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Thermal decomposition of silver hexacyanoferrates(II) and its analytical application

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Abstract

The reaction of thermal decomposition of $Ag_4[Fe(CN)_6]$ has been established on the basis of thermal and X-ray analyses of the solid decomposition products and chemical analysis of gaseous products. It has been found out that on the basis of the loss in mass of silver hexacyanoferrate(II) at 400°C it is possible to determine $Fe(CN)_6^-$ ions in the presence of Cl^-, Br^- or I^-, whose silver salts do not decompose at this temperature.

INTRODUCTION

Thermal decomposition of $Ag_4[Fe(CN)_6]$ was examined by Duval [1], who, using the thermogravimetric curve, found that the compound decomposes over the temperature range 229–812°C. As a result of the decomposition, a mixture of iron and silver oxides is formed. Duval did not present the decomposition reaction or the composition of solid and gaseous decomposition products. The purpose of the present work is to establish the reaction of $Ag_4[Fe(CN)_6]$ decomposition and to examine the possibilities of analytical application of this reaction. Thermal decomposition of silver hexacyanoferrate(II) may be used for determination of $Fe(CN)_6^{4-}$ ions in the presence of halide ions, and for simultaneous determination of $Fe(CN)_6^{4-}$ and Cl^-, $Fe(CN)_6^{4-}$ and Br^-, or $Fe(CN)_6^{4-}$ and I^-.

EXPERIMENTAL

Apparatus

Thermal analysis was carried out using a MOM OD-102/1500°C thermal analyzer (MOM, Budapest, Hungary). The measurements were made in air in the temperature range 20–1000°C at a heating rate of 5°C min^{-1}. The sensitivity of the galvanometers for DTA and DTG curves was 1/5. The

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TG sensitivity was 200 mg. The mass of the sample was 100 mg. α-Al_2O_3 was used as reference material.

The X-ray analysis of sinters was carried out with a DRON-1 X-ray diffractometer (St. Petersburg, Russian Federation) using Cu Kα radiation filtered through a nickel filter. The intensity of the reflections was measured with an SRS-1-0 scintillation counter (St. Petersburg, Russian Federation) for 2θ angles from 2 to 70°.

Thermal decomposition with absorption of gaseous products was made with an assembly composed of electric furnace, programmer for linear temperature increase, absorption tubes and membrane pump.

Reagents

The following solutions were used: potassium hexacyanoferrate(II), 0.05 mol l^{-1}; sodium chloride, 0.1 mol l^{-1}; sodium bromide, 0.05 mol l^{-1}; potassium iodide, 0.05 mol l^{-1}; silver nitrate, 0.1 mol l^{-1}; nitric acid, 2 mol l^{-1}. Chemicals were of analytical grade, produced by Polskie Odozynniki Chemiorne (P.O.Ch), Gliwice, Poland, and were used without further purification.

Thermal analysis

Thermal curves of silver hexacyanoferrate(II) are presented in Fig. 1. The DTA and TG curves show that the decomposition of $Ag_4[Fe(CN)_6]$ begins at 220°C and proceeds in two stages. The first stage corresponds with the first, very intense exothermic peak at 310°C, and the second is related

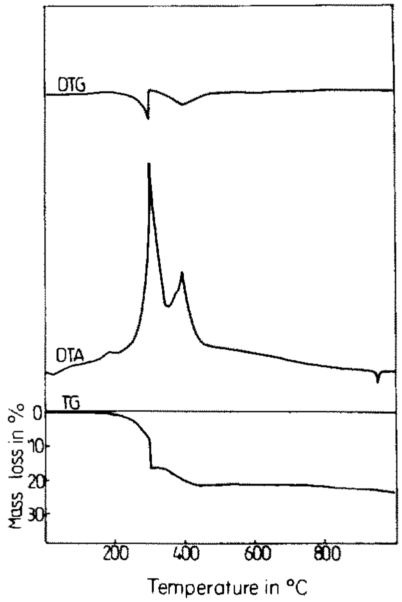

Fig. 1. Thermal analysis curves of $Ag_4[Fe(CN)_6]$.

