CHEMISTRY

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1960

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

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A NEW REARRANGEMENT OF TRIHALOACETOHYDROXAMIC ACIDS

α-Halogenated hydroxamic acids of the fatty series are little-studied compounds. Only monochloro-^(1), dichloro-^(2), monobromo-^(1), and monoiodoacetohydroxamic acids^(1) have been described. Trichloroacetohydroxamic acid has been isolated only in the form of its salt with hydroxylamine^(2). α-Fluorine-containing hydroxamic acids of the fatty series are unknown.

Fig. 1

Fluoro- and chloro-substituted acetohydroxamic acids are readily formed by the interaction of esters of the corresponding haloacetic acids with free hydroxylamine in absolute alcohol solution. In this way monofluoro-, trichloro-, fluorodichloro-, and trifluoroacetohydroxamic acids were prepared; these are colorless hygroscopic crystalline substances, readily soluble in water, alcohols, and acids, and sparingly soluble in most organic solvents.

It is interesting to note that aqueous solutions of trifluoroacetohydroxamic acid show different basicity depending on the length of their storage. This change in the basicity of dilute aqueous solutions of trifluoroacetohydroxamic acid over time is shown in Fig. 1. In this connection, one may assume the existence of a dynamic equilibrium of two tautomeric forms of trifluoroacetohydroxamic acid, with the dilute aqueous solution containing not less than 37% of the dibasic form:

$$CF_3{-}C(=O){-}NH{-}OH \rightleftarrows CF_3{-}C(OH){=}N{-}OH$$

It is known that most hydroxamic acids, as well as their salts and acyl derivatives, are characterized by a tendency toward the Lossen rearrangement, with formation of the corresponding isocyanates or products of their transformations (amines, substituted ureas, urethanes). The rearrangement of halogen-substituted acetohydroxamic acids had previously been studied only in examples of the thermal decomposition of dichloroacetohydroxamic acid and its benzoate^(2). In both cases it was not possible to isolate dichloromethyl isocyanate

or the usual products of its transformations. It was suggested^(3) that the initially formed isocyanate is converted into dichloromethylamine, which is dehydrochlorinated with liberation of hydrocyanic acid.

In this connection it could be assumed that the rearrangement of other halogen-substituted acetohydroxamic acids would also proceed according to the general type of the Lossen reaction, with possible subsequent transformation of the isocyanates.

In order to test this assumption, the thermal decomposition of trichloro- and trifluoroacetohydroxamic acids was studied. It was found that, when these compounds are heated above their melting points, vigorous decomposition occurs, and the main reaction products unexpectedly formed are trichloro- or trifluoronitrosomethane and formaldehyde:

$$CX_3—CO—NH—OH \rightarrow CX_3NO + CH_2O.$$

At the same time, the evolution of small amounts of hydrocyanic acid and carbon dioxide is observed.

The formation of nitroso compounds during the decomposition of hydroxamic acids has not been observed previously. Evidently, in the present case, owing to the peculiar distribution of electron density in the molecules of fully halogenated hydroxamic acids and in the intermediate products of their transformations, a rearrangement takes place that differs from the Lossen reaction. It may be assumed that the initial stage of this rearrangement is the formation of an "azacarbene" derivative ([4]):

$$CX_3 - C(=O) - NH - OH \rightarrow CX_3 - C(=O) - \ddot{N} : + H^+ + OH^-,$$

The generation of the latter is apparently facilitated by the acid–base dissociation of hydroxamic acids:

$$CX_3 - C(=O) - NH - OH \rightleftharpoons CX_3 - C(=O) - NH - O^- + H^+$$

$$CX_3 - C(OH) = N - OH \rightleftharpoons CX_3 - \overset{+}{C} = N - OH + \overline{OH}$$

$$CX_3 - C(=O) - NH - O^- + CX_3 - \overset{+}{C} = N - OH \longrightarrow CX_3 - C(=O) - N(H) - O - C(CX_3) = N - OH$$

