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Abstract

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On Nitroperfluoroalkyl Nitrites

The recently discovered β-nitroperfluoroalkyl nitrites, readily obtained by nitrating fluoroolefins with nitrogen oxides and representing a new type of fluorocarbon derivatives, have proved to be stable and extremely reactive compounds.

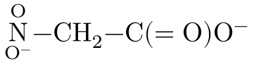
If ordinary nitroalkyl nitrites, upon interaction with water or alcohols, are converted into nitro alcohols, then nitroperfluoroalkyl nitrites, when treated with these same reagents, undergo more complex changes associated with the presence of fluorine atoms in the molecule. Upon hydrolysis, β-nitroperfluoroalkyl nitrites are converted into α-nitroperfluorocarboxylic acids, which are more robust compounds than ordinary α-nitro acids and do not decarboxylate even during distillation:

$$\mathrm{NO_2 - CF}x\mathrm{ - CF_2 - ONO + 2H_2O \rightarrow O_2N - CF}x\mathrm{ - COOH + HNO_2 + 2HF}$$

$$x = \mathrm{F},\ \mathrm{CF_3}\text{ and others.}$$

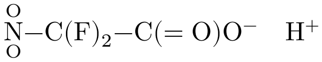
It is known that nitroacetic acid can be preserved for some time without change only under conditions of complete absence of moisture (under dry ether). Its aqueous solutions rapidly decompose with the evolution of CO_2 and the formation of nitromethane. In contrast to nitroacetic acid, difluoronitroacetic acid is a more stable compound; it can be distilled under vacuum and stored for a long time. By repeated distillation it is possible to obtain anhydrous nitrodifluoroacetic acid, which consists of transparent, colorless crystals that deliquesce in air and have a melting point of 37°.

The ease of decarboxylation of nitroacetic acid is apparently the result of fixation of the proton by the oxygen atom of the nitro group, whose electron density is considerably increased owing to the phenomenon of conjugation. The same phenomenon of conjugation is, naturally, manifested to a much lesser degree in the case of difluoronitroacetic acid because of the electron-withdrawing effect of the fluorine atoms.



$$\overset{\mathrm{O}}{\underset{\mathrm{O^-}}{\mathrm{N}}}\mathrm{-CH_2-C(=O)O^-}$$

(I)



$$\overset{O}{\underset{O}{N}}-C(F)_2-C(=O)O^- \quad H^+ \quad (II)$$

$$^-\overset{O}{O}N=CH_2+CO_2$$

Upon hydrolysis of β-nitroperfluoropropyl nitrite and β-nitroperfluoroisobutyl nitrite with a calculated amount of water, α-nitroperfluoropropionic and α-nitroperfluoroisobutyric acids, respectively, were obtained. Both acids proved to be still more stable compounds than nitrodifluoroacetic acid; they likewise distill readily at ordinary pressure.

Preparation of α-nitroperfluoropropionic acid upon hydrolysis of β-nitroperfluoropropylnitrite, and of α-nitroperfluoroisobutyric acid upon hydrolysis of β-nitroperfluoroisobutylnitrite, served as proof of the structure of the nitronitrites and of the order of addition of the nitro and nitrite groups to unsymmetrical fluoroolefins.

By means of the usual esterification reaction, α-nitroperfluoropropionic acid was converted into a series of esters. These esters can be saponified with liberation of the original α-nitroperfluoropropionic acid.

Esters of difluoronitroacetic acid are also readily obtained by the action of alcohols on its anhydride or halo anhydrides. Another important method for preparing esters—direct esterification—proved unsuitable, since in the presence of mineral acids, which serve as esterification catalysts, difluoronitroacetic acid decomposes. The most convenient method for preparing esters proved to be the direct reaction between β-nitroperfluoroethylnitrite and alcohols. Using this reaction as an example, a new method was demonstrated for preparing esters of perfluoronitrocarboxylic acids, which was then extended to other nitroperfluoroalkylnitrites. The overall reaction may be expressed by the following equation:

$$O_2NCF_2CF_2ONO + 2ROH \rightarrow RONO + O_2NCF_2{-}CO{-}OR + 2HF.$$

Apparently, in this process nitroperfluoroethylnitrite is converted successively into nitroperfluoroethyl alcohol, the fluoroanhydride, and then into an ester of difluoronitroacetic acid. In this way the methyl, ethyl, isopropyl, β-fluoroethyl, cyclohexyl, and other esters of difluoronitroacetic acid and α-nitroperfluoropropionic acid were synthesized, as well as some esters of α-nitroperfluoroisobutyric acid. The esters obtained are clear, colorless, readily mobile liquids with a characteristic odor. Their properties are given in Table 1.

