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Abstract

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ANALYSIS OF ORGANIC FLUORINE COMPOUNDS. SIMULTANEOUS MICRODETERMINATION OF FLUORINE AND NITROGEN IN ORGANIC COMPOUNDS

(Presented by Academician M. I. Kabachnik, 8 VII 1958)

In previously published works ([1,2]) it was established that, in the elemental analysis of organic fluorine compounds, magnesium oxide is a reliable reagent for the quantitative binding of fluorine liberated during the decomposition of organic substances. At the same time it was shown that fluorine absorbed by magnesium oxide can be quantitatively liberated from the absorbent layer in the form of HF by hydrolytic decomposition of magnesium fluoride with water vapor at high temperature ([3]). High-temperature hydrolysis, or pyrohydrolysis, proceeds according to the following scheme:

$$MeF_2 + H_2O \rightarrow MeO + HF.$$

On the basis of these facts, we considered it possible to carry out the simultaneous determination of fluorine and nitrogen from one sample by introducing magnesium oxide into the decomposition zone of the substance during the determination of nitrogen by Dumas, capturing the fluorine with magnesium oxide, and subsequently pyrohydrolyzing the magnesium fluoride obtained. For this purpose we used a modification of the microdetermination of nitrogen by Dumas, developed by M. O. Korshun and M. N. Chumachenko and intended for the analysis of difficultly combustible compounds, in which pyrolytic combustion of the sample in a layer of nickel oxide was employed.

Table 1

Combustion in a layer of pure nickel oxide

Substance	Sample, mg	F, % calculated	F, % found	F, % difference
Anilide of α-hydroperfluoroisobutyric acid $C_{10}H_7F_6NO$	7.000	42.04	39.63	−2.41
Anilide of α-hydroperfluoroisobutyric acid $C_{10}H_7F_6NO$	4.790	42.04	41.06	−0.98
Borofluoride of tri-(*m*-nitrophenyl)-oxonium $C_{18}H_{15}BF_4N_3O_7$	5.200	16.20	15.74	−0.46
1-Bromo-2-(trifluoromethyl)-1,1,3,3,3-pentafluoropropane* C_4HBrF_8	6.720	54.09	28.09	−26.00
1-Bromo-2-(trifluoromethyl)-1,1,3,3,3-pentafluoropropane* C_4HBrF_8	4.690	54.09	21.67	−32.42

* B.p. 56°.

The choice of precisely this variant was dictated by the circumstance that pyrolytic combustion according to M. O. Korshun ([4]), carried out in a quartz tube, not only ensured quantitative combustion, but also made it possible easily to replace the reagent that had absorbed the fluorine after each experiment.

The presence in the decomposition zone, in addition to magnesium oxide, also of nickel oxide could not be an obstacle to the pyrohydrolytic determination of fluorine, since nickel fluoride hydrolyzes at a lower temperature than magnesium fluoride ([5]). At the same time, nickel oxide itself at high temperatures does not retain fluorine completely. Table 1 gives the results of fluorine determinations obtained by burning the sample in a layer of pure nickel oxide. Combustion was carried out at 900° using an electric furnace 6 cm long.

Table 2

Determination of fluorine and nitrogen from one sample of 3.5–8 mg

Substance	N, % calculated	N, % found	N, % difference	F, % calculated	F, % found	F, % difference	Note
β-(p-Fluorophenyl)-β-alanine $C_9H_{10}FNO_2$	7.64	7.67 7.55	+0.03 −0.09	10.37	10.12 10.39	−0.25 +0.02	Pyrohydrolysis was carried out in a nickel tube
2,4-Dinitrophenylhydrazone of trifluoroacetone $C_9H_7F_3N_4O_4$	19.18	19.10 19.20	−0.08 +0.02	19.52	19.71 19.88	+0.19 +0.36	Pyrohydrolysis was carried out in a nickel tube
β-Trifluoromethyl-γ-piperidinotrifluoropropenylbenzene $C_{11}H_{15}F_4NO$	5.53	5.35 5.38	−0.18 −0.15	30.02	29.99 29.69	−0.03 −0.33	Pyrohydrolysis was carried out in a nickel tube
N-(α-Trifluoromethyl-β-phenyltrifluoropropenyl-1)-piperidine $C_{15}H_{15}F_6N$	4.34	4.43 4.32	+0.09 −0.02	35.29	35.66 35.60	+0.37 +0.31	Pyrohydrolysis was carried out in a nickel tube
Anilide of α-hydroperfluoroisobutyric acid $C_{10}H_7F_6NO$	5.16	5.08 5.14	−0.08 −0.02	42.04	42.14 42.24	+0.10 +0.20	Pyrohydrolysis was carried out in a nickel tube

