SYNTHESIS AND THERMAL DECOMPOSITION OF POTASSIUM TRIOXALATOALUMINATE HYDRATE

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(Received November 18th, 1971)

ABSTRACT

The preparation of pure $K_3Al(C_2O_4)_3 \cdot mH_2O$ $(2 < m < 3)$ is described. Dependent on the mode of preparation, the following were found to be contaminants of the desired product: $K_2C_2O_4 \cdot 1H_2O$; KHC_2O_4; $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$; $H_2C_2O_4 \cdot 2H_2O$; different forms of aluminium oxide hydrate; $K_4Al_2(OH)_2(C_2O_4)_4 \cdot (2+x)H_2O$ $(0.7 < x < 1.7)$ and $K_2Al_2(H_2O)_2(C_2O_4)_4 \cdot 4H_2O$.

The thermal behaviour of $K_3Al(C_2O_4)_3 \cdot mH_2O$ was investigated by means of thermogravimetry, differential thermal analysis, differential scanning calorimetry, infrared spectral analysis, evolved gas analysis and high temperature X-ray diffraction. The dehydration proceeds via the intermediate 2- and 0.75-hydrates (room temperature to 120°C). The existence of the 3-hydrate could not be confirmed. On increasing the temperature, anhydrous potassium trioxalatoaluminate decomposes into potassium oxalate, potassium carbonate and alumina (320–435°C). The potassium oxalate decomposition (435–475°C) is overlapped by the formation of $KAlO_2$ from potassium carbonate and alumina; the procedural final temperature of the latter process is dependent on the CO_2 partial pressure. After the thermal decomposition of the excess K_2CO_3 present, $KAlO_2$ is the final solid product.

INTRODUCTION

This contribution deals with the following subjects: (*a*) the preparation of a pure stoichiometric potassium trioxalatoaluminate hydrate, (*b*) the discussion of the water content of this compound and the stability of the different hydrates possible, and (*c*) the elucidation of the thermal decomposition process of the anhydrous compound.

During the synthesis of the desired product, the author[1] found other potassium oxalatoaluminates, as well as non-aluminium containing oxalates, to be contaminants. These contaminants are detectable by thermal analysis (TA), infrared spectral analysis (IR), and, especially in low concentrations, by thermogravimetry (TG), because of their differing decomposition pattern.

The purity as well as the definite water content of this compound are interesting for its use as a diluent crystal for the investigation of the trioxalato complexes of

trivalent transition-metal ions by means of crystallographic, structural and spectral methods of analysis. In addition, its application in the field of catalysis, for the preparation of mixed metal oxides by thermal decomposition of mixed oxalates, requires a well-defined starting material.

Surveying the literature about oxalatoaluminates[1] from a synthetical point of view, we found the most thorough work done on potassium trioxalatoaluminate by Rosenheim and coworkers[2,3] and Aronowicz[4], the latter investigator also studying the dehydration of this compound. The vapour pressure of the hydrated species was studied by Wosskressenskaja[5], and its thermal decomposition by Dollimore and coworkers[6].

Up to the present time, the thermal decomposition path is not fully established, possibly due to overlap of the different steps, which hampers stoichiometric calculations based on TG measurements alone. Therefore, we used complementary techniques for the detection of the intermediate products (*e.g.* IR for the occurrence of oxalato- and possible carbonato complexes as well as single oxalate and carbonate anions; evolved gas analysis (EGA) for determination of carbon monoxide and carbon dioxide; differential thermal analysis (DTA) and differential scanning calorimetry (DSC) as finger-print methods and for possible resolution of an overall TG step; and high temperature X-ray analysis (HTX) as a source of survey information and as a complementary check for the other methods mentioned).

The thermal behaviour of this compound is interesting, because it is a straight-forward decomposition of a trioxalato complex of a trivalent metal-ion, *i.e.*, without a subsequent reduction or oxidation step of the central metal ion by the evolved CO or CO_2, as generally occurs in the case of the complexes of transition-metal ions.

EXPERIMENTAL AND RESULTS

Materials

The following chemicals were used in the investigation: $(COOH)_2 \cdot 2H_2O$ (Merck, pA quality), $K_2C_2O_4 \cdot 1H_2O$ (Baker, pA quality), and Aluminium (Merck, pA quality).

*Analytical methods**

TG — A Cahn RH electrobalance in combination with a Dupont 900 differential thermal analyzer were used under the following conditions: Temperature, room temperature–1200°C; heating rate, 5°C min^{-1}; atmosphericconditions, ambient pressure; pure nitrogen, flow rate 28 c.c. min^{-1} at room temperature; pure carbon dioxide, flow rate 34 c.c. min^{-1} at room temperature. The sample was mortared and sieved (nylon sieve) before using 5–10 mg of particle size 58–69 μm.

DTA — A Dupont 900 differential thermal analyzer was used with a heating rate of 10°C min^{-1}. The reference material was α-Al_2O_3 powder. Other operating conditions were the same as for the TG analysis.

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*For extensive experimental details see Ref. 1.

DSC — A Dupont 900 differential thermal analyzer was used in the temperature range: room temperature–600 °C, with a heating rate of 10 °C min^{-1}. Other operating conditions were the same as for the TG analysis.

IR — A Beckman Model IR 8 spectrophotometer was used with the KBr-disc technique, and a scanned region of 2.5–16 μm. The sample was heated to a defined temperature under conditions identical with those used in the TG measurements. Heating was stopped at the chosen temperature value. The sample was cooled to room temperature under dry nitrogen and its infrared absorption spectrum was recorded.

EGA — These measurements were made using a conductometric technique with a diluted aqueous solution of caustic soda as an absorbent, and dry nitrogen as a carrier gas for carbon dioxide, as described by Engelsman *et al.*[7].

