Thermochimica Acta, 39 (1980) 143—149

KINETIC STUDIES ON THE DECOMPOSITION OF CYANO COMPLEXES. I. THE THERMAL DECOMPOSITION OF CYANOFERRATE(II) ACIDS

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(Received 2 January 1980)

ABSTRACT

The formation of HCN from solid iron(II) cyano complex acids is studied by a non-isothermal kinetic method. A derivatograph is used for the measurements and the kinetic parameters are calculated by different methods using the Horowitz—Metzger, Coats—Redfern and Zsako equations. The results are discussed and the kinetic parameters (energy and entropy of activation) are compared with IR and Mössbauer spectroscopic data.

INTRODUCTION

The thermal behaviour of different hydrogen cyano metallates has been investigated previously [1—4], but kinetic calculations have not been made for the elimination of HCN from these solid substances. It is evident that the substitution of one or two cyanide groups by other ligands causes changes in the bonds between the central atom and the CN ligands. It was supposed that these changes could be demonstrated not only spectroscopically but also with the help of kinetic parameters of HCN formation. The following reaction of different iron(II) complexes was studied to prove this supposition.

$$H_{4-x}[Fe^{II}(CN)_{6-x}L_x]_{(s)} \xrightarrow{kT} 4-x(HCN)_{(g)} + [Fe(CN)_2L_x]_{(s)} \qquad (1)$$

where $x = 0$, 1, 2 and L_x = PPh_3, PBu_3, $AsPh_3$, bipy, phen (Ph = C_6H_5, Bu = C_4H_9, bipy = $C_{10}N_2H_8$, phen = $C_{12}N_2H_8$).

EXPERIMENTAL

The following complexes were used as model substances: $H_4[Fe(CN)_6]$, $H_3[Fe(CN)_5PPh_3]$, $H_3[Fe(CN)_5PBu_3]$, $H_3[Fe(CN)_5AsPh_3]$, $H_2[Fe(CN)_4bipy]$ and $H_2[Fe(CN)_4phen]$ prepared by well-known methods [5—7].

The iron contents of the complexes were analyzed spectrophotometrically by bipyridine [8] and the evolved HCN was determined by the thermogas titrimetric (TGT) method [4]. The analytical data are given in Table 1.

TABLE 1

Analytical data of the complexes

Complex	Fe (%)		HCN (mole mole complex^{-1})	
	Calc.	Obs.	Calc.	Obs.
$H_4[Fe(CN)_6]$	25.87	25.9	4	3.98
$H_3[Fe(CN)_5PPh_3]$	11.46	11.5	3	2.94
$H_3[Fe(CN)_5PBu_3]$	14.26	13.8	3	2.92
$H_3[Fe(CN)_5AsPh_3]$	11.27	10.9	3	2.88
$H_2[Fe(CN)_4bipy]$	17.57	17.7	2	1.96
$H_2[Fe(CN)_4phen]$	16.34	16.5	2	1.87

The IR spectra of the complexes were recorded on a double beam Carl Zeiss UR-10 spectrophotometer in KBr.

A ^{57}Co source diffused into Pt was used for Mössbauer measurements. The absorbent was cooled with liquid nitrogen.

The thermal investigations were performed with a MOM 3427/SK type derivatograph in a Pt crucible with α-Al_2O_3 as the inert substance and N_2 as the inert gas. Other operating conditions were T_{Max} 250°C, heating rate 1.5—15°C min^{-1}, TG sensitivity 20, 50 mg, and DTG and DTA sensitivity 1/15 and 1/10, respectively. The weight of the samples was 50—100 mg. The evolved HCN was measured simultaneously by the TGT method [4].

TREATMENT OF DATA

Reaction (1) occurs as a single TG step and it is well separated from the next reactions of $H_4[Fe(CN)_6]$, $H_3[Fe(CN)_5PPh_3]$, $H_3[Fe(CN)_5AsPh_3]$ and $H_2[Fe(CN)_4bipy]$ but elimination of the hetero ligand PBu_3 is superimposed on the final stage in the case of $H_3[Fe(CN)_5PBu_3]$. Therefore, only the TGT curve of $H_3[Fe(CN)_5PBu_3]$, but both the TG and TGT curves of the other complexes were used for the calculation of kinetic data. Good agreement was found between the kinetic parameters obtained from the TG and TGT curves of the same complex.

