The Thermal Decomposition of Solid Hexaamminecobalt(III) Azide

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A qualitative explanation is suggested for the ability of solid $[Co(NH_3)_6](N_3)_3$ to undergo either a fast reaction to CoN, a slow reduction to cobalt(II), or an explosion to cobalt. A competition is assumed between the cobalt(II) reaction and the initiation of an energetic reaction. The latter either produces CoN or explodes depending on the quantity of cobalt(II) complex accumulated prior to the initiation. These processes are strongly influenced by particle size and ammonia.

Introduction

A previous paper characterized the products of the reaction paths by which solid $[Co(NH_3)_6](N_3)_3$ undergoes thermal decomposition.[1] The nature of the factors influencing these reactions is reported in more detail here and a qualitative explanation is suggested.

Experimental

Preparation.—The preparation of crystalline and powder samples of the hexaammine has been described.[1] Microscopic examination and non-rotated X-ray powder patterns reveal crystal sizes of 0.1 to 0.5 mm. for the former and 0.1 to 1 μ for the powder. Samples were stored in a vacuum desiccator over sulfuric acid and kept in the dark.

Procedure.—The apparatus and general procedure have been described.[1] Decompositions were carried out between 110 and 150°. Bath temperatures were controlled within ±0.1°. The volume of the vacuum system ranged from 50 to 70 ml. Samples were *ca.* 10 mg. and contained in small stainless steel cups. The usual run began with the vessel evacuated. Pressure was allowed to build up as the decomposition progressed. Final pressures ranged from *ca.* 80 mm. (eq. 1) to *ca.* 150 mm. (eq. 2). The variation during the runs imposes severe difficulties in treating the data quantitatively, but proved advantageous in revealing the considerable influence of ammonia on the reaction.

The effect of ammonia was investigated by placing a liquid nitrogen trap in the system *ca.* 60 cm. from the hot bath. This removed the ammonia generated by the earliest stages of the run but because of a diffusion problem became less efficient as nitrogen built up in the system. Runs also were made in the presence of an initial pressure of ammonia or nitrogen. The effect of mixing the powder samples with a simple salt, usually KCl, was studied in several runs at 140°.

Results

Three types of decomposition are possible[1]: A slow reaction to a cobalt(II) complex

$$[Co(NH_3)_6](N_3)_3 \longrightarrow Co(NH_3)_2(N_3)_2 + 1.5N_2 + 4NH_3 \quad (1)$$
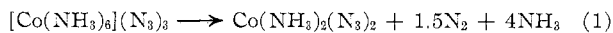
a slow reaction (eq. 1) followed by an explosion to a final stoichiometry of

$$[Co(NH_3)_6](N_3)_3 \longrightarrow Co + {\sim}5.5N_2 + {\sim}3H_2 + {\sim}4NH_3 \quad (2)$$
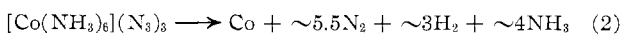
and a reaction with a long induction period followed by a rapid, non-explosive decomposition to a nitride

$$[Co(NH_3)_6](N_3)_3 \longrightarrow CoN + 4N_2 + 6NH_3 \quad (3)$$

Particle size is the most obvious factor affecting these processes. Powder samples generally behave according to (1) and (2) with explosion of the cobalt(II) com-

pound being more likely at the higher temperatures. Figure 1 reports representative experiments at 120 and 140° with the moles of gas evolved per mole of complex (n/n_0) plotted against time. Crystals (Fig. 2) usually follow eq. 3. However, it will be shown that either sample can display the opposite behavior under the appropriate conditions.

Reproducibility is generally good. A fresh sample of powder kept dry and reasonably protected from light gives reproducible data for the slow reaction over a period of a month. Some anomalies occasionally are noted in the curves (for example, Fig. 1, curve B) probably because small portions of the sample experience locally unusual conditions. Similarly, the time at which the solid undergoes an explosion or the rapid reaction to the nitride is variable, presumably because the ignition of the fast reactions results from local overheating during the decomposition. Indeed at low temperatures the explosion itself is not reproducible, the reaction sometimes stopping at the diammine. While different preparations reliably show the same general features, variations in rates are observed. This is an expected consequence of a strong dependence on particle size and, probably, the detailed nature of the surface. Aging over periods of a year was only briefly investigated. It appears to shorten induction periods and somewhat accelerate reaction 1.

