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THE CATALYTIC EFFECT OF CESIUM OXIDES ON THE THERMAL DECOMPOSITION OF CESIUM AZIDE

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ABSTRACT

The thermal decomposition of cesium azide was autocatalyzed by cesium oxides formed in the reaction. The decompositions were performed in ambient atmospheres of oxygen, nitrogen and helium, and in vacuum. Results obtained from the decomposition of sodium azide suggest that an autocatalysis also occurred due to the sodium oxides formed in situ.

INTRODUCTION

The catalyzed thermal decomposition of cesium azide by semiconducting oxides was reported from this laboratory [1]. Recently, it has been found that the decompositions of potassium and cesium azides were catalyzed by transition metals [2]. It has been claimed previously that the decomposition of alkali metal azides (sodium, potassium, rubidium) was catalyzed by the alkali metals formed in situ [3] as described by the overall reaction

$$2\ MN_3 \rightarrow 2\ M + 3\ N_2 \qquad (1)$$

No results on thermal decompositions were reported, to the best of the authors' knowledge, on decompositions of cesium azide under oxidizing atmospheres, such as air or oxygen. The results reported in this study were obtained by differential thermal analysis under oxidizing and inert ambient atmospheres. A comparison with results obtained in vacuum is presented.

EXPERIMENTAL

Materials

Cesium azide (Eastman Organic Chemicals, Ltd.) was crystallized from methanol and contained impurities [1]. Sodium azide (Fluka AG > 99.9%

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purity) was used as obtained. Nitrogen gas used was high purity Matheson (prepurified 99.96%). Oxygen gas was supplied from a local producer (> 99.9% purity).

Apparatus

The controlled atmosphere Differential Thermal Analysis Apparatus Model KA-2H (Robert L. Stone Co., Austin, Texas) was used. The sample holder is built so that the gases pass through the sample. The diluents and reference materials used were alumina (Fisher Laboratory Chemicals) and vitreosil (prepared by grinding tubing, then washing with hydrochloric acid, followed by distilled water and drying at 500°C).

There was no difference in the results using Fisher alumina or vitreosil as diluents.

Procedure

The DTA experiments were carried out by sandwiching the samples between two layers of the diluent (alumina or vitreosil). Each reaction was duplicated and triplicated. The azide was kept in a desiccator and the time of transfer to the DTA apparatus was minimized in order to avoid absorption of water from the atmosphere.

RESULTS

Endothermic transitions

Cesium azide shows three reversible endothermic peaks with tips at 150, 290 and 325°C (Fig. 1). A transition from a tetragonal α-phase to a cubic

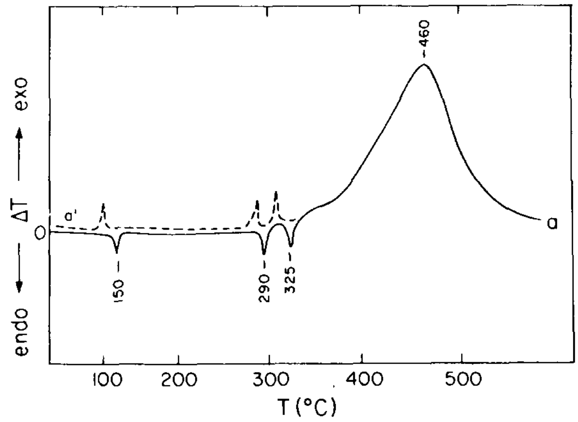

Fig. 1. DTA curves of CsN_3. (a) Heating curve in air (an endothermic peak at 600°C is not shown); (a′) CsN_3 heated to 325°C and cooled.

β-phase takes place at 151°C. The melting point of cesium azide in air is 326°C [4]. The endothermic peak with a tip at 290°C (reversible) is assigned to a solid solution of cesium–rubidium azides [4], because the solid–solid transition and the melting temperatures for rubidium azide have higher values. Heating–cooling cycles have no effect on the transitions (Fig. 1). The hysteresis found by cooling is due to a kinetic effect. There was no effect on the transition temperatures using cesium azide crystallized from water or ethanol, providing the samples were kept under dry conditions and not exposed to the atmosphere for extended periods. Premelting at 325°C and keeping the molten azide for long periods at this temperature had no effect on the endothermic reversible transitions. A small endothermic peak appears with a tip at 600°C which may be assigned to the melting of Cs_2O_2 (594°C) [5].

