THERMAL DECOMPOSITION OF OXALATES. PART 16. THERMAL DECOMPOSITION STUDIES ON CADMIUM OXALATE *

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ABSTRACT

This paper is concerned with the thermal decomposition studies of cadmium oxalate under various conditions. DTA, TG and other complementary techniques are employed to identify the decomposition stages and the nature of the obtained residues when the sample is decomposed in air or in nitrogen. Certain unusual aspects of the cadmium oxalate decomposition are noticed. These are found to be due to high reactivity of the metallic product, which is capable of being oxidised by carbon dioxide gas and the vaporisation of product cadmium at elevated temperatures. The full nitrogen adsorption isotherms on the various heat treated samples are also reported and provides additional information concerning the relevant textural changes which occur in the decomposition process.

INTRODUCTION

There are many reports concerned with the thermal decomposition of oxalates. Comprehensive reports have been produced by various authors [2–12] dealing with a wide range of metal oxalates, but here we deal with cadmium oxalate decomposition in some detail.

Boldyrev et al. [4,6–8] list three possible forms of thermal decomposition of oxalates. The first group comprises oxalates which decompose into carbonate and carbon monoxide

$$MC_2O_4 \rightarrow MCO_3 + CO$$

The second group includes oxalates which usually decompose to form the metal oxide as the solid product and a mixture of carbon monoxide and dioxide as the gaseous products

$$MC_2O_4 \rightarrow MO + CO + CO_2$$

The third group comprises those oxalates which on thermal decomposition form the metal as the solid product and carbon dioxide as the gaseous product

$$MC_2O_4 \rightarrow M + CO_2$$

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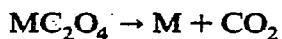
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Some of transition metal oxalates (e.g. Cu, Ni, Co, etc.) often decompose to metal under vacuum or inert flowing gas. In oxygen or air the metal oxidises up to the oxide as formed and in the second group the carbon monoxide produced may be oxidized up to carbon dioxide in the presence of oxygen at a suitable catalyst surface, usually the solid oxide product or the crucible or support material. Cadmium oxalate decomposition has received relatively little attention and the nature of dehydration and decomposition processes has remained uncertain in many details. Previous reports on the mechanism of this compound are contradictory. For example, in the studies by Denk and Dewald [13], the cadmium oxalate is reported to yield metallic cadmium and cadmium oxide on decomposition under vacuum and flowing nitrogen. Different ratios of Cd:CdO are reported, none of which reached the theoretical 1:1 ratio for the formation of Cd_2O. It is suggested that the decomposition of cadmium oxalate to cadmium and cadmium oxide is a single stage process without the formation of any intermediates. Others [5,14] have supported Denk and Dewald's observations and stated that the formation of metal is the result of reduction of oxide by carbon monoxide. Studies by Dell and Wheeler [15] have confirmed that the end product of the decomposition in an inert atmosphere is predominantly metal (92%) with some cadmium oxide (8%). There are, however, other reports [16,17] which suggest either the single stage decomposition of CdC_2O_4 to Cd without the formation of any cadmium oxide or the two stage decomposition of CdC_2O_4 via the formation of $CdCO_3$, the latter acting as an intermediate compound.

EXPERIMENTAL

The trihydrated cadmium oxalate was prepared by the method described by Kapustinskii and Samplavskaya [18]. A large quantity of sample was prepared by precipitation of cadmium oxalate from an aqueous solution of cadmium nitrate and oxalic acid at 60°C. The oxalate sample prepared by this method contained approximately three molecules of water (2.92). The number of crystallised water molecules was found to vary depending on the conditions at which the precipitation is carried out. The potassium permanganate titration method was used to measure the percent oxalate content of the prepared sample. The result of this chemical analysis showed that the prepared sample is free of any oxalic acid impurities and hence can be regarded as pure.

Infrared spectra of the hydrated and anhydrous cadmium oxalate were examined using the compressed KBr disc method and the results were in agreement with previously reported data for cadmium oxalate [12,19]. The spectrum of the anhydrous salt is almost the same as the hydrated salt, except in the region 450–550 cm^{-1}. The peak near 510 cm^{-1} which is attributed mainly to [M–O(ox)] is shifted to higher frequencies (550 cm^{-1}) by the removal of water molecules, where O(ox) represents an oxygen atom of the oxalate ion.

The rising temperature TG experiments using a constant heating rate of 5°C

min⁻¹ were carried out both in flowing air and pure nitrogen using the Stanton TG units model TR01 and 750. The results obtained on both TG units were in very good agreement. Figure 1 shows typical TG traces obtained for dehydration and decomposition when cadmium oxalate is decomposed in air or in nitrogen. It is evident that the sample loses mass in two distinct stages. In air, the dehydration starts at about 52°C and is complete when the temperature reaches 140°C. The decomposition starts at 260°C and finishes at 340°C giving a sigmoid decomposition curve.

