

1184. Thermal Decomposition of Thallous Cyanamide.

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The kinetics of the thermal decomposition of thallous cyanamide have been investigated in the temperature range 460—960°C. Four distinct stages of decomposition are obtained: (1) 460—540°; (2) 500—660°, (3) 660—740°, and (4) 740—960°C. Stages (1), (2), and (3) are adequately described by first-order reactions according to:

$$k_1 \text{ (sec.}^{-1}\text{)} = 8.6 \times 10^5 \exp(-30.8 \text{ kcal./RT})$$

$$k_2 \text{ (sec.}^{-1}\text{)} = 7.9 \times 10^{10} \exp(-56.5 \text{ kcal./RT})$$

$$k_3 \text{ (sec.}^{-1}\text{)} = 1.7 \times 10^{15} \exp(-82.0 \text{ kcal./RT})$$

The percentage total decomposition in terms of nitrogen evolved was (1) 14.4, (2) 25.1, (3) 30.7, (4) ~ 100 at 960°C. The gaseous products are N₂ and (CN)₂, the ratio N₂:(CN)₂ being 3 [stage (1)], 3.4 [stage (2)], and ~ 1 [stage (3)]. Some suggestions are made to account for the main features of this complex decomposition.

THALLOUS CYANAMIDE comprises a linear symmetrical triatomic ion (N=C=N)²⁻ bonded at each end to a thallous ion.¹ The anion is isoelectronic with the azide ion; thus, by analogy with the azide, thallous cyanamide may be expected to decompose thermally according to the general equation:^{2,3}



Considerable information is available about the physical properties of thallous cyanamide;⁴ thus, it undergoes photodecomposition when exposed to a high-pressure mercury lamp with the production of metallic thallium; the ultraviolet absorption edge commences at 5950 Å and, on irradiation by light of 5000—7000 Å, photoconduction associated with an activation energy of 6.3 kcal./mole occurs; from its refractive index (> 1.81) and "static" dielectric constant (~ 7.0) the energy to raise an electron from the full cyanamide band to the conduction band is estimated to be 65 kcal. (optical), or 34.5 kcal. (thermal). Whilst its thermal stability has not previously been studied in detail, decomposition is reported to be considerable at 275°C. At 520°, the solid melts and rapidly decomposes, the nature of the products being unknown.

An attempt has therefore been made to correlate the decomposition kinetics with physical properties and also with the general information available on thallous azide. Unfortunately, the course of the reaction is complex, and is further complicated by a concurrent hydrolysis if water occluded in the crystals is not rigorously removed.

EXPERIMENTAL

Preparation.—By the general procedure of Deb and Yoffe,⁴ a solution of 0.035 mole of Eastman Kodak 90% pure sodium cyanamide in 75 ml. of water was added during 20 min. to a hot solution of 0.029 mole of thallous sulphate in 90 ml. of water. Orange-red crystals of thallous cyanamide were precipitated. The solution was allowed to cool for 1 hr., and the crystals were filtered off, washed with water, ethanol, and anhydrous ether, and then dried and stored over phosphoric oxide in the dark (yield 7.06 g.) (Found: N, 6.41, 6.30. Calc. for CN₂Tl₂: N, 6.24%). The infrared spectrum showed strong absorption (ν₃) at 1845 cm.⁻¹ (cf. 1857 cm.⁻¹ in ref. 4); a band at 2120 cm.⁻¹ associated with sodium cyanamide could not be detected. The purity, determined gravimetrically by precipitation of silver cyanamide with silver nitrate, was 99.3%.

¹ Bredig, *J. Amer. Chem. Soc.*, 1942, **31**, 1730; cf. ref. (4).

² Bollis-Canisella, *Ann. Chim. (Italy)*, 1954, **44**, 1050.

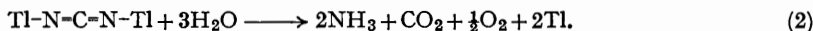
³ Chrelien and Woringer, *Compt. rend.*, 1951, **232**, 1114.

⁴ Deb and Yoffe, *Trans. Faraday Soc.*, 1959, **55**, 106.