Table 1

Formula of substance	B.p., °C	d_4^{20}	n_D^{20}	Analysis found, F (%)	Analysis calculated, F (%)	Analysis found, N (%)	Analysis calculated, N (%)
O_2NCF_2-COOH	80/32 mm	1.438	1.3670	21.5	22.9	7.9	8.5
$CF_3-CF(NO_2)-COOH$	119	1.638	1.3560	39.2	39.8	7.5	7.3
$(CF_3)_2C(NO_2)-COOH$	50/40 mm	–	–	40.5	42.5	–	–
$CF_3-CF(NO_2)CF_2ONO_2$	72–73	1.673	1.3130	44.2	43.2	10.8	10.5
$O_2N-CF(CF_3)-CONH_2$	154/11 mm; m.p. 118°	–	–	40	39.5	14.7	14.3
$CF_3-CF(NO_2)-COOC_2H_5$	107.5	1.412	1.3470	34.6	33.9	6.4	6.0
$O_2NCF_2-COOCH_3$	56/100 mm	1.3790	1.3567	24.5	23.8	9.0	9.7
O_2NCF_2-COCl	52	1.5080	1.3581	23.8	24.3	8.8	8.7
$(O_2NCF_2CO)_2O$	63/35 mm	1.5820	1.3590	28.8	28.6	–	–
O_2NCF_2CN	27	1.4010	1.3229	31.0	28.8	23.0	24.0
$(CF_3)_2C(NO_2)-COOC_3H_7-i$	134	1.441	1.3362	40.3	40.2	4.9	5.2
$CF_3CF(NO_2)COCl$	37	1.6591	1.3502	36.3	37.0	16.9	16.7
$CF_3CF(NO_2)CON(C_2H_5)_2$	149	1.368	1.3715	30.9	31.1	11.3	11.2
$O_2N(CF_2)_4NO_2$	111/18 mm	1.798	1.3410	51.8	50.4	9.6	8.5
$H_2NCOCF_2CF_2CONH_2$	m.p. 250	–	–	40.5	40.4	14.9	14.2

α-Nitroperfluorocarboxylic acids are polyfluoronitro-substituted carboxylic acids; the presence of strongly electronegative substituents has a pronounced effect on the properties of these substances.

Determination of the dissociation constants by the method of measuring the electrical conductivity of solutions showed that difluoronitroacetic acid is a stronger acid than trifluoroacetic acid:

$$\begin{aligned} K_{\mathrm{CNO_2CF_2COOH}} &= 97000 \cdot 10^{-5}; \\ K_{\mathrm{CCF_3COOH}} &= 50000 \cdot 10^{-5}; \\ K_{\mathrm{CCCl_3COOH}} &= 21000 \cdot 10^{-5}; \\ K_{\mathrm{CCH_3COOH}} &= 1.8 \cdot 10^{-5}. \end{aligned}$$

Thus, replacement of a fluorine atom by a nitro group almost doubles the acid’ s ability to ionize. The dissociation constant of nitroperfluoropropionic acid is $K_C = 1875 \cdot 10^{-5}$.

Using nitroperfluoroacetic acid and α-nitroperfluoropropionic acid as examples, the possibility was demonstrated of obtaining various derivatives of nitroperfluorocarboxylic acids. Thus, from nitrodifluoroacetic acid its anhydride, chloro-, bromo-, and fluoroanhydrides were obtained. By reaction of methyl ester or haloanhydrides of nitrodifluoroacetic acid with ammonia, its amide was obtained, which was then converted into the nitrile. By reaction of nitrodifluoroacetic acid with diazomethane, the corresponding ester was obtained, and by treating the acid with dry ammonia, its ammonium salt. It was shown that the acid chloride and the anhydride of nitrodifluoroacetic acid have an acylating action; with aniline and amines they form the anilide and amides. Work with nitronitrites, nitroperfluorocarboxylic acids, and their derivatives requires observance of precautions.

An attempt to obtain metallic salts of α-nitroperfluorocarboxylic acids showed their instability. For example, the silver salt of α-nitroperfluoropropionic acid undergoes destruction with formation of salts of perfluoropyruvic acid. An attempt to obtain the nitrile of nitroperfluoropropionic acid leads to formation of trifluoroacetic acid.

As already mentioned earlier (1), in the nitration of perfluorocyclobutene, along with 1,2-dinitroperfluorocyclobutane, the dinitrite of perfluorocyclobutanediol-1,2 is formed. This substance (with a boiling point of 16°) proved to be extremely reactive. Upon hydrolysis it is converted into perfluoroglutaric acid, upon treatment with ammonia—into the amide, and upon treatment with alcohol—into esters of perfluoroglutaric acid. The latter, evidently, proceeds at the expense of oxidation of the cyclobutane ring by the nitrous acid liberated.

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.

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