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# The Differential Thermal Analysis of Potassium Oxalate[1]

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From the differential thermal and thermogravimetric analyses of potassium oxalate together with the X-ray diffraction studies, three crystallographic modifications of the anhydrous salt were found. When potassium oxalate monohydrate crystals were dehydrated at, *e.g.*, 140°C, phase II, which is stable below 381°C, appears. The crystal in phase II has an orthorhombic unit cell ($a=10.9$, $b=6.11$, and $c=3.44$ Å at 17°C) and transforms at 381°C into phase I, which is stable above 381°C up to the temperature where the decomposition begins. The crystals in phase I belong to the tetragonal system ($a=7.01$ and $c=7.53$ Å at 404°C). The transition between phases II and I is not reversible in an exact sense, and when cooled phase I endures down to 215°C, where it transforms (reversibly) into phase III. Phase III can exist at room temperature. When heated, phase III transforms into phase I at 215°C (often accompanied by a partial transformation to phase II). The resulting phase then transforms into phase II. At all temperatures below 381°C phases I and III are metastable with respect to phase II, and they transform into phase II. The decomposition of potassium oxalate in an oxygen-free atmosphere seems to proceed in two stages.

The thermal decomposition of potassium oxalate complexes of di- and tri-valent metal in the solid state has been studied by several investigators,[2-6] and it has been reported that in many cases potassium oxalate or potassium hydrogen oxalate results as an intermediate decomposition product; this may affect the further decomposition processes of those materials. Many of the reports, however, do not seem to have referred in detail to the thermal behavior of potassium oxalate itself. Studies of the decomposition of potassium oxalate have been made by thermogravimetric analysis (TGA),[6,7] but no differential thermal analysis (DTA) of the material seems to have been reported yet.

In the course of DTA studies of potassium tetroxalate,[8] we found that potassium oxalate has two crystallographically-different phases, I[9] and II[9]. To obtain further information about potassium oxalate, the thermal behavior of the material was studied in more detail by means of DTA, TGA, and X-ray diffraction methods, and another new phase of the anhydrous salt was found. Some features of the decomposition and transitions of potassium oxalate will be reported in this paper.

## Experimental

*Materials.* The potassium oxalate monohydrate was prepared from commercial guaranteed-grade oxalic acid and potassium carbonate and was recrystallized five times from water. The potassium oxalate anhydrate ($K_2C_2O_4$) was obtained by dehydrating the hydrous salt at about 125°C for more than 4 hours.

*Procedures.* The DTA and TGA curves were obtained using a "High-temperature-type Differential Thermal and Thermogravimetric Analyser" (Rigaku Denki Co.). Pt-Pt·Rh (13%) thermocouples were used as the temperature detectors, and $\alpha$-alumina was used as the reference material. The sample material was powdered in an agate motar (powder size smaller than 200 meshes), and about 400 mg of the material was charged in a platinum cell in the manner shown in Fig. 3(f) by tapping the botton of the cell. These procedures were conducted in an dry-air atmosphere when the specimen was the anhydrous salt. When necessary, the specimen was dried again in the DTA-TGA apparatus by evacuation. In most thermal measurements, the heating and cooling rate was about 2.5°C/min unless otherwise specified.

The X-ray diffraction studies at high temperatures were made on a diffractometer equipped with a modified specimen heating apparatus (Rigaku Denki Co.). In X-ray measurements, the heating rate was about 2.5°C/min and the cooling rate was 5—10°C/min. After attaining a given temperature, the specimen was kept at that temperature for about 10 min and diffraction patterns were taken at the scanning speed of 1°/min.

## Results and Discussion

Figures 1(a) and (a′) show the simultaneously-recorded DTA and TGA curves of potassium oxalate monohydrate. The endothermic peak, $P_1$, which is associated with the dehydration of the water of crystallization appears at 135°C (peak temperature, PT). No other peak appears up to 381°C, where the second endothermic peak $P_2$ (PT 391°C) begins to appear. The TGA curve shows a gradual weight loss from around 426°C, indicating the decomposition of $K_2C_2O_4$. The pattern of the DTA curve accompanying this decomposition is strongly affected by the atmospheric conditions. When measurements were made in an atmosphere of flowing dry air (Fig. 1(a)), where a sufficient supply of oxygen gas to the specimen would be expected, the specimen shows two exothermic

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[1] Partly presented at the Chūgoku-Shikoku Meeting of Chemical Society of Japan, Okayama, October, 1967.

