1009. *The Thermal Decomposition of Salts of Mellitic Acid. Part I. Aluminium Mellitate and Natural Mellite*

By A. K. GALWEY

The kinetics of formation of product carbon dioxide and carbon monoxide during the thermal decomposition of aluminium mellitate in a vacuum have been studied. Results showed that three reactions could be recognised in different temperature ranges. (i) The initial reaction (below 250°) where a small yield of gas was formed during dehydration of the reactant. (ii) The low-temperature thermal decomposition studied at 382—485° in which the carbon dioxide reaction obeyed the third-order kinetic equation at ~410° and the second-order kinetic equation at ~460°. The energy of activation was $45 \cdot 5 \pm 1 \cdot 0$ kcal. mole^{-1}. Carbon monoxide formation showed similar kinetic characteristics but the energy of activation was $70 \cdot 0 \pm 1 \cdot 5$ kcal. mole^{-1}. (iii) The high-temperature decomposition (525—593°) in which the rate of formation of both gaseous products obeyed the third-order kinetic equation and the energy of activation was $45 \cdot 0 \pm 2 \cdot 0$ kcal. mole^{-1}.

The reactions of naturally occurring mellite were identical with those of the synthetic salt.

Possible mechanisms for these reactions are discussed.

THERE are many accounts of the thermal decomposition of inorganic ionic salts in the solid phase.[1] Work of this kind has been largely concerned with (a) the determination of the function which expresses the relationship between area of reaction interface and fraction of the salt decomposed (this may give information about the growth of nuclei of product phase), and (b) the identification of the processes involved in the rate-determining step of the reaction. For many inorganic ionic salts, detailed mechanisms for the decomposition have been proposed, but much less information is available about the reactions of metal salts of organic acids. Reasons for this include the observation that many such salts melt before decomposition, and those which do decompose before melting may have complex secondary reactions between the primary products which make accurate kinetic studies difficult. For example[2] nickel phthalate, which decomposed before melting, yielded at least eight products of isothermal decomposition in a vacuum. However, it appeared probable that the decomposition reactions of salts of mellitic acid (benzenehexacarboxylic acid) would provide a simpler system for study since, if water of crystallisation was lost below reaction temperature,[3] the only products expected were oxides of carbon, elemental carbon, and metal and/or oxide. Thus, there is less probability of secondary reactions between products. Furthermore, if acid salt is absent from the reactant it is possible that all the carboxyl groups in the acid radical may be equivalent, thus simplifying the interpretation of the results. It also must be remembered, in comparing results of a study of this type with those given in ref. 1, that the metal–carboxyl group bond may have much more covalent character than the bonds in those ionic solids whose thermal decomposition has been studied in the solid phase.

Aluminium mellitate was selected as being of particular interest since it occurs in brown coal as the mineral mellite. Comparative studies, using synthetic salt and natural mineral, showed that the kinetic results for the thermal decomposition of salts from both sources were identical within experimental error. From this it is concluded that the ageing, pressure treatment, and probable presence of impurities in the mellite did not significantly influence the thermal decomposition.

[1] P. W. M. Jacobs and F. C. Tompkins, "Chemistry of the Solid State," Butterworths, London, 1955, ch. 7.

[2] A. K. Galwey, *J. Catalysis*, 1965, in the press.

[3] M. Chaigneau, *Bull. Soc. chim. France*, 1961, 54.

EXPERIMENTAL AND RESULTS

Reactants Studied. Synthetic aluminium mellitate was supplied by Mining Research Ltd., Essen-Kray, W. Germany. Throughout the present study material from a single batch was used as small (~2 mm. cubes) crystals or as crushed powder which will be referred to as sample 1.

Samples of " Saxony mellite " were supplied by Dr. Ing. Maucher of the South Germany Mineral Centre, München-Pasing. Four single crystals (samples 2—5), each ~0·7 cm.^{3}, were selected for investigation; each crystal was initially broken into fragments of suitable size for kinetic studies. Crystals used as samples 2 and 3 were of good habit, almost transparent, and brown. Samples 4 and 5 were crystals of poor habit, coloured smoke-grey, and contained visible particles of impurity (rock fragments?; coal?). Analyses of samples 1—5 are given in the Table; the small weights of samples 2—5 available made quantitative determinations of concentration of impurity metals (*e.g.*, Mg, Ca) impracticable.

