

THE THERMAL ANALYSIS OF "ARGENTIC OXYNITRATE" AND SILVER OXIDES

J. C. JACK and T. KENNEDY

Department of Chemistry, Paisley College of Technology, Paisley, Scotland

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The precise stoichiometry of "argentic oxynitrate" has been elucidated by analytical and thermal analytical techniques. A decomposition path of the oxynitrate has been proposed and values of the enthalpy changes obtained. TG has been used as the criterion of purity of silver(II) oxide and new values for the heat of formation of silver(I) and silver(II) oxide are reported.

Considerable attention has been focused on the preparation and properties of compounds containing silver in the +2 oxidation state. Perhaps the most important of these compounds is silver(II) oxide, AgO [1-6]. As part of an investigation into the use of silver(II) oxide as an oxidant in the determination of transition and transuranic elements it was necessary to obtain the oxide in a high state of purity by prolonged boiling of an aqueous suspension of the so-called argentic oxynitrate, "Ag₇NO₁₁". There is considerable variation in the literature as to the precise stoichiometry of the oxynitrate, Ag_{28.55}O_{44.86}N_{4.08} [7], Ag₂₈O₄₄N₄ [8] and Ag_{26.57}O_{41.92}N_{3.93} [9] having been variously reported. No direct calorimetric studies of the oxynitrate or indeed of silver oxides appear to have been published. This paper records the results of our thermal analysis investigations of these systems and the resulting stoichiometric implications. The precise route of the thermal decomposition of "argentic oxynitrate" and the associated enthalpy changes are also reported.

Experimental

Materials. Commercial samples of silver(I) oxide and silver(II) oxide (samples A and B) were used without further purification. Silver(II) oxide, sample C, was prepared from "argentic oxynitrate" with precautions to exclude atmospheric carbon dioxide. "Argentic oxynitrate" was prepared by anodic oxidation of silver nitrate solution [10].

Analysis. Total silver was determined gravimetrically as the chloride and volumetrically by the Volhard method, using 0.1M ammonium thiocyanate standardised against 99.995% pure silver. Silver(II) was determined volumetrically by the iodide method [3]. Nitrogen was determined by Devarda's method after reduction of higher valent silver to silver(I) by heating gently with 1.0M

sulphuric acid until the samples were completely dissolved and no further evolution of oxygen was observed. Carbon was determined by combustion using a Perkin-Elmer elemental analyser.

Thermal studies. TG studies were carried out on a Stanton HT-M thermobalance at a heating rate of $2^{\circ} \text{ min}^{-1}$ under dry nitrogen. Samples of 150–500 mg were contained in recrystallised alumina crucibles. Calorimetric studies were carried out on a Perkin-Elmer differential scanning calorimeter, Model DSC I B, under dry nitrogen. Samples of 25–60 mg were encapsulated in aluminium pans or sealed with a pinhole in the lid and scanned at heating rates of 8 or $16^{\circ} \text{ min}^{-1}$ at a sensitivity of 8–32 m·cal·sec⁻¹ full scale deflection, depending on the magnitude of the enthalpy change. Quantitative data was obtained from the appropriate peak areas calibrated against 99.999% pure indium.

Results

Analytical aspects of silver oxides. The results of the chemical and thermogravimetric analysis of silver oxide samples are shown in Table 1.

Table 1
Chemical and thermogravimetric analysis of silver oxides

		Ag ₂ O	AgO (A)	AgO (B)	AgO (C)
Total Ag %	Found	93.0	86.6	87.0	87.0
	Theoretical	93.1		87.1	
Ag ²⁺ %	Found	—	83.8	82.3	85.5
	Theoretical	—		87.1	
Wt. loss %	Found	—	6.24	6.19	6.40
	AgO → Ag ₂ O	Theoretical	—	6.45	
Wt. loss %	Found	6.5	7.15	6.84	6.50
	Ag ₂ O → Ag	Theoretical	6.90	6.45	

Although it has been reported that silver(I) oxide in vacuum loses 5% of its oxygen in the temperature range 100–200° [11], the TG curves define the initiation temperature of decomposition of silver(I) oxide in nitrogen as 350°. Weight losses up to this temperature were regarded as being due to the decomposition of silver(II) oxide to silver(I) oxide. This assumption was justified by the chemical analysis of the oxide isolated at this stage and the fact that no AgO lines were present in X-ray powder photographs of the intermediate oxides.

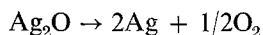
The TG results for silver(II) oxide samples A and B indicate a low first weight loss and a high second weight loss as compared with the theoretical values. Infra-red examination of the gases evolved on heating these samples indicated the presence of carbon dioxide and a subsequent determination of carbon on sample B indicated a carbon content corresponding to 2.8% silver carbonate.

