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THERMOGRAVIMETRIC ANALYSIS OF SOME INTERACTION PRODUCTS OF 1,2,3-BENZOTRIAZOLE HYDROCHLORIDE WITH CERTAIN NEGATIVE CYANO-COMPLEXES OF THE TRANSITION METALS

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Summary—Thermogravimetric pyrolyses of some interaction products of certain negative cyano-complexes of the transition metals with 1,2,3-benzotriazole hydrochloride and identification of several intermediate products formed during the course of the reactions are reported.

THIS paper arises from part of a general study of the interaction products of some of the transition metals with 1,2,3-benzotriazole hydrochloride. Pyrolyses of cyano-complexes of molybdenum, ruthenium, osmium, cobalt, manganese, platinum, palladium and nickel, and of the thiocyano-complex of cobalt have been studied using a thermobalance. It was found that all of the compounds were stable up to at least 45° and that decomposition of the compounds occurred between 45° and 480°. Thermogravimetric analysis of these complex compounds gave support to the proposed formulae of the 1,2,3-benzotriazole hydrochloride interaction products with the aforementioned metal complexes reported by Wilson and James.[2]

The purposes of this study were to use the thermobalance as a means of detecting and following the course of the solid-state reactions of the aforementioned products, and to isolate and attempt to identify some of the intermediate products formed during the course of these reactions.

EXPERIMENTAL

Analyses

Determinations of carbon, nitrogen and hydrogen were provided by commercial analysts. Determinations of the metal content of the compounds were made in this laboratory by decomposing the compounds in air, then reducing the oxides to the pure metal in an atmosphere of hydrogen, employing a Vycor combustion chamber.

Apparatus

The thermobalance and its calibration, operation and use have been reported previously by Wilson and Henry.[3] The furnace temperature was increased at an average rate of 2°/min over a temperature range of room temperature to approximately 600°. A Beckman-IR-5 Spectrophotometer was used for obtaining spectra of various intermediate products, employing the standard potassium bromide-pellet technique in which spectra-grade potassium bromide was used. The intermediate products were obtained according to the procedure reported by Wilson and James.[2]

RESULTS

Thermograms for compounds 1–9 with the respective formulae:

$(C_6H_4N_2NH_2)_4Mo(CN)_8$, $(C_6H_4N_2NH_2)_2(C_6H_4N_2NH)[Pt(CN)_6]$,

$(C_6H_4N_2NH)Ni(CN)_2{\cdot}2HCN$, $(C_6H_4N_2NH_2)_2Ru(CN)_6$,

$(C_6H_4N_2NH_2)_3Mn(CN)_6$, $(C_6H_4N_2NH_2)_2(C_6H_4N_2NH)[Pd(CN)_6]$,

$(C_6H_4N_2NH_2)_3Co(CN)_6$, $(C_6H_4N_2NH_2)_3Co(SCN)_6$

and

$(C_6H_4N_2NH_2)_2Os(CN)_6$,

were obtained as described by Wilson and Henry.[3] The pyrolysis curves are presented graphically in Figs. 1, 2 and 3; the analysis of these curves is given in Table I and analyses for several of the intermediate products formed during the course of the thermogravimetric analyses are given in Table II. For each of the above compounds

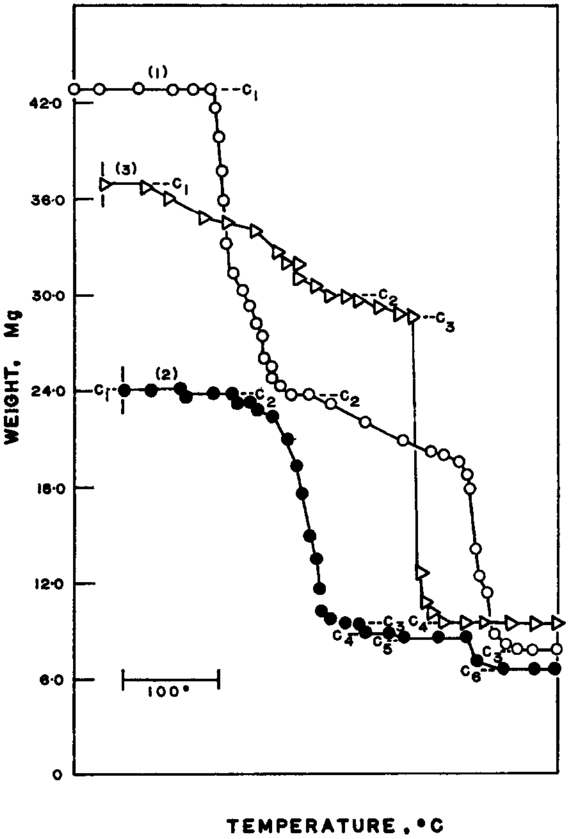

FIG 1.—Thermogravimetric analysis of compounds 1–3:—
(1) $(C_6H_4N_2NH_2)_4$ $Mo(CN)_8$: —○—,
(2) $(C_6H_4N_2NH_2)_2(C_6H_4N_2NH)[Pt(CN)_6]$: —●—,
(3) $(C_6H_4N_2NH)Ni(CN)_2 \cdot 2HCN$: —▷—.