Chemical analyses of aluminium mellitate and of mellite

Ref.	Description	Non-combustible residue (Al_2O_3) (%)	Combustion analysis C (%)	Combustion analysis H (%)	Loss in weight in a vacuum at 200° (H_2O) (%)
1	Synthetic	16·81	21·05	4·81	41·1
2	Mellite (brown)	16·35	21·44	4·77	41·2
3	Mellite (brown)	16·51	21·13	4·83	41·5
4	Mellite (grey)	18·24	20·94	4·80	41·0
5	Mellite (grey)	17·34	21·71	5·15	41·3
Calc. for $Al_2C_{12}O_{12},18H_2O$		14·27	20·17	5·08	45·4
Residue from low-temp. reaction		48·33	37·80	$<0·5$	—
Residue from high-temp. reaction		55·13	39·49	$<0·5$	—

The results in the Table show that all reactants had closely similar chemical compositions; the higher residues from samples 4 and 5 may be attributed to solid particles of impurity. Also recorded in the Table is the loss in weight on heating in a vacuum at 200°, corrected for weight of gaseous products. This represents loss of water of crystallisation, and accounts for virtually all the constituent hydrogen of the reactants.

X-Ray diffraction patterns for samples 1—5 were identical within experimental error. A similarly obtained photograph for sample 1 (after dehydration) gave no sharp lines but only four diffuse halos. This showed that the salt prior to decomposition contained no well defined crystal structure and must be regarded as approaching the vitreous state.

The Thermal Decomposition Reaction.—The kinetics of the thermal decomposition were studied by measuring, with a McLeod gauge, the pressure of gas evolved in a constant-volume vacuum apparatus, while the reactant was held at a constant, measured temperature. A carbon dioxide–acetone (~ −80°) trap or a liquid-nitrogen (~ −195°) trap was placed between the reactant and the pressure gauge. The reactant, contained in a small glass tube, was initially outgassed for 2 hr. at ~10^{-6} mm., and was weighed before and after reaction.

Preliminary experiments showed that decomposition occurred at rates suitable for kinetic studies in three temperature ranges: ~240°, the initial reaction; 382—485°, the low-temperature reaction; and 525—593°, the high-temperature reaction.

Initial Reaction.—On heating below 250°, in a vacuum, aluminium mellitate yielded water (Table) and a small amount of carbon dioxide. The yield of gas was variable, and the kinetics of formation irreproducible; no significant kinetic results were obtained.

Sample 1, after dehydration for 2 hr. at 220°, became hydrated to the original weight after 7 days in saturated water vapour at room temperature, but after dehydration accompanied by slight decomposition (20 hr. at 230°) rehydration was much slower, about 50% of the weight loss being regained after 1 month.

Low-temperature Decomposition.—On completion of this reaction 100·0 mg. of sample 1 yielded 21·2 mg. of carbon dioxide, 2·5 mg. of carbon monoxide, and 35·2 mg. of a black residue, the composition of which is recorded in the Table. Yields for samples 2—5 were identical with those for sample 1. No significant changes in product yields with mass of reactant or reaction temperature were detected. *X*-Ray studies showed the solid residue to be amorphous, and the surface area of the product from completed low-temperature thermal decomposition for sample 1, determined by measurement of nitrogen adsorption at −195° and application of the B.E.T. equation, was 6·0 m.^{2} g.$^{-1}$.

Pressure–time plots for finely crushed material from sample 1 showed the low-temperature thermal decomposition to be deceleratory throughout. Results from typical experiments using a −80° trap are shown in Figure 1; qualitatively similar results were obtained using a −195° trap. The readings did not fit the "contracting cube" or the first-order equations, which have both found application [1] in the study of the thermal decomposition of solids. Results did, however, fit the third-order equation very satisfactorily ($0·1 < \alpha < 0·85$); typical plots are shown in Figure 2. Arrhenius plots using third-order rate constants gave the energy of activation as 45·5 ± 1·0 kcal. mole^{-1} for experiments with the −80° trap (44·0 ± 1·5 was found by use of the less accurately obeyed second-order equation), and 70·0 ± 1·5 kcal. mole^{-1} with the −195° trap. Results of experiments in which samples of mellite, or single crystals of synthetic material, were used all gave rate constants which fell on the same Arrhenius line as that found using powdered material from sample 1, when the same refrigerant trap was used. Slopes of plots of log $(1/1 - \alpha)$ against log t (where α was the fractional decomposition at time t) for all the kinetic data obtained (for all samples and for either cold trap) varied between 0·5 at ~410° (third-order kinetics) and 1·0 at ~460° (second-order kinetics). Thus, the apparent reaction order increased with increasing temperature but results fitted the third-order equation to an acceptable degree of accuracy over the whole range studied.

