NOTE

Differential thermal analysis of some cyano and cyanonitrosyl iron complexes⁽¹⁾

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THE THERMAL decomposition of hexacyanoferrate (II) and (III) compounds and of certain cyanonitrosyl ferrates has been the subject of numerous investigations.⁽²⁻⁸⁾ These early studies were made under a variety of conditions and thus report a variety of decomposition temperatures and products. Only recently has there been a report of a systematic study of several of these compounds using the techniques of differential thermal analysis.⁽⁹⁾ As part of a general investigation in these laboratories of reactions leading to the formation of inorganic macromolecules, the thermal decomposition of a variety of cyano and cyanonitrosyl ferrates has been studied by differential thermal analysis (DTA) and a complementary technique, dynamic gas evolution (DGE).

EXPERIMENTAL

Apparatus

The DTA apparatus was constructed in these laboratories. A cell block was made from a cylindrical nickel rod (1.9 cm dia. by 6.3 cm length) with a face machined along the rod parallel to the long axis and two holes, perpendicular to the axis, drilled to accommodate Pyrex crucibles (1.4 cm dia. by 1.2 cm deep).

The block temperature was measured with a chromel-alumel thermocouple inserted into a hole drilled in the centre of the block perpendicular to the face. The differential thermocouple was of chromel-constantan, held in position by a detachable spacer bar mounted on centring pins. The block temperature was recorded with a Micromax S recorder; the differential temperature with a Sargent MR recorder.

Heating was furnished by a 750 W Hevi-Duty combustion tube furnace fitted with a Vycor tube (2.5 cm by 60 cm). A laboratory-built programmer insured that the temperature of the furnace could be increased at a uniform rate.

The technique of dynamic gas evolution is described elsewhere^(10a,b) as is the detector unit and electrical circuitry.⁽¹¹⁾

All studies were made with carefully dehydrated α -aluminum oxide as reference material, with a sample size of 0.3–0.5 g, a heating rate of 6°C/min, and under a flow of dried oxygen-free nitrogen of 50 cm³/min. The apparatus was calibrated against known lattice transition and melting point temperatures of ammonium nitrate, silver nitrate, potassium dichromate, and sodium molybdate over the temperature range 32.2–687°C.

- ⁽¹⁾ Taken from the thesis submitted by A. F. GREENE, Jr., to the Graduate School of Western Reserve University in partial fulfillment of the requirements for the degree of Master of Science 1961.
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Note

Reagents

All reagents were either obtained commercially in reagent grade purity or prepared in these laboratories.

Lithium, sodium, calcium, and barium hexacyanoferrate (III) were prepared by reaction of silver hexacyanoferrate (III) and the desired metal chloride; lithium, potassium, and barium pentacyanonitrosylferrate (II) by the analogous reactions of silver pentacyanonitrosylferrate (II). Interestingly enough, ethanol and tetrahydrofuran, when added to effect crystallization, gave higher hydrates than when recrystallization was effected from water alone.

ANALYSIS								
1	Calculated (%)				Found (%)			
Compound	Fe	Ca	Ba	H ₃ O	Fe	Ca	Ba	H,O
Li ₃ [Fe(CN) ₆]·8H ₂ O	14.82				14·70 14·93		·	
Ca ₂ [Fe(CN) ₆] ₂ ·18H ₂ O	12.86	13.85			12·72 12·82	13.58		
Ba ₃ [Fe(CN) ₆] ₂ ·18H ₂ O	9.61		35.50		10∙08 10∙10		35·45 35·65	
Li ₂ [Fe(CN) ₅ NO]·4H ₂ O	18.55			13.9	18·15 17·85			13.7
Ba[Fe(CN)5NO]·6H2O	12.12		29.77		12.39		29·35 29·97	

Turnbull's Blue was prepared by the method of WEISER *et al.*⁽¹²⁾ Excess water was removed by drying on the steam bath.

DTA and DGE peaks

Peak temperatures on the differential thermal analysis curves were read at the first point of inflection after the curve departed from the base line. Superimposition of the dynamic gas evolution curves onto the DTA curves clearly showed which DTA peaks were associated with gas evolution and which were due to lattice transformation and melting. Further, the DGE peaks were frequently better resolved than the DTA peaks and allowed more exact determination of the decomposition temperatures.

RESULTS

Complete results are shown in Table 1 and some representative DTA and DGE curves in Fig. 1. Two results are immediately obvious. First, water is removed at temperatures ranging from about 80°C to as high at 180°C, but for most compounds at about 100°C. These reactions are endothermic. Secondly, cyanogen is a common product from all these thermal decompositions and is evolved as the result of an exothermic reaction. Since the formation of cyanogen from cyanide is an oxidation reaction, it seems reasonable to suggest that the metal is being reduced and that the compounds formed as thermal decomposition proceeds contain the metal in successively lower formal oxidation states.

As a general rule, the iron (III) complexes decompose at a markedly lower temperature than the analogous iron (II) species; decomposition is thus to be associated with the ease of reduction of the metal ion and not with any intrinsic stability of the metal-cyanide bond. Both the iron (II) and the

⁽¹²⁾ H. B. WEISER, W. O. MILLIGAN and J. B. BATES, J. Phys. Chem. 46, 99 (1942).