Procedure.—Thermal decomposition was followed by measuring the pressure increase of the gaseous products at appropriate times in a constant-volume system with two McLeod gauges covering the range from 10^{-5} to 2 torr. The cyanamide (25 mg.) was contained in a Pyrex boat (silica for temperatures $> 500^{\circ}\text{C}$), which was towed into a horizontal quartz reaction vessel by means of a magnetically-operated iron slug sealed in glass. The furnace around the vessel was controlled electronically to $\pm 0.5^{\circ}$, the temperature being measured by a calibrated Pt/Pt-Rh thermocouple. A trap, immersed in liquid nitrogen, was inserted between the reaction vessel and the gauges, to condense the cyanogen, and so to enable the rate of evolution of nitrogen to be measured.

RESULTS

In preliminary experiments, gaseous products were evolved between 245 and 325° in an erratic and irreproducible manner owing to reaction with occluded water in the thallos cyanamide:



This hydrolysis, found with the silver salt by Chrelien and Woringer,³ reduced the Tl content by as much as 8% and probably accounts for the apparent melting of the thallos cyanamide at 252° .⁴ This hydrolysis could be eliminated by outgassing the salt at 120° for 12 hr. at 10^{-6} mm. after which no decomposition was detected below 400° .

Kinetics of Nitrogen Evolution.—Nitrogen-evolution rates were obtained with the vapour trap immersed in liquid nitrogen. Four distinct stages of decomposition, depending on the temperature range used, were obtained (Figures). Three of these stages can be described by first-order equations:

$$\ln[p_{\infty}^i/(p_{\infty}^i - p^i)] = k^i t$$

where p^i is the pressure of nitrogen evolved at time t , and p_{∞}^i is the final pressure developed in stage (i) and k^i is the relevant rate constant. Typical α/t plots shown in Figs. 1, 2, and 3 refer

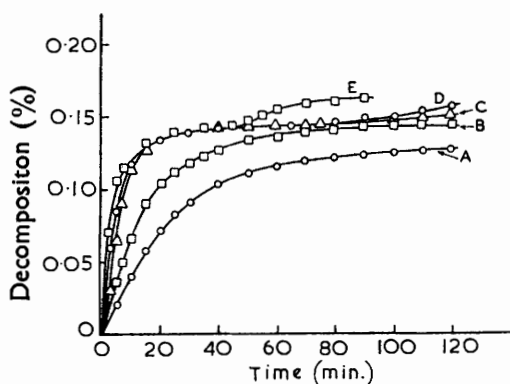


FIG. 1. Plot of percentage decomposition as a function of time in minutes for stage (1) decomposition at various temperatures from 460 to 540° .

A, 460° ; B, 480° ; C, 500° ; D, 520° ; E, 540° .

respectively to stage (1), 400 — 540° ; stage (2), 500 — 660° ; and stage (3), 640 — 740° . The percentage decomposition, α , was calculated in terms of the total amount of nitrogen present initially in the cyanamide. In terms of the equation,



the value 2α gives the percentage of the available nitrogen evolved.

For each stage, activation energies were derived from the linear plots of $\log_{10} k^i$ against $1/T^{\circ}\text{K}$. The velocity constant k_1 of stage (1) is well described by

$$k_1 (\text{sec.}^{-1}) = 8.6 \times 10^5 \exp(-30.8 \text{ kcal./RT}) \quad (3)$$

If the rate-determining step is the excitation of an electron from the valence to the conduction band, an activation energy of around 35 kcal./mole is predicted.

In the analysis of stage (2) decomposition at a temperature T_2 ($> 500^{\circ}$), the amount of gas that

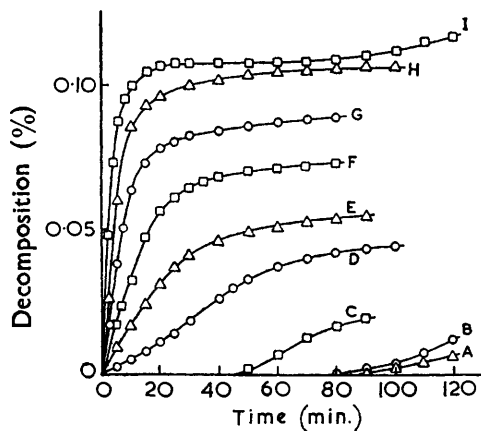


FIG. 2. Plot of percentage decomposition as a function of time in minutes for stage (2) decomposition at various temperatures from 500 to 660°.

