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Abstract

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ON A CASE OF THE MANIFESTATION OF PSEUDOHALOGEN PROPERTIES BY A TRIFLUOROMETHYL GROUP BONDED TO A CARBON ATOM

As is known, the perfluoroalkyl group has a strong electron affinity, and its influence on the character of a molecule can in many cases be compared with the influence of halogens. These properties are most noticeable in the trifluoromethyl group, which is consistent with its high electronegativity (χ_{CF_3} 2.9—3.3), which lies between the electronegativities of fluorine (χ_F 4.0) and chlorine (χ_{Cl} 3.0).

Cases in which the trifluoromethyl group behaves like a halogen are widely known in examples of perfluoroalkyl derivatives of the elements: Hg ([1–3]); Li ([4]), Mg, Zn, Cd ([5]); Si ([6]); P, As, Sb ([7,8]); S ([9]); I ([10]), etc. The most typical example is the hydrolysis of such compounds, in which the trifluoromethyl group is often quantitatively eliminated in the form of fluoroform:

$$(CF_3)_n - \ + nH_2O \rightarrow nCF_3H + \ (OH)_n.$$

Much less studied are those cases in which a perfluoroalkyl group bonded to a carbon atom possesses pseudohalogen properties. Perhaps the only reliable reaction of this kind is the haloform decomposition of perfluoroketones ([11]). However, compounds are known in which the CF_3 group, contrary to expectations, does not exhibit pseudohalogen properties, as, for example, in trifluoroacetic acid.

Because of the greater electronegativity of fluorine, compared with chlorine, the trifluoromethyl group is more electrophilic than the trichloromethyl group; however, trifluoroacetic acid is stable to heating and does not undergo haloform decomposition.

A natural explanation of this fact is the strong electron-donating action of the three fluorine atoms, far exceeding the analogous action of chlorine, as a result of which conjugation of the carbonyl group with the fluorine atoms becomes possible and the C—C bond in trifluoroacetic acid is strengthened (A).

Thus, the accumulation of strong electronegative substituents at the carbon atom in acetic acid first leads to a decrease in the strength of the C—C bond,

and subsequently to its strengthening due to "reverse polarization" of the carbonyl oxygen. This is also illustrated by the example of the unusual stability of difluoronitroacetic acid ([12]) (B).

(A) (B)

The possibility of "reverse polarization" of the carbonyl oxygen would seem to contradict generally accepted views on its reactivity; however, attempts to consider a number of reactions from this point of view may prove very fruitful. As an illustration, let us refer to the known reaction of Perkow ([13]) for obtaining vinyl esters of phosphoric acid, the mechanism of which can be interpreted as a nucleophilic attack by the free electron pair of the phosphorus atom on the positively charged oxygen atom of the carbonyl group, made electrophilic (as a result of "reverse polarization")

$$\mathrm{Cl{-}CCl_2{-}CH{=}O \cdots P(OR)_3 \longrightarrow \overline{Cl} + CCl_2{=}CH{-}O{-}P(OR)_2{=}O + \overset{+}{R}}$$

or the interaction of trichloronitrosomethane with triethyl phosphite, leading to the formation of a dichloroformoxime derivative (14)

$$\mathrm{Cl{-}CCl_2{-}N{=}O \cdots P(OR)_3 \longrightarrow \overline{Cl} + CCl_2{=}N{-}O{-}P(OR)_2{=}O + \overset{+}{R}}$$

Recently an attempt has been made to explain from the same point of view the reaction of obtaining trichlorovinylalkylamines from dialkylamides of trichloroacetic acid (15)

$$\mathrm{Cl{-}CCl_2{-}C(=O)NR_2 \cdots PR'_3 \longrightarrow \left[CCl_2{=}C(NR_2){-}O{-}\overset{+}{P}R'_3\right] \xrightarrow[-(R'_3P\to O)]{} CCl_2{=}CCl{-}NR_2}$$

In studying fluorinated β-hydroxy acids we found a new and clear example of the manifestation of pseudo-halogen properties by the trifluoromethyl group bonded to a carbon atom. During pyrolysis of the potassium salts of β,β-ditrifluoromethyl-β-hydroxypropionic acid (I) and β-trifluoromethyl-β-hydroxybutyric acid (II), elimination of the trifluoromethyl and carboxyl groups occurs, and the corresponding ketones are formed: trifluoroacetone and acetone.

$$\mathrm{CF_3{-}C(R)(OH){-}CH_2{-}COO^- \longrightarrow CF_3^- + R{-}C(OH){=}CH_2 + CO_2}$$

$$\mathrm{I\ R = CF_3;\quad II\ R = CH_3.}$$

A special investigation was devoted to determining the fate of the trifluoromethyl anion, which could either lose a fluoride ion, turning into difluorocarbene and then into tetrafluoroethylene,

$$\overline{CF_3} \rightarrow CF_2 : + \overline{F}; \qquad 2CF_2 : \rightarrow CF_2{=}CF_2,$$

or react with the acetone formed, with formation of fluoroform

$$\overline{CF_3} + RH \rightarrow CF_3H + \overline{R}.$$

It turned out that the trifluoromethyl group is converted practically quantitatively into fluoroform.