Further stabilization of the "azacarbene" is effected by transfer of the trihalogenomethyl cation, with the formation of a new nitrogen–carbon bond through coordination of one of the unshared electron pairs of the nitrogen atom:

$$[X_3C] - C(=O) - \ddot{N} :\longrightarrow: C(=O) - N : -CX_3$$

The resulting bipolar ion is hydrated, and the order of addition of the elements of water is opposite to the direction of the hydration reaction of isocyanates:

$$X_3C - \dot{N} - C \equiv O + H^+ - \overline{OH} \rightarrow X_3C - N(OH) - C(=O)H.$$

The latter compound, which may be regarded as a product of condensation of trihalogenonitrosomethane with formaldehyde, undergoes thermal decomposition with formation of the final reaction products:

$$X_3C - N(O - H) - C(=O)H \longrightarrow X_3C - N = O + H - C(=O)H$$

The decomposition of trihalogenoacetohydroxamic acids, as a result of which trihalogenonitrosomethane and formaldehyde are formed, is a new type of rearrangement of hydroxamic acids.

Experimental Part

Monofluoroacetohydroxamic acid. To a freshly prepared solution of 5.0 g of hydroxylamine in 100 ml of methanol, with stirring and cooling with ice, 16.7 g of methyl fluoroacetate was slowly added dropwise. A slight evolution of heat was observed, and the reaction mixture became light yellow. After completion of the addition of the ester, stirring was continued for another 2 hours, after which the solution was evaporated in vacuo at room temperature to 1/3 of the initial volume; a white crystalline precipitate separated from the solution. The precipitate was filtered off, and the mother liquor was evaporated in vacuo to dryness. The residue, in the amount of 6.7 g, was recrystallized twice from dry ethyl acetate, giving white crystals of monofluoroacetohydroxamic acid with m.p. 75–76°. The yield was 40%.

Found, %: C 25.61; H 4.70; N 15.35; F 20.08
$C_2H_4O_2NF$. Calculated, %: C 25.83; H 4.31; N 15.06; F 20.45

Sodium salt of monofluoroacetohydroxamic acid was obtained by precipitation from a cold methanolic solution of the acid upon neutralization with a solution of sodium methylate or caustic soda in methanol.

Found, %: N 12.32; F 16.14
$C_2H_3O_2NFNa$. Calculated, %: N 12.17; F 16.52

Fluorodichloroacetohydroxamic acid. Similarly, from 4.3 g of hydroxylamine and 16.5 g of methyl fluorodichloroacetate, 10.1 g of fluorodichloroacetohydroxamic acid with m.p. 94.5–95° was obtained (from ethyl acetate). The yield was 61%.

Found, %: C 14.64; H 1.45; N 8.89; F 11.42; Cl 43.60
$C_2H_2O_2NFCl_2$. Calculated, %: C 14.81; H 1.23; N 8.66; F 11.72; Cl 43.85

Trichloroacetohydroxamic acid. Similarly, from 11.2 g of hydroxylamine and 30.0 g of methyl trichloroacetate, 25.5 g of trichloroacetohydroxamic acid with m.p. 78–79° was obtained (from a chloroform–petroleum ether mixture). The yield was 85%.

Found, %: N 8.02; Cl 59.26
$C_2H_2O_2NCl_3$. Calculated, %: N 7.85; Cl 59.62

Sodium salt of trichloroacetohydroxamic acid was obtained by precipitation from a cold methanolic solution of the acid upon neutralization with a solution of sodium methylate or caustic soda in methanol.

Found, %: N 7.14; Cl 52.70; C 12.33
$C_2HO_2NCl_3Na$. Calculated, %: N 6.99; Cl 53.06; C 11.98

The potassium salt of trichloroacetohydroxamic acid was obtained analogously.

Found, %: N 6.50
$C_2HO_2NCl_3K$. Calculated, %: N 6.57

Trifluoroacetohydroxamic acid. Similarly, from 6.4 g of hydroxylamine and 25.0 g of methyl trifluoroacetate, 19.0 g of trifluoroacetohydroxamic acid with m.p. 75–76° was obtained (from a chloroform–petroleum ether mixture), subliming upon heating to 70° in a vacuum of 15–18 mm. The yield was 76%.