The Effect of Ammonia on Powder.—Ammonia remarkably alters the decomposition of both powder and crystalline samples. With powder the most obvious effect is the inhibition of the explosion of the cobalt(II) compound (Fig. 1, curve B′). Moderate ammonia pressures allow the production of $Co(NH_3)_2(N_3)_2$ under conditions which normally produce explosions. The diammine is inert to further decomposition for over an hour although it will slowly evolve gas and ultimately explode. At higher ammonia pressures a tetraammine $Co(NH_3)_4(N_3)_2$ rather than the diammine is formed.[2] This tetraammine is evidently more sensitive and explosions again are noted (Fig. 1, curve C′).

Added ammonia also accelerates reaction 1 with moderate pressures (50, 100 mm.) having the greatest effect. At high pressures some inhibition, even after making allowance for the production of a tetraammine rather than a diammine, was observed.

(1) T. B. Joyner and F. H. Verhoek, *J. Am. Chem. Soc.*, **83**, 1069 (1961).

(2) T. B. Joyner and F. H. Verhoek, *Inorg. Chem.*, **1**, 557 (1962).

Runs in the presence of nitrogen were undertaken to establish that the ammonia effects were specific rather than a general phenomenon brought about by the presence of any gas above the solid. With the slower runs this is clearly the case, the nitrogen producing little alteration in the rates (Fig. 1, curves A and C). With faster runs at 140° some acceleration was noted. This was less than with comparable pressures of added ammonia. It almost certainly may be attributed to a diffusion effect, the evolved ammonia being restricted to the vicinity of the solid and so producing an effective ammonia pressure higher than the solid would have experienced during an initially evacuated run.

Since ammonia inhibits the explosion of $Co(NH_3)_2$-$(N_3)_2$, it is expected that its removal by a cold trap will lead to earlier explosions (Fig. 1, curves D, D'). It is noteworthy, however, that at 120° the behavior of two freshly prepared samples was altered from the customary reactions ((1) and (2)) to the non-explosive production of CoN (eq. 3). A third preparation did not show this effect, the 120° trapped run culminating in the usual explosion.

The Effect of Ammonia on Crystals.—Crystalline samples usually show a long induction period with little gas evolution followed by a rapid, non-explosive reaction to CoN (Fig. 2, curves A, A'). With ammonia initially present (curves B, B') the behavior is altered to a short initial acceleration followed by a long period of slow decomposition producing $Co(NH_3)_2(N_3)_2$ (identified by X-ray powder patterns[2]), and finally, at a time past the rapid reaction of the normal run, a generally weak but audible explosion. The samples usually are not entirely consumed, considerable undecomposed material being scattered outside the hot zone.

A cold trap on the line remarkably shortens the induction period and yields the customary CoN non-explosively (Fig. 2, curves C, C'). The induction period is so curtailed that the rapid reaction begins at a time when very little nitrogen has been observed and, in fact, in a comparable untrapped run no gas evolution would have been observed. While this acceleration may most reasonably be attributed to the removal of ammonia, it is noteworthy that trapping small amounts—virtually undetectable manometrically—could have such a marked effect.

The Effect of KCl on Powder.—The presence of finely ground KCl in the decomposing solid produces no marked change in the course of the decomposition to the diammine. The curves are similar to normal runs, although a slight slowing is noticeable. The probability of explosions is lowered, and it is possible to obtain the cobalt(II) complex under conditions where explosions would normally be expected