HTX — A Nonius high temperature X-ray diffraction camera, model Guinier 3 was used with a heating rate of 4.5 °C h^{-1}, and an atmosphere of dry nitrogen.

A. Preparation of $K_3Al(C_2O_4)_3 \cdot mH_2O$

Up to a few years ago, all the original papers and handbooks reported any form of aluminium oxide hydrate to be a suitable starting material, or an intermediate, in the preparation of $K_3Al(C_2O_4)_3 \cdot mH_2O$. The process involves a substitution of the hydroxyl ligand by the oxalate anion in an acidic, aqueous medium[1]. In a recent paper Broadbent[6] used a modified method by boiling commercially available "basic aluminium oxalate"* with a concentrated solution of potassium oxalate hydrate.

The products obtained by different authors are described by different formulas, because the synthesis of a well-defined trioxalato complex is complicated by the following factors.

(*1*) The conversion Al (s)$\rightarrow$Al$(C_2O_4)_3^{3-}$ (aq) yields a stoichiometric ratio of $C_2O_4^{2-}$ to Al^{3+} deviating from 3, as a result of the low and irreproducible reaction rate at the solid–liquid interface, and the competition between the hydroxyl and oxalate ligands in the complexation of Al^{3+}.

(*2*) The stoichiometric ratio of K$^+$ to Al^{3+} deviates from 3, due to the factors mentioned in (*1*), and the fact, that potassium hydroxide, used as a starting material, is normally neither dry nor carbonate free.

(*3*) The desired product may be contaminated by $K_2C_2O_4 \cdot H_2O$, KHC_2O_4, $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$, $H_2C_2O_4 \cdot 2H_2O$, $K_4Al_2(OH)_2(C_2O_4)_4$ hydrate, $K_2Al_2(H_2O)_2(C_2O_4)_4 \cdot 4H_2O$, and different forms of aluminium oxide hydrate[1].

(*4*) The percentage of hydrate water in $K_3Al(C_2O_4)_3$ hydrate may vary (cf. part *B* of this section).

Requirements for a good preparation are as follows.

(*a*) A source for aluminium with a minimal chance of the formation of relatively stable hydroxyl complexes, *e.g.* amalgamated aluminium, and freshly precipitated aluminium hydroxide or "basic aluminium oxalate".

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*This product, obtained from B. D. H. (crude analysis results; Al$_2$O$_3$, 40% and C$_2$O$_4$, 48%), is hygroscopic and no longer available.

(*b*) A recrystallization procedure which removes contaminants by the use of different solvents, *e.g.*, ethanol or ethanol–water mixtures for the removal of the acidic oxalates, which are soluble in this medium, and water for the removal of the insoluble aluminium hydroxyl compounds. The trioxalatoaluminate can be recrystallized from its aqueous solution because normal potassium dioxalatoaluminate does not interfere, due to the extremely good solubility of the latter compound in water.

(*c*) A $K^+:Al^{3+}$ molar ratio less than 3, to minimize the contamination with potassium oxalate hydrate which is not removed by the above procedures. Hydrolysis of the trioxalatoaluminate should be reduced to a minimum.

(*d*) A good product control at every recrystallization step entailing (*i*) pH control of the liquid for the detection of acidic oxalates; (*ii*) a final crystallization from a previously boiled solution to encourage precipitation of more-insoluble hydroxyl complexes; (*iii*) scanning of the IR spectrum of the solid product to show the presence of hydroxyl groups, indicated by a peak at $1050 \, cm^{-1}$, and free oxalate, indicated by a peak at $770 \, cm^{-1}$ (*cf.* part *C* of this section); and (*iv*) a final product control by means of TG for the detection of small amounts of contaminant, normally potassium oxalate monohydrate (*cf.* part *C* of this section).

*Preparation** — Small cuttings of aluminium chips and a few drops of mercury were added to a warm ($70 \, ^{\circ}C$), concentrated solution of oxalic acid dihydrate. The $C_2O_4^{2-}:Al^{3+}$ molar ratio was chosen somewhat above the critical value of 1.5. A pure nitrogen atmosphere was used to prevent the formation of chemically inert aluminium oxide hydrates.

After stirring, the reaction started and the solution was sometimes cooled to prevent boiling, which results in the formation of hydroxyl complexes, and to retard the vigorous effervescence of hydrogen. The residual mercury was removed, and the stoichiometric quantity of a solution of potassium oxalate monohydrate was added slowly to the cold solution with vigorous stirring to prevent partial hydrolysis. An equal volume of ethanol was added slowly to the initially clear solution, once again with vigorous stirring. As a result, potassium trioxalatoaluminate hydrate was precipitated.

Depending on the resultant product, control recrystallization from water or water–ethanol mixtures was necessary. The hydrate generally contains 2.5–2.8 molecules of water, a figure which is not constant on drying in the air. In a stream of dry nitrogen at room temperature, the 2-hydrate of $K_3Al(C_2O_4)_3$ was finally formed.

B. Dehydration of $K_3Al(C_2O_4)_3 \cdot mH_2O$ $(2 < m < 3)$

From a survey of the literature[1], the stoichiometry and stability of the different possible hydrates of potassium trioxalatoaluminate appears questionable. In order to solve this problem, we placed the sample in a micro-vacuum desiccator above its own saturated, aqueous solution. It was converted into a sticky material after standing

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*Other procedures mentioned in the literature can also lead to a good product, bearing in mind the remarks made before.