A, 500°; B, 520°; C, 540°; D, 560°; E, 580°; F, 600°; G, 620°; H, 640°; I, 660°.

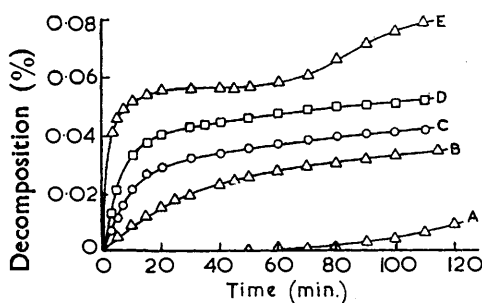


FIG. 3. Plot of percentage decomposition as a function of time in minutes for stage (3) decomposition at various temperatures from 660 to 740°.

A, 660°; B, 680°; C, 700°; D, 720°; E, 740°.

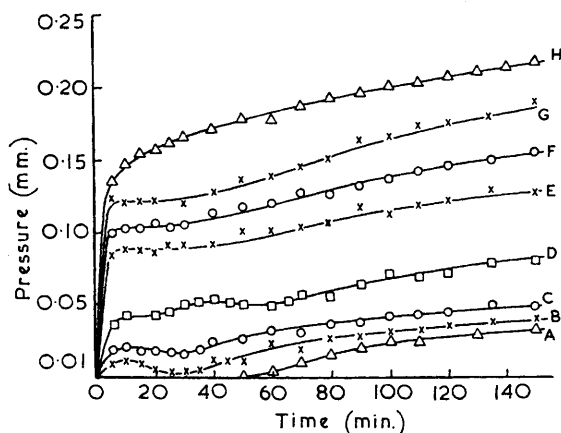


FIG. 4. Stage (4) decomposition; plot of pressure of nitrogen evolved in mm. against time in minutes at various temperatures from 740 to 960°.

A, 740°; B, 760°; C, 780°; D, 800°; E, 840°; F, 880°; G, 920°; H, 960°.

would have been evolved at any time t at this temperature by the stage (1) process was subtracted from the total amount of gas obtained at time t and temperature T_2 , with the aid of equation (4)

$$\log \left(\frac{k_1^{(T_2)}}{k_1^{(480)}} \right) = \frac{E_1}{2.3R} \left(\frac{T_2 - T_{480}}{T_2 T_{480}} \right) \quad (4)$$

where $k_1^{(480)}$, $k_1^{(T_2)}$ are respectively the values of k_1 at 480° for stage (1) (obtained experimentally) and at T_2 , where T_2 is a temperature within the second-stage temperature range. Consequently, the pressure p^1 to be subtracted from the total pressure ($p^1 + p^2$) is given by

$$p^1 = p^1_{\infty} [1 - \exp(-k_1^{(T_2)} t)] \quad (5)$$

From the unimolecular plot of α_2 against time, the velocity constant, k_2 , of stage (2) is then found to be

$$k_2(\text{sec.}^{-1}) = 7.9 \times 10^{10} \exp(-56.5 \text{ kcal./RT}) \quad (6)$$

In the third stage, after similar correction for the preceding stages, k_3 was evaluated as

$$k_3(\text{sec.}^{-1}) = 1.7 \times 10^{15} \exp(-82.0 \text{ kcal./RT}) \quad (7)$$

The extent of decomposition in terms of nitrogen evolved in the various stages were (1) 14.4%, (2) 10.7%, (total 25.1%); (3) 5.6%, (total 30.7%). Thus, the total nitrogen evolution after stage (3) represents 61.4% of that expected from equation (1).