Found, %: C 18.86; H 1.78; N 10.64; F 43.91
$C_2H_2O_2NF_3$. Calculated, %: C 18.61; H 1.55; N 10.86; F 44.17

Sodium salt of trifluoroacetohydroxamic acid was obtained by precipitation from a cold methanolic solution of the acid upon neutralization with a solution of sodium methylate or caustic soda in methanol.

Found, %: N 9.45; F 37.40
$C_2HO_2NF_3Na$. Calculated, %: N 9.28; F 37.75

The potassium salt of trifluoroacetohydroxamic acid was obtained analogously.

Found, %: N 8.52
$C_2HO_2NF_3K$. Calculated, %: N 8.38

Basicity of trifluoroacetohydroxamic acid. To a solution of a weighed portion of trifluoroacetohydroxamic acid (0.1–0.2 g) in 50 ml of water, after various intervals of time, 20 ml of a 0.1 N solution of caustic soda was added, and the excess of the latter was back-titrated with 0.1 N hydrochloric acid using thymolphthalein.* The amount of alkali bound, expressed in equivalents per mole of trifluoroacetohydroxamic acid, is given in Table 1.

Table 1

Duration, hours	Alkali equivalent, weighed portion 1	Alkali equivalent, weighed portion 2	Relative alkali equivalent, weighed portion 1	Relative alkali equivalent, weighed portion 2
0.17	1.20	1.20	1.38	1.36
10	1.12	1.15	1.29	1.31
24	1.04	1.06	1.20	1.21
48	0.975	0.985	1.12	1.12
96	0.92	0.915	1.06	1.04
144	0.87	0.89	1.00	1.01
240	0.87	0.88	1.00	1.00

Thermal decomposition of trichloroacetohydroxamic acid. Into a flask with a delivery tube, connected in series with a receiver cooled with ice and with a trap cooled with an acetone–carbon dioxide mixture, 8.9 g of trichloroacetohydroxamic acid was placed. The latter was carefully heated in vacuo at 20–30 mm to 90–95°. Vigorous decomposition was observed, accompanied by the evolution of gaseous and solid substances. The gaseous substances, colored blue, condensed in the trap as a blue liquid. The solid substances partially sublimed and condensed in the receiver. After the decomposition was complete, the temperature was raised to 140–150°, and heating was continued for about an hour. A resinous residue amounting to 2.1 g remained in the flask.

The condensate, amounting to 4.6 g, was fractionated, and chloronitrosomethane was isolated with b.p. 5–7°/70 mm and d_4^{20} 1.457. The yield was 62%. Molecular weight found 145.0, calculated 148.4.

Found, %: Cl 71.15
$CONCl_3$. Calculated, %: Cl 71.71

In the literature, for trichloronitrosomethane, b.p. 5°/70 mm and d 1.506 are given.

In the off-gases from the distillation of trichloronitrosomethane, hydrocyanic acid (Prussian-blue test) and carbon dioxide (baryta-water test) were detected.

The sublimate, amounting to 0.9 g, was a white amorphous substance, soluble in water, readily and completely sublimable, and was paraformaldehyde. Yield 60%.

Found, %: 1.01 iodine equivalent
CH_2O. Calculated, %: 1.00 iodine equivalent

Thermal decomposition of trifluoroacetohydroxamic acid. By heating 13.0 g of trifluoroacetohydroxamic acid in vacuo at 30–40 mm to 80–85°, trifluoronitrosomethane was similarly isolated, with b.p. from −85° to −82°. The yield was 63%. Molecular weight found 96, calculated 99.

Found, %: F 57.1
$CONF_3$. Calculated, %: F 57.6

In the literature, for trifluoronitrosomethane, b.p. −86° is given.

In the off-gases from the distillation of trifluoronitrosomethane, carbon dioxide was detected; hydrocyanic acid was detected in the residue.

The sublimate, amounting to 2.2 g, was paraformaldehyde. Yield 73%.

Received
15 II 1960

CITED LITERATURE

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* Since the strength of trifluoroacetohydroxamic acid was not determined, the indicator was chosen.

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