overnight at room temperature. During the TG measurement (Fig. 1) in a stream of dry nitrogen, a rapid weight loss was observed due to the evaporation of the excess water, followed by a weak inflexion at a water content of 2.75 moles, a more pronounced inflexion at 2 moles of water, and another weak inflexion at 0.75 moles of water. There was no evidence for the existence of a trihydrate. From our results (Table I) we may draw the following conclusions.
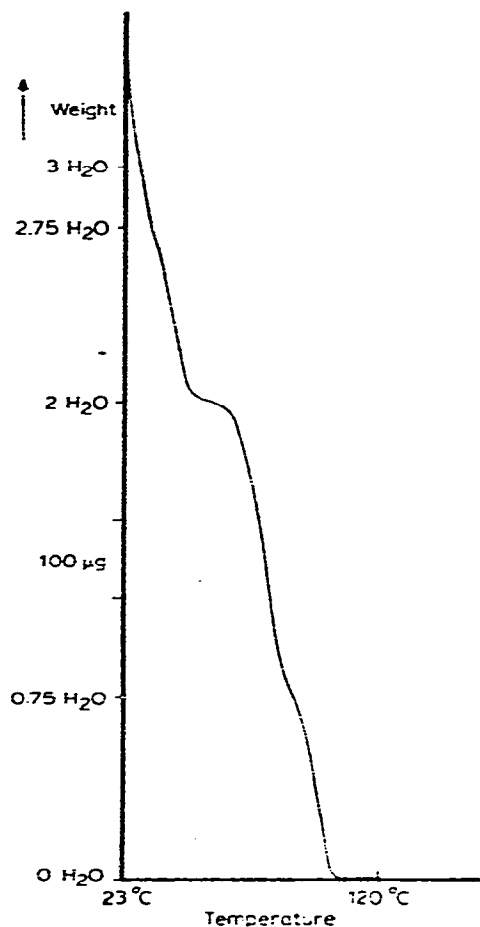

Fig. 1. TG thermogram of the dehydration of $K_3Al(C_2O_4)_3 \cdot mH_2O$ stored above its saturated aqueous solution. There is no evidence for the existence of a trihydrate. Heating rate, $5\,^\circ C\ min^{-1}$; sample holder, Pt, internally coated with Rh; atmosphere, dry nitrogen; flow rate, 28 c.c. min^{-1}; pressure, atmospheric.

(1) The dihydrate is stable at room temperature in a stream of dry nitrogen.

(2) The change in the procedural starting temperature (PST) value, for the dehydration of the 2-hydrate with the premeasurement procedure, is dependent on the amount of sample and the preceding transport facilities for the water vapour. Thus, the stoichiometric calculations and temperature limits, based upon the points of

inflexion in the TG thermogram (Fig. 1), are somewhat uncertain. Moreover for a correct experiment, control of the water-vapour partial pressure should be necessary.

TABLE I

CHARACTERISTIC TG TEMPERATURE VALUES (T, °C) AND WEIGHT LOSSES (W, μmol H_2O) FOR THE DEHYDRATION OF $K_3Al(C_2O_4)_3 \cdot mH_2O$

Experiment	Experimental conditions[x]			
	a	b	c	d
Sample weight (μg)	8775		8958[y]	
Dehydration, >2.75 H_2O T	23–50	23–33		≤25.5
W	9.82			8.55
Dehydration, 2.75 H_2O T		33–57		25.5–32.7
W		13.04		11.16
Dehydration, 2H_2O T	50–99	57–89	39–96	32.7–67.9
W	24.36	21.25	25.63	18.55
Dehydration, 0.75 H_2O T	99–119	89–108	96–119	67.9–89.2
W	13.93	12.98	14.81	13.88
Total μmoles of H_2O/ μmole of anhydrous salt	2.63		2.01	3.35

[x]a, Direct weighing and temperature programming; b, overnight contact with the vapour of its saturated aqueous solution; c, predried with dry nitrogen at room temperature; d, heating rate, 0.5 °C min^{-1} instead of 5 °C min^{-1} at the other measurements, for further conditions, cf. b. [y]Before placing in a stream of dry nitrogen.

(3) The wide scatter of results obtained by other authors from different preparative methods (see A), becomes more comprehensible in view of the possible contaminants and the instability of the 2.75-hydrate.

Our results are in reasonable agreement with those of Wosskressenskaja[5], who inferred the existence of a 3-, 2-, and 0.6-hydrate using vapour pressure measurements. A continuous decay of vapour pressure for compositions from 3 moles H_2O–2.8 moles H_2O per mole of anhydrous salt, is demonstrated by the authoress mentioned, illustrating the dependence of composition on premeasurement procedure and mode of drying and storage of the material. The lower hydrates show the normal phase rule behaviour.

The stepwise dehydration is also confirmed by DTA and DSC measurements (see Figs. 4 and 5), though this process is better resolved by the latter method due to a sample holder geometry, which permits better atmospheric control. (DTA, peak temperature 93 °C, shoulder at 67 °C. DSC, peak temperatures 83 and 109 °C.)

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C. Thermal decomposition of anhydrous $K_3Al(C_2O_4)_3$