Calculations on the final mass loss suggested that the product of decomposition in air is CdO (36% mass loss for the anhydrous samples). This was also confirmed by X-ray diffraction analysis on the residues and chemical analysis.

In nitrogen, the dehydration commences very slowly at about 80°C and is complete at 180°C. The decomposition of anhydrous oxalate in nitrogen initiates at 310°C and is complete at 440°C. More experiments in nitrogen showed further mass loss which is more distinctive when the high heating rates are used. This mass loss can be related to vaporization of the metallic product making the choice of final mass loss difficult.

The TG results of a number of experiments carried out in nitrogen confirmed the considerable percentage of oxide (about 27.5 ± 5%) which may be formed at the end of the decomposition.

X-Ray diffraction analysis was also undertaken on the residues collected from TG runs in nitrogen. Under an atmosphere of nitrogen the procedure involved cooling the residue to room temperature while still under the nitrogen atmosphere. The results generally showed that the diffraction pattern of residues is very similar to that for cadmium oxide yet there are still differences which can be related to the presence of cadmium in the residue. This observation has also been reported by David [5] and later by Straumanis et al. [20]. The thermogravimetric traces confirms the production of about 75% metallic cadmium in the residues; the X-ray diffraction
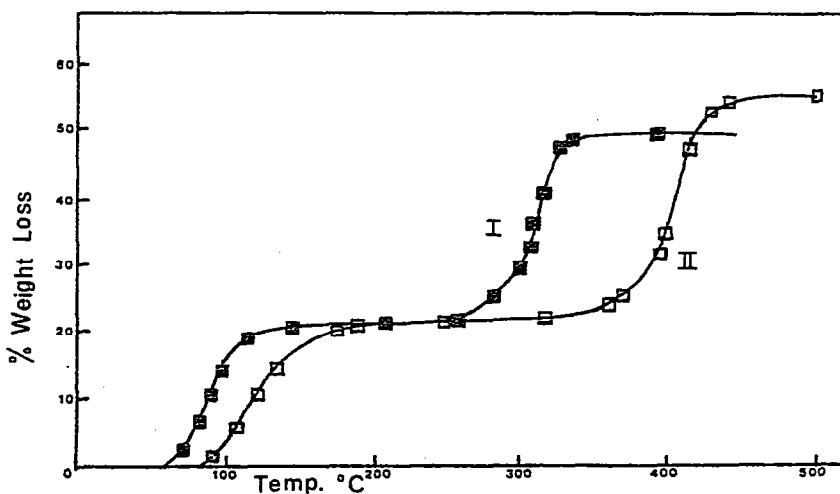

Fig. 1. TG traces for the thermal decomposition of cadmium oxalate. ▨, in air; and □ in nitrogen.

analysis may therefore be regarded as not a very sensitive technique to detect the correct concentration of cadmium and cadmium oxide in the mixtures.

Based on the obtained TG results from the decomposition of cadmium oxalate in nitrogen it can be said that no real correlation is found between the obtained amount of oxide in the residue with the initial mass of sample, nature of the flowing inert gas, different heating rates, preparation procedure or the number of water molecules contained in the original compound. The chemical analysis on residues using the method suggested by David [5] (reaction with $KMnO_4$ and back titration) gave only an average of 0.4% for the concentration of cadmium. This is to be expected since the metallic cadmium can be vaporised at temperatures higher than 350°C and any free metal in the residue can be oxidised at room temperatures.

The observations on the thermal decomposition of CdC_2O_4 and the residues obtained in nitrogen can be summarized as follows.

(1) The product of thermal decomposition in nitrogen is always a mixture Cd + CdO regardless of the size of the sample, shape of the crucible and the nature of flowing inert gas.

(2) The decomposition is a complex one and the experimentally found mass loss is often different from that of the expected mass loss.

(3) This difference in mass loss can be related to either the formation of CdO in appreciable quantities or the vaporization of metallic product at elevated temperatures.

(4) No significant difference in the composition of the mixture is observed when different heating rates are used.

The DTA experiments were carried out using both the Netzsch model 404 and the DuPont 900 apparatus. In each experiment, in order to reduce the thermal conductivity between two cells the sample was diluted to 10% in α-alumina and heated under the same conditions as in thermogravimetric work.

In air, two distinct processes are noticed when the hydrous material is subjected to heat treatment (Fig. 2). (1) The dehydration process which starts at about 75°C and is complete at 140°C giving an endothermic peak with a peak temperature of 100°C and (2) the exothermic peak due to the decomposition of anhydrous cadmium oxalate starting at about 272°C, giving a peak temperature at 325°C. The latter process can be related to the formation of CdO resulting from the simultaneous oxidation of any possible metallic cadmium which might have been formed as a result of this process.

The DTA experiments carried out in nitrogen confirmed the existence of three endothermic peaks; these are as follows.

(1) An endotherm peak corresponding to the dehydration process occurring at 105°C and slowly disappearing at about 150°C (Fig. 2).