In the highest temperature range, 740–1000°, the pressure–time plots were complex. In general, at below 960°, there is a high initial rate followed below 960° by a period of about $\frac{1}{2}$ hr. during which the nitrogen pressure is either roughly constant, or, at the lower temperatures 760–780°, even decreases. This plateau is followed by a slow evolution of nitrogen over long periods. Undoubtedly, the nitrogen reacts with the thallium metal produced in the decomposition and/or with other products since a brownish black residue begins to accumulate, the amount being quite substantial at 960°. This residue is insoluble in the usual solvents and is unaffected by hot alkalis and acids; it is probably a polymer, such as carbon nitride $(\text{C}_3\text{N}_4)_x$, obtained when cyanamide is heated to high temperatures, together with thallium carbide.

Since this work was completed, Sole and Yoffe⁵ have reported some brief work on the thermal decomposition of thallos cyanamide; their results do not agree with ours. Their "initial small irreproducible bump" probably arises from the hydrolysis since no special precautions were taken to remove completely the occluded water. The decomposition is stated to follow equation (1), the reaction being rapid and decomposition apparently complete above 520°. We find the extent of decomposition to be only 25% at this temperature. The reason for the disagreement is that they used a bucket made of platinum, which we found to catalyse the reaction. Unless the furnace design is suitable (as in our experiments) there is indeed loss of material by sublimation. In some preliminary work we endeavoured to prevent this by enclosing the cyanamide in platinum foil but found that even at 470° both stages (1) and (2) occurred simultaneously, apparently as a single process. Without the presence of platinum the temperature required to simulate this single process is 640°. Their decay period also followed a unimolecular law, but the activation energy of 47.5 kcal./mole was, as would be expected, between those determined by us for stages (1) and (2), *viz.*, 30.8 and 56.5 kcal./mole, respectively.

Nitrogen:Cyanogen Ratio.—A series of experiments was undertaken to measure the ratio of nitrogen to cyanogen evolved during the decomposition at various temperatures. The Table summarizes the main results. In series I, the cyanogen was condensed during the decomposition in the trap cooled by liquid nitrogen. At the end of the experiment, the trap was warmed to room temperature and the total gas pressure recorded; the cyanogen pressure was then obtained by difference. In series II, the total pressure of nitrogen + cyanogen evolved was measured, the cold trap being at room temperature, and on completion of the run, the cyanogen was condensed by cooling the trap to 77°K, and the pressure of the remaining nitrogen recorded. The Table shows that the amount of nitrogen evolved in the first three stages of decomposition was independent of whether the cyanogen was removed by condensation during reaction. The Table also shows that gaseous cyanogen reacts with the other products of the decomposition to form a non-volatile solid or a solid polymer. Cyanide ion can be detected in the residue; thus some of the cyanogen must react with the thallium produced in the decomposition. If it is assumed that no cyanogen is lost during series I, the ratio of evolved nitrogen to cyanogen is about 3:1 in stage (1). This ratio is maintained throughout the course of the decomposition, since in one run at 480° with the liquid-nitrogen trap immediately adjacent to the reaction vessel for maximum efficiency of removal of gaseous cyanogen, the thallos cyanamide sample was removed at 10 min. intervals from the hot reaction vessel into a cool part of the apparatus and the $\text{N}_2:(\text{CN})_2$ ratio determined from the pressures recorded with the trap first at liquid-nitrogen and then at room temperature. The gaseous products were removed, the sample returned to the reaction vessel, and the measurements repeated at subsequent 10 min. intervals. The ratio remained constant at 3:1 throughout the whole of the stage (1) decomposition, and the rate of evolution of cyanogen obeyed first-order kinetics throughout.

⁵ Sole and Yoffe, *Proc. Roy. Soc.*, 1964, A, **277**, 523.

Nitrogen: cyanogen ratios.

Liquid-nitrogen runs ^{a, b} (series I)					Total pressure runs ^a (series II)			
Temp.	α_T	$\alpha_{N_2^1}$	$\alpha(CN)_2^1$	$N_2^1:(CN)_2^1$	α_T	$\alpha_{N_2^1}$	$\alpha(CN)_2^1$	$N_2^1:(CN)_2^1$
460°	18.7	13.4	4.7	2.85:1	15.0	13.3	1.7	7.8:1
480	19.1	14.3	4.8	3.0:1	16.9	14.1	2.8	5.0:1
480	19.1*	14.4	4.9	2.9:1	17.6	14.3	3.3	4.3:1
480	—	—	—	—	19.5	14.3	5.2	2.75:1
500	19.3 ^c	14.4	4.9	2.9:1	—	—	—	—

