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THERMAL DECOMPOSITION OF SOLID ISOTHIOCYANATE COMPLEXES

PART II. KINETIC PARAMETERS

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ABSTRACT

A computational method has recently been used to obtain kinetic parameters from differential enthalpimetric data[1]. This method was applied to a limited number of metal complexes in addition to some standard substances for which satisfactory agreement with previously determined values was obtained. In the present paper, a systematic kinetic study of the complexes $MPy_4(NCS)_2$ (M = Mn, Fe, Co, Ni, Cu, and Zn; Py = pyridine) is presented.

EXPERIMENTAL

A Perkin–Elmer differential scanning calorimeter (DSC-1) was used for the kinetic measurements. The procedure was identical to that described previously[2]. The sample weight was usually less than 10 mg in order to ensure temperature uniformity. The heating rate was 16°K·min^{-1} in each case. The IBM 1620 of the Wolverhampton College of Technology was used for the computational work.

RESULTS AND DISCUSSION

It was assumed that the decompositions could be described by an equation of the form

$$\partial\alpha/\partial t = A(1-\alpha)^n \cdot \exp(-E/RT) \qquad (1)$$

in which α is the fractional extent of the reaction, A is a pre-exponential factor, E is the activation energy, and n is the "order of reaction". The latter quantity may possess only particular values[3], and in the least squares analysis employed here, n probably represents an average value for a large portion of the experimental curve. The rate of reaction, $\partial\alpha/\partial t$, is proportional to $\partial H/\partial t$, the rate of change of enthalpy of the sample. These two quantities are related by the equation

$$\partial H/\partial t = \partial\alpha/\partial t(\Delta H \cdot \omega/M) \qquad (2)$$

in which ΔH is the enthalpy change per mole of sample, ω is the weight of sample, and M is its molecular weight. Inasmuch as $\partial H/\partial t$ can be measured with a differential scanning calorimeter[4], it is possible to calculate $\partial\alpha/\partial t$ (Eqn. 1). A least squares analysis of Eqn. 1 in linear form yields values for A, n, and E.

Beech[1] has shown that for the metal complexes ML_4Cl_2 (M = Co or Ni; L = pyridine, 3- and 4-methylpyridine), the activation energies for the reaction

$$ML_4Cl_2\ (\text{cryst.}) \rightarrow ML_2Cl_2\ (\text{cryst.}) + 2L\ (g)$$

exceeded the heats of decomposition and were dependent upon the basicity of L. This was compatible with an endothermic reaction for which the rate-controlling step was the metal–ligand bond cleavage. It was also shown that the activation energies were more sensitive to changes in L than were the heats of reaction.

In the present paper we report kinetic parameters for the decomposition of the solid complexes $MPy_4(NCS)_2$ (M = Mn, Fe, Co, Ni, and Zn; Py = pyridine). In Part I of the present series[5], we discussed the thermochemistry of these complexes and found their heats of decomposition to be very similar. If bond cleavage were the rate-determining step in these decompositions, the activation energies would be expected to provide a more sensitive measure of bond strength than the overall heat of reaction inasmuch as the latter includes variations in the crystal-packing forces in the decomposition product.

The kinetic parameters which we have calculated are shown in Table I. For small values of α, the activation energies exceed those characteristic of later stages of the reaction, perhaps because this region is associated with nucleation of the crystal, a process which proceeds at only a limited number of sites that are subject to local disorder[6]. Propagation of the reactant–product interface proceeds more easily, and, for an endothermic reaction, the activation energy is similar to, or greater than, the heat of decomposition[6,7].

Inasmuch as the structures of the compounds are similar[5], the crystal field-dependent part of the activation energies for these decompositions is equal to the difference in stabilisation energy between the approximately octahedral reactant and the intermediate, of unknown structure, at the reactant-product interface. Because the thiocyanate ion produces a smaller crystal field than does pyridine[8,9], the change in crystal field stabilisation energy (CFSE) should be reflected in the magnitudes of the activation energies.

For the more extended ranges of α and for $\alpha \nless 0.4$, E_A increased smoothly from Mn (about 16 kcal·mole^{-1}) to Co (about 20 kcal·mole^{-1}). Smaller values of α gave characteristically larger E_A values with differing values of n, and it is probable that nucleation becomes increasingly important in these regions. E_A for the Zn complex was very similar to that for the Co complex, but E_A for the Ni complex was difficult to measure because of the inflexion point in the thermogram corresponding to the formation of the tripyridine complex, a point that is discussed more fully in Part I of this series[5]. It is possible that a tripyridine complex is the common intermediate or transition state in the decomposition of each of the solid tetrapyridine

TABLE I

KINETIC PARAMETERS FOR $MPy_4(NCS)_2$

M	*Range of* x	A	E_A (*kcal·mole*$^{-1}$)	n
Mn	0.03–0.82	6.3	16.0	0.43
	0.03–0.88	7.0	16.9	0.52
	0.16–0.88	5.8	14.8	0.42
	0.03–0.26	10.4	23.3	0.23
	0.03–0.22	9.2	20.6	1.5
Fe	0.03–0.84	7.2	18.2	0.32
	0.12–0.90	7.0	17.8	0.25
	0.03–0.17	6.9	17.7	0.77
	0.03–0.25	9.1	21.5	0.65
Co	0.03–0.89	8.6	21.4	0.37
	0.02–0.91	8.6	20.9	0.47
	0.13–0.89	6.9	17.9	0.25
	0.02–0.21	11.1	25.5	1.26
	0.03–0.45	11.5	26.7	1.23
Ni	0.01–0.87	7.1	18.4	0.43
	0.13–0.87	5.0	14.5	0.24
	0.04–0.71	6.8	17.9	0.42
	0.01–0.42	9.4	22.3	1.3
	0.04–0.35	10.2	24.2	1.8
Zn	0.02–0.86	9.9	19.5	0.38
	0.04–0.88	10.3	19.9	0.47
	0.02–0.31	10.4	20.2	0.62
	0.12–0.84	10.3	20.1	0.44

complexes but that this tripyridine complex is particularly stable in the case of nickel. If this is correct, the activation energy for the decomposition of a stable intermediate would be expected to be lower than that of the reactant. This would seem to be true for the Ni complex, for which E_A is markedly dependent upon the range of x (Table I). It is therefore possible that the solid state decomposition during the propagation period may be represented by the reaction scheme

$$ML_4(NCS)_2 \text{ (cryst.)} \rightarrow ML_3(NCS)_2 \text{ (cryst.)} \rightarrow ML_2(NCS)_2 \text{ (cryst.)}$$

The values of log E_A were found to be somewhat lower than the values previously found for dehydration and related reactions (normally[7] 11–12). An independent thermogravimetric investigation by Murgulescu *et al.*[10], for the solid $NiPy_4(NCS)_2$, however, yielded values of $E_A \approx 20$ kcal·mole^{-1}, $A_x \approx 10^4$–10^5 (using our value of n), and $n = 0$. The low values of the "order of reaction", n, do not support a diffusion mechanism for any of the reactions studied.

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