(2) The decomposition peak appearing at 350°C which is without any shoulder and disappears at 385°C. This observation, however, was repeated several times at different heating rates and using other insert gases. The experiments gave no indication of the possible formation of $CdCO_3$ as an intermediate compound. Although the DTA traces show no indication of the formation of stable intermediate
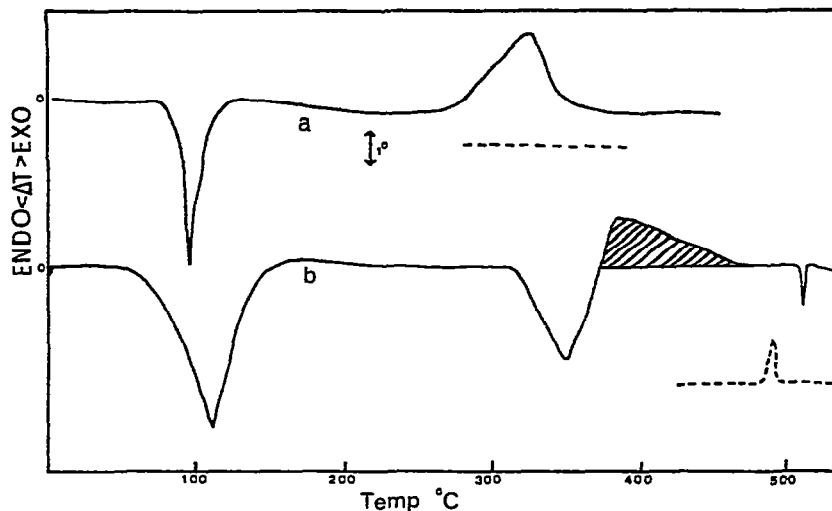
Fig. 2. DTA curves for trihydrated CdC₂O₄. (a), in air; and (b), in nitrogen. ——————, heating curve; — — —, cooling curve.

carbonate, the possibility of the existence of cadmium carbonate was also tested by a series of experiments carried out on premade mixtures of anhydrous $CdCO_3$ and CdC_2O_4 (Fig. 3). These experiments showed that the decomposition peaks for both compounds are totally separated on mixing and this is repeatedly observed for all experiments independent of different heating rates and various percentages of mixing.

(3) The third and small endothermic peak appearing at $510°C$ which is exothermically reversible at $491°C$ on the cooling cycle.

It was mentioned earlier that the vaporization of the metallic product can be enhanced at the elevated temperatures since its melting point was within the range of decomposition. Thus, as far as the phase transformation of metallic cadmium is concerned, the peak temperature of $510°C$ cannot be related to such a process. Moreover, in addition to a phase change, a DTA signal may appear which is large and increasingly endothermic (Fig. 4). The signal is found to normally appear at $600°C$, remaining at a constant value and then progressively becoming smaller as the rate of rise of the temperature decreased. No reversible exothermic peak is observed on the cooling cycle in this case. Also since the appearance of this signal is random, many experiments were carried out to stabilize the conditions at which only the third endothermic peak could appear. To do this, the low temperature head DuPont unit was used to closely investigate these observations with higher accuracies. It should be pointed out that the infrequent appearance of this endothermic signal could be observed with either the platinum–rhodium or chromel–alumel thermocouples regardless of the nature of sample crucibles and inert gas atmospheres.

The result of these and similar experiments suggested that the initial mass of material and the position of thermocouple play an important role in the appearance of the large endothermic signal. To avoid this, the different diluted mixtures of

CdC_2O_4/Al_2O_3 were used and the sample temperature thermocouple was positioned on the surface of the mixture rather than in the sample. This, however, minimized the possibility of corrosion of the thermocouple resulting from the reaction of very
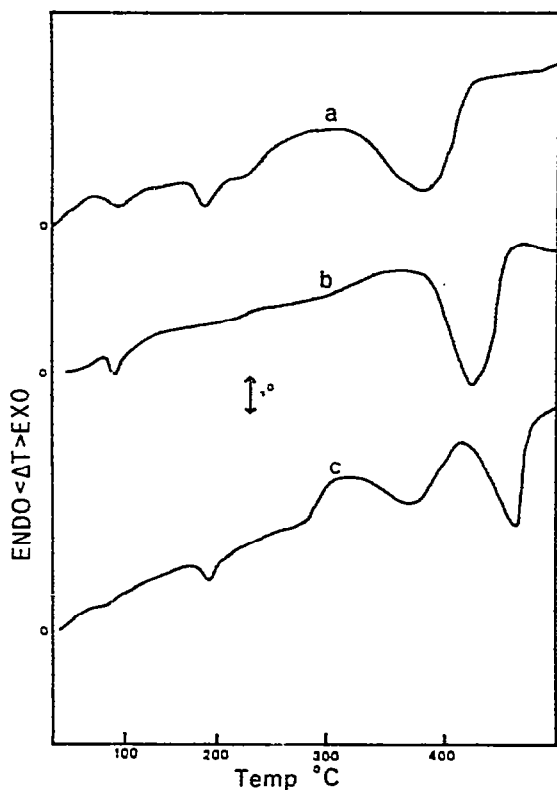