TABLE 1

Diffractometric identification of compounds in the sinter obtained by heating $Ag_4[Fe(CN)_6]$ at 450°C.

X-ray data		Literature data	
2θ in deg	d/n in Å	d/n in Å	Compound
33.25	2.69	2.69	Fe_2O_3
34.40	2.61	unidentified	
35.75	2.51	2.51	Fe_2O_3
38.15	2.36	2.36	
41.70	2.17	Unidentified	
44.40	2.04	2.04	Ag
49.50	1.84	1.84	Fe_2O_3
64.55	1.44	1.44	Ag

to the exothermic peak at 400°C. The first exothermic peak is connected with a rapid loss in mass, whereas the rate of mass loss in the second stage is distinctly slower. The first stage ends at 340°C, and the second at about 450°C. In the thermal curves obtained under different conditions (lower DTA sensitivity, 1/15; larger sample, 200 mg), the first exothermic peak is split into several peaks which are close to each other (270, 300, 330°C), but the temperature at which these changes end is similar (350°C) to the temperature at which the first stage of decomposition terminates (Fig. 1). The further run of the curves is similar.

To establish the reaction of thermal decomposition at 400°C, sinters were prepared at 450°C and analyzed by X-ray diffractometry (Table 1). The released carbon dioxide was also determined by absorption on ascarite while oxygen or air was let through the apparatus used for thermal decomposition. The acount of carbon dioxide released and absorbed in oxygen atmosphere was 40.0% (the amount calculated according to eqn. (1) was 41.04%). The loss in mass determined on the basis of the TG curve was 21.0%, and the loss in the mass of singers prepared at 450°C was 20.10%, whereas the loss in mass calculated according to eqn. (1) was 20.06%. The above results indicate the following reaction in oxygen:

$$2Ag_4[Fe(CN)_6] + 13.5O_2 \rightarrow 8Ag + Fe_2O_3 + 12CO_2 \quad (1)$$

The results of determination of carbion dioxide in air indicate incomplete oxidation of carbon to carbon dioxide. The following equation illustrates the decomposition reaction:

$$2Ag_4[Fe(CN)_6] + 11O_2 \rightarrow 8Ag + Fe_2O_3 + 10CO_2 + 2CO \quad (2)$$

The calculated amount of CO_2 is 34.20%, and the determined amount is 34.85%. The loss in mass in the same for both equations.

Determination of hexacyanoferrates(II) in the presence of chlorides, bromides and iodides

The principle of the method consists in precipitating the silver salts, drying the precipitate at 110°C and weighing it (initial mass), then heating it to 400°C and weighing again (final mass). On the basis of percentage of mass loss at 400°C, and the mass loss of the reference sample which contained only $Ag_4[Fe(CN)_6]$ precipitated and heated under the same conditions as the examined samples, the percentage of $Ag_4[Fe(CN)_6]$ in the precipitate was determined.

Performance of the determination

The solution containing hexacyanoferrate(II) and chlorides, bromides or iodides was diluted to 100 ml, 10 ml of HNO_3 solution were added, and $AgNO_3$ solution was gradually added at room temperature, the mixture being stirred. The precipitate was filtered through a G4 Schott crucible, washed with sold water, dried at 110°C and weighed, then heated in an electric furnace to 400°C and kept at this temperature for 0.5 h. The result is calculated on the basis of the initial mass of the precipitate (110°C), the loss in its mass at 400°C, and the loss in the mass of the reference sample $Ag_4[Fe(CN)_6]$.

The results of determination of Fe(CNr4 – 6 in the presence of Cl^-, Br^- or I^- are listed in Table 2.

TABLE 2

Results of determination of hexacyanoferrates(II) in the presence of chlorides, bromides and iodides.