Because of the apparent ease with which silver(II) oxide may be contaminated with carbonate attempts to obtain pure silver(II) oxide were directed towards the method described by Noyes et al. [10] with the modification that de-gassed water was used throughout and all operations were carried out in an atmosphere of carbon dioxide free nitrogen.

The TG results for "carbonate free" silver(II) oxide prepared in this manner were very close to the theoretical values and carbon dioxide was not detected in these decomposition reactions, but replicate determination of Ag^{2+} by the iodide method gave results which were consistently 98.0% of theoretical. Thus the iodide method gave only a 98% yield of the actual Ag^{2+} content. In Table 2 is given the composition of silver(II) oxide, sample B, calculated on the basis of total silver, Ag^{2+} and carbon analyses, together with an interpretation of the TG curve for the same material, based on the first weight loss being due solely to the reaction:



and on the second weight loss being due to the reactions:



and

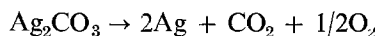


Table 2

Composition of silver(II) oxide, sample B. Based on analytical and TG results

	Analysis	TG
AgO %	96.4	96.1
Ag ₂ O %	2.75	2.60
Ag ₂ CO ₃ %	0.90	1.30

The results indicate that TG provides a rapid and convenient method for the analysis of silver(II) oxide.

Determination of stoichiometry of "argentic oxynitrate". Freshly prepared samples of "argentic oxynitrate", dried by washing with pure dry acetone and storing in a desiccator over molecular sieve for 12 hours gave the following typical analysis:

Total silver: 79.5%, nitrogen: 1.65%, oxygen (by difference): 18.85%

It was not possible to determine the oxidising power of the oxynitrate by the iodide method because of side reactions involving loss of oxygen which reacted in a random manner with the iodide.

The above results for the oxynitrate gave $\text{Ag}_{6.25}\text{NO}_{10}$ or $\text{Ag}_{25}\text{N}_4\text{O}_{40}$ as the empirical formula, which may be rewritten as $\text{Ag}_{21}\text{O}_{28} \cdot 4\text{AgNO}_3$. We believe that the reported variations in the oxynitrate stoichiometry [4, 7-9] are the result of spontaneous oxygen loss from oxynitrate observed by us, which has led us to investigate only freshly prepared material.

TG of "argentic oxynitrate". The TG results are shown in Table 3 and Fig. 1.

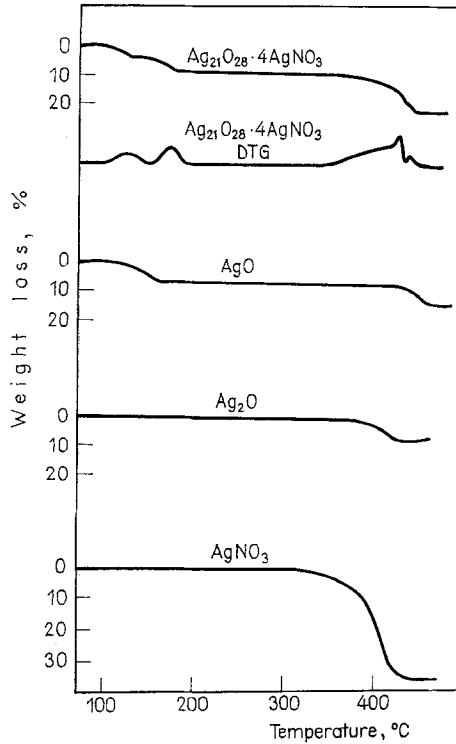


Fig. 1. TG curves of "argentic oxynitrate", silver nitrate and silver oxides

Table 3

TG of "argentic oxynitrate" ($\text{Ag}_{21}\text{O}_{28} \cdot 4\text{AgNO}_3$)

Stage	Initiation temp. °C	Loss %	
		Found	Theor.
1	80-85	3.3	3.4
2	115-120	5.0	5.3
3	350	6.4	6.2
4	425	5.9	6.0
5	435	0.94	0.93

Table 4

ΔH values for the decomposition of argentic oxynitrate
($\text{KJ mol}^{-1} \text{Ag}_{21}\text{O}_{28} \cdot 4\text{AgNO}_3$)

Stage	Initiation temp. °C	ΔH
1	85	-244
2	140	- 75.8
3	350	659
4+5	440	338

The enthalpy changes for silver nitrate and silver(I) and silver(II) oxides are shown in Table 5. The results, expressed as KJ mol^{-1} reactant, are derived from direct measurement of the reacting species and indirectly from "argentic oxynitrate" and the species formed by stage 1 of the decomposition of the oxynitrate, i.e. $21\text{AgO} + 4\text{AgNO}_3$, isolated on the thermobalance.

