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# Thermal decomposition of potassium dioxodiaquaperoxyoxalatouranate(VI)

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## Abstract

Potassium dioxodiaquaperoxyoxalatouranate(VI) was obtained by reaction of uranyl nitrate with oxalic acid and then hydrogen peroxide in the presence of potassium ion. The complex was subjected to chemical analysis. The thermal decomposition behavior of the complex was studied using TG, DTA and DTG techniques. The solid complex salt and the intermediate product of its thermal decomposition were characterized using IR absorption and X-ray diffraction spectra. Based on the data from these physicochemical investigations, the structural formula of the complex was proposed as $K_2[UO_2(O_2)C_2O_4(H_2O)_2]$.
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*Keywords:* Thermal analysis; Peroxy; Uranium(VI); Potassium salt; X-ray diffraction; IR data

## 1. Introduction

Owing to an intrinsic interest in [1–4] and practical use of [5,6] peroxometal compounds there has been an upsurge of research in their chemistry. Although peroxoactinides are known [7–11] molecular complexes are rather few [12,13]. This aspect of uranium chemistry is complicated [7]. $[UO_2(O_2)]\cdot nH_2O$ ($n = 2$ or 4) is the best characterised. In addition $[UO_2(O_2)L]$ L = $Ph_3PO$, $Ph_3AsO$ or pyridine N-oxide [12] and a few diperoxouranium(VI) complexes with Schiff bases as coligands [13] are known. The compound $[UO_2(O_2)]\cdot 4H_2O$ oxidises olefins to epoxides and oxidative-cleavage products [6]. It has been observed [8–11] that $[UO_2]^{2+}$ reacts with $H_2O_2$ to generate $[UO_2(O_2)]$ in solution which suggested that a similar reaction in the presence of an appropriate coligand would provide access to molecular peroxo-complexes of the metal.

As with molybdenum and tungsten, the peroxide chemistry of uranium is confined to the +6 oxidation state; in view of the small potential for the +6/+5 change (0.063 V). The best characterised peroxy derivative is the tetroxide (commonly called uranyl peroxide), $UO_4\cdot nH_2O$ (where $n$ is 2 or 4); many peroxy uranates are known, in which the ratio of peroxide to uranium is 3:1, 5:2, 2:1, 3:2, 1:1 and 1:2 and in addition to these, a series of mixed ligand peroxy compounds have been described. In general, the peroxide content increases with pH; acids decompose the compounds to uranium (VI) salts and oxygen, while the triperoxyuranate ion is stable at pH 12–14.

In the present work the potassium dioxodiaquaperoxyoxalatouranate(VI) complex was prepared by reaction of ${UO_2}^{2+}$ with oxalic acid and then hydrogen peroxide in the presence of potassium ion. The thermal decomposition of the complex has been studied and a detailed account of the mechanism has been

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worked out on the basis of the thermal data, infrared spectroscopic and X-ray diffraction studies.

## 2. Experimental

### 2.1. Instrumentation

### 2.1.1. Thermal analysis unit

A SEIKO combined thermal analysis system (TG/DTA-32), with temperature programmable thermal balance, and platinum crucible is used for taking thermograms in air. The rate of heating is fixed at 10 K/min. The sensitivity of the instrument is 0.1 mg.

### 2.1.2. Infrared spectra

The infrared spectra of the complexes are recorded on SHIMADZU FTIR-8201 PC Infrared Spectrophotometer in KBr pellets.

### 2.1.3. X-ray diffraction data

X-ray diffractometer (RICH SEIFERT & Co.) attached to a microprocessor is used for taking X-ray diffraction patterns at wave length of Cu K$\alpha$1 = 1.540598 Å.

### 2.2. Preparation and analysis

The potassium dioxodiaquaperoxyoxalatouranate-(VI) complex salt is prepared by adopting the following procedure [14].

About 1.0 g (1.99 mmol) $UO_2(NO_3)_2{\cdot}6H_2O$ was dissolved in water (10–15 cm$^3$) followed by addition of 10% potassium hydroxide solution with stirring until the yellow precipitate ceased to appear. The yellow precipitate was filtered off and washed free of potassium and nitrate ions. To an aqueous suspension of the product was added 4 cm$^3$ of concentrated oxalic acid (10 mmol) to obtain a clear solution, which was stirred for ca. 5 min. A 25 cm$^3$ (220.5 mmol) sample of 30% $H_2O_2$ was added, while the U:$C_2O_4$:$H_2O_2$ ratio was maintained at 1:5:122.5 and the solution was stirred for ca. 15 min followed by careful addition of the potassium hydroxide solution until the pH was raised to 6, where upon a yellow product just began to appear. An equal volume of ethanol was added with occassional stirring to obtain the yellow microcrystalline complex of potassium dioxodiaquaperoxyoxalatouranate(VI). The compound was allowed to settle for ca. 20 min, separated by centrifugation, purified by washing with ethanol (3–5 times) and finally dried in vacuo over silica gel. The compound thus obtained is tested to confirm the absence of nitrate.