Discussion

The decomposition of $[Co(NH_3)_6](N_3)_3$ is inherently complex, involving a possible transfer of three electrons from azide to cobalt, and is further complicated by the ligand sphere of ammonias. The kinetic behavior, which includes a number of almost contradictory obser-
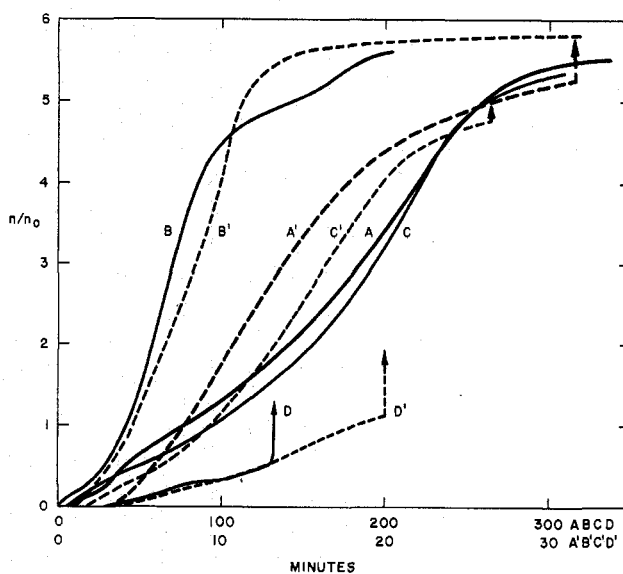

Fig. 1.—Thermal decomposition of $[Co(NH_3)_6](N_3)_3$ (powder). A, 120°, initially evacuated; B, 120°, 100.4 mm. NH_3 initially present; C, 120°, 100.0 mm. N_2; D, 120°, trapped; A', 140°, initially evacuated; B', 140°, 106.4 mm. NH_3; C', 405.5 mm. NH_3; D', 140°, trapped.
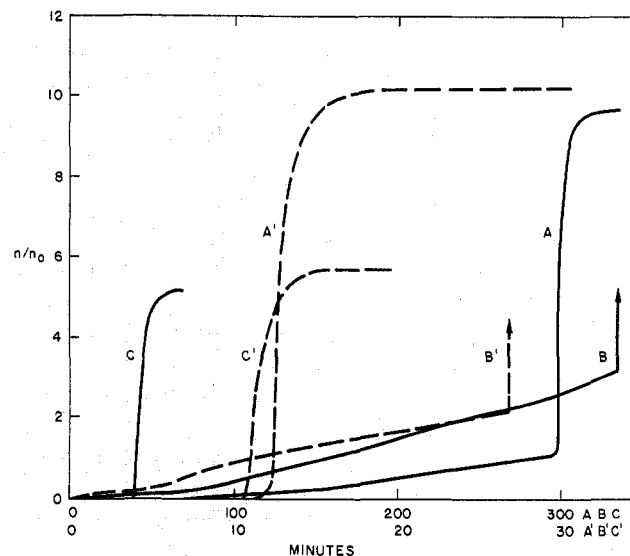

Fig. 2.—Thermal decomposition of $[Co(NH_3)_6](N_3)_3$ (crystals). A, 130°, initially evacuated; B, 130°, 101.0 mm. NH_3 initially present; C, 130°, trapped; A', 150°, initially evacuated; B', 150°, 100.7 mm. NH_3; C', 150°, trapped.

vations, reflects this complexity. Consequently, it is desirable to provide a consistent, qualitative explanation of the relationship between the various reactions which can occur during the decomposition.

To be accounted for are: (1) powder samples are more labile than crystals; (2) crystals usually show a long induction period and a fast, non-explosive reaction to CoN, but added ammonia will promote the formation of $Co(NH_3)_2(N_3)_2$ and inhibit the rapid CoN reaction, the run then terminating in an explosion; (3) crystals exposed to a cold trap produce CoN smoothly with shortened induction periods; (4) the CoN reaction is inhibited by very tiny amounts of ammonia; (5)

powder proceeds slowly to $Co(NH_3)_2(N_3)_2$ at low temperatures or in the presence of added ammonia, at higher temperatures the diammine explodes; (6) powder exposed to a cold trap explodes with shortened induction periods except at 120° when it may produce CoN smoothly; (7) the one-electron reduction to cobalt(II) (eq. 1) is accelerated by moderate ammonia pressures, inhibited by higher pressures.

