Thermochimica Acta, 99 (1986) 139–143
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

# SILVER TELLURITES AND THEIR THERMAL DISSOCIATION

G.G. GOSPODINOV and T.S. TODOROV

*Department of Inorganic Chemistry, Higher Institute of Chemical Technology, Bourgas 8010 (Bulgaria)*

(Received 23 August 1985)

## ABSTRACT

In order to elucidate possible tellurites, the three-component system $AgNO_3$–$Na_2TeO_3$–$H_2O$ was studied at 25 and 100°C by the method of residual solubility and through the pH of solutions. Crystallographic data were adduced. The thermal stability of the $Ag_2TeO_3$ obtained was studied.

## INTRODUCTION

Investigations of silver tellurites are scarce and limited to the synthesis of silver tellurite by precipitation of $AgNO_3$ and sodium tellurite in stoichiometric quantities or with a slight excess of $Na_2TeO_3$ [1–4]. Data concerning the composition and type of precipitate are contradictory. According to refs. 1–3, the tellurite obtained is $Ag_2TeO_3$, and according to ref. 4, it is $Ag_2TeO_3 \cdot 6H_2O$.

The colour of the precipitate differs, depending on the ratio between the solutions mixed together. When $AgNO_3$ is in excess of the stoichiometric amount, a light-yellow precipitate is obtained, and when there is a shortage of it, the precipitate is white. According to ref. 2, if precipitation is done without excess $Na_2TeO_3$, the precipitate is light-yellow and in two or three weeks becomes dark-blue, due to decomposition of adsorbed $AgNO_3$.

According to ref. 4 the colour of the precipitate does not depend on the order in which the solutions are mixed (a solution of $AgNO_3$ with $Na_2TeO_3$ or vice versa). In both cases a yellow flocculant precipitate is formed and, when dried at 90–100°C, it becomes grey and then dark-blue.

The present study aims to clarify this contradiction in the literature concerning silver tellurites and to find tellurites of different composition and study their thermal stability.

0040-6031/86/$03.50 © 1986 Elsevier Science Publishers B.V.

## EXPERIMENTAL

In order to determine the concentration interval in which silver tellurite exists and establish tellurites of different composition, the system $AgNO_3$–$Na_2TeO_3$–$H_2O$ was studied at 25 and 100°C. The initial substances were analytical grade $AgNO_3$ and $Na_2TeO_3 \cdot 5H_2O$. The samples were thermostatted at 25°C in glass thermostatting vessels, continuously circulating water being introduced from an ultrathermostat (U-10). The required amounts of $AgNO_3$ and $Na_2TeO_3 \cdot 5H_2O$ were dissolved separately in a 50-ml measuring bottle and were put together in the bottles for thermostatting. They were stirred continuously with a magnetic stirrer. The $Na_2TeO_3/AgNO_3$ mole ratio were: $n = 0.2$, 0.5, 1, 2 and 3. The system $AgNO_3$–$NaTeO_3$–$H_2O$ was studied at 100°C by mixing aqueous solutions of $Na_2TeO_3$ and $AgNO_3$ (50 ml each) in glass ampoules, the $Na_2TeO_3/AgNO_3$ mole ratios being: $n = 0.25$–10. Then the ampoules were sealed and thermostatted at $100 \mp 1$°C for 3 months. The solid phase was separated from the liquid phase by filtration with a G-3 filter.

Both at 25 and 100°C the liquid and solid phases, after being separated, were subjected to chemical analysis. The solid phases were further subjected to X-ray and thermal analyses. pH measurements of the equilibrium mother solutions were conducted with a laboratory digital LP-17-type pH-meter. X-ray and X-ray phase analyses were accomplished on a DRON-2 apparatus using $CuK_\alpha$ emission and a nickel filter for the $\beta$-emission. Chemical analysis for the concentration of $Ag^+$ was made argentometrically [5], and $TeO_3^{2-}$ was determined gravimetrically as elementary tellurium [6]. The thermal stability of the system was studied using an OD-102-type derivato-

