

The Influence of Semiconducting Oxides on the Thermal Decomposition of Cesium Azide

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The influence of *n*- and *p*-type oxides on the thermal decomposition of solid and molten cesium azide was studied and a decrease found in the catalytic activity on nickel oxides in the order $\text{NiO}(\text{Li}) > \text{NiO} > \text{NiO}(\text{Cr})$. Zinc oxide with an *n*-type behavior inhibited the decomposition, while *n*-type cadmium oxide catalyzed the reaction. An explanation is given.

INTRODUCTION

The thermal decomposition of the azides of sodium and potassium has been extensively studied (1, 2, 3). However, no study on the thermal decomposition of cesium azide (CA) has been published.

The present paper reports a study on the thermal decomposition of CA in which the influence of some semiconducting oxides was investigated. In a recent study (2) on the influence of oxides on the thermal decomposition of potassium azide, it was concluded that the catalyzing agent was the metal produced by the reduction of the oxide by potassium. To the best of the authors' knowledge, no study has been published on the influence of both *p*- and *n*-type semiconductors on the thermal decomposition of CA.

EXPERIMENTAL

Apparatus. The decompositions were carried out in a vacuum apparatus in which a pressure of 10^{-6} torr was obtainable. Pressures were measured with two McLeod gauges—for lower and higher pressure ranges. The volume calibration was carried out by heating the quartz reaction chamber at 370° , the mean temperature of the ex-

periments. The traps were cooled by immersion in liquid-air-filled Dewar flasks. The other parts of the apparatus were at room temperature.

Furnace and temperature control. A homemade tubular furnace was used. The temperature was automatically controlled by a West Gardsman and was recorded by an additional Chromel-Alumel thermocouple connected to a Doran potentiometer. The temperature constancy was kept at $\pm 0.5^\circ$.

X-ray analyses. The residues were analyzed by X-ray with a Phillips Diffractometer ($\text{Cu } K_\alpha$ Ni-filtered radiation).

Materials. *Cesium azide.* (Eastman Organic Chemicals Ltd.) was recrystallized by dropwise addition of ethyl alcohol to a concentrated aqueous solution of CA which was kept at 0°C . Small platelets were obtained. The crystals were dried in a vacuum desiccator. No alcohol was present, as was shown by IR analyses. Emission spectroscopy analysis showed the presence of metallic impurities as follows:

Li, 100_{ppm}; Na, 100_{ppm}; K, 100_{ppm}; Rb, 1%;
Cu, 0.01%.

The rubidium was present as the azide, shown by determining its melting point by differential thermal analysis. The melt-

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ing point of potassium azide was not observed with this technique.

Nickel oxide was prepared by the decomposition of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (BDH Analar) in air. The heating sequence was as follows: (a) A temperature of 700° was maintained for 3 hr. (b) It was then raised to 800° and kept there for 2 hr. (c) The final stage was sintering at 1000° for 12 hr. The nickel oxide was colored green.

Doped nickel oxide. (a) *Lithiated nickel oxide* was prepared by the same thermal sequence as used for the preparation of nickel oxide, except that to a concentrated aqueous solution of nickel nitrate an aqueous solution of lithium nitrate was added to make it a 1 atom % lithium concentration. The solution was evaporated on a sand bath at 280° , and then transferred to an unglazed porcelain crucible. From this stage the treatment was as for nickel oxide. The lithium was determined by flame photometry. The lithium content was found to be 0.57% atom. (b) *Chromiated nickel oxide* was prepared following the same procedure as for the lithiated oxide, except that a solution of ammonium dichromate was added to the nickel nitrate solution. A 1 atom % chromiated nickel oxide was prepared.

Zinc oxide, containing 13 ppm of free zinc, was used (4); 1 atom % lithiated zinc oxide was prepared as described previously (5).

Cadmium oxide was prepared from cadmium hydroxide (6). The hydroxide was heated at 100° while pumping for 30 min. The temperature was raised to 400° and the sample was heated while continuously pumping for 1 hr. A brown preparation was obtained.

Finely divided *nickel* was prepared by Mond's procedure (7). All other chemicals used were of reagent grade.

