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Note

KINETIC PARAMETERS OF THE THERMOGRAVIMETRIC DISSOCIATION OF DI-, TRI- AND TETRAMINE COMPLEXES OF COPPER(II) NITROSOPENTACYANOFERRATE(II)

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The use of thermogravimetric analysis as a technique for determining the bonding and structure of complexes has increased greatly in the last few years. Most thermal studies on complexes have been of a qualitative nature, but recently considerable work has been done on kinetic and thermodynamic aspects of reactions in the solid state. Transition metal complexes containing nitrogen donor ligands, e.g. ammonia and aliphatic di-, tri- and tetramines have also been studied recently [1–5]. Studies on the thermal dissociation and kinetic parameters of copper(II) complexes have been made but the complexes of the type where cation and anion are both complex have not been studied systematically [6].

EXPERIMENTAL

The thermogravimetric analysis was done on a thermobalance supplied by FCI, Sindri. Mass loss was determined at a heating rate of 10°C min^{-1} up to 1073 K.

RESULTS AND DISCUSSION

The rate of thermal decomposition of a complex has been determined by the rate at one or more stages [7]. Computation of TGA data was carried out in order to calculate the rate constant and apparent energy of activation from the plots of $[-\log_e(1-\alpha)]^{1/n}$ vs. time and $-\log_e[-\log_e(1-\alpha)]^{1/n}/T^2$ vs. $10^3/T$, where $n = 1$. Similar plots were obtained for all the four complexes from 573 K but different plots were obtained between 293 and 573 K. The plots of the complex $[Cu(en)(H_2O)_2][Fe(CN)_5NO]\cdot H_2O$ are given in

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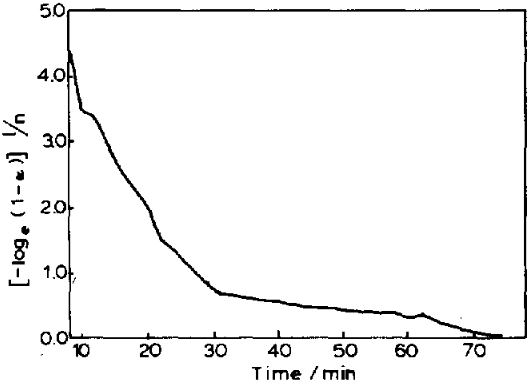

Fig. 1. Relation between $[-\log_e(1-\alpha)]^{1/n}$ and time for the complex [Cu(en)-$(H_2O)_2$][$Fe(CN)_5NO$]·H_2O.

Figs. 1 and 2 for clarity. Values of α were calculated from mass-loss data using the expression $\alpha = (w_t - w_f)/(w_0 - w_f)$, where w_t = mass at time/temp., w_0 = initial sample mass, and w_f = residual mass at the end of the process.

All four complexes contain lattice water and coordinated water molecules are present in ethylenediamine, propylenediamine and diethylenetriamine complexes. The triethylenetetramine complex does not contain coordinated water. Thermal decomposition begins with weight loss at 333 K, resulting in loss of lattice water molecules. The de-aquation of lattice water molecules is

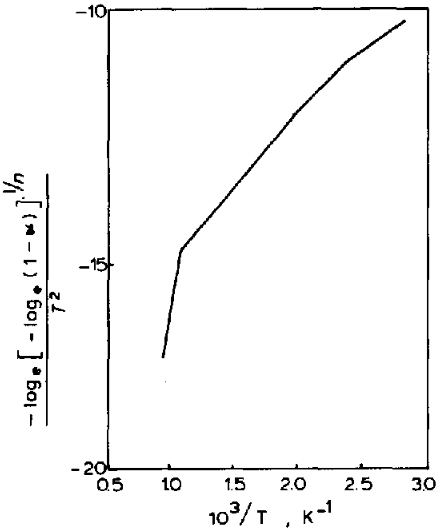

Fig. 2. Relation between $-\log_e[-\log_e(1-\alpha)^{1/n}/T^2$ (where $n = 1$) and $10^3/T$ for the complex [Cu(en)$(H_2O)_2$][$Fe(CN)_5NO$]·H_2O.