$Fe(CN)_6^{4-}$/mg		Difference/%	Content of anions/mg		
Calc.	Found		Cl^-	Br^-	I^-
15.31	15.53	+1.5	21.2	20.0	31.7
30.62	31.00	+1.3	21.2	40.0	63.4
45.93	45.03	−2.0	21.2	20.0	31.7
61.26	60.61	−1.1	21.2	20.0	31.7
30.62	30.24	−1.3	42.4	20.0	63.4
61.26	61.87	+1.0	42.4	40.0	63.4

Simultaneous determination of hexacyanoferrates(II) and iodides

The possibilities of applying thermal decomposition of silver hexacyanoferrate(II) for developing methods of determination of $Fe(CN)_6^{4-}$ and Cl^-, $Fe(CN)_6^{4-}$ and Br^- and $Fe(CN)_6^{4-}$ and I^- were examined. The

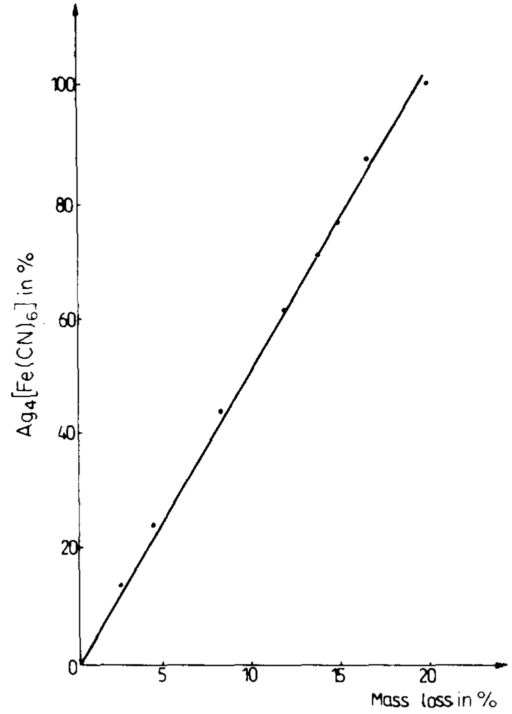

Fig. 2. Curve of the mass loss of the precipitate composed of $Ag_4[Fe(CN)_6]$ and AgI at 500°C.

precipitates were obtained by a method similar to the one previously described, and their composition was established on the basis of the loss in their mass and the analytical curve.

The mass loss for the precipitate of $Ag_4[Fe(Cn)_6]$ and AgCl, $Ag_4[Fe(Cn)_6]$

TABLE 3

Results of the determination of hexacyanoferrates(II) and iodides by the thermogravimetric method.

Calc./mg		Mass loss/%	Content of $Ag_4[Fe(CN)_6]$/%	Found/mg		Difference/mg	
$Fe(CN)_6^{4-}$	I^-			$Fe(CN)_6^{4-}$	I^-	$Fe(CN)_6^{4-}$	I^-
5.92	63.60	2.70	13.46	6.01	63.45	+1.5	−0.2
11.83	63.60	4.59	22.88	11.65	64.43	−1.5	+1.6
29.58	63.60	8.57	42.72	29.23	64.32	−1.2	+1.1
59.15	63.60	12.20	60.82	59.09	62.48	−0.1	−1.8
88.73	63.60	14.10	70.29	89.77	62.26	+1.2	−2.1
59.15	31.80	15.00	74.78	58.60	32.43	−1.0	+2.0
118.30	63.60	15.28	76.17	119.90	62.40	−1.3	−1.9
118.30	31.80	17.10	85.24	117.30	32.54	−0.9	+2.3

and AgBr was determined at 400°C, whereas for $Ag_4[Fe(CN)_6]$ and AgI the loss in mass was measured at 500°C. The analytical curve of the loss in mass was prepared by obtaining precipitates from standard solutions and determining the dependence of the percentage of $Ag_4[Fe(CN)_6]$ in the precipitate upon the loss of mass at 400 or 500°C. Figure 2 presents the curve of the loss in mass for $Ag_4[Fe(CN)_6]$–AgI. The precipitate composed of $Ag_4[Fe(CN)_6]$ and AgI was heated at 500°C for several minutes. The results obtained for this system were the best as regards repeatability. They are presented in Table 3.

