Chemistry

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1960

SovietRxiv

Abstract

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A New Method for the Simultaneous Determination of Silicon and Halides in Organosilicon Compounds

(Presented by Academician M. M. Shemyakin, February 15, 1960)

In earlier published works ($^{1-4}$) it was shown that a reductive method for decomposing organic substances by heating them with metallic potassium in a hermetically sealed steel microbomb is effective and rapid. The effectiveness of this method is due to the fact that at 850—900° metallic potassium, being in the vapor state, ensures complete reduction of all elements entering into the composition of the organic molecule. We have applied the indicated reductive decomposition method to organosilicon compounds for the purpose of determining silicon. It is known that when inorganic silicon compounds are fused with metallic potassium, silicon is reduced to the elemental state (^{5}), which dissolves well even in weak alkali solutions with the formation of soluble silicate.

In the present work we have shown that the above-mentioned properties of silicon can be used in the analysis of organosilicon compounds. When organosilicon compounds are fused with metallic potassium and the resulting melt is then dissolved in water, potassium silicate is formed; for its determination one can use volumetric, colorimetric, and amperometric determination methods ($^{6-8}$).

Another important advantage of this method consists in the fact that, during fusion of organic compounds containing silicon and fluorine, no volatile silicon-fluorine compounds are formed, which is characteristic of oxidative decomposition methods. Owing to this, the possibility is created for the simultaneous determination of silicon and fluorine.

A weighed portion of the substance, from 5 to 15 mg, is placed in the steel test tube of the microbomb together with 25–100 mg of metallic potassium. The bomb is hermetically sealed and heated in a furnace for 5 min at 850—900°, then cooled, and the melt is dissolved in water; the solution is quantitatively transferred to a beaker made of organic glass and placed for 10–15 min on a boiling water bath. After cooling, the solution is transferred to a volumetric flask made of alkali-resistant glass, filtered from carbon, and after this aliquot samples are taken for the determination of silicon.

Colorimetric determination of silicon. 10–25 ml of the solution is placed in a 50-ml flask, water is added to 35 ml, then 1 ml of $5\,N\ H_2SO_4$ and 3 ml of a 5% ammonium molybdate solution are added. The solution is mixed and left for 10 min. Then 4 ml of 8 N H_2SO_4 is added to the flask in small portions. It is diluted with water to 45 ml and a drop of 30% $SnCl_2$ solution is added. The solution in the flask is brought to the mark with water, mixed, and after 5 min the intensity of the color is measured. The amount of silicon in milligrams is determined graphically.

Amperometric titration. 5–25 ml of the solution is placed in the cell and the volume is brought to 50 ml with 0.1 N KNO_3 solution. Iz-

measurements are carried out under a continuous stream of nitrogen. A solution of $Pb(NO_3)_2$ is gradually added from a burette and, after 1.5-2 min, the galvanometer readings are recorded. The voltage is 1.5 V. The equivalence point (e.p.) is determined graphically (Fig. 1). The results of analyses of pure substances obtained by the colorimetric and amperometric methods are given in Table 1.

Amperometric determination of silicon is based on the interaction of soluble silicates with fluorides in the presence of a definite amount of HCl, with formation of potassium silicofluoride K_2SiF_6 (^{6}, ^{9}, ^{10}). The results of analyses are given in Table 2.

Simultaneous determination of silicon and halogens. The melt solution is brought to a definite volume and subjected to determination in the form of aliquot portions, which makes it possible to determine several elements from a single sample. In the present case we simultaneously determined silicon and halogens.

Fig. 1

Table 1

Colorimetric and amperometric determinations of silicon

Substance	Calculated Si, %	Colorimetric determination of Si, % found	Colorimetric determination of Si, % difference	Amperometric titration of Si, % found	Amperometric titration of Si, % difference
Diethylsilanediol $C_4H_{12}OSi$	23.35	23.37	+0.02	23.29	−0.06
Diethylsilanediol $C_4H_{12}OSi$	23.35	23.07	−0.28	23.11	−0.24
Triphenylethylsilane $C_{20}H_{20}Si$	8.67	8.50	−0.17	8.60	−0.07
Triphenylethylsilane $C_{20}H_{20}Si$	8.67	8.87	+0.20	8.52	−0.15
Trimethylbutylsilane $C_7H_{18}Si$	21.73	21.50	−0.23	21.67	−0.06
Trimethylbutylsilane $C_7H_{18}Si$	21.73	21.32	−0.41	21.68	−0.05
Tetraethylsilane $C_8H_{20}Si$	19.44	19.57	+0.13	19.33	−0.11
Tetraethylsilane $C_8H_{20}Si$	19.44	19.23	−0.21	19.35	−0.09
1,4-di-(trimethylsilyl)benzene $C_{12}H_{22}Si_2$	25.22	24.50	+0.28	25.20	−0.02