Fig. 3. DTA curves in nitrogen for (a), anhydrous $CdCO_3$: (b), CdO_2O_4, and (c), 50% mixture of CdC_2O_4 and $CdCO_3$.
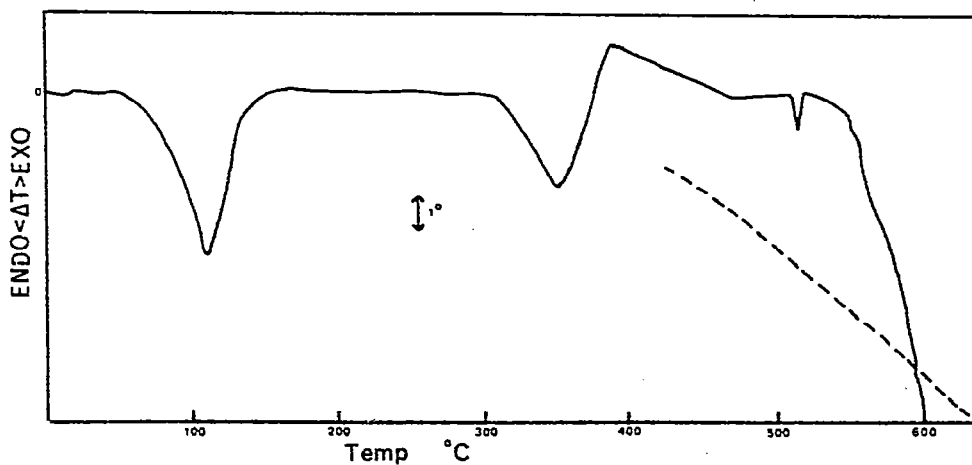

Fig. 4. DTA curve for cadmium oxalate trihydrate in nitrogen. —————, heating curve; — — —, cooling curve.

reactive metallic cadmium with either chromel or alumel or both. It is found that the dilution of a 4% sample in α-alumina can relatively stabilize the conditions at which the phase change peak can consistently be produced.

The changes in surface characteristics of hydrous cadmium oxalate heated at constant temperatures in the range 100–600°C for one hour in air were investigated by the series of low temperature nitrogen adsorption isotherm experiments (Figs. 5–7). These experiments were carried out using a BET volumetric unit described by Faith and Willingham [21]. Calculations on the results obtained were carried out both by using the conventional BET method of analysing the data and the De Boer's *t*-plot method [22].

The sample heated at 100°C [Fig. 5(a)] showed a hysteresis loop which appeared at higher relative pressures indicating a macro-porous structure giving a surface area of 18.3 m² g⁻¹. This value and the macroporous nature of the surface is also confirmed by the *t*-plot method of analysing the data (Fig. 8). The plot clearly shows the upward deviation of points from an ideal non-porous structure model (De Boer's standard reduced isotherm) which occurs at a relative pressure of about 0.5. The calculation of pore size distribution using Dollimore and Heal's method [23] gave
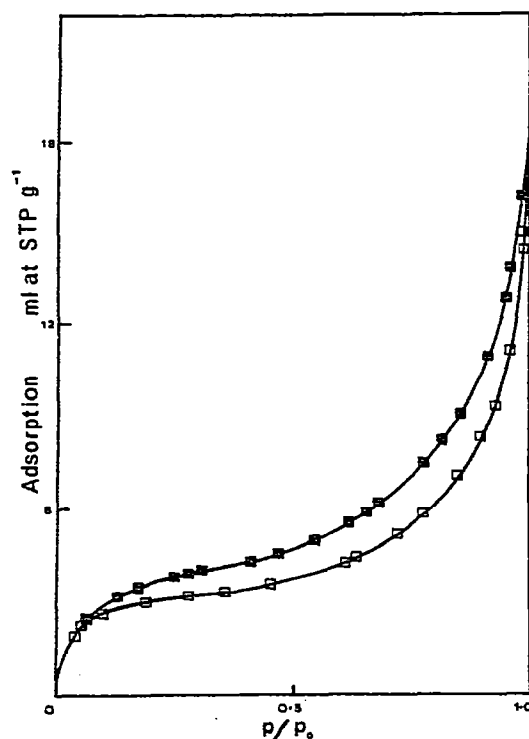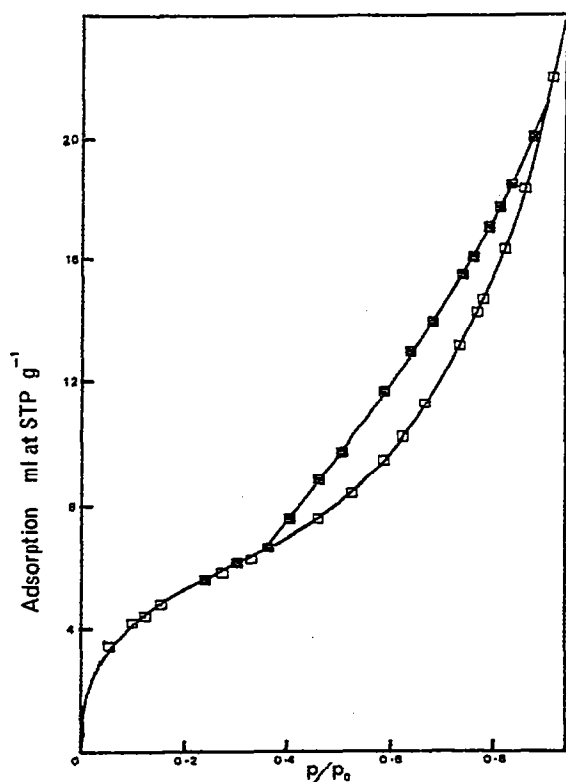