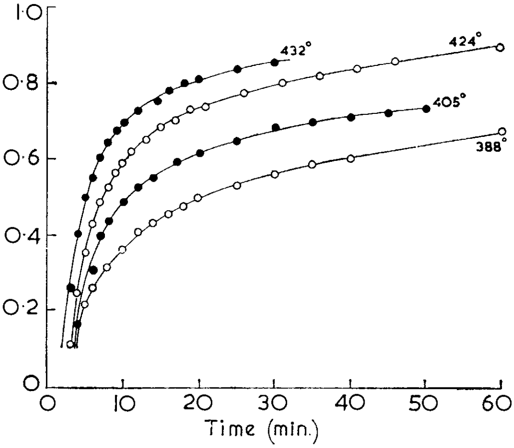

FIGURE 1. Fractional decomposition (α) against time plots for the low-temperature thermal decomposition of aluminium mellitate (sample 1) at several temperatures, with a −80° refrigerant trap

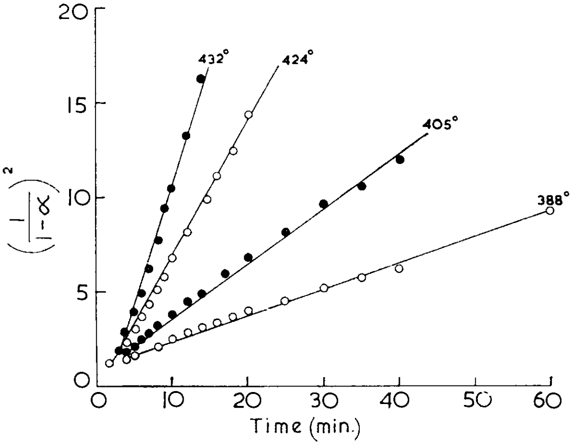

FIGURE 2. Third-order plots for the data in Figure 1

High-temperature Decomposition.—On completion of decomposition, 100·0 mg. of the original sample 1 yielded (in this reaction) 5·3 mg. of carbon dioxide, 1·6 mg. of carbon monoxide, and

28·3 mg. of a black, non-volatile residue, the chemical composition of which is shown in the Table. No crystalline structure was found in this residue by *X*-ray studies, and surface-area measurements gave 4·2 m.^{2} g.$^{-1}$. The product yields were independent of mass of reactant and reaction temperature (525—593°), except that a slight increase in the carbon monoxide yield was observed at higher temperatures. Product yields from the decomposition of mellite were identical with those found for sample 1.

Kinetic studies of this reaction were complicated by the uncertainty, with each sample, as to whether the low-temperature reaction had been completed or whether slight high-temperature reaction had occurred. This reaction was deceleratory throughout, and results for the decomposition of powdered sample 1 fitted the third-order equation satisfactorily ($0 < \alpha < 0{\cdot}8$); typical results are shown in Figure 3. All results obtained with material from samples 1—5 with a $-80°$ or a $-195°$ trap gave third-order rate constants which fell on a single line on the Arrhenius plot, from which the activation energy 45·0 ± 2·0 kcal. mole^{-1} was found. The kinetics of evolution of both gases were identical, and also the kinetic behaviour of decomposition of natural and synthetic material were similar within experimental error. Plots of $\log (1/1 - \alpha)$ against $\log t$ for all data gave slopes between the extreme limits 0·35 and 0·7, but most results showed kinetic behaviour to be very close to third order. No trend of change of reaction order with temperature was found. The rate constants of this reaction was not apparently influenced by the temperature at which the low-temperature decomposition had occurred. There was no evidence that the solid product catalysed the formation of carbon dioxide from carbon monoxide as would be shown by a decrease in product pressure at the end of experiments in which a $-195°$ trap had been used.

