for rendering water- and oil-repellent properties to cloths [39], materials for microelectronics [40], surfactants for olefin polymerisation processes [36], systems exhibiting high stability to electron impact and X-rays [41−43] *etc.*

The data on the acute toxicity of some fluorine-containing acrylates [44] and metacrylates [34] obtained in the studies with white of no breed mice in the doses 800−5000 g/kg after single intragastric introduction are listed in Table 2. For all the doses tested, we observed insignificant suppression of the central nervous system with respiratory depression and disorders of the coordination of movements; for doses above 1000 mg/kg, the anaesthetic and spasmodic effects were observed. They are more clearly exhibited for fluorinated metacrylates. It follows from the data shown in Table 2 that the fluorinated acrylates under investigation belong to the III or IV class of danger (moderately of low toxic substances).

TABLE 2

Toxicological characteristics of fluorine-containing acrylates

Compound	LD_{50}, mg/kg	LD_{100}, mg/kg	Class of danger
CH_2=CHC(O)$OCH_2CF_2CF_2H$	3300	5000	III
CH_2=CHC(O)$OCH_2(CF_2CF_2)_2H$	2250	4000	III
CH_2=CHC(O)$OCH_2(CF_2CF_2)_3H$	4080	6000	III
CH_2=CHC(O)$OCH_2(CF_2CF_2)_4H$	2670	5000	III
CH_2=CHC(O)$OCH_2(CF_2)_5CF_3$	4330	5500	III
CH_2=CHC(O)$OCH_2CF_2(OCF_2CF_2)_2OCF_3$	4420	6000	III
CH_2=C(CH_3)C(O)$OCH_2CF_2(OCF_2CF_2)_2OCF_3$	5000		IV
CH_2=C(CH_3)C(O)$OCH_2(CF_2CF_2)_2H$	3330	5000	III
CH_2=C(CH_3)C(O)$OCH_2(CF_2)_5CF_3$	5875	6500	IV
CH_2=C(CH_3)C(O)$OCH_2(CF_2CF_2)_3H$	3330	5000	III

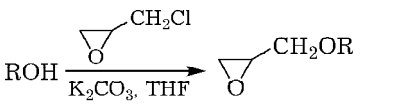
DERIVATIVES OF OLEFINS AND EPOXIDES CONTAINING FLUOROALKYL SUBSTITUENTS

The products of the reaction of polyfluorinated telomere alcohols with epichlorohydrine are important initial compounds for obtaining polymeric materials. They are synthesized by the interaction of fluoroalcohols with epichlorohydrine in the presence of bases (Scheme 1) [30].

It was shown previously [45] that the telomere alcohol $HCF_2CF_2CH_2OH$ in dimethylformamide enterst he reaction with allyl chloride and forms partially fluorinated alkyl allyl ether. We developed [30] this approach using telomere alcohols $H(CF_2CF_2)_nCH_2OH$ (n = 2–4) and partially fluorinated alcohols synthesized by us (Scheme 2).

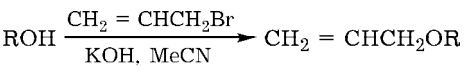
Dehydration of secondary and tertiary alcohols under the action of concentrated sulphuric acid on safe non-toxic zeolites NaA, NaX, CaA and other results in the formation of polyfluorinated olefins (Scheme 3) [46].

For some fluorinated derivatives of ethylene and epoxides [30], investigations of the acute toxicity were carried out with white of no breed mice in the doses 1000–4000 mg/kg after single intragastric introduction (Table 3). One can see that the olefins under investigation belong to the III or IV class of danger (moderately or low toxic substances). The derivatives of ethylene with the linear polyfluorinated framework having the length of the carbon chain more than 5 in the subtoxic dose (1000 mg/kg) cause suppression of the central nervous system which is exhibited as the strong sedative effect, while the derivatives branched at he oxygen atom promote development of the narcotic state. A similar situation is also observed for epoxides (suppression of the central nervous system, distortion of the coordination of movements and development of the anaesthetic state). The compounds belong to the III class of danger (moderately dangerous substances).



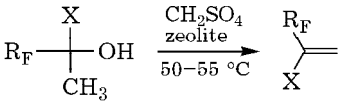
R = $HCF_2CF_2CH_2$, $H(CF_2CF_2)_2CH_2$, $H(CF_2CF_2)_3CH_2$, CF_3CHFCF_2–CH(CH_3)$_2$

Scheme 1.