Procedure. The vacuum apparatus was pumped out for several hours at a pressure of 10^{-6} torr. During the pumping the furnace was hot, but the sample was at room temperature. Reactions were not started until the air leak was less than 2×10^{-5} torr/hr. The test tube containing the azide

was brought home to the hot zone by using a magnet. Zero time was taken at the moment the sample reached the position of the thermocouple. The progress of the reaction was followed by measuring the pressure of the evolved nitrogen. When constant pressure was attained, the sample was left in contact with the evolved gas for periods between 12 and 24 hr. No pressure drop was observed. In slow reactions, i.e., at lower temperatures, the sample was left overnight in contact with the nitrogen, and the pressure recorded in the morning. A second pressure reading was taken after 1 hr. Great care was taken to keep the Dewar flasks filled with liquid air. Although the sample test tubes were weighed after removal from the reaction chamber, they were not assessed because of secondary reaction in the atmosphere of the residue. Some parallel runs were carried out in quartz test tubes. It was found that the same results were obtained using borosilicate glass and quartz. The study was continued in borosilicate test tubes.

Samples for the catalyzed reactions were prepared by adding a weighed amount of the azide to a preweighed quantity of the catalyst and mixing in an agate mortar.

RESULTS

Cesium azide. Heating the solid azide at 200° and 293° for 48 hr in vacuum resulted in the very small decomposition of 0.28% and 1.11% respectively. At 360° , when CA is in the molten state (m.p. 325°), 1.21% had decomposed after 70 min, 1.55% after 200 min, and 2.95% was observed after 36 hr, the pressure not reaching a constant value. At 380° decomposition of molten CA was still slow, 16.2% being decomposed after 24 hr. The irradiation at room temperature in vacuum of cesium azide by a high-pressure mercury lamp resulted in 2% decomposition to give a yellowish-brown-tinted solid. Bringing home the irradiated azide to the hot zone at 390° showed the reaction to be identical to that with unirradiated CA. At temperatures higher than 400° the thermal decomposition is distinct. From the above results, which

were reproducible to about 1%, it may be concluded that the thermal decomposition of CA at temperatures lower than 400° is negligible.

NiO, NiO (1% Li), NiO (1% Cr). The formula weight ratios of CA to the oxide here are 1:1. At 240° a slow reaction developed with NiO. The decomposition after 8 and 16 hr was 7.98% and 25.9%, respectively. This reaction takes place in the solid state. The mixture of nickel oxide

and cesium azide decomposed completely after 12 hr, at 280°.

Doped nickel oxide was found to have an interesting influence on the thermal decomposition of cesium azide. The shortest induction period was with lithiated nickel oxide (Fig. 1). Chromiated nickel oxide was less active, while the activity of nickel oxide lies between NiO(Li) and NiO(Cr) (Fig. 1). Nevertheless, even with the chromiated nickel oxide, the reaction