A survey of the literature dealing with oxalate decompositions shows, in general, that the following species might occur as transition states or intermediate products during these decompositions: (a) Metal ions with a valence modified during the process, e.g. $Al^{3+} \rightarrow Al^{+}$; (b) the anions O^{2-}, O_2^{2-}, $C_2O_4^{2-}$, $C_2O_3^{2-}$, $C_2O_2^{2-}$, CO_3^{2-}, CO_2^{-}, $CO_2CO_2^{-}$, $C_nO_n^{2-}$ ($n = 3-8$), and $C_6O_6^{m-}$ ($m = 2,3,4$); (c) mixtures of the ions mentioned in (b); (d) complexes of metal ion and ligand with different coordination numbers, eventually mixtures of these complexes; (e) metal carbides and carbonyls.
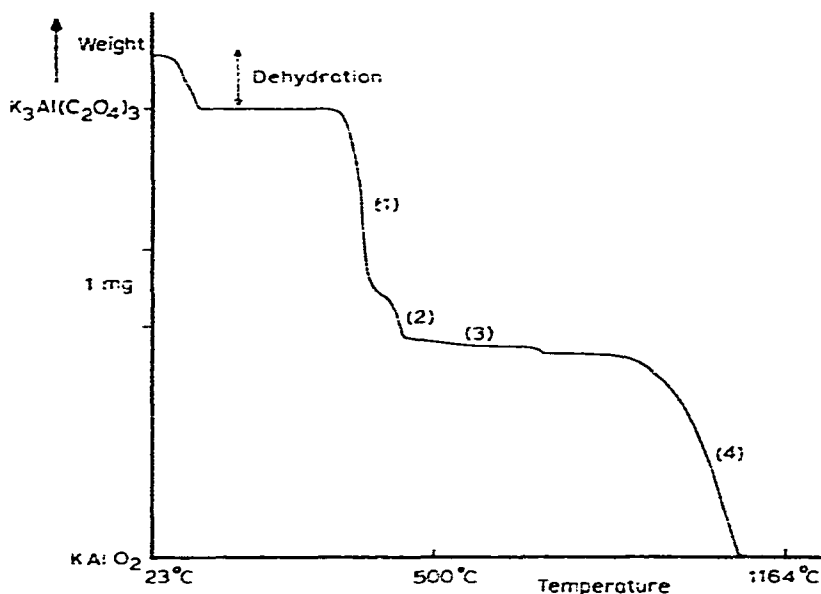

Fig. 2. Survey TG thermogram of $K_3Al(C_2O_4)_3 \cdot mH_2O$ ($m = \pm 2.8$). Heating rate, $5^{\circ}C$ min^{-1}; sample holder, Pt, internally coated with Rh; atmosphere, dry nitrogen; flow rate, 28 c.c. min^{-1}; pressure, atmospheric. (1), Trioxalatoaluminate decomposition; (2), Oxalate decomposition; (3), Aluminate formation; (4), Potassium carbonate decomposition.

TG results

The TG thermogram of the anhydrous compound in dry nitrogen (Fig. 2 and Table II) is characterized by a rapid large weight loss (step 1, 320–435°C), superposed by a rapid second step (435–475°C). The third step is a very slow one, starting at 475°C, accelerating towards its procedural final temperature (PFT), the value of which can vary from measurement to measurement (660–780°C, cf. Table II, 9). The fourth step with varying PST value and, therefore, varying PFT value (cf. Table II, 10), leads finally to a solid residue.

Assuming anhydrous $K_3Al(C_2O_4)_3$ to be the starting material, which is confirmed by IR (see *IR results*), $KAlO_2$ is supposed to be the final solid product. This supposition is in reasonable good agreement with the calculated and measured residual weight (cf. Table II, 4).

TABLE II

CHARACTERISTIC TG WEIGHT AND TEMPERATURE VALUES (T)
FOR THE THERMAL DECOMPOSITION OF ANHYDROUS $K_3Al(C_2O_4)_3$

Experiment	a	b	c	d	e
1. Weight (hydr., μg)	8775	8958	8687	8416	7209
2. Weight (dehydr., μg)	7908	8229	7763	7543	6412
3. $K_3Al(C_2O_4)_3$ (μmol.)	19.36	20.15	19.01	18.48	15.68
4. $KAlO_2$ (μmol.)	17.42	19.78	17.33	18.32	14.70
5. K_2CO_3 (μmol.)	20.25	20.67	19.47	19.06	16.80
6. C_2O_3 3 (μmol.)	19.30	20.09	19.10	18.29	15.82
7. T, 1st. step (°C)	316–435	323–434	308–419	329–436	260–420
8. T, 2nd. step (°C)	435–477	434–478	419–469	436–474	420–470
9. T, 3rd. step (°C)	477–695	478–732	460–704	474–777	470–658
10. T, 4th. step (°C)	748–1056	754–1100	740–1046	949–1166	741–1011

The fourth step of the decomposition is in very good agreement with the thermal decomposition of potassium carbonate. This assumption is based on characteristics already found for this decomposition[3]: i.e. relatively large temperature range; shift of temperature range dependent on partial pressure of carbon dioxide; disturbance in the reproducibility of the measured temperature range of this step, due to the gas transport reaction character of the decomposition; possibility of reaction of the evolved gaseous products (K_2O) with the alumina reaction tube; and reformation of potassium carbonate between two subsequent measurements, from potassium aluminate formed and carbon dioxide from the ambient atmosphere. Hence, the carbon dioxide partial pressure is ill-defined during the experiments. The production and removal of CO_2 in the preceding step, also determines the behavior in the subsequent steps. One mole of potassium carbonate per mole of anhydrous salt is volatilized in this fourth step (cf. Table II, 5), with the formation of gaseous potassium oxide and carbon dioxide. Attempts to make stoichiometric calculations for the first three steps of the decomposition were not very successful, due to their mutual overlap[1]. The measured points of inflexion in the TG curve are unsuitable for stoichiometric calculation due to the asymmetric thermal behaviour of the overlapping processes on both sides of the relevant point.

Based on TG analysis, only the high reaction rate of the first two decomposition steps and the slow rate of the third one are notable. The PFT value of the latter process is dependent on CO_2 partial pressure.

Assuming that $KAlO_2$ is the solid residue, a stoichiometric calculation for evolved "C_2O_3"* in the first three steps, including the CO_2 evolution in the fourth step, gives a good correspondence with the expected value (cf. Table II, 6). This procedure is only permitted in the absence of carbon formation by the well-known Boudouard equilibrium. Only an observed slight greying justifies this assumption.

Complementary techniques are used in order to give a correct interpretation of the first three steps.

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*C_2O_3 stands for molar ratio $CO:CO_2 = 1$.

IR results

Surveying the infrared spectral analysis of solid oxalates and carbonates[1] the following conclusions can be drawn.

(*1*) A free oxalate anion with three strong bands in the NaCl region can be distinguished from a coordinated oxalate anion with six strong bands in this region.