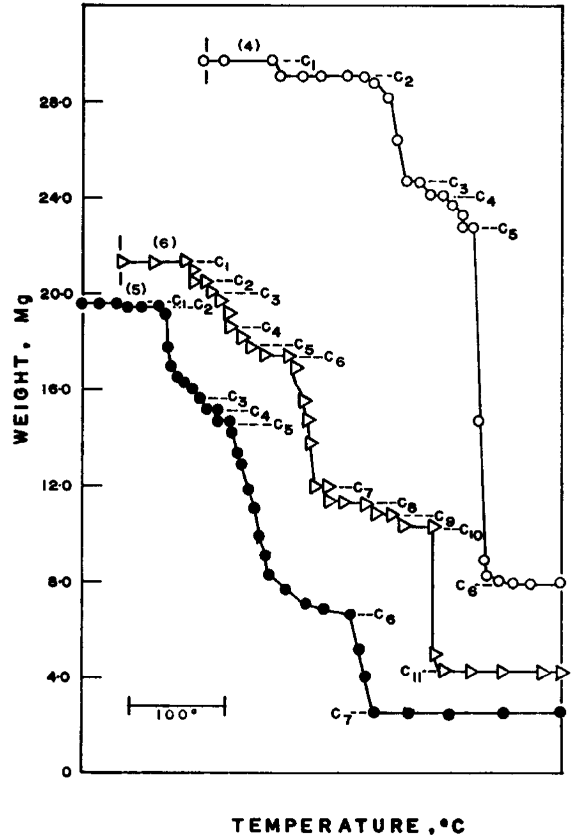

FIG. 2.—Thermogravimetric analysis of compounds 4–6:
(4) $(C_6H_4N_2NH_2)_2Ru(CN)_6$: —○—,
(5) $(C_6H_4N_2NH_2)_3Mn(CN)_6$: —●—,
(6) $(C_6H_4N_2NH_2)_2(C_6H_4N_2NH)[Pd(CN)_6]$: —▷—.

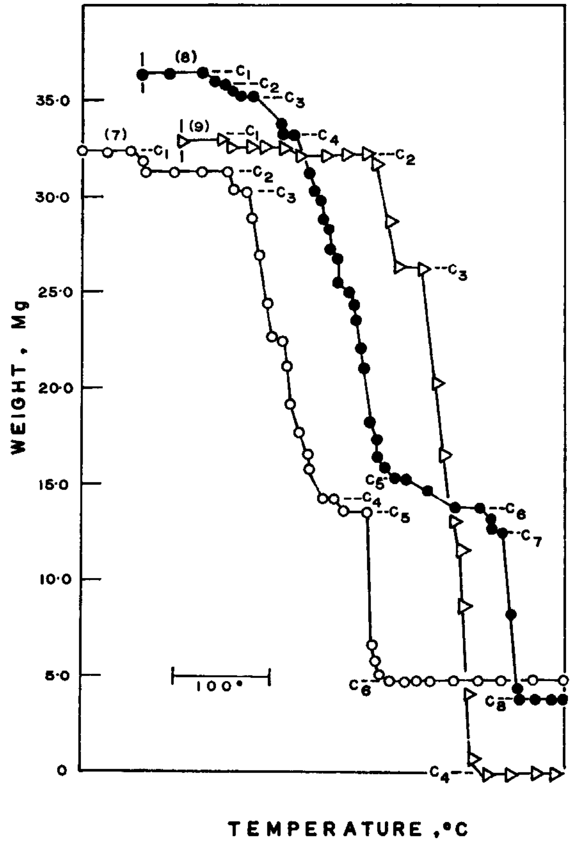

FIG. 3.—Thermogravimetric analysis of compounds 7–9:
(7) $(C_6H_4N_2NH_2)_3Co(CN)_6$: —○—,
(8) $(C_6H_4N_2NH_2)_3Co(SCN)_6$: —●—.
(9) $(C_6H_4N_2NH_2)_2Os(CN)_6$: —▷—.