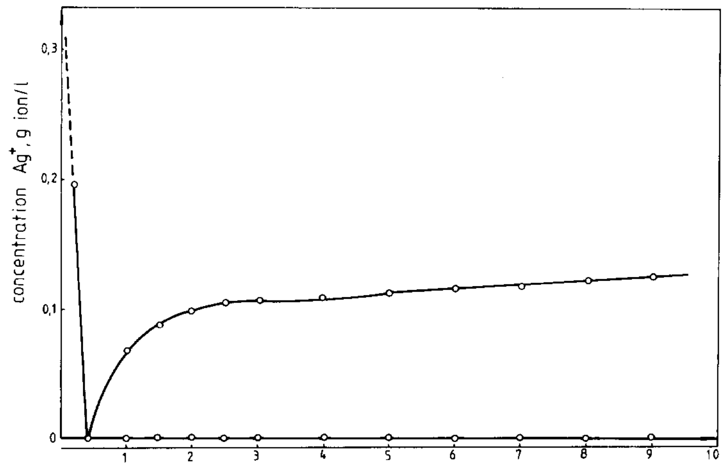

Fig. 1. Solubility isotherm of the system $AgNO_3$–$Na_2TeO_3$–$H_2O$ at 100°C.

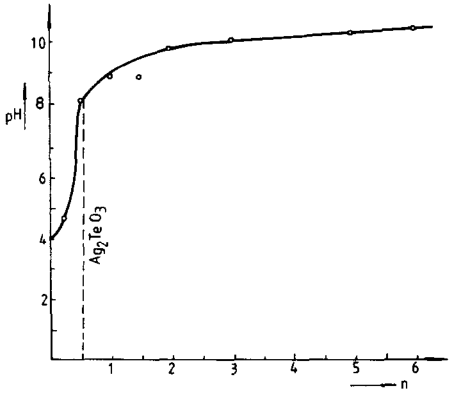

Fig. 2. Dependence of pH of equilibrium solution on the mole ratio $n = Na_2TeO_3/AgNO_3$.

graph. Tests at 25°C showed that only $Ag_2TeO_3$ is always obtained, independent of the mole ratio ($Na_2TeO_3/AgNO_3$, $n = 0.5–3$). Excess $Na_2TeO_3$ stabilizes $Ag_2TeO_3$ and the latter retains its colour after drying. X-ray phase analysis revealed that although precipitation takes place at room temperature, the tellurite obtained is always in the crystal state and its composition is $Ag_2TeO_3$. Therefore, assertions that $Ag_2TeO_3$ exists in the amorphous state [1], and that $Ag_2TeO_3 \cdot 6H_2O$ is synthesized [4] are groundless and inconsistent. The dependence of pH on $Na_2TeO_3/AgNO_3$ mole ratio is also in favour of an analogous process in the precipitation of the solid phase. As the isotherm for the whole interval under study (Fig. 1) and the pH dependence (Fig. 2) show, only one compound is obtained in the system. This compound has a very good crystallinity which is due to both the effect of the high temperature, and, probably the higher pH values. When an excess of $Na_2TeO_3$ is present ($n = 3–10$), the crystal phase is impurified by a small quantity of elemental silver resulting from the photochemical effect of light.

TABLE 1

X-ray pattern of $Ag_2TeO_3$

| *I* | *d* (Å) | *hkl* | *I* | *d* (Å) | *hkl* |
|---|---|---|---|---|---|
| 1 | 4.9022 | 001 | 2 | 2.7184 | 211 |
| 1 | 4.2029 | 120 | 22 | 2.4779 | 230 |
| 1 | 3.7106 | 111 | 100 | 2.4544 | 002 |
|  | 3.4901 | 200 | 6 | 1.7615 | 232 |
| 3 | 2.9116 | 220 | 6 | 1.7571 | 060 |
| 12 | 2.8823 | 201 | 5 | 1.7502 | 450 |
| 13 | 2.8535 | 031 | 2 | 1.7464 | 142 |
| 14 | 2.8133 | 201 | 7 | 1.730 | 142 |
| 2 | 2.7792 | 211 | 5 | 1.7262 | 410 |

