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THERMAL DECOMPOSITION KINETICS OF BISTHIOUREA CADMIUM(II) TETRATHIOCYANATO DIAMMINE CHROMATE(III)

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ABSTRACT

Cadmium thiourea reineckate undergoes a two-stage thermal decomposition on heating. The DTG peak temperatures are 291 and 469 °C and the corresponding DTA temperatures are 255 and 490 °C. The kinetic parameters for the first stage decomposition are $E^* \approx 120$ kJ mole^{-1}; $Z \approx 1.2 \times 10^8$ cm^3 mole^{-1} sec^{-1} and $\Delta S^* \approx -95$ J mole^{-1} K^{-1}. For the second stage, $E^* \approx 133$ kJ mole^{-1}; $Z \approx 6.1 \times 10^5$ cm$^{-\frac{3}{2}}$ mole$^{\frac{1}{2}}$ sec^{-1} and $\Delta S^* \approx -142$ J mole^{-1} K^{-1}.

INTRODUCTION

The method by Rulfs et al.[1] for the semi-micro gravimetric determination of cadmium is based on the precipitation of cadmium as bis-(thiourea)cadmium(II) tetrathiocyanato diammine chromate(III), or cadmium thiourea reineckate (hereafter abbreviated to $CdTu_2R_2$). A titrimetric modification of this procedure based on the oxidation of $CdTu_2R_2$ with chloramine-T has recently been developed[2].

The drying temperature recommended[1] for the precipitate of $CdTu_2R_2$ is 110 °C. Kiba and Sato[3] recommended a drying temperature of 110 to 140 °C, whereas Mahr and Ohle[4] state that the complex is stable up to 167 °C. Apart from these early investigations, no systematic work on the thermal decomposition of $CdTu_2R_2$ seems to have been reported in the literature. It was therefore considered worthwhile to study the thermal decomposition of $CdTu_2R_2$ by TG and DTA in detail, as part of our programme of an investigation on the thermal behaviour of metal complexes[5]. The decomposition kinetics of $CdTu_2R_2$ have been investigated for the first time by a mathematical analysis of the TG curve and the results are presented in this communication.

EXPERIMENTAL

Preparation of the sample

A pure sample of $CdTu_2R_2$ was prepared by standard methods[6].

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Instruments

TG and DTA curves were recorded on a Stanton recording thermobalance Model TR-01. Heating rate, 4°C min^{-1}; chart speed, 3 in. h^{-1}; atmosphere, static air; crucible (DTA), Pt; reference substance (DTA), alumina.

Pyrolysis experiments

In separate pyrolytic experiments, weighed samples of $CdTu_2R_2$ were heated in open porcelain or silica crucibles to a temperature of ca. 800°C. It was found that the sample swelled up at first. A vigorous reaction then set in and the mass burned with a blue flame. The flame soon died away, but glowing particles persisted for some time. Finally, the mass crumbled to a compact bluish-green powder.

Analysis of the final pyrolytic residue showed the absence of sulphide, but indicated the presence of sulphate. Therefore a quantitative analysis of the residue was carried out which showed the residue to be an equimolar mixture of $CdSO_4$ and Cr_2O_3. In the absence of sophisticated instrumental facilities for a quantitative analysis of the gaseous products of decomposition, only qualitative tests could be carried out; these revealed the presence of ammonia and sulphur dioxide among them.

Treatment of data

The instrumental curves were redrawn as the mass versus temperature (TG) curve and also as the rate of loss of mass versus temperature (DTG) curve. The curves were drawn using standard curve sets. The instrumental DTA curve was used as such.

The TG curves were studied in greater detail. Two non-overlapping decomposition stages were observed. Kinetic data, viz., activation energy (E^*), entropy of activation (ΔS^*), order of reaction n and pre-exponential factor (Z) were calculated for both these decomposition stages.

Mathematical analysis of the TG curve

The order of reaction n was first determined from the equation[7]:

$$C_s = n^{(1/1-n)} \tag{1}$$

where C_s is the value of C at the temperature T_s corresponding to the DTG peak, i.e., the temperature at which dC/dT is a maximum. C is the weight fraction present at temperature T and is defined as $C = (w_\infty - w)/w_\infty$ where w_∞ is the total mass loss for the particular stage and w is the mass loss up to temperature T. T_s is obtained from the DTG curve and the corresponding C_s is obtained from the TG curve. A theoretical curve of n versus C_s was drawn using data computed from eqn (1), by calculating various values of C_s corresponding to $n = 0$, 1/2, 1, 3/2 etc. The value of n in the present case was read off from this "master curve" corresponding to the value of C_s determined from the TG curve.

The value of n was found to be 2 for the first stage and 1/2 for the second stage.