Three different methods based on the well-known kinetic equation

$$\frac{d\alpha}{dT} = \frac{k(T)}{\phi} f(\alpha) \qquad (2)$$

where $k(T) = A \exp(-E/RT)$, $f(\alpha) = (1-\alpha)^n$, α is the ratio of the amount of reacted substrate to the initial amount of substrate, T is the temperature, k is the rate constant of the reaction at T, ϕ is the heating rate, A is the pre-exponential factor, E is the apparent activation energy, R is the gas constant, and n is the reaction order, were chosen for the calculation of E, A and n. The methods were

(a) The Horowitz—Metzger equations (H—M) [9]

$$\ln\ln\frac{1}{1-\alpha}=\frac{E}{RT_{\max}^{2}}\,\theta \tag{3}$$

if $n = 1$, and

$$\ln\left[1-\left(\frac{1}{1-\alpha}\right)^{n-1}\right]=\ln(1-n)-\frac{E}{RT_{\max}^{2}}\,\theta \tag{4}$$

if $n \neq 1$, where $T_{\max}$ is the temperature at the DTG peak, and $\theta = T - T_{\max}$.

(b) The Coats—Redfern equations (C—R) [10]

$$\ln\frac{\ln[1/(1-\alpha)]}{T^{2}}=\ln B-\frac{E}{RT} \tag{5}$$

if $n = 1$, and

$$\ln\frac{1-[1/(1-\alpha)]^{n-1}}{(1-n)\,T^{2}}=\ln B-\frac{E}{RT} \tag{6}$$

if $n \neq 1$ and

$$B=\frac{AR}{E}\left(1-\frac{2RT}{E}\right) \tag{7}$$

(c) The Zsako method Zs [11]

$$\ln\int_{\alpha_0}^{\alpha_i}\frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)}-\ln\int_{T_0}^{T_i}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T=\text{constant}_i=\left(\ln\frac{A}{\phi}\right)_i \tag{8}$$

$$\sigma^{2}=\frac{\sum_{i=1}^{r}(C_i-\bar{C})^{2}}{r}=\mathrm{f}(E,n) \tag{9}$$

where C_i is the value of $\ln(A/\phi)$ belonging to the measured α_i, T_i is a point on the TG curve, $\bar{C}$ is the average value of $\ln(A/\phi)_i$, and r is the number of points used for the calculations from the TG curve.

The calculations have been made for values of n of 1/3, 1/2, 2/3, 1, 3/2, 2 and values of E, A and n were accepted at the best regression of eqns. (3) or (4) and (5) or (6) and at the minimum of σ^2 using expression (8) and (9).

On the basis of these primary kinetic data, the activation free energy (ΔG^{1}) and activation entropy (ΔS^{1}) were calculated from the equations

$$\Delta S^{'}=R\left[\ln\frac{Ah}{kT}-1\right] \tag{10}$$

$$\Delta G^{'}=E-T(R+\Delta S^{'}) \tag{11}$$

where k is the Boltzmann constant and h the Planck constant.

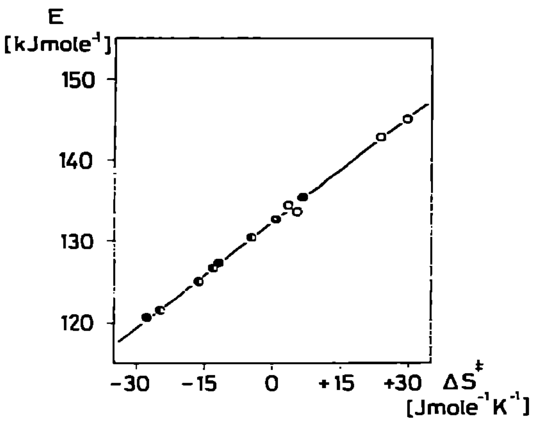

Fig. 1. Activation energy vs. activation entropy for the thermal decomposition of $H_4[Fe(CN)_6]$. E and $\Delta S^‡$ were calculated (n = 1) by the Coats—Redfern (●), Horowitz—Metzger (○), and Zsako (◐) methods.

RESULTS AND DISCUSSION

The calculated figures for the reaction orders for these compounds decomposed at any heating rate differed from one in only a few cases. Therefore the formation of HCN from these complexes was considered to be a first-order reaction.

The activation energy values calculated by the Coats—Redfern and Zsako methods showed good agreement while it was found that the third method gave systematically larger activation energies.

If the heating rate was increased, the E values decreased, but the kinetic compensation effect [12] was experienced as a linear function $E(\Delta S^‡)$ (Figs. 1 and 2).