Table 5

ΔH values for silver nitrate and silver oxides

Reaction	Source species	ΔH	Initiation temp. °C
AgNO_3 (s)	$\text{Ag}_{21}\text{O}_{28} \cdot 4\text{AgNO}_3$	11.2	187
↓	AgNO_3	11.8	186
AgNO_3 (l)	$21\text{AgO} + 4\text{AgNO}_3$	10.6	193
AgNO_3 (s, α)	$\text{Ag}_{21}\text{O}_{28} \cdot 4\text{AgNO}_3$	2.0	154
↓			
AgNO_3 (s, β)	AgNO_3	2.3	157
AgO	$\text{Ag}_{21}\text{O}_{28} \cdot 4\text{AgNO}_3$	-2.62	139
↓			
$1/2\text{Ag}_2\text{O} + 1/4\text{O}_2$	AgO	-2.51	147
	$21\text{AgO} + 4\text{AgNO}_3$	-2.42	135
Ag_2O	$\text{Ag}_{21}\text{O}_{28} \cdot 4\text{AgNO}_3$	23.0	442
↓			
$2\text{Ag} + 1/2\text{O}_2$	AgO	23.2	417
	Ag_2O	21.5	397
	$21\text{AgO} + 4\text{AgNO}_3$	24.2	440
AgNO_3	$\text{Ag}_{21}\text{O}_{28} \cdot 4\text{AgNO}_3$	127.6	352
↓			
$1/2\text{Ag}_2\text{O} + \text{NO}_2 + 1/4\text{O}_2$	$21\text{AgO} + 4\text{AgNO}_3$	130.0	360

The enthalpy of decomposition of silver nitrate could only be measured indirectly as attempts to decompose silver nitrate directly produced very finely divided silver which coated the sample holder and damaged the thermistors of the calorimeter.

Discussion

There is no evidence for the formation of a molecular complex at stage 1 of the oxynitrate decomposition. The silver(II) oxide and silver nitrate behave as an intimate mixture. Thus extraction of this phase with cold water gave 21.0% soluble silver expressed as silver nitrate [theoretical for $(\text{Ag}_{21}\text{O}_{21} \cdot 4\text{AgNO}_3) = 20.5\%$]. X-ray powder photographs of this mixture showed no significant difference from the superimposed patterns of silver nitrate and silver(II) oxide. There is a significant difference in the initiation temperatures of the decomposition of silver(I) and silver(II) oxides, depending on the source of the measurements. Thus, initiation temperatures of species which contain nitrate are consistently higher than for the silver oxides alone. This may be the result of the state of oxide aggregation being influenced by the presence of nitrate.

Previously reported measurements of the enthalpy changes derived from electrochemical studies of silver oxides [2] are compared with those from this study in Table 6.

Table 6
Enthalpy changes for silver oxides

Reaction	ΔH (KJ mol ⁻¹)	
	Ref. [2]	This study
$\text{Ag}_2\text{O} \rightarrow 2\text{Ag} + 1/2\text{O}_2$	-31.1	-23.0
$\text{AgO} \rightarrow \text{Ag} + 1/2\text{O}_2$	-12.2	-9.0
$\text{AgO} \rightarrow 1/2\text{Ag}_2\text{O} + 1/4\text{O}_2$	-3.3	-2.5

The enthalpy change found for the reaction



$\Delta H = +128.9$ KJ mol⁻¹, compares well with the calculated value, $\Delta H = +136.3$ KJ mol⁻¹ (taking $\Delta H_{f(\text{NO}_2)}^\circ = +138.09$ KJ mol⁻¹ [12]).

It has been proposed that "argentic oxynitrate" produced electrolytically is converted on drying to a higher silver oxide of unspecified composition and a measurable amount of silver nitrate [9]. A structural study of silver(II) oxide has established that the lattice comprises Ag(III) coordinated with four dsp² hybridised oxygen atoms in a square planar arrangement and Ag(I) with two sp hybridised oxygen atoms [1]. On the basis of magnetic and neutron diffraction studies it was concluded that Ag(II) is not present in AgO [13, 14]. No evidence has so far been produced to suggest the existence of any allotropic modification of AgO [9].

The oxynitrate has been shown to crystallise in the cubic space group Fm3M, the structure being described as a supporting Ag₃O₄ structure with the nitrates

ZUSAMMENFASSUNG — Die genaue Stöchiometrie des "Silberoxynitrats" wurde durch analytische und thermoanalytische Prüfung geklärt. Der Zersetzungsvorgang des Oxynitrats wurde verfolgt und die Enthalpieänderungen beobachtet. Die Reinheit von Silber(II)oxyd läßt sich thermogravimetrisch kontrollieren. Es wurden neue Werte für die Bildungswärmen des Silber(II)oxyds und Silber(I)oxyds gefunden.

Резюме — Аналитическим и термоаналитическим методами исследована стехиометрия оксинитрата серебра. Приведен предполагаемый ход распада оксинитрата и получена величина изменения энтальпии. В качестве критерия чистоты окиси серебра (II) использована кривая ТГ. Установлены новые величины теплот образования окисей серебра (I) и (II).