Preparation and Thermal Decomposition of [Cr (salen) (H$_2$O)$_2$] Cl

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Abstract: A complex of N,N'-ethylenebis (salicylideneiminato) diaquochromium (III) chloride, [Cr (salen) (H$_2$O)$_2$] Cl was prepared, and its decomposition mechanism was studied by TG and DTA. The IR spectrum of the product of thermal decomposition was examined at the first stage. Kinetic results were obtained from the analysis of TG-DTG curves with three different methods. The most probable kinetic functions were suggested by comparison of kinetic parameters.

Keywords: Chromium (III) complex, thermal decomposition, non-isothermal kinetics.

Chromium (III) is an essential trace element[1]. In an active form, chromium (III) as a component of glucose tolerance factor (GTF) can improve insulin biological activity. Cr supplementation in humans and animals reduces symptoms of Type II diabetes and hypoglycemia. For a better understanding of the nature of biologically active chromium (III) complex, many GTF model complexes have been studied previously[2]. Here, one GTF model complex of N,N'-ethylenebis (salicylideneiminato) diaquochromium (III) chloride, [Cr (salen) (H$_2$O)$_2$] Cl was prepared and characterized, and the mechanism of thermal decomposition of the complex was studied. For the TG-DTG curve, the Achar differential equation[3], the Coats-Redfern integral equation[4] and our reduced equations[5] were used to analyze the non-isothermal decomposition process. The integral, differential and our reduced equations are as follows:

$$\text{Ln} (g (\alpha)/T^2)=\ln(AR/\beta E)-E/RT \qquad (1)$$
$$\text{Ln}[(d\alpha/dt)/f (\alpha)]=\ln A-E/RT \qquad (2)$$
$$E/(RT_m^2)+A (1/\beta)f'(\alpha_m)\exp [-E/(RT_m)]=0 \qquad (3)$$
$$E/(RT_i^2)+3A (1/\beta)f'(\alpha_i)\exp [-E/(RT_i)]-2/T_i=0$$

In the above equations, α is the fractional decomposition, T the absolute temperature (K), $d\alpha/dt$ the reaction rate, A the preexponential Arrhenius factor, β the heating rate (deg.min^{-1}), E the apparent activation energy (kJ.mol^{-1}), R the gas constant (kJ.mol^{-1}K^{-1}), f (α) and g (α) the differential and integral functions respectively, f'(α) the differentiation of f (α), the subscript m and i the point of the maximum transformation rate and the point of the inflection of DTG curve respectively.

Experimental

Preparation of [Cr (salen) $(H_2O)_2$] Cl: Salicylaldehyde (0.1 mol) and ethylenediamine (0.05 mol) were added to a solution of chromium (III) chloride hexahydrate (0.05 mol) in ethyleneglycol-water-methanol (1: 1: 3, 150 ml).   After the mixture was refluxed for 30 min, sodium carbonate (0.03 mol) was gradually added to the solution, followed by reflux of the solution about three to four hours.   Concentrating the solution yielded a reddish brown precipitate, which was recrystallized from 80% methanol to give reddish orange crystals. Analysis for [Cr(salen)$(H_2O)_2$] Cl [Cr $(C_{16}H_{14}N_2O_2)$ $(H_2O)_2Cl$] C: 49.42 (49.30);   H: 4.85 (4.65);   N: 7.05 (7.19);   Cr: 13.83 (13.42).

Physical measurement: TG analysis was carried out on a Perkin Elmer TGA-7 thermogravimetric analyzer, at a N_2 flow rate of 60 ml.min^{-1} and a heating rate 5.00 deg.min^{-1}.   The amount of sample used was 3.244 mg, and the temperature range was 313.15 to 773.15 K.   IR spectrum of the complex [Cr (salen) $(H_2O)_2$] Cl was examined on a Perkin Elmer 983 infrared spectrophotometer (KBr disc, 4000~400 cm^{-1}, CsI disc, 400~180 cm^{-1}), IR spectrum of the product of thermal decomposition was examined on a Shimadzu 403 infrared spectrophotometer (KBr disc, 4000~650cm^{-1}). Molar conductance was obtained with DDS-11A conductivity detector.

Component analysis: Cr content in complex was determined according to the reported general procedure[6]. C, H and N content were determined using a Perkin Elmer 240 elemental analyzer.

Result and discussion

Molar conductance: The complex is soluble in common solvents such as water, methanol, alcohol, DMF, acetone *etc*   The molar conductance in water solution is 96±2 s.cm^2.mol^{-1} (298.15 K, 1.0×10^{-3} mol/L).   This datum gives, as expected, a 1:1 electrolytic value.

IR spectrum: The IR spectrum of the complex shows the absorption at 1627 cm^{-1}, 1597 cm^{-1} and 1340 cm^{-1} attributable to C=N, C=C and γ_{C-O}(phenolic) stretching frequencies of salen ligand respectively, and the absorption at 2600~3300 cm^{-1} attributable to coordination water and γ_{C-H} stretching frequencies.   The IR bands observed around 385 cm^{-1}, 375 cm^{-1} are assigned to γ_{Cr-N}, and the band at 512 cm^{-1} to γ_{Cr-O} (phenolic), and the bands at 800 cm^{-1} 540 cm^{-1} 499 cm^{-1} to ρ_r, ρ_w and γ_{Cr-O} stretching frequencies of coordination water molecules.   These studies as well as the result of molar conductance infer that an octahedral structure complex of chromium (III) are completed by a salen tetradentate Schiff base and two water ligands.