Horowitz–Metzger equation[7]

Since $n \neq 1$, the Horowitz–Metzger equation, applicable to non-first order processes, was employed.

$$\log \frac{1-C^{(1-n)}}{1-n} = \frac{E^* \theta}{2.303\, RT_s^2} \tag{2}$$

Here, $\theta = T - T_s$ and R is the gas constant. A plot of the left-hand side expression of eqn (2) versus θ was drawn and was found to be linear. From its slope E^* was calculated.

Coats–Redfern equation[8]

This equation was used in the form

$$\log \frac{1-C^{(1-n)}}{(1-n)T^2} = \log\left[\frac{Z}{\phi}\frac{R}{E^*}\left(1-\frac{2RT}{E^*}\right)\right] - \frac{E^*}{2.303\, RT} \tag{3}$$

where ϕ is the heating rate in °C min^{-1}. E^* is usually of the order of hundred thousands of joules, $R = 8.3$ J K^{-1} mole^{-1} and $T < 1000$ K. Hence $2\,RT/E^* \approx 0$ and $1-(2RT/E^*) \approx 1$. This reduces the first term on the right-hand side of eqn (3) to a constant. A plot of the left-hand side expression of eqn (3) against $1/T$ should therefore be a straight line. This was found to be so in practice. From the slope of this linear plot, E^* was calculated. Knowing the value of E^*, the value of Z was calculated from the intercept of the same linear plot. The entropy of activation, ΔS^* was calculated from the relation,

$$Z = \frac{kT_s}{h} e^{\Delta S^*/R} \tag{4}$$

where k is the Boltzmann constant, h is Planck's constant and e is the base of the natural logarithms.

All the linear plots were drawn by the method of least squares and the correlation coefficients (r) were also calculated. First all the numerical calculations were made using logarithm tables and then checked using an electronic calculator.

RESULTS AND DISCUSSION

Tables 1 and 2 present data concerning thermal behaviour and Tables 3 and 4 present mathematical analysis data concerning decomposition kinetics.

Thermal behaviour

It may be seen from the TG and DTG curves (Table 1, Fig. 1) that there are two definite decomposition stages, which do not overlap. The DTG peaks (Fig. 1) can clearly be seen at 291 and 469 °C. There are no other significant peaks in the DTG curve. The DTA curve shows two peaks, both exothermic, at 255 and 490°C. While these do not quite coincide with DTG peaks, the correspondence is obvious. It may also be noted that the peak widths are greater in DTG (220–350°C and 370–570°C) than in DTA (245–260°C and 445–510°C). The stability range extends from 40 to 200°C, so that a drying temperature of 100°C reported in the literature[1] is quite adequate and safe.

TABLE 1

PEAKS AND PLATEAUS IN TG, DTG AND DTA CURVES

exo = exothermic, w = weak, s = strong.

Peaks in DTA (°C)	*Peaks in DTG (°C)*	*Stability range in TG (°C)*	*Peak width range in DTG (°C)*	*Peak width range in DTA (°C)*
255 exo w	291	ambient to 200	220–350	245–260
490 exo s	469		370–570	455–510