Fig. 5. Nitrogen adsorption isotherm (−195.8°C) of sample heat treated at 100°C. □, adsorption; ■, desorption.

Fig. 6. Nitrogen adsorption isotherm (−195.8°C) of sample heat treated at 200°C. □, adsorption; ■, desorption.
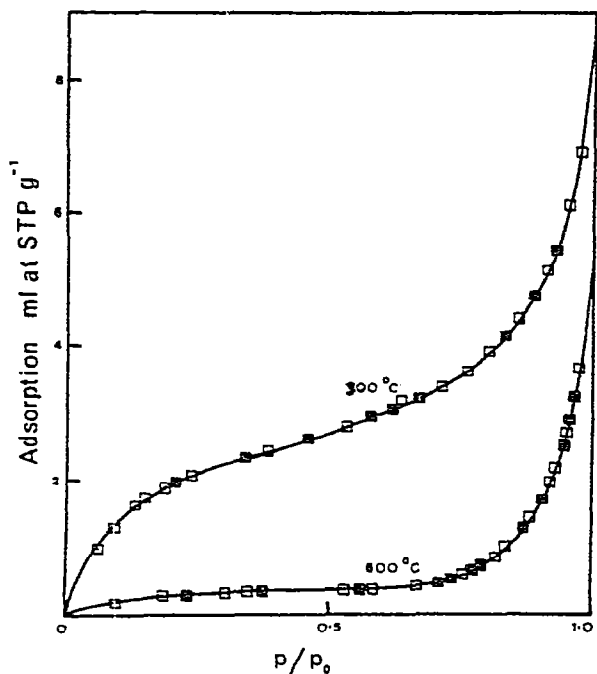
Fig. 7. Nitrogen adsorption isotherm (−195.8°C) of samples heat treated at 300 and 600°C. □, Adsorption; ▓, desorption.

values of 0.03 ml g^{-1} and 1.85 Nm for the total pore volume and the mean pore radius, respectively (Fig. 9).

On the sample heated at 200°C (Fig. 6), the hysteresis loop appears at lower relative pressures, giving an indication of appearance of micro pores together with the deterioration of the previously existing macro pores. The specific surface area
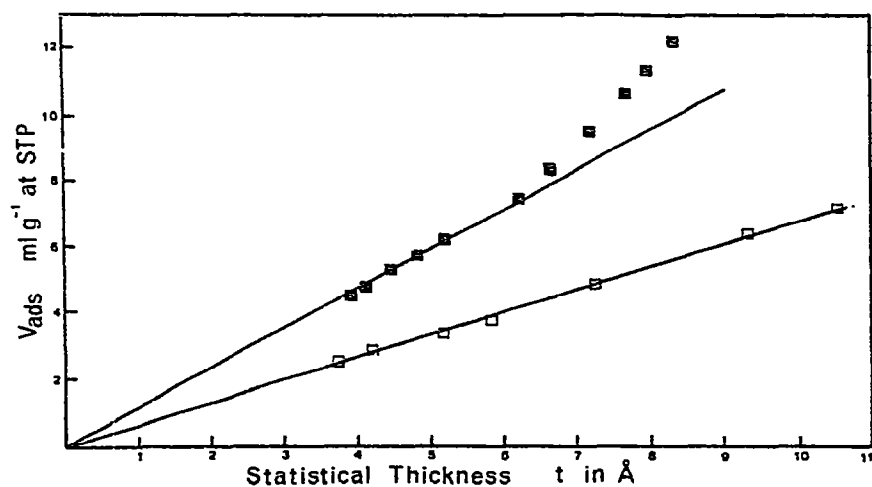