R = $H(CF_2CF_2)_2CH_2$, $H(CF_2CF_2)_3CH_2$, $H(CF_2CF_2)_4CH_2$, CHF_2CF_2–CH(CH_3)$_2$, CF_3CHFCF_2–CH(CH_3)$_2$

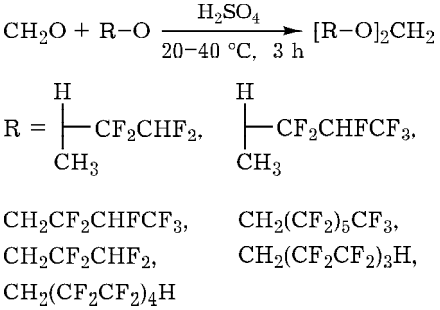
Scheme 2.



1a-d **2a-d**

$R_F = HCF_2CF_2$, X = H(**a**),
HCF_2CF_2, X = CH_3 (**b**),
HF_3CHFCF_2, X = H(**c**),
HF_3CHFCF_2, X = CH_3 (**d**)

Scheme 3.



Scheme 4.

A number of fluoroalcohols react with formaldehyde in concentrated sulphuric acid to form formal (Scheme 4) [47, 48].

These acetales may be efficient heat carriers; their further fluorination with elemental fluorine allows one to obtain promising dielectrics with variable boiling points.

For partially fluroianted acetales obtained in the work we studied their acute toxicity for white of no breed mice. The results are shown in Table 4. One can see that the compounds under investigation belong to the III or IV class of danger (moderately or low toxic substances). The general action on the animals is expressed as the suppression of the central nervous system and respiratory function, and distortion of the coordination of movements. No basic indices of intoxication were detected.

ESTERS OF DICARBOXYLIC ALIPHATIC ACIDS

The need for high-temperature lubricating oil to treat the moving parts and thus increase the operation lifetime of the mechanisms due to the low coefficients of friction is rather high. Esters of dicarboxylic aliphatic acids found application as efficient lubricants and hydraulic liquids [49]. Along with this, these exists the need for lubricants for rolling mills, not only for steel but also for other metals. In addition, they are used as coatings of petroleum equipment and oil-pipelines because, unlike for mineral oil, these lubricants do not get washed out with organic substances. The possibility of esterification of a number of aliphatic dicarboxylic acids under the action of partially fluorinated alcohols in the presence of concentrated sulphuric acid was demsontrated (Scheme 5) [50–53].

TABLE 3

Toxicological characteristics of fluorinated derivatives of ethylene and epoxides

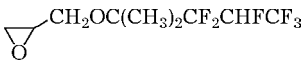
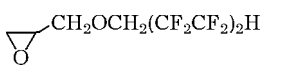
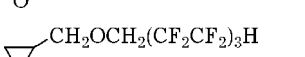
Compound	LD_{50}, mg/kg	LD_{100}, mg/kg	Class of danger
$CH_2=CHCH_2OC(CH_3)_2CF_2CHFCF_3$	2210	3500	III
$CH_2=CHCH_2OCH_2(CF_2CF_2)_2H$	2750	4000	III
$CH_2=CHCH_2OCH_2(CF_2CF_2)_3H$	5000		IV
$CH_2=CHCH_2OCH_2(CF_2CF_2)_4H$	5000		IV
$CH_2=C(CH_3)CF_2CHF_2$	1334	3000	III
$CH_2=C(CH_3)CF_2CHFCF_3$	1800	3000	III
	1800	3000	III
	3000	5000	III
	3830	6000	III

TABLE 4

Some toxicological characteristics of fluorine-containing compounds

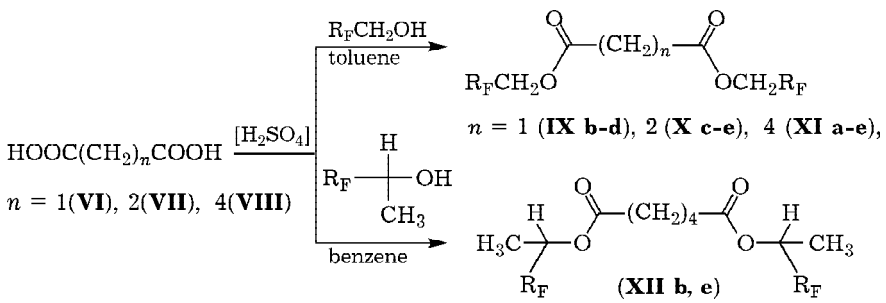
Compound	LD_{50}, mg/kg	LD_{100}, mg/kg	Class of danger
$[HCF_2CF_2CH(CH_3)O]_2CH_2$	1917	5000	III
$[CF_3CHFCF_2CH(CH_3)O]_2CH_2$	4330	5500	III
$[CF_3(CF_2)_5CH_2O]_2CH_2$	>5000		IV
$[CHF_2CF_2CH_2O]_2CH_2$	2290	6000	III
$[H(CF_2CF_2)_3CH_2O]_2CH_2$	>5000		IV
$[H(CF_2CF_2)_4CH_2O]_2CH_2$	>5000		IV
$[H(CF_2CF_2)_2CH_2O]_2CH_2$	5000		IV
$[CF_3CHFCF_2CH_2O]_2CH_2$	2290	6000	III