A reasonable picture may be formed in terms of an over-all decomposition involving two major processes. One is the (probably) only moderately energetic one-electron reduction (eq. 1), the other a very exothermic decomposition to the final product, either cobalt (eq. 2) or CoN (eq. 3). Once the latter is well initiated, the energy liberated is sufficient to ensure rapid propagation through the solid by either the non-explosive reaction to CoN or, alternately, an explosion to cobalt. Which of these paths will be followed will depend on the time of initiation of the energetic reaction relative to the progress of the one-electron reduction.

The over-all decomposition may be thought of as a competition between the one-electron reduction and the *initiation* of the rapid exothermic reaction (without being specific as to the nature of the latter). Once the exothermic reaction begins, the quantity of cobalt(II) present determines whether it goes smoothly to the nitride or explodes. If the initiation occurs early relative to the progress of the one-electron reaction, a large amount of the original hexaammine still will be present and the energetic decomposition will proceed smoothly to CoN. Conversely, if the one-electron reaction has progressed far, the composition of the solid will have been altered by the accumulation of cobalt(II) complexes. Initiation of an exothermic reaction will now lead to an explosion of these compounds. The explosion, in turn, will destroy any remaining hexaammine.

Ammonia affects both processes, accelerating the one-electron reaction and inhibiting the initiation of the exothermic reaction. First considering large crystals, the effect of minute quantities of ammonia may be understood in terms of surface adsorption. It is reasonable to assume that reaction begins most readily on and near the surface since powder, with a high surface to volume ratio, is more labile than larger crystals. If it is further assumed that the ammonia produced in the early stages of the reaction is adsorbed on the surface, an explanation of the inhibiting action of small quantities of ammonia is possible. While the reaction is young, having produced a microscopic amount of solid product and a manometrically undetectable quantity of gases, sufficient decomposition will have occurred to surround the site with adsorbed ammonia. This ammonia, by acting directly on the young reaction site, can strongly influence the course of the reaction.

Decomposition thus may be visualized as beginning on the surface, rapidly consuming the surface layers (and, perhaps, regions of internal imperfection) but penetrating the bulk of the crystal slowly. The adsorbed ammonia inhibits the energetic reaction and the total decomposition remains small. Eventually the inhibition is overcome, probably by local overheating, and the reaction propagates through the crystal (still primarily $[Co(NH_3)_6](N_3)_3$) to yield CoN. Reducing the adsorbed ammonia with a cold trap permits an earlier initiation of the energetic reaction and so shortens the induction period.

Conversely, excess ammonia not only more effectively inhibits the initiation of the energetic reaction, but also accelerates the one-electron reduction (as shown by experiments with the powder). Thus in the presence of added ammonia a considerable amount of the diammine may be produced prior to the rapid reaction. When the energetic reaction finally is initiated the diammine explodes, shattering the crystal and scattering some of the still unreacted hexaammine out of the hot zone of the reaction vessel.

With microcrystalline powders the situation is altered by a surface area 100 to 1000 times greater than in the visibly crystalline samples. The initial surface reaction thus generates considerable ammonia. This promotes the reduction to cobalt(II) and inhibits the initiation of the energetic reaction. Moreover, a surface reaction penetrating only a short distance into small crystals consumes a large percentage of the sample. (For instance, a uniform penetration of only ten molecular layers would consume about 35% of a 0.1 μ crystal.) Consequently, by the time local overheating could overcome the ammonia's inhibition and initiate the energetic reaction, the sample would consist largely of $[Co(NH_3)_2(N_3)_2]$ and an explosion would result.

The explosion can be avoided by completely inhibiting its initiation with added ammonia (at low temperatures the product ammonia is sufficient) or by mixing the solid with KCl. The latter probably decreases the chance of local overheating by acting as a heat sink. Alternately, the powder can follow the non-explosive CoN path if the one-electron reduction is slowed relative to the time needed to initiate the energetic reaction. Thus at 120°, with a cold trap providing the most favorable situation for initiation, the fast reaction can commence before much cobalt(II) has accumulated and so go non-explosively to CoN. That these are borderline conditions is indicated by two samples following the CoN path while a third exploded. The existence, therefore, of two possible paths will account for the general characteristics of the decomposition of $[Co(NH_3)_6](N_3)_3$. This explanation should provide a base for detailed studies of the reaction mechanisms.