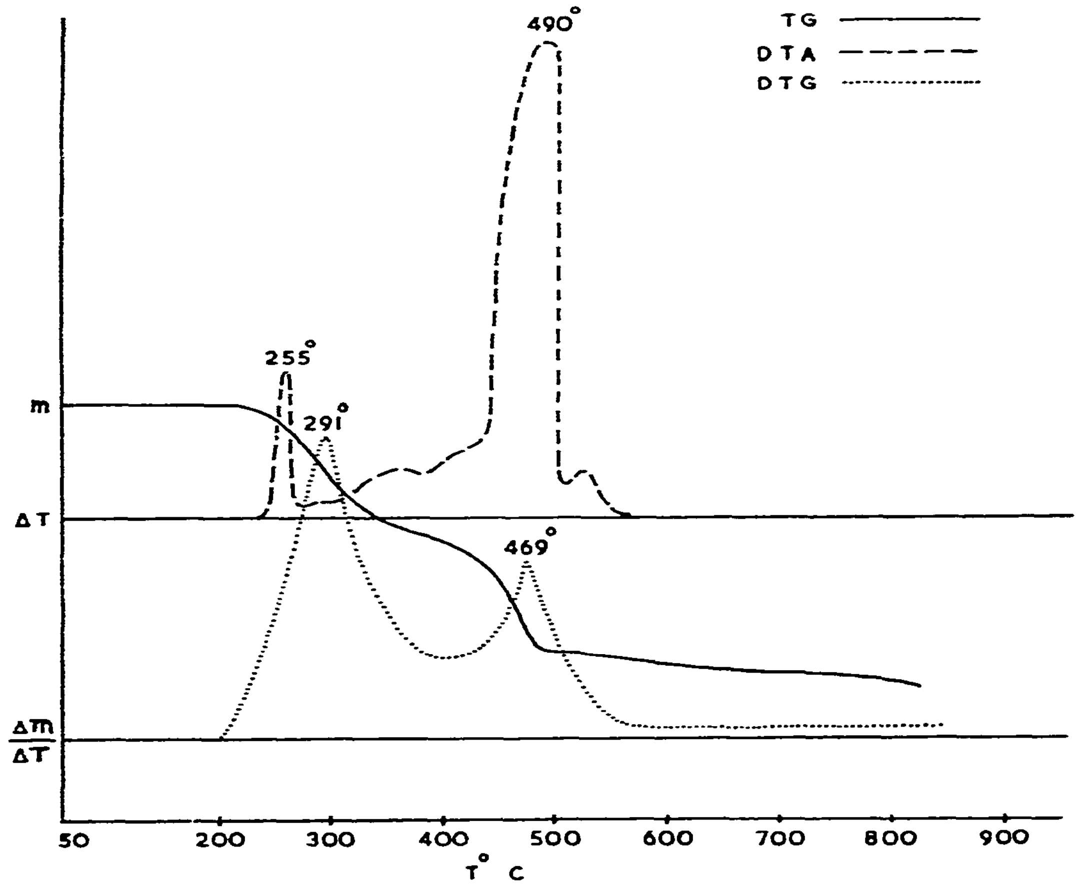

Fig. 1. Thermal decomposition of cadmium thiourea reineckate.

It is interesting to note that, while the first DTG peak temperature is higher than that of the corresponding DTA peak, and the DTG peak is further shifted from the DTA peak, the reverse is the case with the second peak. A tentative explanation is offered to this. During independent pyrolytic experiments in a crucible, it was noted that $CdTu_2R_2$ on heating swelled up at first and finally crumbled to a compact residue. In the first instance the gaseous decomposition products may be considered to be occluded in the solid, from which they would subsequently have to be expelled by heating. If the solid is bulky (as in stage 1) this would mean that the observed DTG peak temperature would be somewhat higher than the "true" DTG peak temperature. During the second stage, the solid residue is compact and hence the DTG and DTA peaks could correspond more closely.

It may be seen from Table 2 that the observed mass loss in the first stage is 25.93%. This corresponds satisfactorily with the loss of mass theoretically required (24.44%) for the decomposition of $CdTu_2R_2$ to a hypothetical complex of the formula $Cd[Cr(CNS)_4]_2$.

TABLE 2

PYROLYSIS DATA

Probable pyrolytic residue		*% Loss of mass*				
after stage 1	*final*	*after stage 1 (from TG data)*	*after stage 1 (calculated)*	*final (from independent pyrolysis)*	*final (from TG data)*	*final (calculated*
$Cd[Cr(CNS)_4]_2$	$CdSO_4 + Cr_2O_3$	25.93	24.44	59.89	58.89	59.98

The total loss of mass observed at the end of the final stage is 58.89% in the TG analysis, and 59.89% in independent pyrolytic experiments. The loss of mass theoretically required for the conversion of $CdTu_2R_2$ to a mixture of $CdSO_4$ and Cr_2O_3 would be 59.98%, which agrees very closely with the experimental values. In the light of this observation, it may be concluded that $CdTu_2R_2$ decomposes to a mixture of $CdSO_4$ and Cr_2O_3 when heated in air to 800 °C. This result is confirmed by actual quantitative analysis of the residue. It may be noted that $CdSO_4$ is stable up to 906 °C, while $Cr_2(SO_4)_3$ decomposes completely to Cr_2O_3 above 700 °C (Ref. 9). If the temperature is increased further, $CdSO_4$ may ultimately decompose to give the oxide. In fact, Kiba and Sato[3] report that the final products are CdO and Cr_2O_3 when heating $CdTu_2R_2$ to 940 °C.

Decomposition kinetics

It may be seen from Tables 3 and 4 that the order of reaction $n = 2$ for the first stage and $n = 1/2$ for the second stage. Such non-unity values are not uncommon for solid state decompositions[10].

TABLE 3

KINETIC DATA FOR FIRST STAGE OF DECOMPOSITION

$w_\infty = 11.80$ mg; $T_s = 564$K; $n = 2$; $r = 0.99$; $Z = 1.22 \times 10^8$ cm^3 mole^{-1} sec^{-1}; $\Delta S^* = -95.43$ J K^{-1} mole^{-1}.