TABLE I

Compound	C_1			C_2			C_3			C_4		
	Initial weight, *mg*	Weight corrected for moisture, *mg*	Temp range, °*C*	Weight, *mg* Calc.	Weight, *mg* Meas.	Temp range, °*C*	Weight, *mg* Calc.	Weight, *mg* Meas.	Temp range, °*C*	Weight, *mg* Calc.	Weight, *mg* Meas.	Temp range, °*C*
1. $(C_6H_4N_2NH_2)_4Mo(CN)_8$	42·9		<140	24·0	23·9	225–240	7·9	7·8	>480			
2. $(C_6H_4N_2NH_2)_2(C_6H_4N_2NH)[Pt(CN)_6]$	24·2	24·0	<60									
3. $(C_6H_4N_2NH)Ni(CN)_2{\cdot}2HCN$	37·1		<45	30·0	30·0	45–250				9·5	9·6	>400
4. $(C_6H_4N_2NH_2)_2Ru(CN)_6$	29·7	29·1	<75									
5. $(C_6H_4N_2NH_2)_3Mn(CN)_6$	19·6	19·4	<50									
6. $(C_6H_4N_2NH_2)_2(C_6H_4N_2NH)[Pd(CN)_6]$	21·3		<70									
7. $(C_6H_4N_2NH_2)_3Co(CN)_6$	32·4		<50				30·9	30·9	155–165	14·4	14·3	270–295
8. $(C_6H_4N_2NH_2)_3Co(SCN)_6$	36·5		<65									
9. $(C_6H_4N_2NH_2)_2Os(CN)_6$	33·0	32·4	<45				26·4	26·3	220–240	0.0	0·0	>430

TABLE I.—(CONTD.)

Compound	C_5			C_6			C_7			C_8			C_{11}		
	Weight, *mg* Calc.	Weight, *mg* Meas.	Temp range, °*C*	Weight, *mg* Calc.	Weight, *mg* Meas.	Temp range, °*C*	Weight, *mg* Calc.	Weight, *mg* Meas.	Temp range, °*C*	Weight, *mg* Calc.	Weight, *mg* Meas.	Temp range, °*C*	Weight, *mg* Calc.	Weight, *mg* Meas.	Temp range, °*C*
1. $(C_6H_4N_2NH_2)_4Mo(CN)_8$															
2. $(C_6H_4N_2NH_2)_2(C_6H_4N_2NH)[Pt(CN)_6]$	8·3	8·4	290–350	6·6	6·7	>375									
3. $(C_6H_4N_2NH)Ni(CN)_2{\cdot}2HCN$															
4. $(C_6H_4N_2NH_2)_2Ru(CN)_6$	22·8	22·7	260–270	8·0	7·9	>280									
5. $(C_6H_6N_2NH_2)_3Mn(CN)_6$	14·9	14·9	130–145				2·7	2·6	>305						
6. $(C_6H_4N_2NH_2)_2(C_6H_4N_2NH)[Pd(CN)_6]$										11·3	11·3	225–260	4·2	4·3	>335
7. $(C_6H_4N_2NH_2)_3Co(CN)_6$				4·7	4·8	>320									
8. $(C_6H_4N_2NH_2)_3Co(SCN)_6$				14·0	13·9	330–350				4·0	3·9	>400			
9. $(C_6H_4N_2NH_2)_2Os(CN)_6$															

TABLE II

Initial compound	Description	Temp. range, °C	Intermediate compound	Description	Temp. range, °C	Calculated (Found) for % intermediate compounds,			
						Carbon	Nitrogen	Hydrogen	Metal
$(C_6H_4N_2NH_2)_4Mo(CN)_8$	Yellow, crystalline compound	<140	$(C_6H_4N_2NH)_2Mo(CN)_4$	Black, crystalline compound	215–225	43·85 (44·24)	31·96 (31·49)	2·30 (2·54)	21·89 (21·73)
$(C_6H_4N_2NH_2)_2Ru(CN)_6$	Light grey, powdery compound	<160	$(C_6H_4N_2N)_2Ru(CN)_2$	Blue-black, crystalline compound	255–265	43·12 (43·03)	28·73 (28·94)	2·07 (2·24)	26·08 (25·79)
$(C_6H_4N_2NH_2)_3Co(CN)_6$	White, crystalline compound	<55	$(C_6H_4N_2NH)Co(CN)_3$	Black, crystalline compound	275–300	42·21 (42·06)	32·82 (32·75)	1·97 (1·72)	23·01 (23·47)
$(C_6H_4N_2NH_2)_2Os(CN)_6$	Light blue, powdery compound	<190	$(C_6H_4N_2N)_2Os(CN)_2$	Blue-black, crystalline compound	230–250	35·14 (35·02)	23·42 (23·04)	1·69 (1·54)	39·75 (40·40)

the weights for the breaks $C_2, C_3, \ldots, C_n$ were calculated on the basis of the following reactions:

Compound 1

$$C_2\text{: } 2(C_6H_4N_2NH_2)_4Mo(CN)_8 \xrightarrow[\Delta]{(140\text{–}225)^\circ}$$
$$4C_6H_4N_2NH\uparrow + 8HCN\uparrow + 2(C_6H_4N_2NH)_2Mo(CN)_4$$

$$C_3\text{: } 2(C_6H_4N_2NH)_2Mo(CN)_4 + 3O_2 \xrightarrow[\Delta]{(240\text{–}480)^\circ}$$
$$4(CN)_2\uparrow + 4C_6H_4N_2NH\uparrow + 2MoO_3$$

Compound 2

$$C_5\text{: } (C_6H_4N_2NH_2)_2(C_6H_4N_2NH)[Pt(CN)_6] \xrightarrow[\Delta]{(115\text{–}290)^\circ}$$
$$2HCN\uparrow + 3C_6H_4N_2NH\uparrow + (CN)_2\uparrow + Pt(CN)_2$$

$$C_6\text{: } Pt(CN)_2 \xrightarrow[\Delta]{(350\text{–}375)^\circ} Pt + (CN)_2\uparrow$$

Compound 3

$$C_2\text{: } 2(C_6H_4N_2NH)Ni(CN)_2\cdot 2HCN \xrightarrow[\Delta]{(45\text{–}230)^\circ}$$
$$4HCN\uparrow + 2(C_6H_4N_2NH)Ni(CN)_2$$

$$C_4\text{: } 2(C_6H_4N_2NH)Ni(CN)_2 + O_2 \xrightarrow[\Delta]{(255\text{–}400)^\circ}$$
$$2(CN)_2\uparrow + 2C_6H_4N_2NH\uparrow + 2NiO$$

Compound 4

$$C_5\text{: } (C_6H_4N_2NH_2)_2Ru(CN)_6 \xrightarrow[\Delta]{(260\text{–}270)^\circ} 4HCN\uparrow + (C_6H_4N_2N)_2Ru(CN)_2$$

$$C_6\text{: } (C_6H_4N_2N)_2Ru(CN)_2 + O_2 \xrightarrow[\Delta]{(270\text{–}280)^\circ} G\uparrow + RuO_2$$

where G represents the volatile organic pyrolytic products formed during the course of the chemical process.

Compound 5

$$C_5\text{: } 3(C_6H_4N_2NH_2)_3Mn(CN)_6 \xrightarrow[\Delta]{(130\text{–}145)^\circ}$$
$$15HCN\uparrow + 3(C_6H_4N_2NH)(C_6H_4N_2N)_2Mn(CN)$$

$$C_7\text{: } 3(C_6H_4N_2NH)(C_6H_4N_2N)_2Mn(CN) + 2O_2 \xrightarrow[\Delta]{(150\text{–}305)^\circ}$$
$$3C_6H_4N_2NH\uparrow + G\uparrow + Mn_3O_4$$

Compound 6

$$C_8\text{: } 2(C_6H_4N_2NH_2)_2(C_6H_4N_2NH)[Pd(CN)_6] \xrightarrow[\Delta]{(70\text{–}206)^\circ}$$
$$4HCN\uparrow + 4C_6H_4N_2NH\uparrow + 2(C_6H_4N_2NH)Pd(CN)_4$$

$$C_{11}\text{: } 2(C_6H_4N_2NH)Pd(CN)_4 + O_2 \xrightarrow[\Delta]{(305\text{–}335)^\circ}$$
$$4(CN)_2\uparrow\ 2C_6H_4N_2NH\uparrow + 2PdO$$

Compound 7

$$C_3\text{: } 4(C_6H_4N_2NH_2)_3Co(CN)_6 \xrightarrow[\Delta]{(55\text{–}160)^\circ}$$
$$4HCN\uparrow + 4(C_6H_4N_2NH)(C_6H_4N_2NH_2)_2Co(CN)_5$$

$$C_4\text{: } 4(C_6H_4N_2NH)(C_6H_4N_2NH_2)_2Co(CN)_5 \xrightarrow[\Delta]{(165\text{–}270)^\circ}$$
$$8HCN\uparrow + 8C_6H_4N_2NH\uparrow + 4(C_6H_4N_2NH)Co(CN)_3$$

$$C_6\text{: } 4(C_6H_4N_2NH)Co(CN)_3 + 3O_2 \xrightarrow[\Delta]{(300\text{–}320)^\circ}$$
$$6(CN)_2\uparrow + 4C_6H_4N_2NH\uparrow + 2Co_2O_3$$