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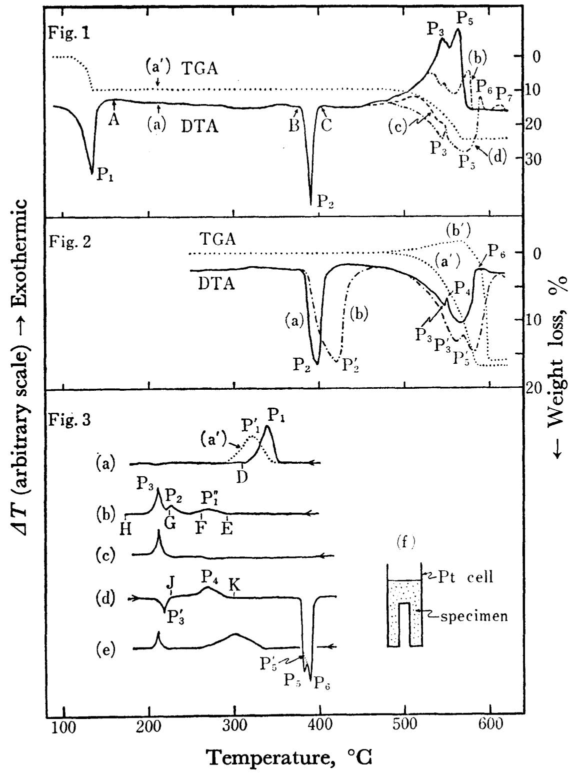
[9] In Ref. 8, phase II in this paper is referred to as phase I and phase I in this paper, as phase II.



Figs. 1 and 2. Simultaneously recorded DTA and TGA curves of potassium oxalate. 1(a): $K_2C_2O_4 \cdot H_2O$, in air with flow; 1(b): in air with no flow; 1(c): in $N_2$ gas with no flow; 1(d): in $N_2$ gas with flow.

2(a): $K_2C_2O_4$ *in vacuo*; 2(b): *in vacuo*, heating rate 5°C/min.

Fig. 3. Cooling DTA of $K_2C_2O_4$ ((d): heating DTA).

peaks, $P_3$ and $P_5$, probably due to the combustion of the carbon monoxide gas produced by the decomposition. When the heating rate was 1°C/min, the separation of these two peaks was less clear. After thermal measurements up to about 612°C the resulting solid substance was potassium carbonate. Figure 1(b) is the DTA thermogram when the measurement was made in dry air at 1 atm with no flow. The exothermicity of the decomposition is decreased compared with the case of a flowing atmosphere, and the temperature of completion of the decomposition becomes higher. Figure 1(d) shows the DTA curve when the measurement was made in dry nitrogen gas with a flow at 1 atm. In this case, two endothermic peaks, $P_3$ and $P_5$ (PT 547 and 570°C respectively), appear corresponding to the decomposition of $K_2C_2O_4$. When the measurement was made in $N_2$ gas at 1 atm with no flow, the thermogram (c) in Fig. 1, which is rather similar to Fig. 1(b), was obtained. The (b) and (c) curves have features intermediate between the former two cases (Figs. 1(a) and 1(d)).

Figure 2(a) shows the DTA thermogram for the measurement in the vacuum of the order of $10^{-2}$ mmHg. This curve, showing endothermic peaks of $P_3$ and $P_5$, is quite similar to the (d) curve in Fig. 1 except that the shape of the $P_2$ peak is deformed more broadly and its peak temperature is shifted to the higher side because of the smaller thermal conductivity of the specimen in a vacuum. The apparent exothermic peak, $P_4$, at 555°C, appears clearly in a flowing $N_2$ gas atmosphere and *in vacuo*, but we could find, by the X-ray diffraction method, no evidence for it as a real peak. The TGA curve in Fig. 2 indicates that the apparent peak, $P_4$, is accompanied by a clear change in the decomposition rate; this is supported by X-ray diffractometry and pressure measurement of the evolved gases. Figure 2(b) shows the thermogram obtained *in vacuo* when the heating rate was 5°C/min. The curve is displaced to the higher-temperature side as a whole as a result of the increase in the heating rate. The TGA curve (b') shows an apparent weight increase accompanying the endothermic peak, $P'_3$, instead of showing a weight loss. This phenomenon may be due to the proper jetting of the resulting gases, which might be effective in a vacuum.

In the case of the measurements in $N_2$ gas and *in vacuo*, the temperature of the completion of the decomposition becomes higher and an exothermic peak, $P_6$, in Figs. 1 and 2 sometimes appears just before the completion of the decomposition. (Otherwise, $P_7$ in Fig. 1 often appears). The weight change accompanying $P_6$ is small; this might suggest that $P_6$ in Figs. 1 and 2 corresponds to the improvement of the crystallinity of the $K_2CO_3$ resulting from the decomposition process. The decomposition products in these cases were gray or dark gray, indicating the presence of carbon.