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Compound		Gaseous Products	
	Temp. (°C) Characteristics		
Li ₃ [Fe(CN) ₆]·8H ₂ O	148	endo, s	H ₂ O
	240	endo, m	
	266	exo, sp	C_2N_2
Na ₃ [Fe(CN) ₆]·2H ₂ O	128	endo, s	H_2O
	280	exo, s, sp	C_2N_2
K ₃ [Fe(CN) ₆]	340	exo, vs, vsp	C_2N_2
Ca ₃ [Fe(CN) ₆] ₂ ·18H ₂ O	84	endo, sh	H₂O
	100	endo, s	$H_{2}O$
	150	endo, m	H ₂ O
	272	exo, m, b	C_2N_2
	318	endo, m, b	C_2N_2
$Ba_3[Fe(CN)_6]_2 \cdot 18H_2O$	68	endo, sh	H_2O
	82	endo, sh	H_2O
	116	endo, s	H_2O
	216	exo, s, sp	C_2N_2
	262	endo, vb	C_2N_2
	(286)	(DGE peak maximum)	
Na ₄ [Fe(CN) ₆]·10H ₂ O	88	endo, sh	H₂O
	116	endo, s	H_2O
	600	exo, w, vb	C_2N_2
K ₄ [Fe(CN) ₆]·3H ₂ O	100	endo, s	H*O
	588	endo, w, vb	C_2N_2
Na ₃ [Fe(CN) ₅ NH ₃]·3H ₂ O	148	endo, s	H ₂ O, NH ₃
	298	exo, sh	C_2N_2
	352	exo, m	C_2N_2
	600	endo, w, b	C_2N_2
Turnbull's Blue KFe[Fe(CN)6]·xH2O	100	endo, m, vb	H ₂ O
	196	exo, s, b	C_2N_2
	290	endo, m, b	C_2N_2
	324	exo, s, b	C_2N_2
	398	endo, s	C_2N_2
	470	exo, w, sh	C_2N_2
	605	exo, s, sp	N_2
Prussian Blue KFe[Fe(CN) ₆]·yH ₂ O	100	endo, m, vb	H_2O
	196	exo, s, b	C_2N_2
	270	endo, m, b	C_2N_2
	324	exo, s, b	C_2N_2
	380	endo, s	C_2N_2
	433	exo, w, sh	C_2N_2
	605	exo, s, sp	N ₂

TABLE 1.—THERMOLYSIS TEMPERATURES AND CHARACTERISTICS

Note

<u> </u>	DT	Gaseous		
Compound	Temp. (°C)	Characteristics	Products	
Li ₂ [Fe(CN) ₅ NO]·4H ₂ O	86	endo, m	H₂O	
	122	endo, s	H ₂ O	
	294	endo, s	NO	
	338	exo, sh	C_2N_2	
Na₂[Fe(CN)₅NO]·2H₂O	158	endo, vs	H₂O	
	309	endo, s	NO	
	338	exo, sh	C_2N_2	
K₂[Fe(CN)₅NO]·2H₂O	92	endo, sh	H₂O	
	120	endo, s	H₂O	
	286	exo, w	NO	
	306	exo, s	C_2N_2	
	639	endo, m	melting	
Ba[Fe(CN)₅NO] 6H₂O	94	endo	H₂O	
	180	endo	H ₂ O	
	324	(DGE peak only)	NO	
	334	exo, vs, sp	NO, C ₂ N ₂	
K ₃ [Co(CN) ₆]	420	endo, w, b	C_2N_2	
	559	endo, m, sp	l.t.	
	665	exo, w, b	C_2N_2	

TABLE 1-(cont'd)



A. $K_{3}[Fe(CN)_{6}]$ B. $Na_{2}[Fe(CN)_{5}NO] \cdot 2H_{2}O$ C. Turnbull's Blue D. $K_{4}[Fe(CN)_{6}] \cdot 3H_{2}O$ E. $K_{3}[Co(CN)_{6}]$

Note

iron (III) complexes are high field-low spin species; the d^5 iron (III) is readily reduced whereas the d^6 iron (II) species is resistant to further reduction. This resistance of high field d^6 cyano complexes to thermal decomposition is expected and observed in potassium hexacyanocobaltate (III). It should also be noted that the strong, sharp exothermic decomposition observed for both Turnbull's Blue and Prussian Blue at 605° corresponds to the ultimate decomposition to iron carbide, carbon and nitrogen as reported by SIEFER^(10b).

The cyanonitrosyl complexes decompose first to lose nitric oxide, then at higher temperatures cyanogen is evolved. Formally, iron may be considered to exhibit a +2 oxidation state in these complexes; elimination of nitric oxide thus involves an oxidation of iron to a +3 state and cyanogen formation a reduction back to iron (II). The comparatively low temperatures (ca. 300°) for cyanogen evolution are consistent with this interpretation.

Preliminary weight loss studies, infrared examination of the decomposition residues, and the generally intractable nature of these solids indicate that stable, polymeric materials involving metalcyanide-metal bridging are formed. Characterization of these residues is now in progress as is further study of cyano and cyanonitrosyl complexes of molybdenum, chromium, and vanadium.

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