(*2*) Information about the number of coordinated oxalate groups (1, 2 or 3) can be given. (*a*) An uncoordinated oxalate group or monooxalato complex does not show band splitting compared with an oxalate anion in D_{2h} symmetry, *e.g.*, in $K_2C_2O_4 \cdot 1H_2O$. (*b*) A dioxalato complex, square planar or octahedral in *trans* configuration, shows, in comparison with a 1:1 complex, no splitting of bands or some weak splitting ($5\,\mathrm{cm}^{-1}$). An octahedral dioxalato complex in *cis* position, shows splitting of bands in the same way as binuclear tetraoxalato complexes. (*c*) For an octahedral trioxalato complex, a stronger splitting of bands ($\pm 20\,\mathrm{cm}^{-1}$) is observed.

(*3*) A carbonate anion can be distinguished from an oxalate anion.

(*4*) The presence of OH and H_2O groups can easily be confirmed.

Therefore, IR is capable of monitoring a decomposition by registering, at room temperature, the different infrared absorption spectra of samples, which have been previously heated to a well-defined temperature, *e.g.* the inflexion point of the TG curve (see *Analytical methods section*).

The following results have been obtained (Fig. 3). At $320\,^\circ\mathrm{C}$ (Fig. 3, b), the OH stretching vibration at about $3400\,\mathrm{cm}^{-1}$ has disappeared, and the salt is dehydrated. The trioxalatoaluminate complex is unchanged, confirmed by the remaining band splitting at about $1300\,\mathrm{cm}^{-1}$ and $800\,\mathrm{cm}^{-1}$. At $350\,^\circ\mathrm{C}$ (Fig. 3, c), some trioxalatoaluminate still remains, but a strong intensification of bands occurs at about $765\,\mathrm{cm}^{-1}$, $1305\,\mathrm{cm}^{-1}$ and $1630\,\mathrm{cm}^{-1}$, peaks which correspond to the $\delta(\mathrm{O\text{-}C\text{=}O})$, $\nu_s(\mathrm{O\text{-}C\text{=}O})$ and $\nu_a(\mathrm{O\text{-}C\text{=}O})$ vibration modes, respectively, of the oxalate anion. At this temperature, trioxalatoaluminate is converted into oxalate. Neither a dioxalatoaluminate, detectable by a decrease in band splitting, nor a carbonate or carbonato complex, were observed at this temperature.

At $370\,^\circ\mathrm{C}$ (Fig. 3, d), the IR spectrum of potassium oxalate heated to $420\,^\circ\mathrm{C}$ (Fig. 3, e) is predominant, with some rudimentary peaks of trioxalatoaluminate indicating the completion of the decomposition.

At $420\,^\circ\mathrm{C}$ (Fig. 3, f), the transition between the first and second steps of the decomposition in the TG curve, potassium oxalate is still predominant with the start of a band formation in the $800\text{--}900\,\mathrm{cm}^{-1}$ region and intensification of the $1400\text{-}\mathrm{cm}^{-1}$ peak, due to potassium carbonate formation (Fig. 3, h).

At $470\,^\circ\mathrm{C}$ (Fig. 3, g), the PFT value of the second step, carbonate is present and oxalate has disappeared (no band at $770\,\mathrm{cm}^{-1}$). An intermediate carbonato complex of Al^{3+} is improbable. At $690\,^\circ\mathrm{C}$ (Fig. 3, h) the KAlO_2 spectrum is superposed on the spectrum of potassium carbonate. At $910\,^\circ\mathrm{C}$ (Fig. 3, j) the potassium carbonate peak at about $880\,\mathrm{cm}^{-1}$ is no longer visible, due to a broad potassium aluminate peak.
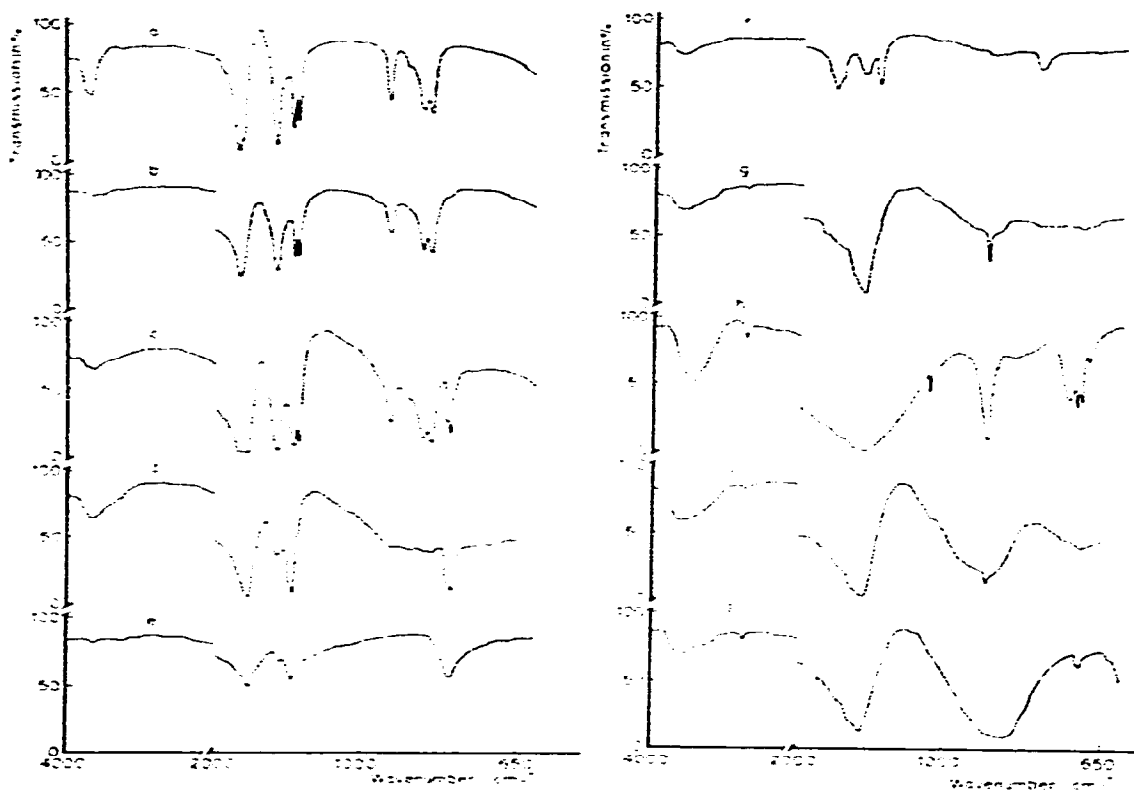
Fig. 3. Infrared absorption spectra of $K_3Al(C_2O_4)_3 \cdot mH_2O$ ($m = \pm2.8$), measured at room temperature on samples, previously heated to different well-defined temperatures (°C). a, room temperature; b, 320; c, 350; d, 370; e, $K_2C_2O_4$ ("anhydrous"); f, 420; g, 470; h, K_2CO_3 ("anhydrous"); i, 690; j, 910.