Thermal decomposition process: The TG-DTG curves are shown in **Figure 1**. The TG-DTG curves indicate that the compound [Cr (salen) $(H_2O)_2$] Cl undergoes a two-stage decomposition process.   The IR spectrum of the product of thermal decomposition at the first stage was examined.   The IR spectrum of the residue is similar to that of [Cr (salen) $(H_2O)_2$] Cl. The IR bands of salen ligand are observed at 1622 cm^{-1} 1594 cm^{-1} and 1330 cm^{-1} for its C=N, C=C and γ_{C-O}(phenolic) stretching f r e q u e n c i e s   r e s p e c t i v e l y .

Figure 1. TG and DTG curves of [Cr (salen) (H₂O)₂] Cl
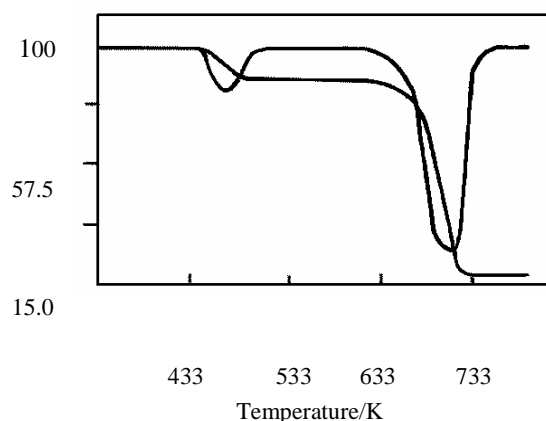
A broad band in the region 3300~3600 cm^{-1} is assigned to γ_{OH} showing the involvement of hydroxide in coordination. This shows that the salen ligand is still present in the tested substance. TG studies at this stage showed a mass loss corresponding to one H_2O and one HCl molecules. Thus, the probable product of decomposition at this stage is Cr (salen) OH [mass loss (%): calc: 13.98, found: 13.27]. The final substance is considered to be Cr_2O_3 [mass loss (%): calc: 80.05, found: 80.22]. These results suggested a possible decomposition processes of N,N'- ethylenebis (salicylideneiminato) diaquo chromium (III) chloride as the following:

$$[Cr\ (salen)\ (H_2O)_2]\ Cl \xrightarrow{\ 360\sim552\ K\ } Cr\ (salen)\ OH \xrightarrow{\ 552\sim741\ K\ } Cr_2O_3$$
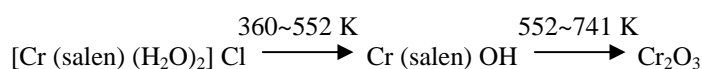
Table 1. TG-DTG data on the thermal decomposition of [Cr (salen) (H₂O)₂] Cl

	The first stage				The second stage		
No.	T (K)	α	$d\alpha/dt$	No.	T (K)	α	$d\alpha/dt$
1	448.15	0.1366	0.3914	1	658.15	0.0814	0.1863
2	451.15	0.1761	0.5263	2	663.15	0.1118	0.2739
3	454.15	0.2262	0.6687	3	668.15	0.1553	0.4055
4	457.15	0.2850	0.8553	4	673.15	0.2146	0.5863
5	460.15	0.3522	0.9968	5	678.15	0.2901	0.7562
6	463.15	0.4481	1.2830	6	683.15	0.3775	0.8712
7	466.15	0.5321	1.3684	7	688.15	0.4723	0.9534
8	469.15	0.6153	1.4276	8	693.15	0.5702	0.9973
9	472.15	0.6975	1.4046	9	698.15	0.6691	1.0268
10	475.15	0.7708	1.3355	10	703.15	0.7673	1.0279
11	478.15	0.8328	1.2171	11	708.15	0.8663	1.0372
				12	713.15	0.9529	0.9151
				13	718.15	0.9788	0.5534

Non-isothermal kinetic studies: The possible forms of f (α), g (α) and f'(α) are found from reference[5]. The original data on the decomposition processes of

N,N'-ethylenebis(salicylideneiminato)diaquochromium (III) chloride are listed in **Table 1**, the data of T_m, α_m, T_i and α_i are 472.15 K, 0.6975, 461.15 K, 0.3842 for the first decomposition process and 708.15 K, 0.8663, 695.65 K, 0.6197 for the second decomposition process respectively. Using the possible forms of f (α), g (α) and f'(α) in reference[5], the data in **Table 1** and the data of T_m, α_m, T_i and α_i are analyzed by use of equations (1), (2) and (3). For equations (1), (2) and (3), the kinetic analysis are completed by a computer. The calculated results clearly show that the values of E and A yielded by three methods are approximately the same and the linear correlation coefficients are better when the probable functions of the mechanism are f (α)=2$(1-\alpha)^{1/2}$, g (α)=1-$(1-\alpha)^{1/2}$, f'(α)=-$(1-\alpha)^{-1/2}$, for the first decomposition process and the same forms of function for the second decomposition process. The results are as: lnA=30.37, E=118.30 kJ/mol, r=0.9804; lnA=28.87, E=120.91 kJ/mol, r=0.9951; and lnA=26.06, E=124.97 kJ/mol at the first decomposition process, and lnA=32.68, E=190.09 kJ/mol, r=0.9862; lnA=30.32, E=189.80 kJ/mol, r=0.9936; and lnA=26.89, E=196.87 kJ/mol at the second decomposition process for equations (1), (2) and (3) respectively. It can be concluded that the probable functions of the mechanism of the first and simultaneously the second decomposition processes of [Cr (salen) $(H_2O)_2$] Cl are as the functions f (α)=2 $(1-\alpha)^{1/2}$, g (α)=1-$(1-\alpha)^{1/2}$ and f'(α)=-$(1-\alpha)^{-1/2}$. Thus the kinetic equations of the first and the second decomposition processes are all as follows:

$$d\alpha/dt = A\exp(-E/RT)\, 2\, (1-\alpha)^{1/2}.$$

Acknowledgments

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