During pyrolysis of the potassium salt of hydroxy acid I, another direction of the reaction was also observed, namely, with a yield of 30%, β,β-ditrifluoromethyl-β-propiolactone (III) was obtained, the properties of which we had studied earlier (16)

$$(CF_3)_2C(OH){-}CH_2{-}COOK \longrightarrow (CF_3)_2C{-}CH_2O{-}\overset{|}{C}O + KOH$$

It was of interest also to investigate the behavior of the trifluoromethyl group in salts of β,β-ditrifluoromethylacrylic acid (IV) and β-trifluoromethylcrotonic acid (V).

During pyrolysis of the potassium salt of β,β-ditrifluoromethylacrylic acid, its acid fluoride (VI) was obtained, identified in the form of the anilide (VII)

$$(CF_3)_2C{=}CH{-}COOK \xrightarrow{200^\circ} (CF_3)_2C{=}CH{-}COF \xrightarrow{C_6H_5NH_2} (CF_3)_2C{=}CH{-}CONHC_6H_5$$

(IV) (VI) (VII)

On thermal decomposition of the potassium salt of β-trifluoromethylcrotonic acid, only trifluoroisobutylene was isolated in low yield

Table 1

Compound	Amount, g	Decomp. onset temp., °C	Reaction products	Amount, g (yield, %)	Mol. wt. found	Mol. wt. calc.	Constants	Lit. data	Analysis, % found	Analysis, % calc.	Characterized by conversion into known
$(CF_3)_2C(OH)-CH_2-COOK$*	12.78	190	CF_3COCH_3; $(CF_3)_2C(-CH_2-CO-O-)$ (lactone)	3.17 (59); 2.67 (26)			B.p. 21–25°; B.p. 90–94°, n_D^{20} 1.3244	([16]) B.p. 94.5–95°, n_D^{20} 1.3240			2,4-Dinitrophenylhydrazone; Anilide of β,β-ditrifluoromethyl-β-oxopropionic acid ([16])
$(CF_3)(CH_3)C(OH)-CH_2-COOK$	23.42	195–200	CF_3H; CH_3COCH_3	7.10 (91); [illegible] (65)	68.2	70	B.p. −81 – (−79.5°); B.p. 57–59°		C 17.14 H 1.43 F 81.41	17.14 1.43 81.42	2,4-Dinitrophenylhydrazone
$(CF_3)_2C{=}CH-COOK$	19.20	190–200	$(CF_3)_2CH{=}CH-COF$	8.6 (52)			B.p. 64–65°/752 mm, n_D^{20} 1.3010, d_4^{20} 1.5275, found MR 25.78, calc. 25.82		C 28.60 H 0.49 F 63.34	28.55 0.48 63.35	Anilide of β,β-ditrifluoromethylacrylic acid ([17])
$(CF_3)(CH_3)C{=}CH-COOK$	20.23	270	$(CF_3)(CH_3)C{=}CH_2$	2.62 (23)	110.4	110.0	B.p. 3.6–3.7°	([18]) b.p. 6.4°	C 24.30 H 0.55 F 66.30	24.23 0.50 67.19	

* Pyrolysis was carried out in vacuum.

Thus, the trifluoromethyl group bound to carbon in the second valence state is immobile, analogously to "vinylic" chlorine, which may also be regarded as a manifestation of its pseudohalogen properties.

Experimental part

Preparation of potassium salts of the acids. The salts were readily obtained by neutralizing the acids with a small excess of dry bicarbonate, followed by drying in air and recrystallization from a suitable solvent. The properties of the salts obtained are given in Table 2.

Table 2

Compound	Solvent for recrystallization	m.p., °C	Analysis, %, found	Analysis, %, calculated
I $CF_3-C(CF_3)(OH)-CH_2COOK$	Reprecipitated in the cold from ethyl acetate	182	C 22.70H 1.13F 40.93	22.681.1743.19
II $CH_3-C(CF_3)(OH)-CH_2COOK$	Same	156–160 (decomp.)		
IV $CF_3-C(CF_3)=CHCOOK$	Abs. dioxane	168		
V $CH_3-C(CF_3)=CHCOOK$	As for I	236–238	C 24.22H 0.44	24.400.41

$$CH_3-C(CF_3)=CH-COOK \xrightarrow{300^\circ} C(CF_3)(CH_3)=CH_2$$

(V) (VIII)

Thermal decomposition of salts. Pyrolysis of the dry salts was carried out by heating them in a Pyrex flask on a metal bath. The reaction products were collected in a trap cooled either to −78° or to −110° C. The gases were then distilled off from the high-boiling fraction on a Podbielniak column. The residue was fractionated on an ordinary column. Pyrolysis of the salts in vacuo was carried out in a glass apparatus with ground joints. The salt was placed in a test tube, which was then connected to a trap equipped with a stopcock for evacuating the system. Upon reaching a vacuum of 0.05 mm Hg, the stopcock was closed, the trap was cooled with liquid nitrogen, and pyrolysis was carried out.

After the reaction was complete, the products were separated as in experiment 1. The results of the pyrolysis of the salts are given in Table 1.

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

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