Summarizing, we can infer that trioxalatoaluminate is converted into oxalate between 320°C and 420°C, the oxalate is converted into carbonate between 420°C and 470°C, and mono- or dioxalatoaluminates, or carbonatoaluminate complexes, are improbable intermediates in the decomposition.

DTA and DSC results

In the DTA thermogram (Fig. 4), and DSC thermogram (Fig. 5) the resolution of trioxalatoaluminate and oxalate decomposition is clear. In comparison with the results obtained for pure potassium oxalate[8], in this case, the temperature traject of the oxalate decomposition is shifted to lower values, possibly caused by the degree of granular dispersion. A characterization of the involvement of potassium oxalate (using its phase transition at 390°C) by heating a sample of potassium trioxalatoaluminate to its first decomposition peak temperature, was not successful. However, this attempt is not useful, because in a "blank" experiment, with heating of *pure* potassium oxalate to decomposition followed by cooling, the phase transition peak was also unobservable in the DTA thermogram.

Further, the aluminate formation with a small thermal effect at 774 °C, and the final carbonate melting and reaction with Al_2O_3 at 891 °C, are visible.
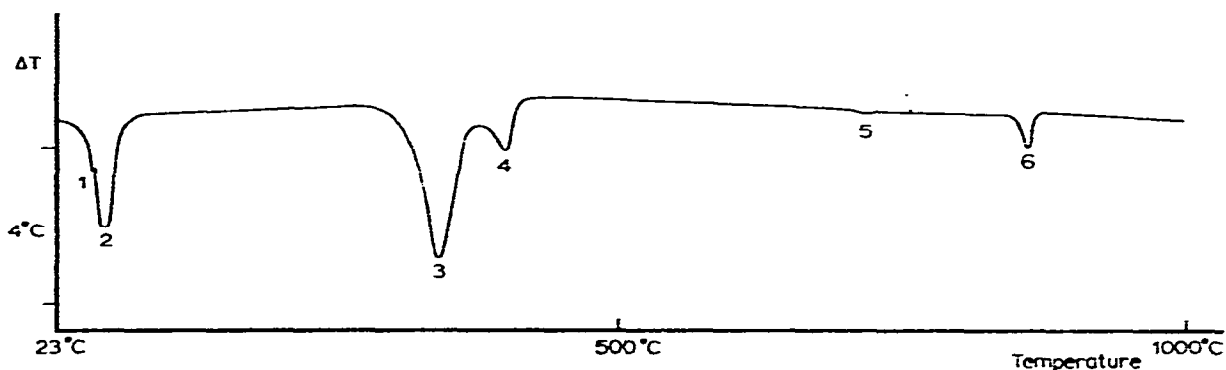

Fig. 4. DTA thermogram of $K_3Al(C_2O_4)_3 \cdot mH_2O$ ($m = \pm 2.8$). Heating rate, $10 °C\ min^{-1}$. α-Al_2O_3 powder between sample and thermocouple. Atmosphere, dry nitrogen; flow rate, 28 c.c. min^{-1}; pressure, atmospheric. Peak temperatures (°C): Dehydration, 67 (1), 93 (2); trioxalatoaluminate decomposition, 423 (3); oxalate decomposition, 481 (4); aluminate formation, 773 (5); potassium carbonate melting and reaction, 891 (6).
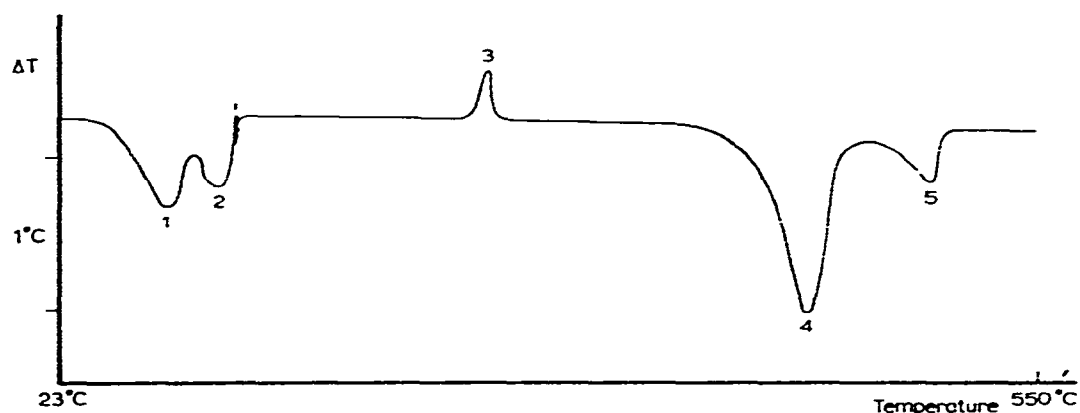

Fig. 5. DSC thermogram of $K_3Al(C_2O_4)_3 \cdot mH_2O$ ($m = \pm 2.8$). Heating rate, $10 °C\ min^{-1}$; atmosphere, dry nitrogen; flow rate, 28 c.c. min^{-1}; pressure, atmospheric. Peak temperatures (°C): Dehydration, 83 (1), 109 (2); phase transition (not always detectable), 265 (3); trioxalatoaluminate decomposition, 425 (4); oxalate decomposition, 491 (5).