Temp. (°*K*)	*w* (*mg*)	$C = \frac{w_\infty - w}{w_\infty}$	$\frac{1-C^{1-n}}{1-n}$	*Horowitz–Metzger method*[a]		*Coats–Redfern method*[b]	
				$\theta = T - T_s$	$\log\left(\frac{1-C^{1-n}}{1-n}\right)$	$\frac{1}{T} \times 10^3$	$\log\left(\frac{1-C^{1-n}}{(1-n)T^2}\right)$
533	9.42	0.7983	0.2528	−31	−0.597	1.876	−6.051
543	8.22	0.6966	0.4355	−21	−0.361	1.842	−5.831
553	6.96	0.5898	0.6955	−11	−0.168	1.808	−5.642
563	5.57	0.4721	1.1190	−1	+0.049	1.776	−5.453
573	4.23	0.3584	1.7900	+9	+0.253	1.745	−5.264
583	3.09	0.2619	2.8190	+19	+0.450	1.715	−5.091
593	2.11	0.1788	4.5920	+29	+0.662	1.686	−4.894
603	1.48	0.1254	6.9720	+39	+0.843	1.658	−4.717

[a] $E^* = 125.1$ kJ mole^{-1}. [b] $E^* = 115.2$ kJ mole^{-1}.

TABLE 4

KINECTIC DATA FOR SECOND STAGE OF DECOMPOSITION

$w_\infty = 13.00$ mg; $T_s = 742$K; $n = 1/2$; $r = 0.99$; $Z = 6.06 \times 10^5$ cm$^{-3/2}$ mole^{-1} sec$^{\frac{1}{2}}$; $\Delta S^* = -141.8$ J K^{-1} mole^{-1}.

Temp. (°*K*)	*w* (*mg*)	$C = \frac{w_\infty - w}{w_\infty}$	$\frac{1-C^{1-n}}{1-n}$	*Horowitz–Metzger method*[a]		*Coats–Redfern method*[b]	
				$\theta = T - T_s$	$\log\left(\frac{1-C^{1-n}}{1-n}\right)$	$\frac{1}{T} \times 10^3$	$\log\left(\frac{1-C^{1-n}}{(1-n)T^2}\right)$
693	2.85	0.7808	0.2332	−49	−0.6322	1.443	−6.315
703	3.63	0.7208	0.3022	−39	−0.5197	1.422	−6.214
713	4.60	0.6462	0.3922	−29	−0.4065	1.402	−6.113
723	6.25	0.5192	0.5588	−19	−0.2528	1.382	−5.971
733	8.37	0.3562	0.8062	−9	−0.0936	1.364	−5.824
743	10.40	0.2000	1.1056	+1	+0.0434	1.346	−5.698
753	12.00	0.0769	1.4448	+11	+0.1599	1.329	−5.594

[a] E^* (Horowitz-Metzger) = 143.6 kJ mole^{-1}. [b] E^* (Coats-Redfern) = 122.2 kJ mole^{-1}.

The activation energy for stage 1 was found to be 125.1 kJ mole^{-1} (Ref. 7) and 115.2 kJ mole^{-1} (Ref. 8). The agreement can be considered to be satisfactory. The correlation coefficients for both the linear plots were found to be 0.99 indicating near-perfect fit. The pre-exponential factor and the entropy of activation calculated from eqn (8) for the first stage were: $Z = 1.22 \times 10^8$ cm^3 mole^{-1} sec^{-1} and $\Delta S^* = -95.43$ J K^{-1} mole^{-1}. The somewhat lower value for E^* indicates that neither in energy nor in configuration does the activated complex differ much from the reactant and further-more that the bonds involved are rather weak. The negative entropy of activation shows that the activated complex is more ordered than the reactant.

Although the second stage is kinetically of the order 1/2, its E^* and ΔS^* values are comparable with the corresponding values for the first stage. Thus for the second stage, $E^* = 143.6$ kJ mole^{-1} (Ref. 7) and 122.2 kJ mole^{-1} (Ref. 8), $Z = 6.06 \times 10^5$ cm$^{-\frac{1}{2}}$ mole$^{\frac{1}{2}}$ sec^{-1} and $\Delta S^* = -141.8$ J K^{-1} mole^{-1}. The near-unity values ($r = 0.99$) for the correlation coefficients for both the linear plots for the second stage also indicate good agreement with the kinetic data. The negative value for ΔS^* and the low value for E^* would imply that the activated complex for stage 2 is also highly ordered and that the bonds involved are rather weak.

The ligancies of Cd and Cr in $CdTu_2R_2$ are 4 and 6, respectively. In the hypothetical intermediate product, $Cd[Cr(CNS)_4]_2$, Cr would probably have a ligancy of 4 but Cd is not bound to any ligand. However, it is likely that Cd may have its usual coordination number of 4 in the crystal. In the final products ($CdSO_4$ and Cr_2O_3) the crystal coordination number of Cd would be 4 and that of Cr would be 6 (Ref. 11). Since the coordination numbers of Cd^{2+} and Cr^{3+} remain more or less the same in the original reactant, in the hypothetical intermediate product and in the final products, a similar situation is likely to prevail in the activated complexes of both the decomposition stages also. The comparatively low values of E^* for the decomposition steps could perhaps be attributed partly to the above circumstance.

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