From these findings, it might be said that the supply of $O_2$ gas or the ease of carrying off the resultant gases plays an important role in the decomposition mechanism, and that the decomposition of $K_2C_2O_4$ in an $O_2$-free atmosphere proceeds through two stages. The first stage might be associated mainly with the $K_2C_2O_4 \rightarrow K_2CO_3 + CO$ reaction, and the second one, with $2\,K_2C_2O_4 \rightarrow 2\,K_2CO_3 + C + CO_2$.

The TGA curve (a') in Fig. 1 shows that there is no weight change accompanying the $P_2$ endothermic peak (PT 391°C), which begins to appear from 381°C. When the specimen was once heated up to 408°C (over the $P_2$ peak) and then submitted at once to the cooling DTA, the thermogram shown in Fig. 3(a) was obtained. A broad exothermic peak, $P_1$ (PT 341°C), appears from around 360°C, but no other peak appears below the peak temperature. As the period of heat-treatment increases, the peak which corresponds to $P_1$ in Fig. 3(a) shifts to the lower-temperature side and its peak area decreases (Fig. 3(a')). When the original specimen was heated to a temperature above *ca.* 410°C, treated for a longer time (*e.g.*, 1 hr), and then subjected to the cooling DTA, the thermogram shown in Fig. 3(b) was obtained. A very broad exothermic peak, $P''_1$ (PT 267°C), in Fig. 3(b) appears from around 304°C, and two other exothermic peaks, $P_2$ and $P_3$, appear at 226 and 212°C (PT) respectively. The $P_3$ peak is less displaced than $P_2$ when the cooling rate is changed. If the specimen is heat-treated at 420°C for 1 hr (TGA shows that about 0.6% of the specimen is decomposed by this heat-treatment), the broad peak, $P''_1$, in Fig. 3(b) almost disappears. When the specimen which had undergone the thermal-treatment heating above 390°C and cooling below 210°C was further heat-treated above *ca.* 410°C for a long enough time (*e.g.*, 1 hr), the peak which corresponds to $P_2$ in Fig. 3(b) did not appear (Fig. 3(c)).

After the original specimen had been heat-treated at, *e.g.*, 420°C for a longer time (1 hr), it was cooled to around 145°C and then heated again for the heating DTA (Fig. 3(d)). There thereupon appeared an endothermic peak, $P'_3$ (PT 219°C), which corresponds to the exothermic peak, $P_3$, in Fig. 3(b), and a broad exothermic peak at around 265°C. The endothermic peak at around 390°C, which may correspond to $P_2$ in Fig. 1, appears as a clear double peak. When this specimen was submitted again to the cooling DTA just after attaining 420°C, the thermogram (e) in Fig. 3 was obtained. It should be noted that the peaks which correspond to $P_1$ in Fig. 3(a) and $P_3$ in Fig. 3(b) appear, but not the peak which corresponds to $P_2$ in Fig. 3(b). On the other hand, when the specimen which has shown the thermogram in Fig. 3(d) was submitted from the K point to the cooling DTA, it did not show any peak.

The specimen once heated to 408°C and quickly cooled to, *e.g.*, 360°C does not show in the heating DTA the endothermic peak which corresponds to $P_2$ in Fig. 1, indicating that the change associated with the peak is not reversible. This peak does appear, however, if the specimen once heated to 408°C and then quickly cooled to 360°C is kept there for a longer time. This is true even for the specimen heat-treated at higher temperatures (*e.g.*, 370°C). The lower the temperature, and the longer the heat-treatment, the larger the peak area of the endothermic peak which corresponds to $P_2$ in Fig. 1.

When the specimen once heated around or above 408°C is cooled quickly below 351°C, it often shows, in the heating DTA, an endothermic shoulder peak, $P'_5$ (PT 388°C) in Fig. 3(d), in addition to the peak which corresponds to $P_2$ in Fig. 1. It seems interesting that the temperature of 351°C coincides with that where the broad exothermic peak $P_1$ in Fig. 3(a) begins to appear. When the specimen once heated to 400°C was quenched to 0°C, kept there for about 2 min, and quickly heated (to 310°C in 14 min, then to 400°C at 2.5°C/min), it showed the shoulder peak. When this specimen was further heat-treated at 400°C for 1 hr, quickly cooled to 273°C, and then heated as before, it shows a clear double peak. By the repetition of the heating, cooling, and heat-treatment descrived above, the shoulder peak $P_5$ (or $P'_5$) in Fig. 3(d) becomes the main peak, while the original main peak, $P_6$, becomes the shoulder. Similar phenomena were observed for the specimen heat-treated at other temperatures. The shoulder peak, $P_5$ (or $P'_5$), in Fig. 3(d) disappears if the specimen so treated as to show the peak is further heat-treated at 360°C for 12 hr, though it does not disappear upon heat-treatment at 306°C for 1 hr.