Only for a mixture of esters of adipinic acid obtained by esterification with a mixture of telomere alcohols $H(CF_2CF_2)_nCH_2OH$ (n = 4, 6), the data on LD_{50} are available (5000 mg/kg) [54]. An important aspect is the investigation of the acute toxicity of esters of malonic acid modified at the ester part with fluorine atoms. Investigation with white of no breed mice under intragastric introduction int eh doses 800–4000 mg/kg was carried out (Table 5). One can see that all the compounds investigated belong to the III class of danger according to the State Standard GOST 12.1.007–76 (moderately toxic substances). Esters of malonic acid with linear polyflorinated fragments with the length of carbon chain up to 5 in the sub-toxic dose (1000 mg/kg) after single action cause suppression of the respiratory centre, distortion of the coordination of movements in mice, and also disorder to the central nervous system which is expressed as a strong sedative effect. Esters of adipinic acid with a short carbon chain in doses above 1000 mg/kg cause the anaesthetic state. These neurotoxic effects get reverted to the physiological norm after 24 h. No death cases were observed during the experiment.

After the intragastric introduction of the esters of maleic acid containing linear polyfluorinated carbon chains with the length more than five in the aster part, we observed insignificant (within the first 4 h) total depression. The compounds belong to the IV class of danger (moderately toxic) (see Table 5).

EXPERIMENTAL

The purity of the fluorinated compounds under investigation was checked using ^1H and ^{19}F NMR, IR spectroscopy and gas chromatography mass spectrometry (energy of ionising electrons 70 eV) recording with the chromatograph with the mass selective detector (Hewlett Packard G 1800 A GCD) (column 30 m, 0.25 mm



R_F = $CF_3(CH_2)_5$ (**a**), HCF_2CF_2 (**b**), $H(CF_2CF_2)_2$ (**c**), $H(CFCF_2)_3$ (**d**), CF_3CHFCF_2 (**e**)

Scheme 5.

TABLE 5

Toxicological characteristics of fluorine-containing esters of dicarboxylic aliphatic acids

Compound	LD_{50}, mg/kg	LD_{100}, mg/kg	Class of danger
$CHF_2CF_2CH_2OC(O)CH_2C(O)OCH_2CF_2CHF_2$	3000	5000	III
$H(CF_2CF_2)_2CH_2OC(O)CH_2C(O)JCH_2(CF_2CF_2)_2H$	4875	5000	III
$CHF_2CF_2CH(CH_3)OC(O)(CH_2)_4C(O)OCH(CH_3CF_2CHF_2$	1667	3000	III
$CHF_2CF_2CH_2OC(O)(CH_2)_4C(O)OCH_2CF_2CHF_2$	2167	3000	III
$H(CF_2CF_2)_2CH_2OC(O)CH{=}CHC(O)OCH_2(CF_2CF_2)_2H$	4500	5500	IV
$H(CF_2CF_2)_3CH_2C(O)OCH{=}CHC(O)OCH_2(CF_2CF_2)_3H$	5000	–	IV

in diameter, coated inside with a layer of copolymer of 5 % diphenyl – 95 % dimethylsiloxane (HP-5) 0.25 μm thick, carrier gas: helium, 1 ml/min, evaporator temperature 280 °C). Column temperature was raised at a rate of 10 °C/min from 50 to 280 °C (retention time 2 and 5 min, respectively). Analysis of the reaction mixtures was carried out with LKhM 72 chromatograph (15 % SE-30, SKTF-803), QF-1, khromosorb W, column 4000 mm, diameter 4 mm).

Acute toxicity was determined for white outbred mice with a mass of 22–25 g and doses 500 to 5000 mg/kg after peroral introduction according to Cerber's method.

CONCLUSION

The data on the toxicity of several classes of compounds allowed us to conclude that these compounds belong to the III or IV class of danger (moderately or low toxic substances) and are safe for working with them in order to obtain various fluorine-containing materials, which broadens the area of their application.

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