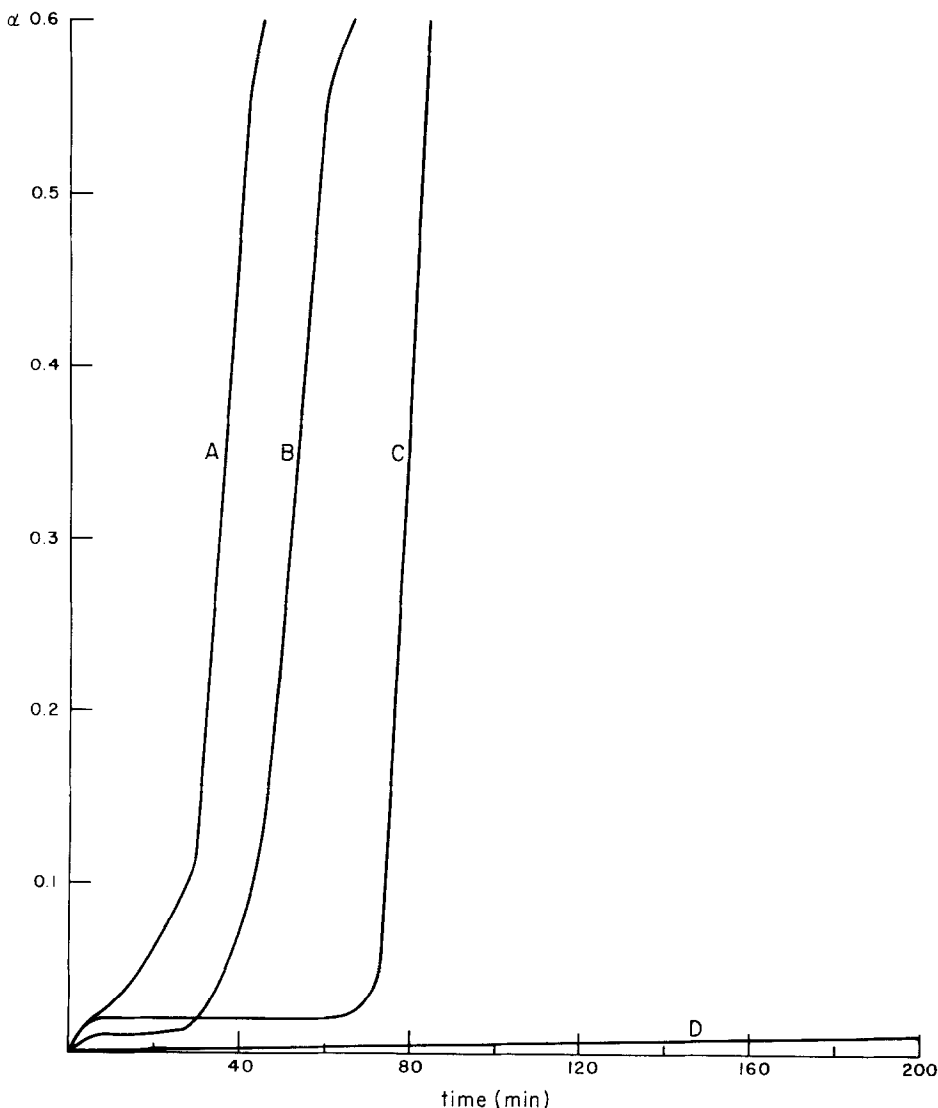


FIG. 1. Thermal decomposition curves of cesium azide in the presence of oxides at 380°C: A, $\text{CsN} + \text{NiO}$ (% Li); B, $\text{CsN}_3 + \text{NiO}$; C, $\text{CsN}_3 + \text{NiO}$ (1% Cr); D, CsN_3 .

was much faster than in CA without additives (Fig. 1). The reaction with the above-mentioned semiconducting oxides reached completion. The residues contained metallic nickel, as was confirmed by X-ray analyses.

Nickel oxide was also identified by the X-ray analyses. Its presence may be explained by the high activity of the freshly deposited nickel metal, which is oxidized partly in air before being sealed in the capillary tube.

Ni. Two decompositions were carried out by adding metallic nickel to CA. In the first run, a mixture of nickel supplied by Fisher (rinsed with acetone and dried) and CA (1:1 formula weight ratio) were heated at 360°. The reaction rate was found to be much slower than with nickel oxide. In a second experiment, nickel prepared by Mond's method was mixed with the azide. The reaction rate with this preparation of nickel was faster than with the commercial nickel, but still was slower than with nickel oxide.

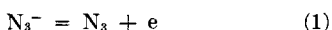
CsN₃ + ZnO. At 360°, for a mixture of 1:1 formula weight ratio, a decomposition of 1.36% was reached after 70 min. No further decomposition was observed even after 24 hr. This result, compared to those obtained by heating CA without additives, indicated that zinc oxide inhibits the decomposition.

CsN₃ + ZnO (1% Li). At 360°, for a mixture of 1:1 formula weight ratio, after 70 min the decomposition was 1.79%. After 24 hr the decomposition was 2.15%, the pressure not reaching a plateau.

CsN₃ + CdO. At 360°, for a mixture of 1:1 formula weight ratio, the decomposition was 1.93% after 70 min, and 13.3% after 24 hr, the reaction not reaching a constant pressure.