EGA results

Using the sensitive micromethod for continuous determination of carbon dioxide content in evolved gas, as described by Engelsman et al.[7], the following brief conclusions can be drawn.

(*1*) The agents used for drying and deoxygenating of carrier-gas are relatively good absorbers of carbon dioxide, and regeneration *in situ*, immediately prior to the measurements, is necessary.

(*2*) The measuring room must be evacuated in order to prevent carbon dioxide absorbance on the walls. Nevertheless, absorption occurs again when carbon dioxide is a product of the decomposition process studied.

(*3*) An alumina reaction tube or even a chemically inert reaction tube is not adequate in view of condensation effects (K_2CO_3) caused by temperature non-homogeneity and the dynamic method of analysis used[8].

(*4*) An atmosphere with a controlled partial pressure of carbon dioxide is impossible under the applied conditions.

(*5*) Due to the applied conditions, the measurement of the carbon dioxide produced is less sensitive, as a result of the smoothing effects mentioned, but in general, we can conclude that in the first three steps of the decomposition, carbon dioxide is produced in an amount decreasing in the following sequence: step 1 > step 3 > step 2.

HTX results

The results obtained from high temperature X-ray diffraction measurements support the conclusions drawn from the other techniques, *i.e.*, the occurrence of a phase transition in the dehydrated trioxalatoaluminate, followed by trioxalatoaluminate decomposition, oxalate decomposition, aluminate formation and potassium carbonate decomposition.

DISCUSSION

Dehydration

Some discussion about the stoichiometry of the possible hydrates still remains. A slow weight loss in the overlap region between two successive steps, which is small per unit of time, cannot be interpreted in terms of the preceding or the subsequent steps. At lower heating rates (Expt. *d*, Table I), this weight loss becomes more important, and can lead to stoichiometric conclusions which deviate from those drawn from measurements at higher heating rates (Expt. *a*, *b* and *c*). This results from the decomposition kinetics of the material and the transport facilities of the gas produced, the latter having different time constants for production and off-transport during time intervals, dependent on the heating rate chosen. These factors determine which part of a decomposition step belongs to the overlap region measured. Nevertheless, hydrates with a composition around 2.75, 2 and 0.75 moles of water per mole of anhydrous salt are most probably realistic, although measurements with a controlled partial pressure of water should have a better resolving power for a reversible dehydration study.

Trioxalatoaluminate decomposition

Stoichiometric conclusions about the potassium trioxalatoaluminate decomposition and the subsequent reactions at higher temperatures cannot be drawn from the measurements of Broadbent *et al.*[6]. Only the identification of the subsequent

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intermediates ($K_2C_2O_4$ and K_2CO_3) and a trace of the final product ($KAlO_2$) in the case of a nitrogen atmosphere at 900 °C (assuming a solid-state reaction between potassium carbonate and amorphous alumina), is reported. A correct model for the splitting of the subsequent steps in the thermal degradation can only be given when these steps are considered in connection with one another. The final formation of one mole of $KAlO_2$ per mole of Al present is verified by TG, while its identification is supported by HTX (visible from 584 °C) and IR (Fig. 3, i).

The presence of K_2CO_3 is confirmed by its characteristic, carbon dioxide partial-pressure dependent, decomposition step in TG, its melting peak in the 900 °C region in DTA, its IR spectrum (Fig. 3, f–i), and by the HTX results (visible from 403–810 °C). TG measurements demonstrate the decomposition of 1 mole of previously formed K_2CO_3 per mole of anhydrous $K_3Al(C_2O_4)_3$. The overall process of the first three steps of the thermal decomposition of $K_3Al(C_2O_4)_3$ is correctly represented by the following equation:

$$K_3Al(C_2O_4)_3 \text{ (s)} \rightarrow KAlO_2 \text{ (s)} + K_2CO_3 \text{ (s)} + 3CO \text{ (g)} + 2CO_2 \text{ (g)}$$
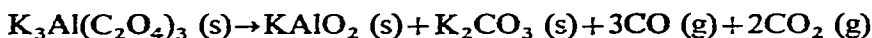
Partially from a comparison with the decomposition of potassium dioxalato-aluminates (to be published), the facts substantiate four overlapping steps.

First step. — Trioxalatoaluminate is degradated to oxalate (IR) with evolution of carbon monoxide and carbon dioxide (EGA). Some potassium carbonate is already observable (HTX, 403 °C).

Second step. — Oxalate is converted into carbonate (IR). The decomposition of 1 mole of potassium oxalate per mole of anhydrous trioxalatoaluminate is possible (TG) if overlap with the subsequent step is assumed. The weight loss of this step is dependent on the number of moles of oxalate present per mole of anhydrous salt.

Third step. — Aluminate formation from carbonate and alumina with evolution of carbon dioxide is evident for the following reasons: (a) Detection of aluminate by IR and HTX analysis; (b) thermodynamical possibility of the process; (c) dependence on carbon dioxide partial-pressure; (d) the amount of carbon dioxide evolved per mole of anhydrous salt is the same for the di- and trioxalatoaluminates (Al-content dependence).