Compound 8

$$C_6\colon\ 4(C_6H_4N_2NH_2)_3Co(SCN)_6 \xrightarrow[\Delta]{(60\text{–}330)^\circ} 8H_2\uparrow$$

$$+\ 8(SCN)_2\ 8C_6H_4N_2NH\uparrow + 4(C_6H_4N_2N)Co(SCN)_2$$

$$C_8\colon\ 4(C_6H_4N_2N)Co(SCN)_2 + 3O_2 \xrightarrow[\Delta]{(355\text{–}450)^\circ} G\uparrow + 2Co_2O_3$$

Compound 9

$$C_3\colon\ (C_6H_4N_2NH_2)_2Os(CN)_6 \xrightarrow[\Delta]{(190\text{–}225)^\circ} 4HCN\uparrow + (C_6H_4N_2N)_2Os(CN)_2$$

$$C_4\colon\ (C_6H_4N_2N)_2Os(CN)_2 + 2O_2 \xrightarrow[\Delta]{(250\text{–}420)^\circ} G\uparrow + OsO_4\uparrow$$

Isolation of pyrolysis products

The aforementioned thermogravimetric data, obtained from the pyrolysis of the products resulting from the interaction of certain negative metal ion complexes with the hydrochloride of 1,2,3-benzotriazole, suggested the presence of several decomposition products. To ascertain some further proof of the intermediate products and a qualitative indication of the composition of the volatile organic residue given off over selected temperature ranges, the decomposition vapours resulting from these pyrolyses were trapped and partially analysed. The special all-glass decomposition apparatus, as well as the procedure for isolating the pyrolytic products, have been described previously by Wilson and James.[2] Each of the starting metal-complex compounds was heated separately in the special decomposition apparatus to a temperature slightly above that required to obtain complete decomposition of the compounds. All of the cyano-complex compounds studied, with the exceptions of the ruthenium and osmium compounds, gave decomposition products whose infrared spectra contained all of the principal absorbance bands corresponding to the spectra of pure 1,2,3-benzotriazole in addition to several other absorbance bands which could not be associated directly with 1,2,3-benzotriazole. The presence of 1,2,3-benzotriazole was further verified by dissolving the condensed vapours in water and precipitating the 1,2,3-benzotriazole from an ammoniacal EDTA solution using aqueous silver nitrate, because silver cyanide is highly soluble in such a medium.[1] All of these compounds decomposed to give hydrogen cyanide and/or cyanogen, with the exception of the thiocyanate complex of cobalt, which was precipitated from aqueous silver nitrate solutions as silver cyanide.

For the ruthenium and osmium compounds, the infrared spectra of the volatile organic portion of the residue, after removing any cyanide or cyanogen present, were quite similar and indicated that the residue contained a cyano-compound of 1,2,3-benzotriazole which was not the same, but contained a structure similar to that of *o*-aminobenzonitrile. Similar spectra for the organic portions of the residues of the other seven complex compounds were obtained. These spectra were very similar and indicated that 1,2,3-benzotriazole was the principal organic portion of the residue.

DISCUSSION

These data indicate that complete decomposition of the interaction products of some of the transition metals with 1,2,3-benzotriazole hydrochloride occurs over a temperature range of 45° to 480°. Complete qualitative and quantitative analyses of the organic vapours produced in the thermal decomposition reactions could not readily be obtained because, in most reactions, a small concentration of impurities and/or 1,2,3-benzotriazole derivatives were produced. These could not be easily separated from the 1,2,3-benzotriazole because of the close similarity between these products and 1,2,3-benzotriazole. Decomposition of the complexed compounds gave the metal oxide or mixed metal oxide and in one instance the pure metal, hydrogen cyanide, cyanogen, 1,2,3-benzotriazole, and in one case hydrogen and thiocyanogen.

Zusammenfassung—In dieser Arbeit wird über thermogravimetrische Pyrolysen von Produkten der Reaktion negativer Cyanokomplexe der Übergangsmetalle mit 1,2,3-Benztriazolhydrochlorid berichtet und mehrere Zwischenprodukte identifiziert.

Résumé—On décrit des pyrolyses thermogravimétriques de quelques produits d'interaction de certains complexes négatifs cyanés des métaux de transition avec le chlorhydrate du benzotriazole-1,2,3 et identifie quelques composés intermédiaires produits au cours de cette réaction.

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