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THERMAL DECOMPOSITION KINETICS FOR NICKEL /II/ OXALATE DIHYDRATE

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ABSTRACT

The thermal decomposition of nickel oxalate dihydrate /$NiC_2O_4.2H_2O$/ has been studied in detail in a nitrogen atmosphére. Two clear-cut and non-overlapping stages are found :
Step 1 = dehydration, $NiC_2O_4.2H_2O \longrightarrow NiC_2O_4 + 2H_2O$, and
Step 2 = decomposition, $NiC_2O_4 \longrightarrow NiO + CO + CO_2$.
The temperatures of inception /Ti/, completion /Tf/ and maximum rate of decomposition /Ts/ are recorded. Kinetic parameters /E and $\log_{10}A$/ have been computed by the Coats-Redfern method. E ranges from 15 to 20 K cal mole^{-1} for step 1 and from 50 to 70 K col/mole for step 2. $\log_{10}A$ varies from 5 to 8 for step 1 and from 18 to 25 for step 2.

INTRODUCTION

Oxalate decomposition is a time-honoured route for the preparation of metal oxalates has been studied by a large number of workers from very early times. Recently, increasing interest has been bestowed on the Kinetics of thermal decomposition of metal oxalates.[1,2] As part of a programme of study encompassing simple inorganic compounds, minerals and polymers, we undertook a study of nickel/II/ oxalate dihydrate. The results are presented in this communication. Measuring methods and apparatus a Netszch Combined thermobalance DTA apparatus was employed in preliminary studies and later the detarled studies were made with a Dupont thermobalance 990-951 model.

The studies were acrried out in a dynamic nitrogen atmosphere /gas flow 50 cm^3 min^{-1}/. Three sample masses /5,10 and 20 mg/ and three heating rates /2^o, 5^o and 10^o per minute/ were employed. Temperatures of inception /Ti/, completion /Tf/ and maximum decomposition /Ts/ were recorded. Kinteics parameters /E=energy of activation and A=pre-exponential factor/ were calculated using the Coats-Redfern Equation.

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RESULTS AND DISCUSSION

The results are presented in tables 1 and 2. Table 1 presents the phenomenological data and table 2 gives the kinetics parameters. Table 1 shows that Ti tends to very only slightly when m or Ø are varied, whereas Tf and Ts very more markedly. This is in accordance with observations of earlier workers.[3] It may be seen from table 2 that E ranges from 15 to 20 Kcal $mole^{-1}$ for step 1 and from 50 to 70 Kcal $mole^{-1}$ for step 2, omitting values for which the correlation coefficient is low. $\log_{10}A$ varies from 5 to 8 for step 1 and from 18 to 25 for step 2. Quantitative correlations, however, could not be made for these variations.

REFERENCES

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Tabele 1. Effect of variation of m and ϕ on Ti, Tf and Ts

Reaction →		step 1			step 2		
m (mg)	ϕ $(^{\circ}C\ min^{-1})$	Ti	Tf	Ts	Ti	Tf	Ts
5	2	383	488	476	518	618	603
	5	408	518	493	568	638	619
	10	398	533	508	563	648	635
10	2	398	518	483	548	618	604
	5	423	526	503	563	645	623
	10	423	553	518	578	653	635
20	2	398	528	498	548	618	603
	5	418	523	508	568	648	604
	10	416	558	528	563	623	608

Explanations :
m = mass of sample ; ϕ = heating rate ;
Ti, Tf and Ts are given in °Kelvin

Tabele 2. Effect of variation of m and ϕ on E and A

Reaction → Order →		Step 1 ; x=0,65			Step 2 ; x=0,35		
m (mg)	ϕ $(^{\circ}C\ min^{-1})$	E	A	γ	E	A	γ
5	2	16,84	$2{,}17 \times 10^{6}$	0,9820	35,92	$2{,}11 \times 10^{11}$	0,9388
	5	20,74	$1{,}73 \times 10^{8}$	0,9890	55,69	$4{,}53 \times 10^{18}$	0,9805
	10	16,52	$2{,}95 \times 10^{6}$	0,9890	61,75	$4{,}74 \times 10^{20}$	0,9894
10	2	17,56	$3{,}12 \times 10^{6}$	0,9900	70,44	$1{,}47 \times 10^{24}$	0,9906
	5	20,72	$1{,}03 \times 10^{8}$	0,9980	76,38	$9{,}28 \times 10^{25}$	0,9993
	10	18,57	$1{,}17 \times 10^{7}$	0,9970	72,22	$1{,}74 \times 10^{24}$	0,9950
20	2	16,72	$7{,}32 \times 10^{5}$	0,9924	48,01	$3{,}75 \times 10^{15}$	0,9660
	5	17,36	$2{,}92 \times 10^{6}$	0,9960	70,12	$5{,}80 \times 10^{23}$	0,9977
	10	15,70	$5{,}20 \times 10^{5}$	0,9970	38,10	$1{,}19 \times 10^{12}$	0,9777

Explanations : E = energy of activation /in Kcal $mole^{-1}$/
A = pro-experimential **factor**/in sec^{-1}/
n = order parameter
γ = correlation coefficient