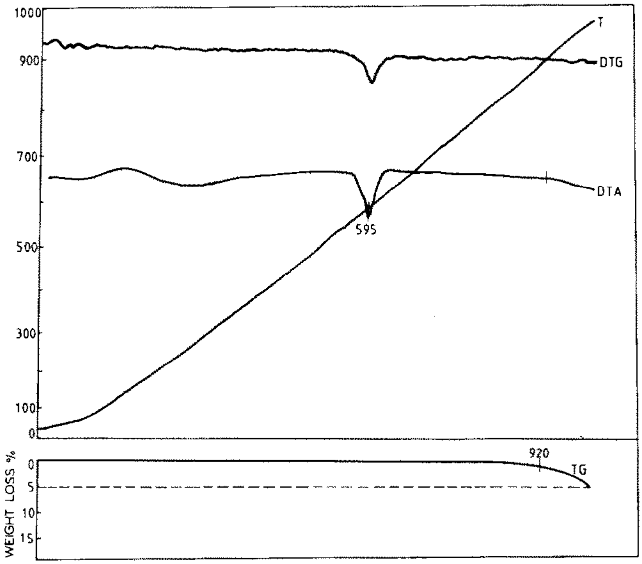

Fig. 3. Derivatogram of $Ag_2TeO_3$.

Its quantity increases with increasing excess of $Na_2TeO_3$, which probably activates that process. The reason for the assertion concerning the existence of $Ag_2TeO_3 \cdot 6H_2O$ [4] may, therefore, be due to a failure to recognize the presence of that phase by chemical analysis.

X-ray analysis showed that $Ag_2TeO_3$ crystallizes in a monoclinic system with a $P2_1/a$ space group and the following parameters of the elementary cell: $a = 7.002$, $b = 10.53$, $c = 4.912$ Å and $\beta = 51°49'$. These values are in good agreement with the literature data [7]. Lines not belonging to the $Ag_2TeO_3$ phase and owing to impurity phases were not observed (Table 1).

An exothermal peak is observed at 595°C on the derivatogram of $Ag_2TeO_3$ (Fig. 3). This peak is reversible and is not accompanied by a weight loss of the sample. Visual observations of a sample heated to 595°C show that the tellurite melts.

Silver tellurite is thermostable to 920°C. At higher temperatures it begins to decompose. The thermogravimetric curve shows that at 1000°C the weight loss due to decomposition of $Ag_2TeO_3$ is only 5%. After heating the sample for 1 h at 950°C the decomposition products of $Ag_2TeO_3$ contain two phases: $Ag_2TeO_3$ and metallic silver. Since $Ag_2O$ is unstable at high temperature and decomposes to Ag and $O_2$, it is $TeO_2$ and $O_2$ that are supposed to form in the gas phase. Based on these results, the scheme of thermal dissociation is suggested as

$$Ag_2TeO_3 \xrightarrow{t>920°C} 2Ag + TeO_2 + 1/2O_2$$

## REFERENCES

1 V. Lenher and E. Wolensky, J. Am. Chem. Soc., 35 (1913) 727.
2 M.A. Berchenco, A.I. Bilyaev and Z.L. Leshchinskaya, Zh. Phys. Khim., 43 (1969) 1403.
3 B.H. Tavernier, Z. Anorg. Allg. Chem., 373 (1966) 327.
4 E.Sh. Ganelina and T.N. Pozhidaeva, Z. Prikl. Khim. (Leningrad), 38 (1965) 2210.
5 B.N. Zagortchev, Anal. Khim. Izd. Tech., (1967) 587.
6 I.I. Nazarenko and E.I. Ermakov, Analititchna Himia Selena i Telura, Nauka, Moscow, 1974, p. 59.
7 R. Masse, J.C. Guitel and I. Todjman, Mater. Res. Bull., 15 (1980) 431.