The X-ray diffraction method was employed to elucidate what phenomena or changes these peaks correspond to.

Figure 4(a) shows the X-ray powder diffraction pattern of $K_2C_2O_4$ at room temperature for the Cu-$K\alpha$ radiation. The crystallographic data of the $K_2C_2O_4$ crystal have not yet been reported. One may index the diffraction lines assuming that $K_2C_2O_4$ crystal has an orthorhombic unit cell with cell constants of $a$=10.90, $b$=6.11, and $c$=3.44 Å at 17°C. From the observed density data (2.381 g/cc at 25°C) of the material, a unit cell can be said to contain 2 chemical units.

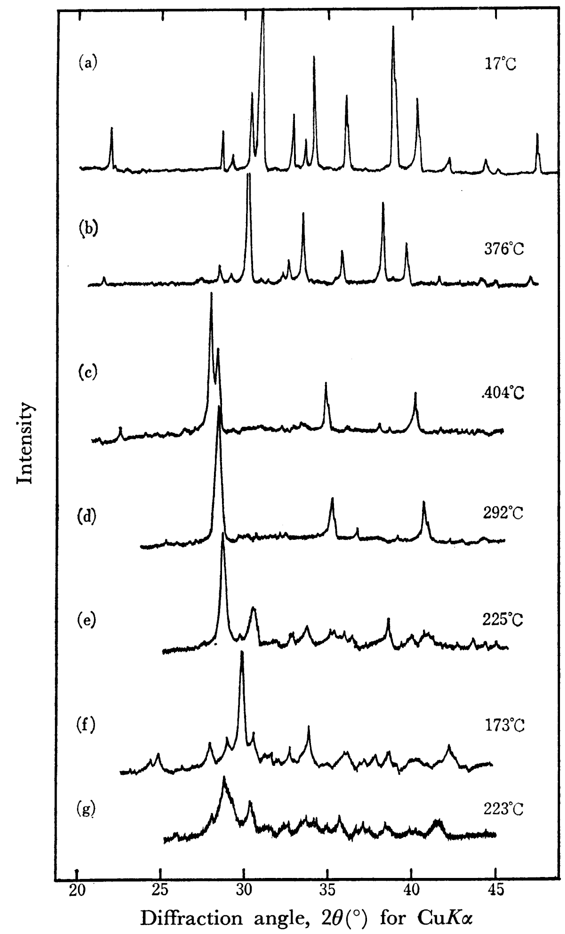


Fig. 4. X-Ray diffraction patterns of $K_2C_2O_4$. (d)—(f): in cooling process.

When $K_2C_2O_4$ crystals were heated in the X-ray high-temperature apparatus up to 376°C (B in Fig.1), the specimen shows the diffraction pattern shown in Fig. 4(b). We may index the diffraction lines in this pattern assuming that $K_2C_2O_4$ crystals have lattice parameters of $a$=11.01, $b$=6.16, and $c$=3.56 Å. When the specimen was heated to 404°C and treated there (C in Fig. 1), it showed the diffraction pattern shown in Fig. 4(c). This pattern has no similarity with the pattern (b) in Fig. 4. One may index the diffraction lines assuming that the crystals have a tetragonal unit cell with cell constants of $a$=7.01 and $c$=7.53 Å. From these facts, it may be concluded that the endothermic peak, $P_2$, in Fig. 1 corresponds to the polymorphic transition of potassium oxalate anhydrate crystals. As has been stated above, this transition does not occur reversibly in an exact sense. We shall refer to the phase stable below 381°C as phase II, and to that phase stable above 381°C, as phase I.