2nd Stage								
	α_T	$\alpha_{N_2^2}$	$\alpha(CN)_2^2$	$N_2^2:(CN)_2^2$	α_T	$\alpha_{N_2^2}$	$\alpha(CN)_2^2$	$N_2^2:(CN)_2^2$
640	36.4	25.2	11.2	1.73:1	36.0	25.6	10.4	—
640	43.9*	25.0	18.9	1:1.33	—	—	—	—
660	36.8 ^d	25.4	11.4	1.65:1	36.8	25.2	11.6	—
660	44.1* ^d	24.9	19.2	1:1.35	—	—	—	—

3rd Stage								
	α_T	$\alpha_{N_2^3}$	$\alpha(CN)_2^3$	$N_2^3:(CN)_2^3$	α_T	$\alpha_{N_2^3}$	$\alpha(CN)_2^3$	$N_2^3:(CN)_2^3$
720	54.0*	30.0	24.0	1.2:1	48.6	29.8	18.8	—
720	46.2	30.2	16.0	—	—	—	—	—

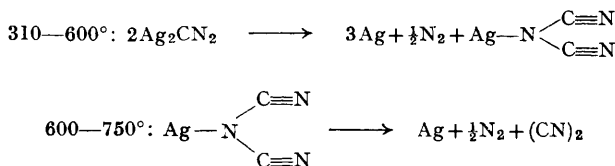
^a All experiments conducted for 150 min. using 25 mg. of thallium cyanamide. ^b Cyanogen condensed out by diffusion into liquid-nitrogen trap. ^c Experiment run for 40 min. ^d Experiment run for 60 min.

* Cyanogen condensed out by direct passage through nitrogen trap.

In stage (2), the reaction which causes loss of cyanogen from the gas phase is evidently more rapid; the faster this gas is removed by condensation the greater is the yield. Thus, at 640°, in the run designated by an asterisk, the yield is much higher ($\alpha = 18.9$) than in the corresponding run at the same temperature ($\alpha = 11.2$) where the condensation was less efficient. This result is in contrast to the corresponding two experiments at 480° where α is the same in each. In stage (3) for the decompositions at 720°, the cyanogen is clearly removed from the gas phase by reaction unless it is efficiently condensed out. The minimum values of the $N_2:(CN)_2$ ratio for stages (2) and (3) are 3:4 and about 1:1, respectively, though these do not correspond to no loss of cyanogen.

DISCUSSION

The gaseous products of decomposition are predominantly nitrogen and cyanogen, as expected from the analogous azide reaction. Below the m. p. of the dried salt (520°), gaseous cyanogen reacts with the other products, in particular with thallium metal to form cyanide. Nevertheless, the results suggest that N_2 and $(CN)_2$ are not produced in equal quantities according to equation (1). Silver cyanamide is reported to decompose by two consecutive first-order processes,³ viz.,



With the thallous salt, evolution of cyanogen occurs even at the lowest temperatures so that a similar mechanism is not applicable. More probably the unit of decomposition comprises more than one molecule; in this connexion we note that the sodium salt of dicyano-imide $Na-N(-C \equiv N)_2$ trimerizes on heating, forming the trisodium salt of tricyanomelamine $Na_3C_6N_9$. If, therefore, a ratio of 3:1 is accepted for the relative amounts of N_2 and $(CN)_2$ evolved, the unit of decomposition may well be an anionic "trimer," which is probably cyclic. The low frequency factor of 10^5 sec.^{-1} compared with a "normal" value of $10^{13} \text{ sec.}^{-1}$ would be consistent with a decomposition involving free rotation of this "trimer" at the onset of

reaction, which decomposes by a first-order process to give three molecules of N_2 and one of $(CN)_2$, together with some thallium and solid residue. The latter decomposes at higher temperatures giving approximate equal amounts of N_2 and $(CN)_2$, suggesting that the residue comprises in part the trithallium salt of tricyanomelamine. The processes occurring in the last stages above 740° are complicated by side-reactions of the products; at 960° , almost the stoichiometric amount of N_2 is evolved so that the unreactive residue is presumably thallium carbide.

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