Exothermic peaks

In air

An exothermic peak with a tip at 460°C is obtained (Fig. 1). This peak was not reversible. Thermogravimetry in air showed a mass loss in this temperature region.

In oxygen

Cesium azide showed the same exothermic peak as in air with a tip at 460°C, when heated in oxygen (Fig. 2).

In helium and nitrogen

The exothermic reaction here showed a peak with a tip at 520°C (Fig. 2). In addition to the delay in the tip temperature of the exothermic peak, a pronounced difference in the curves' slopes (Fig. 2A, B) were obtained. The slopes for the inert gases are smaller compared to those for air (Fig. 1) and oxygen (Fig. 2).

In vacuum

Isothermic reactions in the vacuum line at temperatures up to 390°C were slow [1] and it took a long time until the reaction reached completion (calculated from the amount of nitrogen evolved). Metallic cesium was deposited on the cold walls of the reactor. The metallic mirror changed in color with time to yellow-gold (in vacuum). A colored residue remained at the completion of the reaction. Calculations based on the weight of the residues could not bring a conclusion as to the stoichiometry of the oxide. The weights did not agree with the formulae of cesium oxides. This disagreement could be a result of the evaporation of metallic cesium and the possibility of obtaining a mixture of cesium oxides, formed during the reaction and by exposure to air, when the sample was taken out of the reactor.

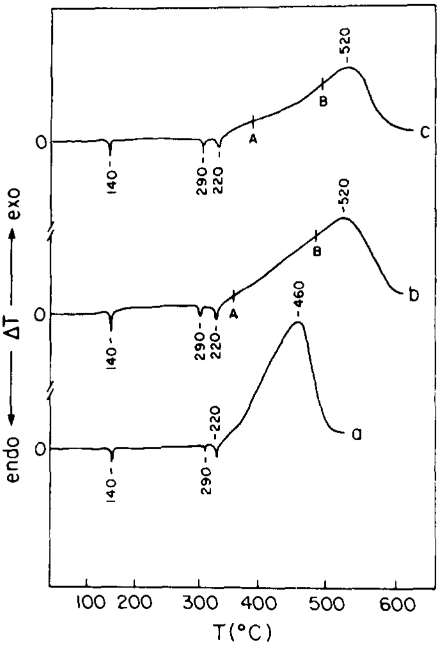

Fig. 2. DTA curves of CsN_3 in flowing gases. (a) Oxygen; (b) helium; (c) nitrogen.

At higher oxygen pressures (3μ) the reaction at 360°C was fast and came to completion in a short period of several hours.

Heating for extended periods at the solid–solid phase transition temperature (i.e., 150°C) did not result in a decomposition.

For sodium azide

An exothermic reaction with a peak tip at 420°C was observed by heating in air (Fig. 3). The reaction was delayed to 480°C when the heating took

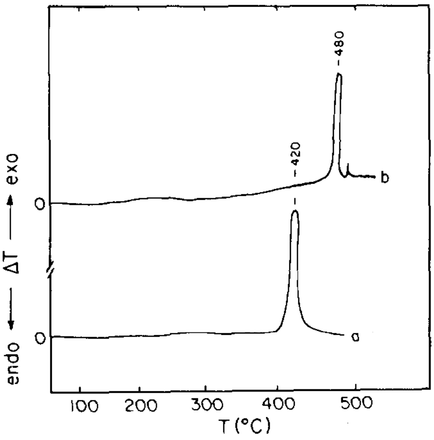

Fig. 3. DTA curves for NaN_3. (a) Air; (b) nitrogen.

place in a nitrogen flow (Fig. 3). No endothermic transition was observed either on heating in air or nitrogen.