Substance	N, % calculated	N, % found	N, % difference	F, % calculated	F, % found	F, % difference	Note
p-Toluidine salt of phenylfluorophosphinic acid $C_{13}H_{15}FNO_2P$	5.24	5.15	−0.09	5.26	+0.02	7.10	7.15	6.94	+0.05	−0.16	Pyrohydrolysis was carried out in a nickel tube
Anilide of difluorochloroacetic acid $C_8H_6ClF_2NO$	6.81	6.94	+0.13	6.84	+0.03	18.49	18.39	18.69	−0.10	+0.20	Pyrohydrolysis was carried out in a platinum tube
Borofluoride of tri-(*m*-nitrophenyl)oxonium $C_{18}H_{15}BF_4N_3O_7$	8.89	8.76	−0.13	8.82	−0.07	16.20	16.09	16.51	−0.11	+0.31	Pyrohydrolysis was carried out in a platinum tube
2,4-Dinitrophenylhydrazone-α,β,β,β-tetrafluoropropiophenone $C_{15}H_{10}F_4N_4O_4$	14.51	14.65	14.70	+0.14	+0.19	19.43	19.85	19.57	+0.42	+0.14	Pyrohydrolysis was carried out in a platinum tube

Substance	N, % calculated	N, % found	N, % difference	F, % calculated	F, % found	F, % difference	Note
Nitrile of α-hydro-β-methoxyperfluoropropionic acid *$C_4H_3F_3NO$	10.15	10.13 10.28	−0.02 +0.13	40.98	41.02 40.97	+0.04 −0.0	Pyrohydrolysis was carried out in a platinum tube
Piperidide of α-hydroperfluoroisobutyric acid $C_9H_{11}F_6NO$	5.32	5.27 5.36	−0.15 +0.04	43.31	43.19 43.09	−0.12 −0.22	Pyrohydrolysis was carried out in a platinum tube

* B.p. 106°.

For the simultaneous determination of fluorine and nitrogen, a 3-8 mg sample of the substance is placed in a quartz combustion test tube 9 cm long, covered with a granular preparation of nickel oxide containing 15-20 wt.% MgO, the test tube is inserted into a quartz combustion tube, and pyrolytic combustion is carried out at 900-950° in an atmosphere of CO_2. Samples of liquids are taken in a thick-walled quartz capillary, which is also placed in the test tube and covered with oxidant. After completion of combustion of the substance and displacement of the nitrogen into the azotometer, the contents of the quartz test tube

is poured into the tube for pyrohydrolysis proposed by N. E. Gel' man and K. I. Glazova, through which steam is passed at 1000° at a rate of 0.5 ml of condensate per minute. The duration of pyrohydrolysis is 20-25 min. Fluorine is titrated in the condensate with thorium nitrate ([6]), and nitrogen is determined from the volume collected in the azotometer. For pyrohydrolysis a platinum or nickel tube is used. When working with a nickel tube, empirical corrections are introduced for the loss of fluorine in the apparatus during pyrohydrolysis.

Nitrogen is determined with an accuracy of up to 0.2%, fluorine—up to 0.5% abs. The results of analyses of pure substances are given in Table 2.

The determination of fluorine and nitrogen from a single sample of an organic

substance has been carried out by us for the first time.

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