When the $K_2C_2O_4$ specimen is once heated to 410°C, kept for a rather short time—until the diffraction lines which belong to phase II disappear, and cooled to 310°C (D in Fig. 3(a)), extra lines which seem to belong to phase II are observed in the diffraction pattern. Figure 4(d) shows the diffraction pattern when the specimen which has been heat-treated at 410°C for a long enough time, is cooled to 292°C (E in Fig. 3(b)). No extra line is seen in this pattern. When a similarly heat-treated specimen is cooled to 225°C (G in Fig. 3(b)), some extra diffraction lines appear (Fig. 4(e)) in addition to the lines in Fig. 4(d). If the specimen which had experienced a transformation history such as II →I→III (see below)→II→I is heat-treated at 410°C for a long enough time and then cooled to 310°C, it gives the diffraction lines of phase I only. When this specimen is cooled to 263°C (F in Fig. 3(b)), some extra diffraction lines appear (prominently at $2\theta=30.4°$). These new peaks disappear when this specimen is cooled to 231°C. When this specimen is further cooled to and kept for a long time at 226°C, it gives a pattern similar to Fig. 4(e). At 225°C, we may index the original diffraction lines assuming that the specimen has lattice constants of $a=6.94$ and $c=7.45$ Å.

Thus, the broad exothermic peak, $P'_1$, in Fig. 3(b) as well as the $P_1$ peak in Fig. 3(a) may be regarded as the peaks accompanying the transformation from phase I to phase II. The cause for the appearance of the $P_2$ peak in Fig. 3(b) is not clear. This peak might also correspond to the I→II transformation. However, the findings with respect to the peak seem to be more favorably explained if we say that the peak is due to rearrangement of the molecules in the lattices with less regularity, which might exist in phase I or which might have resulted from the I→II transformation at a lower temperature (*e.g.*, 250°C), to a structure more stable at the temperatures which the peak covers.

When the specimen heat-treated well at above 410°C is cooled down to H in Fig. 3(b) (173°C), it gives the diffraction pattern shown in Fig. 4(f), which is not at all similar to the (d) or (e) patterns in Fig. 4 or to that of the original specimen at the same temperature. Thus, the sharp exothermic peak, $P_3$, in Fig. 3 (b)is due to the second phase transition. We call this new phase as phase III. In a dry-air atmosphere, phase III is fairly stable at room temperature, especially when it has been properly prepared. It seems interesting that when the specimen completely transformed into phase I is quenched to 0°C, phase I still remains (though it is only a small portion )and the main portion is not phase III but phase II.

When the specimen which gives the diffraction pattern of phase III is heated again to 223°C (J in Fig. 3(d)) it gives the pattern shown in Fig. 4(g). The presence of the diffraction lines of phase I indicates that the transition between phases III and I occurs (at least partly) reversibly; this is supported by the DTA findings. We can also find in Fig. 4(g) many diffraction lines which belong to phase II; this means that the transition from phase III to phase II occurs to a considerable extent. As may be seen from Fig. 4(g), the crystallinity of the resultant phases is poor. If we heat this specimen up to K (*e.g.*, 300°C) over the peak, $P_4$ (PT 265°C), in Fig. 3(d), it gives a diffraction pattern of phase II with an improved crystallinity. Thus, the exothermic peak, $P_4$, in Fig. 3(d) may correspond both to the transformation of $K_2C_2O_4$ from phase I to phase II and to the improvement of the crystallinity of the resulting phase II.

As has already been stated, the heating DTA of the specimen which is in phase III gives an endothermic double peak at around 390°C. If, however, we heat-treat the specimen in phase III at, *e.g.*, 360°C for 12 hr, it shows a single peak. The double peak may then be explained as follows. The first endothermic peak ($P_5$ in Fig. 3(e)) may correspond to the transformation into phase I of the poor-crystalline or amorphous part of the specimen resulting from a transformation history such as II→I→III→II, rather than be due to the presence of another new phase, II′. The poor-crystalline part may be more easily and completely transformed into phase I than the crystalline part of phase II. The second endothermic peak corresponds to the transformation from phase II to phase I.

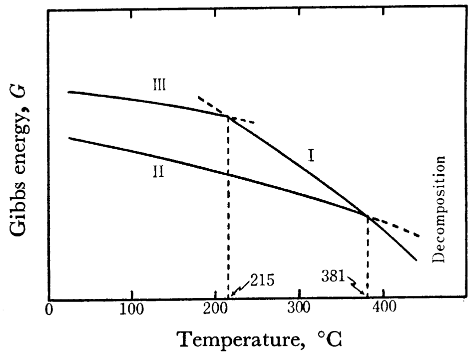


Fig. 5. Schematic representation of phase diagram of $K_2C_2O_4$.

The results discussed above may be summarized schematically as is shown in Fig. 5. Phase II is stable below 381°C, and phase I is stable above that temperature. When crystals in phase I are cooled, phase I endures down to 215°C, where phase III appears and exists below that temperature. At all temperatures below 381°C, phase I and III are meta-stable with respect to phaseII.