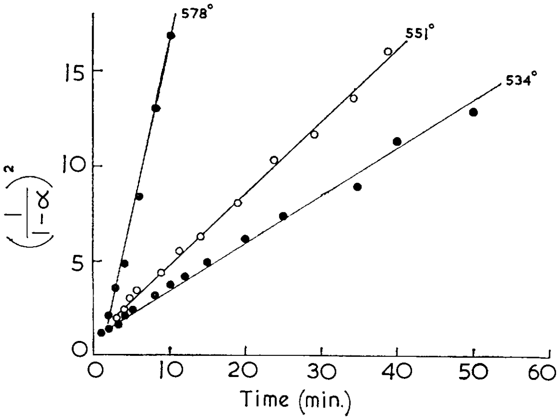

FIGURE 3. Third-order plots for the high-temperature thermal decomposition of aluminium mellitate (sample 1) at several temperatures, with a $-80°$ refrigerant trap

DISCUSSION

Stoicheiometry of Reaction.—The compositions of reactant samples 1—5 were all within relatively narrow limits (Table); samples 4 and 5 contained small amounts of visible impurities. The calculated results below refer to data obtained for sample 1 but results obtained for mellite were identical with these within experimental accuracy. For convenience in discussion, one " mole " of reactant is taken as that weight which contained 12·00 g.-atoms of carbon. The Al : C ratio for sample 1, as prepared, was 2·255 : 12·00 (from Table); thus, an appreciable fraction of the aluminium was present as basic salt or as alumina. On completion of the reaction in the low-temperature decomposition range, each " mole " of reactant yielded 3·90 moles of product gas, 18·4% of this being carbon monoxide and the remainder carbon dioxide. The former was produced in reactions accompanying the decomposition process, since the relative yields of the two products were the same whichever cold trap was used, as might be expected if it was formed in secondary reactions of carbon dioxide at the surface. In the high-temperature reaction, 1·21 moles of gas were given from each " mole " of reactant in the original salt.

The solid residue on completion of this reaction contained more oxygen than that expected if alumina and carbon were the only non-volatile products (Table), indicating that at this temperature not all the " carboxyl group " oxygen had been converted into gaseous products and alumina.

No simple stoicheiometric relationship between product yield and reactant composition was apparent, though closely similar yields were found for reactions of the different source materials. It is concluded, therefore, that a constant fraction of the acid radicals of the reactant decomposed in each of the two reactions. This model is preferred to a mechanism based on the formation of an intermediate compound, for example, a complex containing phenol groups bonding aromatic rings to the aluminium atoms, since no evidence for the existence of such a species was apparent.

Kinetics and Mechanism of the Decomposition Reaction.—There was no evidence that the reactant melted during decomposition, which yielded a brittle black solid having an apparently similar range of particle sizes to that of the reactant used and a relatively low ($\sim$5 m.^{2} g.$^{-1}$) surface area. *X*-Ray studies showed that the dehydrated or decomposed material had no crystal structure, which contrasts with the highly crystalline original reactants. A considerable change in the structure of the solid must therefore accompany dehydration. This may be envisaged as the transition of an ionic salt, containing water of crystallisation, to a covalent crystal in which random bonding in three dimensions was between the terdentate aluminium radicals and the sexidentate mellitate radicals to give the amorphous solid. Hydrolysis and rehydration occurred slowly in material in which little decomposition had occurred. Slight decomposition accompanied dehydration ($\sim$5% of the carbon dioxide yield of low-temperature decomposition). We believe that this represented decomposition of traces of free acid formed by hydrolysis during dehydration; separate experiments showed that pure mellitic acid underwent decomposition under these reaction conditions. Furthermore, on completion of the low-temperature reaction, just detectable amounts of a black residue (carbon) on the walls of the reaction vessel and a white sublimate just outside the heated zone were observed; similar deposits, but in very much greater yield, were found when pure mellitic acid was heated under the same conditions.