Fig. 8. t-Plots for nitrogen adsorption data of sample heat treated at 100 and 200°C. ▓, Sample heated at 100°C; □, Sample heated at 200°C.
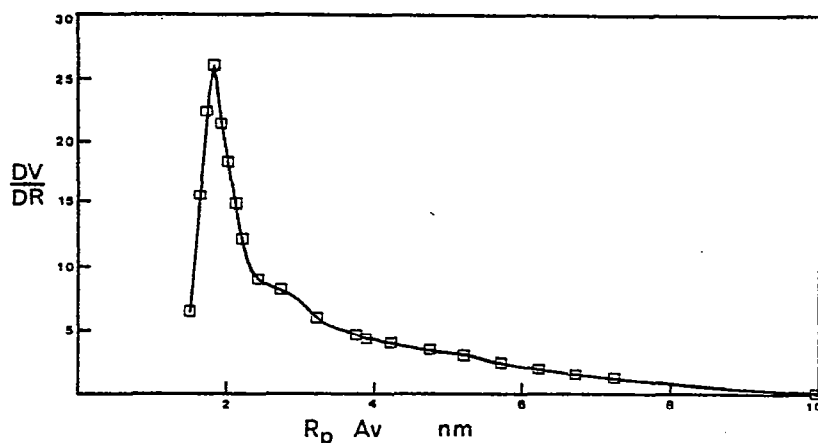
Fig. 9. Pore size distribution plot for sample heat treated at 100°C.

calculated both from the BET and t-plot methods gave the averaged value of 10.6 m^2 g^{-1}. The calculation of pore size distribution gave values of 0.021 ml g^{-1} and 1.55 Nm for the total pore volume and the mean pore radius, respectively.

The adsorption isotherms obtained on other heat treated samples gave no indication of hysteresis loops and the t-plots showed good straight lines up to even high relative pressure values confirming the non-porous nature of the samples. The results obtained (Table 1) show the decrease in surface area from 6.7 to 0.7 m^2 g^{-1} as the temperature is increased from 300 to 600°C. Based on the results obtained it is apparent that the residues are subjected to an overall sintering effect; the originally formed active non-porous cadmium oxide of high surface area sintered to an extent determined by the temperature applied.

TABLE 1

Nitrogen adsorption results on the heat treated samples

Sample [a]	S_{BET} [b] (m^2 g^{-1})	S_t [c] (m^2 g^{-1})	% Weight loss	Total pore volume (ml g^{-1})	Mean pore radius (Nm)
100	18.3	18.50	20.60	0.030	1.85
200	10.6	10.4	26.60	0.021	1.55
300	7.2	6.7	49.20		
400	6.2	5.7	49.23	Non-porous	
500	4.0	5.3	49.44		
600	1.0	0.7	49.74		

[a] Numbers refer to the temperature at which the sample is heat treated.
[b] S_{BET} is the specific surface area calculated from the BET plot.
[c] S_t is the specific surface area calculated by de Boer's t plot method.

DISCUSSION

TG studies in nitrogen show metallic cadmium to be the major product of thermal decomposition, but the appreciable quantities of cadmium oxide (about 2.7%) found in the residue must be regarded as an important feature. This confirms earlier reports concerning the production of a mixture of Cd/CdO [5,14] and would appear to be due to

$$Cd + CO_2 = CdO + CO \qquad (1)$$

The DTA results in air (Fig. 2) agree with previously reported DTA studies [3,15]. Here the exothermic peak can be related to the oxidation of metallic cadmium to the oxide. In nitrogen, however (Figs. 2 and 3), the DTA experiments clearly reject the possibility of the formation of $CdCO_3$ as an intermediate compound and the proposed mechanism by Priblyov and Fazlullina [17] must be regarded as questionable.

There are two interesting observations of the DTA data which may be noted, (i) a slight exothermic drift of the base line (Fig. 2) which is observed on the deflection of the endothermic decomposition peak and, (ii) the third and small endothermic peak observed at 510°C which is exothermically reversible on the cooling cycle.

The general information regarding the application of thermodynamic data on the general reaction

$$M + CO_2 = MO + CO \qquad (2)$$

(where M represents a metal) is to be found in the earlier publication by Dollimore et al. [16] where the product of the thermal decomposition of transition metal oxalates is explained based on the data given in the Ellingham free energy diagrams [24]. This argument leads to the conclusion that the decomposition of CdC_2O_4 in nitrogen is a single stage process (as is also evident from both the TG and DTA traces (Figs. 1 and 2) involving the formation of metallic cadmium and two molecules of carbon dioxide. As the reaction progresses and the rate of reaction increases then the flowing nitrogen gas can no longer preserve the highly reactive metal and thus some oxide production is possible. It may also be plausible to say that at points close to the maximum rate of reaction where the pressure (or presence) of CO_2 at the reaction zones is indeed more than that for the initial and final stages of the decomposition, the oxidation reaction for metal is more favoured. The energy thus liberated from this process causes an exothermic drift of the base line of the DTA trace at the end of the decomposition peak.