TABLE 1

Thermal decomposition data for the complexes

Complex	Temp. (K)	% Wt. loss		Gaseous product	Energy of activation		Rate of reaction (min^{-1})
		Obs.	Calcd.		(k.cal mole^{-1})	(kJ mole^{-1})	
$[Cu(en)(H_2O)_2][Fe(CN)_5NO]\cdot H_2O$	273–973	69.50	69.64				
	333–413	3.82	4.57	H_2O lattice	8.74	36.53	$4.75-10^{-1}$
	413–473	11.04	9.15	2 H_2O coordinated	11.35	47.44	1.32×10^{-1}
	473–553	15.75	15.25	$C_2H_8N_2$	14.67	61.32	1.10×10^{-1}
	573–593	6.38	7.62	NO	10.05	42.00	1.35×10^{-2}
	593–973	32.1	33.05	5 CN	139.00	581.02	1.20×10^{-2}
$[Cu(pn)(H_2O)_2][Fe(CN)_5NO]\cdot 2\ H_2O$	273–953	69.10	71.92				
	333–453	8.98	8.46	2 H_2O lattice	9.66	40.38	6.30×10^{-1}
	453–473	7.23	8.46	2 H_2O coordinated	11.98	50.07	2.1×10^{-1}
	473–563	16.00	17.32	$C_3H_{10}N_2$	16.47	68.84	1.85×10^{-2}
	573–593	6.00	7.05	NO	11.88	49.65	2.40×10^{-2}
	593–953	30.89	30.56	5 CN	144.6	604.43	2.8×10^{-2}
$[Cu(dien)(H_2O][Fe(CN)_5NO]\cdot 3\ H_2O$	273–993	68.68	73.72				
	333–473	10.96	11.88	3 H_2O lattice	9.98	41.71	2.99×10^{-1}
	473–493	3.09	3.96	H_2O coordinated	12.35	51.62	1.3×10^{-1}
	493–573	21.16	22.67	$C_4H_{13}N_3$	16.10	67.29	1.65×10^{-1}
	573–593	4.65	6.60	NO	10.12	42.30	8.0×10^{-2}
	593–993	28.82	28.61	5 CN	139.84	584.93	2.8×10^{-2}
$[Cu(trien)][Fe(CN)_5NO]\cdot 2\ H_2O$	273–933	68.19	74.12				
	333–433	6.93	7.80	2 H_2O lattice	8.46	25.39	1.6×10^{-1}
	433–573	28.32	31.64	$C_6H_{18}N_4$	13.36	55.18	1.19×10^{-1}
	573–593	5.78	6.50	NO	11.04	46.15	2.9×10^{-2}
	593–933	27.16	28.18	5 CN	134.20	560.95	3.55×10^{-2}

completed at 413, 453, 473 and 433 K, respectively, in the four compl mentioned. This stage is indicated by the presence of a break in the curve. The de-aquation of coordinated water molecules in the first t complexes is completed at 473, 473 and 493 K, corresponding to a mass of 2, 2 and 1 water molecules, respectively. The energy of activation coordinated water has higher values than for lattice water, as expected.

The absence of any horizontal plateau in the TG curve indicated successive decomposition steps overlap with one another. De-amina begins at 473, 473, 453 and 433 K and is completed at 553, 513, 573 573 K, corresponding to weight loss of ethylenediamine, propylenedian diethylenetriamine and triethylenetetramine, respectively. These results pear reasonable as ethylenediamine and propylenediamine are of al equal strength as diethylenetriamine and triethylenetetramine in the spe chemical series.

A small break is observed at 573 K in all four complexes, then complex anion $[Fe(CN)_5NO]^{2-}$ begins to decompose with the evolutio brown fumes of the NO group. This decomposition is completed at 59 The CN groups decompose in the range 593–973 K for all complexes. A last stage, between 973 and 1073 K, the weight becomes constant a black residue, which is probably composed of metal carbides and nitrid formed. All the observed and calculated values are given in Table 1.

Thus, it can be concluded that the cation portion in all the complex less stable than the anionic portion. This is because the anion po contains *pi* bonding ligands, e.g. NO and CN, which have empty anti-b ing orbitals and accept the electron density from the metal atom for stronger bonds. All the reactions have been found to be first order. ligands can, thus, the arranged in the order of increasing strength: lattice < H_2O coordinated < ethylenediamine ~ propylenediamine < die enetriamine ~ triethylenetetramine < NO < CN.

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