Substance	Calculated Si, %	Colorimetric determination of Si, % found	Colorimetric determination of Si, % difference	Amperometric titration of Si, % found	Amperometric titration of Si, % difference
1,4-di-(trimethylsilyl)benzene $C_{12}H_{22}Si_2$	25.22	25.01	−0.21	25.20	−0.02

Table 2

Substance	Sample, mg	Si, % calculated	Si, % found	Si, % difference
Octamethyltetracyclosiloxane $C_8H_{24}O_4Si_4$	11.120	37.80	37.58	−0.22
Octamethyltetracyclosiloxane $C_8H_{24}O_4Si_4$	8.964	37.80	37.62	−0.18
Hexamethyldiphenyltetracyclosiloxane $C_{18}H_{22}O_4Si_4$	18.615	26.66	26.82	+0.16
Hexamethyldiphenyltetracyclosiloxane $C_{18}H_{22}O_4Si_4$	13.521	26.66	26.61	−0.05
Tetraethyldiphenylsiloxytitanium $C_{40}H_{60}O_4Si_4Ti$	7.670	14.68	14.54	−0.14
Tetraethyldiphenylsiloxytitanium $C_{40}H_{60}O_4Si_4Ti$	8.722	14.68	14.71	+0.03
Trimethylhexylsilane $C_9H_{22}Si$	14.520	17.73	17.70	−0.03
Trimethylhexylsilane $C_9H_{22}Si$	8.870	17.73	17.62	−0.11

In one aliquot portion the determination of silicon was carried out by any of the methods indicated above, and in another—the determination of chlorine, bromine, iodine, and fluorine; Cl and Br were determined mercurimetrically, I iodometrically ([1], [2]), and F thorimetrically ([3]). The experimental results are presented in Table 3.

Table 3

Simultaneous determination of silicon and halides

Substance	Silicon, % calculated	Silicon, % found	Silicon, % difference	Halide, % calculated	Halide, % found	Halide, % difference
Methylethyldichlorosilane $C_3H_8Cl_2Si$	19.58	19.60 19.57	+0.02 −0.01	49.48	49.53 49.40	+0.05 −0.08
1,5-Hexamethyl-2,3,4-trichlorophenyl-2,3,4-trimethylpentasiloxane $C_{27}H_{39}O_4Cl_3Si_5$	20.82	20.85 20.76	+0.03 −0.06	15.76	15.70 15.60	−0.06 −0.16
Bis-iodomethyltetramethyldisiloxane $C_6H_{16}O_2Si$	13.55	13.65 13.60	+0.10 +0.05	61.29	61.45 61.55	+0.14 +0.26

Substance	Silicon, % calculated	Silicon, % found	Silicon, % difference	Halide, % calculated	Halide, % found	Halide, % difference
Diethylsilanedichl + bromobenzoic acid	23.35	23.40 23.45	+0.05 +0.10	39.76	39.70 39.65	−0.06 −0.11
Diethylsilanedichl + Teflon	23.35	23.35 23.44	0.00 +0.09	76.00	76.20 75.90	+0.20 −0.10

We also analyzed γ-(α,α,β-trifluoro-β-chloroethoxy)-propylmethyldichlorosilane. From a single sample, the percentage contents of Si, F, and Cl were determined.

Found, %: Si 9.73; 9.73; F 19.75; 19.99; Cl 36.73; 36.72
Calculated, %: Si 9.69; F 19.68; Cl 36.74

Thus, a new method has been developed for determining silicon, based on the reductive decomposition of organosilicon substances with metallic potassium. It has been shown that the silicon contained in organic substances, after their decomposition with metallic potassium in a hermetically sealed bomb at 850–900° and dissolution of the melt in water, is quantitatively converted into soluble silicate K_2SiO_3. Amperometric titration has been applied in determining silicon in organic compounds. The possibility has been established of the simultaneous determination of Si and halides, including fluorine, with an accuracy of determination for silicon of $±$0.2% by the amperometric method, $±$0.5% by the colorimetric method, $±$0.3% by the volumetric method, and $±$0.3% for halides.

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Received
13 II 1960

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