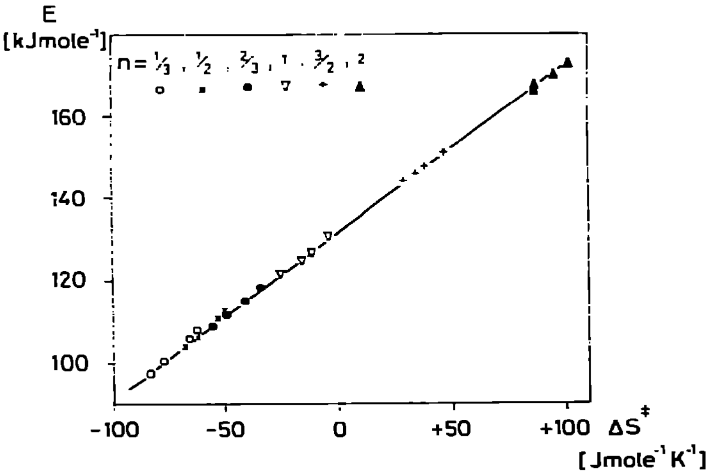

Fig. 2. Activation energy vs. activation entropy for the thermal decomposition of $H_4[Fe(CN)_6]$. E and $\Delta S^‡$ were calculated by the Zsako method for values of n between 1/3 and 2.

TABLE 2

The values of E, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ for $H_4[Fe(CN)_6]$ calculated by different methods

ϕ ($K\ s^{-1}$)	E ($kJ\ mole^{-1}$)			$\Delta S^{\ddagger}$ ($J\ mole^{-1}\ K^{-1}$)			$\Delta G^{\ddagger}$ ($kJ\ mole^{-1}$)		
	C—R	H—M	Zs	C—R	H—M	Zs	C—R	H—M	Zs
0.024	135.5	145.2	130.3	+6.44	+30.01	−4.54	127.1	128.7	128.6
0.048	132.5	143.0	125.0	+0.05	+24.00	−16.30	128.9	128.9	128.6
0.087	127.4	135.0	126.9	−11.90	+4.99	−12.0	129.0	129.1	128.6
0.156	120.7	134.8	121.3	−27.90	+5.59	−24.8	129.6	129.4	128.6

TABLE 3

Comparison of the activation free energy for HCN elimination with the chemical isomer shift and CN frequency of the investigated complexes

Complex	$\Delta G^{\ddagger}$ (kJ mole^{-1})	δ (mm s^{-1})	ν_{CN} (cm^{-1})
$H_4[Fe(CN)_6]$	128.6	−0.48	2073, 2101
$H_3[Fe(CN)_5PPh_3]$	125.9	−0.39	2033, 2060, 2084, 2130, 2146
$H_3[Fe(CN)_5AsPh_3]$	124.8	−0.36	2097
$H_3[Fe(CN)_5PBu_3]$	119.8	−0.35	2080, 2108
$H_2[Fe(CN)_4bipy]$	117.5	−0.25	2080, 2110
$H_2[Fe(CN)_4phen]$	113.6	−0.25	2090, 2120

Since the activation free energy, $\Delta G^{\ddagger}$, also seemed to be independent of the heating rate and the calculation method used (Table 2), it had to be considered that $\Delta G^{\ddagger}$ is more characteristic for this type of decomposition reaction than the apparent activation energy.

It is noticeable that $\Delta G^{\ddagger}$ and the $E(\Delta S^{\ddagger})$ function of the investigated reaction changed as a result of the substitution of HCN by other ligands (Table 3 and Fig. 3).

Comparison of the values of the activation free energy, the chemical isomer shift and the C—N stretching vibration of complexes showed that, while the values of $\Delta G^{\ddagger}$ were decreasing, those of σ were increasing characteristically and the υ_{CN} frequencies shifted to higher values by a few wavenumbers only.

These results led to the conclusion that the decrease in $\Delta G^{\ddagger}$ can be attributed to the decrease of electron density at the iron atom and also to the decrease of $d \rightarrow \pi$ back donation to the CNH ligand. It proves that it is the Fe—CNH bond which is responsible for the magnitude of the activation free

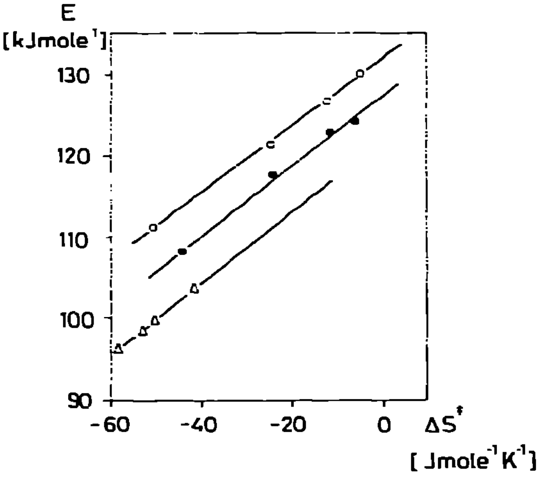

Fig. 3. Activation energy vs. activation entropy of formation of HCN from $H_4[Fe(CN)_6]$ (○), $H_3[Fe(CN)_5PPh]$ (●), and $H_2[Fe(CN)_4bipy]$ (△).

energy of the HCN elimination reaction and its change as a result of substitution causes the change of $\Delta G^{\ddagger}$.

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