The dehydrated vitreous phase, discussed above, decomposed when heated. Three main mechanisms of decomposition may be considered: (i) nucleation and growth of a product phase; (ii) progression of a decomposition interface into the particles of reactant at a direction normal to the original surfaces of the particle; and (iii) decomposition in the matrix, as in the homogeneous phase, with negligible surface effects. None of the kinetic equations derived from models (i) and (ii), which have found [1] extensive application in studies of the thermal decomposition of solids, fitted the present experimental data. Furthermore, crushing [4] or ageing [5] of the reactant did not significantly influence reaction rate, in contrast to observations on some of the reactions of type (i). The kinetic data are, however, consistent with model (iii), in that readings fitted the third-order equation, which has been observed to fit rate processes occurring in the homogeneous phase. The following model is proposed to account for the results. Reaction occurred by a bimolecular process involving two reactant species which, at reaction temperature, have a limited freedom of movement in the vitreous solid by interchange of bonds between the different ligands. The reaction rate decreased as reactant was used, and a further reduction in rate resulted from a decrease in the ease of mobility of the ligands as product alumina increasingly entered the vitreous phase. Thus, it is suggested that two mellitate radicals take part in the bimolecular process leading to reaction. If it is assumed that the influence of the ease of diffusion decreased in importance at the higher-temperature end of the range studied, this accounts for the apparent decrease in reaction order with increasing temperature. Product gases could diffuse from the reaction site to the gaseous phase as reaction

[4] P. W. M. Jacobs and A. K. Galwey, *Proc. Roy. Soc.*, 1960, *A*, **254**, 455.

[5] J. Simpson, D. Taylor, and D. M. W. Anderson, *J.*, 1958, 2378.

proceeds, but any voids left in the solid must be removed by sintering since a solid product with a relatively low surface area remained on completion of the reaction.

The difference in rates of formation of carbon dioxide and carbon monoxide in the low-temperature range indicated that different rate processes were responsible for the formation of the greater part of the yield of each product. The occurrence of two reactions at somewhat different rates accounts for departure from strict linearity of the plots in Figure 2. It is suggested that the low-temperature reaction ceased when sufficient alumina was present in the vitreous matrix to reduce mobility of the two reactants to the point where formation of the decomposition transition complex was prevented. At increased temperatures, however, the reactant radicals again became mobile, and further decomposition occurred by a bimolecular process in a medium in which resistance to diffusion of reactants again increased during the course of the high-temperature reaction, resulting in apparent third-order kinetics. The energy of activation of this process was close to that found for the formation of the main product in the low-temperature reaction. A single rate process probably yielded both products in the high-temperature reaction since rate constants for the formation of both gases gave a single line on the Arrhenius plot. The species formed in the rate-determining step were not identified from the data available but it is suggested that the bond between a metal atom and a carboxyl group of the transition complex was broken in the first step, since nickel and cobalt salts of mellitic acid yielded [6] metal as the main solid product. Secondary reactions between the initially formed species then yielded the products observed.

Natural and Synthetic Reactants.—The close similarity of analytical and kinetic measurements obtained for natural and synthetic reactants showed that the effect of ageing, possible impurities, and prolonged high-pressure annealing during formation in the host rock of the former salt, as compared with the latter, did not influence the kinetics of the thermal decomposition. The mechanism of reaction discussed above is consistent with these observations since it is suggested that complete rearrangement of the radicals within the solid occurred on dehydration immediately before the decomposition reaction. Thus, any differences in the original concentrations or disposition of defects in mellite, as compared with synthetic aluminium mellitate, were destroyed in the transition from ionic to covalent salt before reaction started. This contrasts with the effect of ageing on ionic salts,[5] where it may modify the course of the decomposition reaction; the mineral used in the present study may have been formed up to 200 million years ago, and any ageing process must be assumed to be complete.

Conclusions.—Many equations have been developed [1] to express the kinetics of thermal decomposition of solids; the reactant of the present study did not melt, and at the same time did not obey a rate equation characteristic of reactions of solids. This apparent inconsistency was resolved by the assumption that the present reactant was more accurately represented as a vitreous phase and that decomposition involved rupture of covalent bonds in the homogeneous reactant matrix. This contrasts with results of studies of the thermal decomposition of ionic solids, where charge-transfer has often been considered [4] to be the first step in reaction. Other salts which decompose without melting and obeyed kinetic equations characteristic of reactions occurring in the homogeneous phase include nickel and cobalt mellitate [6] and nickel phthalate.[2]

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Department of Chemistry, The Queen's University,
Belfast, Northern Ireland.

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[6] A. K. Galwey, unpublished results.