A Simple Digestion Method for the Quantitative Analysis of Metal in Some Organometallic Compounds[*]

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Metal in organometallic compound can be quantitatively determined as metallic oxide by either the combustion method or the digestion method. Since the latter procedure is simpler than the former, the digestion method has been extensively applied in various ways through the years by many workers[1]. In this digestion, generally, the complete decomposition of organometallic compounds can be achieved by treatment with concentrated sulfuric acid alone or with an accompanying oxidizing agent, such as nitric acid, perchloric acid and hydrogen peroxide.

In a preceding paper[2], the present author has proposed an analytical method in which organosilicon compounds were completely decomposed in a mixture of concentrated sulfuric acid and perchloric acid, silica being left. However, this method was unsuitable for the determination of tin in organotin compounds, since lower analytical values were

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[*] Added in proof: This study was presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

[1] Cf. R. W. Leeper, L. Summers and H. Gilman, *Chem. Revs.*, **54**, 158 (1954); T. W. Campbell, H. G. Walker and G. M. Coppineer, ibid., **50**, 282 (1952); C. A. Burkhard, E. G. Rochow, H. S. Booth and J. Hartt, ibid., **41**, 138 (1947); R. K. Ingham, S. D. Rosenberg and H. Gilman, ibid., **60**, 519 (1960).

[2] S. Kohama and S. Fukukawa, *Sci. and Ind.* (*Kagaku to Kogyo*), **32**, 113 (1958).

TABLE I. CHANGES OF TRIBENZYLTIN CHLORIDE IN VARIOUS REAGENT MIXTURES
Sample 0.5 g. Temp. 150～200°C

No.	Reagent solution		Observation
	Conc. H_2SO_4 cc.	Oxidizing reagent	
1	5	None	Required long time for digestion
2	—	Fuming HNO_3 $5^{cc.}$ alone	Difficult to dissolve and carbonize
3	5	Fuming HNO_3 $2^{cc.}$	By adding HNO_3, separation of sample and then carbonization occured
4	5	Conc. $HClO_4$ $2^{cc.}$	Volatilization of tin chloride
5	—	Conc. $HClO_4$ $2^{cc.}$ + Fuming HNO_3 $2^{cc.}$	Vigorous oxidation and frequent explosion
6	5	NH_4NO_3 crystal 1.4 g.	Moderate and complete Decomposition

TABLE II. RESULTS OF ANALYSIS
Sample 100～200 mg. Conc. H_2SO_4 $3^{cc.}$

Compound	NH_4NO_3 g.	Metal Calcd. %	Metal Found %	Daviation %
$(C_4H_9)_3SnCl$	0.8	36.46	36.42	−0.10
$(C_4H_9)_2SnCl_2$	0.8	39.06	38.98	−0.20
$(C_8H_{17})_2SnCl_2$	1.0	28.52	28.50	−0.07
$(C_8H_{17})_2SnO$	1.0	32.86	32.86	±0.00
$(C_6H_5CH_2)_3SnCl$	1.0	27.76	27.75	−0.03
$(C_6H_5CH_2)_2SnCl_2$	1.0	31.92	31.86	−0.19
$(C_6H_5)_3SnOOCCH_3$	1.0	29.02	29.23	+0.72
$(C_6H_5)_4Sn$	1.0	27.79	27.67	−0.43
$(i\text{-}C_3H_7O)_4Ti$	0.4	16.85	16.79	−0.36
$(n\text{-}C_4H_9O)_4Ti$	0.4	14.07	14.05	−0.14
$(C_6H_5)_2SiCl_2$	0.8	11.08	11.02	−0.54
$(C_6H_5)_2Si(OOCCH_3)_2$	0.8	9.35	9.39	+0.43
$C_6H_5Si(OOCCH_3)_3$	0.8	0.95	10.01	+0.60
$(C_6H_5)_2Si(OC_2H_5)_2$	0.8	10.31	10.34	+0.29
$C_6H_5Si(OCH_2CH{=}CH_2)_3$	0.6	10.16	10.20	+0.39
$(CH_3)_3SiOC_3H_7{}^i$	0.6	21.24	21.23	−0.04
$(CH_3)_2Si(OC_3H_7{}^i)_2$	0.6	15.93	15.88	−0.31
$CH_3C_2H_5Si(OH)_2$	0.6	26.45	26.28	−0.64
$CH_3(CH_2{=}CH)Si(OH)_2$	0.6	26.96	26.88	−0.29
$CH_3(C_6H_5CH_2)Si(OH)_2$	0.8	16.69	16.65	−0.24
$(C_6H_5)_2Si(OH)_2$	0.8	12.99	12.93	−0.46
$(CH_3)_2(p\text{-}ClC_6H_4)SiOH$	0.8	15.04	15.06	+0.13
$((CH_3)_2SiO)_4$	0.8	37.87	38.05	+0.48
$((C_6H_5)_2SiO)_3$	1.0	14.16	14.27	+0.78
$((C_6H_5)_2SiO)_4$	1.0	14.16	14.11	−0.35
$(p\text{-}BrC_6H_4)_2Si(CH_3)_2$	1.0	7.58	7.61	+0.33
$1,4\text{-}(CH_3)_3SiC_6H_4Si(CH_3)_3$	1.0	12.62	12.57	−0.39