DISCUSSION

The reaction of thermal decomposition of silver hexacyanoferrate(II) occurs at a relatively low temperature (450°C) and as a result, apart from gaseous products, only two solid products (ferric oxide and silver) are formed. This indicates that this reaction can be used in chemical analysis to determine $Fe(CN)_6^{4-}$ ions in the presence of halide ions which form silver salts with much higher breakdown temperature. The present work shows that by thermal decomposition of $Ag_4[Fe(CN)_6]$, it is possible to determine hexacyanoferrates in the presence of chlorides, bromides and iodides, and that it is possible to determine $Fe(CN)_6^{4-}$ and I^- simultaneously.

The developed method for simultaneous determination of hexacyanoferrates(II) and iodides is very simple, although it relates to ions of similar properties. Iodides and hexacyanoferrates(II) usually react in a similar way in the course of precipitation and oxidation. The precipitates obtained exhibit similar solubility, e.g. AgI and $Ag_4[Fe(CN)_6]$ are not soluble in ammonia. This renders the application of the method of separation used for $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ impossible, since the method is based on the different solubility of silver salts of these ions in ammonia [2].

The present method involves thermal decomposition of $Ag_4[Fe(CN)_6]$ at 500°C. As it was developed on the basis of thermogravimetric curves and the loss in mass determined, it is referred to as a thermogravimetric method, although it does not consist of registration of mass depending on temperature or time.

The curve of the mass losses (Fig. 2) is of straight line character over a wide range of $Ag_4[Fe(CN)_6]$ percentage content in precipitates consisting of $Ag_4[Fe(CN)_6]$ and AgI. This fact, and the determination results (Table 3), indicate that it is possible to determine both large and small amounts of $Fe(CN)_6^{4-}$ in the presence of large amounts of iodides. Iodides can be determined if they occur in considerable amounts, because otherwise a slight error in determination of $Fe(CN)_6^{4-}$ will greatly affect the results of determination of iodides. The mass ratio of iodides to hexacyanoferrates(II) should not be less than 1:4.

According to Duval [1], silver bromide is stable up to 950°C, and silver chloride up to 600°C. Silver iodide exhibits stability similar to that of silver bromide (up to 900°C). However, the comparison of results of determination of $Fe(CN)_6^{4-}$ and Cl^- or Br^- with those of determination of $Fe(CN)_6^{4-}$ and I^- proves that the latter results are more precise. The $Ag_4[Fe(CN)_6]$–AgI system exhibits highest thermal stability, and at 500°C the decomposition of AgI present in the precipitate consisting of hexacyanoferrate(II) and silver iodide is not observed. In precipitates composed of $Ag_4[Fe(CN)_6]$ and AgCl or of $Ag_4[Fe(CN)_6]$ and AgBr, cases were observed in which, apart from hexacyanoferrate(II), silver chloride or bromide were partly decomposed at 500°C. This was indicated by the loss in the mass of the precipitate higher than that resulting from $Ag_4[Fe(CN)_6]$ content. Therefore the decomposition is carried out at a lower temperature, i.e. at 400°C. This temperature is sufficient to decompose silver hexacyanoferrate(II) because the presence of silver chloride or bromide reduces the breakdown temperature, and because at 400°C the precipitate is heated for a longer time than at 500°C. For $Ag_4[Fe(CN)_6]$–AgCl and $Ag_4[Fe(CN)_6]$–AgBr the curves of mass losses at 400°C are also of straight line character, which implies that it is possible to determine hexacyanoferrates and chlorides and hexacyanoferrates and bromides. However, these systems require further study. Our work demonstrates that the $Ag_4[Fe(CN)_6]$–AgI system is most suitable to perform thermogravimetric methodological analyses. Methodological analysis are meant here as different ways of determining in the precipitate the content of a compound which undergoes thermal decomposition in the presence of a thermally stable compound under the given conditions.

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