The thermodynamical possibility of this solid–solid reaction is well established because the "amorphous" alumina present here is thermodynamically more active than the well known x- and γ-Al_2O_3 forms. Moreover, its large surface area enhances the reaction rate. Though the thermodynamic data of $KAlO_2$ are not available in the literature up to the present time, a calculation can be made for the Gibbs free energy change of the reaction

$$K_2CO_3 \text{ (s)} + Al_2O_3 \text{ (s)} \rightarrow 2KAlO_2 \text{ (s)} + CO_2 \text{ (g)};$$
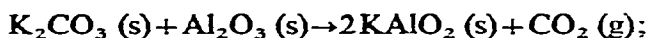
for both x- and γ-Al_2O_3, including its dependence on temperature. Using (i) the virtually temperature-independent Gibbs free energy change reported by Broers and van Ballegoy[9] for the reaction $2NaAlO_2 \text{ (s)} + K_2CO_3 \text{ (l)} \rightarrow 2KAlO_2 \text{ (s)} + Na_2CO_3 \text{ (l)}$, $\Delta G° = +3.2 \pm 0.2 \text{ kcal/mole}$;

(*ii*) the ΔG° (formation) values given in the JANAF tables[10] for $NaAlO_2$ (s), Na_2CO_3 (s), CO_2 (g), α-Al_2O_3 (s), γ-Al_2O_3 (s), and (*iii*) the free energies of melting for Na_2CO_3 (s) and K_2CO_3 (s), we were able to calculate the results given in Table III.

TABLE III

TEMPERATURE DEPENDENCE OF THE GIBBS FREE ENERGY CHANGE AND CO_2 EQUILIBRIUM PRESSURE FOR THE REACTION $Al_2O_3(s) + K_2CO_3(s) \rightarrow 2KAlO_2(s) + CO_2(g)$ USING α- AND γ-Al_2O_3

Quantity calculated	Temperature (°K)					
	600	700	800	900	1000	1100
$\Delta G^{\circ}_{reaction}$ (α-Al_2O_3) (kcal/mol)	+14.6	+11.2	+7.9	+4.6	+1.4	−1.6
CO_2 equilibrium pressure (atm. $\times 10^{-3}$)	0.005	0.32	7.2	7.3	490	2100
$\Delta G^{\circ}_{reaction}$ (γ-Al_2O_3) (kcal/mol)	+10.6	+7.3	+4.1	+1.0	−2.0	−4.9
CO_2 equilibrium pressure (atm. $\times 10^{-3}$)	0.14	5.4	77	580	2800	9400

It seems reasonable to assume aluminate formation during and after the oxalate decomposition step, in accordance with a CO_2 partial-pressure lower than during the oxalatoaluminate decomposition in the first step of the decomposition. The results of Gal *et al.*[11] (starting temperature of the reaction; for α-Al_2O_3, 600°C; β-Al_2O_3, 800°C; γ-Al_2O_3, 300°C) should lead to the same conclusion, but we did not use these results, because the authors give no information about the atmospheric conditions, regarding moisture and carbon dioxide partial-pressure, applied during their measurements.

Fourth step. — This step can be ascribed to the potassium carbonate decomposition already investigated elsewhere[1,8]. This assignation is based on the characteristic dependence on CO_2 partial-pressure of the relatively large temperature range visible in TG analysis, the melting endotherm in DTA analysis, the K_2CO_3 observable in the IR spectrum, and its disappearance at higher temperatures in the X-ray pattern.

The following scheme of decomposition gives the best fit to the data obtained:
1. Trioxalatoaluminate decomposition (320–435°C): $K_3Al(C_2O_4)_3$ (s)$\rightarrow K_2C_2O_4$ (s)$+$ $0.5K_2CO_3$ (s) $+0.5Al_2O_3$ (s)$+2CO$ (g)$+1.5CO_2$ (g), with aluminate formation hampered by the relatively large CO_2 partial-pressure and by the lower temperature, overlapped and followed by *2.* Oxalate decomposition (435–475°C): $K_2C_2O_4$ (s)$\rightarrow$ K_2CO_3 (s)$+CO$ (g), as a result of the lower CO_2 partial-pressure, overlapped and followed by *3.* Aluminate formation (PFT value (475°C) dependent on CO_2 partial-pressure): $0.5\ K_2CO_3$ (s) $+0.5Al_2O_3$ (s)$\rightarrow KAlO_2$ (s) $+CO_2$ (g), followed by *4.* Potassium carbonate decomposition (PST and PFT values dependent on CO_2 partial-pressure): K_2CO_3 (s, 1)$\rightarrow K_2O$ (g)$+CO_2$ (g), accompanied by potassium carbonate melting (900°C) leaving residual $KAlO_2$.

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CONCLUSION

The applied methods of analysis (IR, DTA, DSC, EGA and HTX used as "finger-print" methods, and TG as a means of stoichiometric calculation and determination of small amounts of contaminants) have given a good solution for the main problems reported in this paper, i.e., the synthesis of pure $K_3Al(C_2O_4)_3$ hydrate, the interpretation of the dehydration pattern and the detection of stable hydrates, and the elucidation of the thermal behaviour of the anhydrous compound at increasing temperature.

Criteria for a rapid preparation of a pure product are given, making available all the methods already known for this purpose. A new method for the preparation is also given.

The percentage of hydrate water is not found to be constant (2.6–2.9 moles of H_2O per mole of anhydrous salt). Only the 2-hydrate is stable at room temperature in a dry nitrogen atmosphere. There is no evidence for the existence of the 3-hydrate, as reported in most of the literature. Intermediate 2.75- and 0.75-hydrates are formed on dehydration.

The thermal behaviour of the anhydrous compound can be described by a phase transition at $\sim 265°C$, followed by a decomposition which starts in a dry nitrogen atmosphere at $320°C$.

The thermal decomposition of this compound, representing the decomposition of a trioxalatometal complex without changes in valence of the central metal ion, can be fully described by the four-step scheme given.

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