always obtained because of the volatilization of some tin compounds.

For the quantitative analysis of tin in organotin compounds, a procedure[3] has recently been recommended in which the tin compound was first converted into less volatile bromide with bromine in carbon tetrachloride and then digested by the usual way; however, this method disadvantageously requires a long time (about six hours) for a run of analysis.

In order to select a suitable oxidizing agent for tribenzyltin chloride, which is known to be difficult to decompose, digestions were carried out in concentrated sulfuric acid with the usual oxidizing reagents and with ammonium nitrate. The results are shown in Table I.

It is found that ammonium nitrate is superior to other oxidizing reagents in digesting the tin compound. Hence, the author carried out

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[3] H. Gilman and W. B. King, *J. Am. Chem. Soc.*, **51**, 1213 (1929).

the quantitative estimation of the metal in some organometallic compounds, using ammonium nitrate as an oxidizing reagent. The results on a number of organosilicon compounds, organotin compounds and organotitanium compounds are indicated in Table II; it has thus been found that almost all of the metal in these compounds could be determined accurately.

The values given in Table II are the average of three determinations in most cases.

Thus, the method seems to be a convenient procedure for the determination of the metal in various organometallic compounds. By using ammonium nitrate as a reagent, the loss of the metal salt owing to the volatilization can be completely avoided. There are two further advantages as well; solid ammonium nitrate dissolves uniformly in the solution without forming a separate phase, as in the case of liquid oxidizing agents, and the colorless solution can be obtained by about 30 min. of heating, without any spattering of the sample.

Experimental

All the reagents used were of analytical grade. The organometallic compounds subjected to the tests were partly commercial products and partly compounds which had been synthesized in this Institute. Most of them were further purified according to the methods of the literature.

The Observation of Changes of Tribenzyltin Chloride in Digesting a Solution Containing Perchloric Acid.—A small amount of tribenzyltin chloride was placed in concentrated sulfuric acid containing perchloric acid and then heated to 150～200°C for 5 min., at which time a vigorous reaction started, accompanied with white vapor; this vapor was then passed into dilute aqueous ammonia through a delivery tube. The white precipitate formed in the absorbing solution was identified as tin oxide after ignition.

Analytical Procedure.—About 0.2 g. of a sample is placed in previously-weighed platinum crucible (40 ml.). Then 3 ml. of concentrated sulfuric acid is added, and the mixture is carefully warmed to dissolve the sample. After the mixture has then been cooled somewhat, a spoonful of crystalline ammonium nitrate (about 0.2 g.) is added, with gentle shaking. Gradual oxidation begins as the crystal dissolves into the solution, and the mixture is kept standing for 5 min. In many cases, the content is not yet decolorized, and another spoonful of ammonium nitrate is added, the mixture is then heated carefully so as to avoid spattering. When the mixture is difficult to decolorized, the above procedure is repeated until a colorless solution is obtained. The maximum weight of ammonium nitrate required for the completion of the reaction is about one gram. The contents of the platinum crucible are heated moderately during evaporation and finally ignited intensively until the constant weight of the metallic oxide is attained. The metal is weighed as metallic oxide. The whole procedure takes about 50 min.

Summary

A new, modified digestion method for the quantitative analysis of metal in various organometallic compounds containing silicon, tin and titanium has been developed by the use of ammonium nitrate as a new oxidizing reagent. It has been shown that this method can be carried out more rapidly and more accurately than the other known methods.

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