DISCUSSION

Cesium azide was decomposed in air only after melting (Fig. 1). The metallic cesium formed initially (eqn. 1) is consecutively oxidized to cesium oxides. Most of the cesium is oxidized to Cs_2O_2 as can be judged from its melting point at 600°C [5]. Another reaction can take place between the cesium and the alumina (diluent)

$$Al_2O_3 + 3\ Cs \rightarrow 2\ Al + \tfrac{3}{2}\ Cs_2O_2 \qquad (2)$$

The calculated ΔF for this reaction is positive [6] and therefore the production of metallic aluminum is not feasible. A possibility of the formation of lower oxides of aluminum, is favored providing that the reaction products are removable. From our results it seems that there is no reaction between the cesium and the alumina, because similar results are obtained in air when vitreosil is used as a diluent. The vapor pressure of cesium at the reaction temperatures is high and there is a possibility of its evaporation from the reaction site. However, in air at atmospheric pressures, the probability of the fast oxidation of cesium is high.

It is proposed that the thermal decomposition of cesium azide is autocatalyzed by cesium oxides formed in situ by the oxidation of the molten metal. This suggestion is supported by experiments carried out in various ambient gases. Heating in flowing pure oxygen did not have a significant influence on the molten cesium azide decomposition showing a peak tip at 460°C. The possibility that metallic cesium will be swept away from the reaction site by the flow of oxygen is excluded because of the fast oxidation. The possibility of the formation of aluminum suboxides which may be swept away by the oxygen flow is not feasible because of the expected higher rate of oxidation of the cesium by gaseous oxygen.

The reactions under the flow of helium and nitrogen are similar (Fig. 2). They start very slowly after melting (320°C) and reach the peak tip at 520°C (Fig. 2). In temperature region 320–560°C a variety of concurrent or consecutive reactions take place, e.g., the decomposition of the azide (reaction 1) and the oxidation of cesium. The decomposition temperature peak tip for the cesium azide is higher in helium or nitrogen than in air or oxygen because the amount of oxygen (present as an impurity) is low and it takes time for the accumulation of cesium oxides. The fast stage of the decomposition starts at 520°C when a critical mass of cesium oxide is formed. The similarity in the decompositions under helium and nitrogen may exclude an argument that delay in the peak is caused by cooling. Although helium is a much better heat conductor than nitrogen, the curves (Fig. 2) are nearly identical. The reaction conditions were identical in the reactions of heating under oxygen and inert gases.

The reactions in vacuum in the temperature region of 325–390°C are also slow, because of the low number of oxygen molecules ($\sim 10^{-13}\ l^{-1}$). The solid oxide residue at this temperature region (and also at higher temperatures) may support our proposal of the catalyzing effect of cesium oxides on the decomposition of cesium azide. The high volatility of cesium at these temperatures [7] may indicate that metallic cesium is not the only catalyst for this reaction. Moreover, the enhancement of the reaction at an initial pressure of 3μ of oxygen substantiates the proposal that cesium oxides are needed for catalyzing the decomposition of cesium azide. The delay in the appearance of the reaction peak for sodium azide when heated under a nitrogen flow may indicate that the decomposition of other alkali azides are autocatalyzed by the alkali oxides formed (Fig. 3).

REFERENCES

1 Y. Sears and M. Steinberg, J. Catal., 11 (1968) 25.
2 H.C. Egghart, J. Catal., 79 (1983) 410.
3 M.E. Brown, D. Dollimore and A.K. Galway, in C.H. Bamford and C.F.H. Tipper (Eds.), Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Amsterdam, 1980.
4 H.J. Mueller and J.A. Joebstl, Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem., 121 (1965) 385.
5 Mellors, Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. II, Suppl. III, Longmans, London, 1963, p. 2345.
6 Handbook of Chemistry and Physics, 47th edn., Chemical Rubber Co., Cleveland, Ohio, 1966–1967, pp. S22-D27.
7 J.B. Taylor and L. Langmuir, Phys. Rev., 51 (1937) 753.