The volatilization of Cd at elevated temperatures is also an important factor which should be considered here. This process, however, is reported to initiate at temperatures around 350°C which in turn makes the overall decomposition mechanism more complicated. This would make the total weight loss as recorded by TG dependent upon decomposition, volatilization and the oxidation–reduction processes.

The last endothermic peak (exothermically reversible on the cooling cycle) appearing at 510°C in Fig. 2 can be correlated with observations of Low and Kamel [25] and Straumanis et al. [20]. They showed that cadmium oxide can normally be

decomposed at elevated temperatures according to

$$CdO \rightarrow Cd + \tfrac{1}{2}O_2 \qquad\qquad (3)$$

whereby some of the free Cd can be dissolved in the remainder of CdO causing a small lattice expansion together with increase in its electrical conductivity. The latter, however, is decreased upon heating the oxide in air or oxygen.

The dissolution of metallic cadmium in CdO by an endothermic peak at 510°C which segregates upon slow cooling within the CdO crystallites more or less completely, gives rise to the observed exothermic peak at 491°C (Fig. 2). This behaviour is consistent with the observations of Faivre [26] who studied the lattice expansion of CdO due to the dissolution of free metallic cadmium.

It was pointed out that the formation of excess metallic product could cause the corrosion of thermocouples giving rise to a large endothermic signal at about 600°C and the process was said to be irreversible on cooling (Fig. 4). Thus, in agreement with Straumanis et al. [20] and Low and Kamel [25] it is possible to say that the dissolution of Cd in CdO produced as a result of cadmium oxalate's decomposition in nitrogen gives an endothermic peak which can be explained as follows.

A very small excess of Cd is always present in CdO and this according to Straumanis is reported to have a formula $Cd_{1.0005}O$. It is possible that the ionized part of these excess metallic atoms is responsible for the electrical conductivity rather than the oxygen vacancies. However, for Cd in CdO the ionization reaction may be written as

$$Cd \rightarrow Cd^{2+} + 2\,e \qquad\qquad (4)$$

The solubility of Cd in CdO found in this study (about 0.4%) is very limited because upon cooling the former segregates from the lattice of the oxide. It may thus be possible that, upon heating, some of the oxygen atoms leave the structure of CdO, transferring their two valence electrons more or less completely to the Cd^{2+} ions [eqn. (4)]. These saturated ions represent the Cd excess in the lattice of CdO causing an increase in electrical conductivity of the oxide. The large endothermic signal appearing after the third endothermic phase change peak in Fig. 4 can thus be explained as an artifact produced by electrical leakage between the thermocouple and relatively high electrical conductivity of Cd dissolved in CdO system. It is evident that if the solid solution is heated in oxygen or air, the excess Cd is nearly completely oxidized, the electrical conductivity decreases and thus no endothermic signal appears at high temperatures (Fig. 2).

The full nitrogen adsorption isotherm experiments on the residues obtained by heating the cadmium oxalate samples at various temperatures in air for one hour did not exhibit a maximum for the surface area within the temperature range studied (100–600°C). This indicates that the activation process probably predominates at temperatures lower than 100°C which is subsequently followed by sintering of the solid at higher temperatures (Table 1). The system is characterized by the fact that the activation process is very mild compared with the sintering process. The solid is activated at very low temperatures (probably just after the dehydration process is completed) accompanied by the increase in the porous nature of the substance and

hence the appearance of the hysteresis loop (Fig. 5). The data in Table 1 indicates that at 200°C the amount of oxide formed is probably only a few layers thick on the surface. It can be assumed that as soon as the conversion to the oxide takes place at temperatures higher than 100°C, sintering becomes a predominant factor and hence the porous nature of the solid is seriously affected (deterioration of the hysteresis loop at 200°C and its disappearance at temperatures higher than 200°C). The mechanism of sintering of CdO is discussed by Mikhail and Kamel [27]. The non-stoichiometric nature of CdO and the presence of both oxygen vacancies and interstitial cations in the lattice is believed to accelerate the sintering mechanism.

One can use the information reported here to speculate on the reaction pathway in the thermal decomposition of CdC_2O_4 to metallic cadmium in nitrogen. The schematic representation of the oxalate molecule is
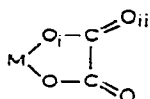