DISCUSSION

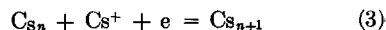
The thermal decomposition of cesium azide can be described as taking place in the following consecutive steps (3): (i) the formation of an excited azide ion, (ii) the formation of an azide radical



(a reversible step), (iii) the reaction of two azide radicals to the formation of three nitrogen molecules



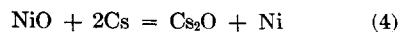
(iv) the absorption of a positive ion at a metal nucleus and electron capture



The "rate-controlling step" is the formation of the azide radical. A *p*-type semiconductor oxide may catalyze (1). Moreover, comparing the nickel oxide catalysts used in the present study, it was expected that the controlled *p*-type lithiated nickel oxide would have the most pronounced catalytic effect on the decomposition. The expected activity would decrease in the order NiO(Li) > NiO > NiO(Cr) (8). On the other hand, the *n*-type zinc oxide might not influence the reversible step (1), whereas ZnO(Li) would accelerate the reaction, the lithium doping producing a *p*-type behavior (9). The *n*-type cadmium oxide (8) would not be expected to catalyze the decomposition.

The experimental data show that the nickel oxide preparation and undoped zinc oxide behaved as expected *a priori*. The nickel oxides influenced the induction periods of the thermal decomposition, while the *n*-type zinc oxide inhibited the reaction. However, lithium-doped zinc oxide did not catalyze the reaction, whereas the *n*-type cadmium oxide had a pronounced influence on the decomposition. The experimental data demonstrate that the full understanding of the catalytic process shows it to be more complicated than the idealized mechanism postulated above. Borekov expressed the opinion (10) that for the full understanding of a catalytic process it is necessary not only to take into account the influence exerted by the catalyst on the reacting molecules, but also the changes in the catalyst itself, as a result of its interaction with the reactants.

The presence of metallic nickel in all the residues shows that the reduction



takes place.

When the reduction is thermodynamically possible, the catalytic influence is pronounced. From Table 1 it appears that reductions of nickel and cadmium oxides are possible, while zinc oxide will not be reduced.

From this estimation it may be concluded that, although the electrical behavior of the oxide is of importance, the reduction plays a most significant part in this catalytic process. The catalyzed decomposition may thus be described as taking place in the following steps.

TABLE 1
STANDARD FREE ENERGIES OF REACTION
 ΔF (kcal mole⁻¹), AT 360° FOR
 $MO + 2Cs = Cs_2O + M^a$

MO: ΔF :	NiO -5.53	CdO -1.69	ZnO +19.26
Catalytic activity	+	+	-

^a Reference (11).

The formation of the N₃ radical is influenced by the electrical behavior of the oxide. In a *p*-type oxide the acceptor centers accelerate the rate of nitrogen formation (1), followed by the formation of metallic cesium. The cesium formed reacts in a secondary reaction with the oxide to form the metal (4). The formation of these species is inhibited by *n*-type oxides. On the surface of the *p*-type (9) lithiated zinc oxide a somewhat faster reaction takes place, but the decomposition is 2.15% only after 24 hr, not reaching a plateau. The reduction of zinc oxide by cesium is not possible thermodynamically (Table 1), thus the cesium evaporates, its vapor pressure being 8.187 torr at 360° (13). It is here assumed that the free energy of formation ΔF is identical for doped and undoped nickel and zinc oxides. Now, with *n*-type cadmium oxide, the reaction is slow but significant. The cesium formed reacts with the oxide (Table 1) and the decomposition is catalyzed.

After the reduction of nickel oxide (both doped and undoped), the sample contains metallic nickel, nickel oxide, and cesium oxide. No cesium being observed on the

cold part of the reactor, it appears that all the cesium produced was oxidized by nickel oxide. Metallic nickel was not very reactive on cesium azide decomposition, so that it may be concluded that the cesium oxide formed is the catalytic agent in this decomposition. A more detailed study is needed on the influence of nickel on the decomposition.

The problem then arises as to the catalytic effect of cadmium oxide. Deposition of cadmium mirror at the cold part of the reactor was observed (14) when heating cadmium oxide in vacuum at 360°. Oxygen is evolved simultaneously with the cadmium. There is a possibility of oxidation by the oxygen of cesium nuclei to cesium oxide, this product being the catalyzing agent. However, it was observed that very small amounts of oxygen were evolved (0.02 μ) by heating cadmium oxide in vacuum at 500° for 15 min.

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