The extent to which the $M-O_i$ bond is covalent depends on the electronegativity of the metal. According to the studies of Fugita et al. [10], as the $M-O_i$ bond becomes stronger (i.e. M is more electronegative), the $C-O_i$ bond is lengthened and the $C-O_{ii}$ bond is shortened. Dollimore et al. [16] used this idea and suggested that for those oxalates which produce metal in nitrogen the decomposition temperature represents the temperature at which the $M-O_i$ link is ruptured and will depend critically on the size and charge of the metal ion, whereas in those decompositions where the oxide is produced in nitrogen the decomposition temperature represents the energy required to break the $C-O_i$ bond and this will depend less critically on the nature of the cation. It must be noted that these generalizations cannot always be regarded as valid since the decomposition temperature of any solid material is dependent upon many factors (e.g. particle size, porosity, preparation procedure, impurities, surface dislocations, ageing, packing, etc.) and the ionic radii of the metal is only one of these factors. The nature of the possible bond rupturing in the extreme cases portrayed above which might occur may be discussed. Considering M to have a high electronegativity value, according to Fujita the $M-O_i$ link becomes stronger and the $C-O_{ii}$ bond is shortened and therefore the rupture of $O-O_i$ bond is more feasible. Using this idea we may write
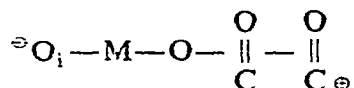

and depending on the rupture of a) C–C or b) M–O bonds two possible mechanisms can thus be considered
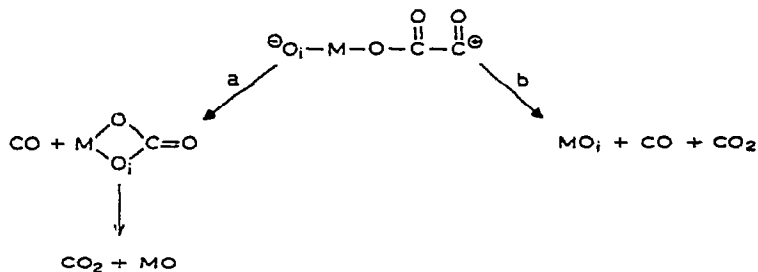
In considering the case where the $M-O_i$ link is not a strong bond in comparison with $C-O_i$ (i.e., M has a bigger ionic radius and less electronegativity), the M–O link might be regarded as the most likely bond to be ruptured and thus we can write

$$^\ominus O- \underset{C}{\overset{O}{\parallel}} - \underset{C}{\overset{O}{\parallel}} -O_i -M_\oplus$$
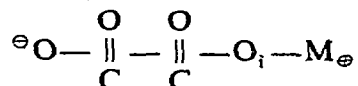
Depending on the rupture of (a′) C–C or (b′) $M-O_i$ or (c′) O_i-C bonds, three alternative mechanisms may now be written as
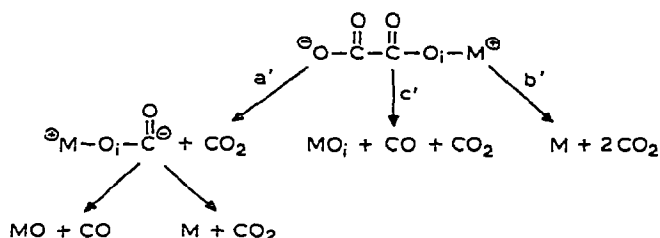
It should be remembered that the above mechanisms are all considered based on the most possible single stage bond breakings within an oxalate molecule on a consecutive basis. In reality, this might be quite different as there is a possibility that the other bonds may also be ruptured simultaneously. The above mechanisms illustrate the difficulties involved in accepting (or rejecting) any of the mentioned forms in which an oxalate molecule can be decomposed to produce metal. It should be noted, however, that four out of the above five different mechanisms lead to the production of metal oxide as a product.

As regards the infrared studies, the discussion on the bond breaking stages can be extended by using Nagase's data [12] on various transition metal oxalates. The increase of the bond energies on removing the coordinated water molecules is reported to increase in the order Ni > Co > Fe > Zn > Mn. Based on the infrared studies reported in this paper, the frequency shift for Cd–O(ox) is observed to be 40 cm^{-1}. Thus, by using the Nagase data, the order Ni > Co > Fe > Zn ≈ Cd > Mn can be obtained.

Table 2 indicates the electronegativity and ionic radii values for some transition metals [28]. The increase in electronegativity values is in the form of Cu = Ni > Co > Fe > Pb > Cd whilst for the ionic radii it takes the form of Ni < Cu = Co < Fe < Cd < Pb. Based on this and also by considering the infrared data, it can be suggested that in an oxalate molecule, the bond energy of M–O(ox) depends very much upon

TABLE 2

Electronegativity and ionic radius valves for some transition metals

Metal	Cu	Ni	Co	Fe	Pb	Cd
Ionic radius (Å)	0.72	0.69	0.72	0.74	1.20	0.97
Electronegativity	1.75	1.75	1.70	1.64	1.55	1.46

the ionic radius and the electronegativity of the metal. The smaller the ionic radius and the higher the ionization potential, the stronger the $M-O_i$ link becomes and hence the bond's length decreases. On heat treatment therefore it is more likely that the other bonds will be initially ruptured. If the opposite case existed, the $M-O_i$ link is perhaps the most likely bond to be ruptured. These considerations show the relative position of cadmium in these sequence considerations but the actual decomposition temperature for cadmium oxalate must also reflect the other factors already mentioned and this could obscure the correlations based on bond rupture.

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