The reaction of hydrogen peroxide with uranyl ion leading to a complex peroxyuranate(VI) of a definite composition is highly dependent on the pH of the reaction medium. Thus, evaluation of an appropriate pH for successful synthesis of a peroxyuranate species is an important prerequisite. The suitable pH for bringing about coordination of both peroxide and oxalate with the uranyl center was ascertained to be 6. The compounds isolated at a relatively lower pH (e.g. ca. 4) did not show the presence of peroxide at the desired level (i.e. U:$O_2^{2-}$ as 1:1), indicating therefore that the $O_2^{2-}$ uptake process was in progress but was not complete.

The compound was analysed for its uranium(VI), oxalate and peroxide contents. Uranium(VI) was estimated by photochemical reduction with alcohol [15] and oxalate and peroxide by volumetric titration with standard cerium(IV) sulphate [16,17]. The potassium and water content were determined by difference and from thermal data. The data corresponds to the mole ratio of U(VI):$C_2O_4$:$O_2^{2-}$ to be 1:1:1 suggesting the molecular formula to be $K_2[UO_2(O_2)C_2O_4(H_2O)_2]$.

## 3. Results and discussion

### 3.1. Thermal analysis

### 3.1.1. Thermogravimetric analysis (TGA)

The thermogram of potassium dioxodiaquaperoxyoxalatouranate(VI) and the data obtained from it are given in Fig. 1 and Table 1, respectively. The TG curve shows that the loss of coordinated water may take place below 106 °C and this accounts for 8.32% (ca. 7.14%) weight loss of the complex. The anhydrous product seems to be stable up to about 106 °C. A sharp weight loss between 200 °C and 248.2 °C may be attributed to the formation of a carbonate intermediate with a calculated weight loss of 18.77% against the observed weight loss of 19.95%. This intermediate, possibly a mixture of potassium carbonate and uranium trioxide, being unstable under the conditions, is likely to decompose to potassium

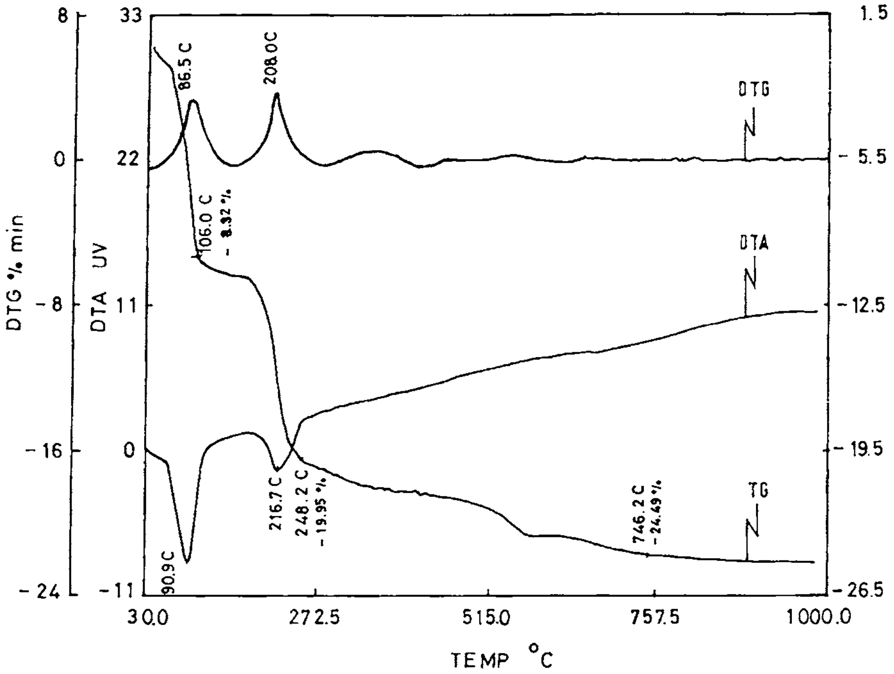

Fig. 1. TG/DTA curve of potassium dioxodiaquaperoxyoxalatouranate(VI).

uranate [18]. The observed weight loss of 24.49% at 746.2 °C against the calculated 24.60% confirms the formation of potassium monouranate.

### 3.1.2. Differential thermogravimetric analysis (DTG)

The DTG data of potassium dioxodiaquaperoxyoxalatouranate(VI) is shown in Fig. 1. On the DTG curve, there is indication for the existence of two significant weight losses. The first peak, having $\Delta T_{\max}$ at about 86.5 °C indicates the formation of anhydrous product from the loss of two molecules of coordinated water. The second significant loss at 208 °C is attributed to the decomposition of the latter to the carbonate intermediate. However, the final stage of the reaction corresponding to the decomposition of potassium carbonate and uranium trioxide to potassium uranate observed in the TG could not be seen in the DTG curve because of the spread of the reaction over a long range of temperature. As such the effect is not pronounced in the DTG curve.

### 3.1.3. Differential thermal analysis (DTA)

DTA results of the compound are also shown in Fig. 1. From the DTA curve it is evident that the endothermic peak with $\Delta T_{\min}$ at 90.9 °C indicates the dehydration of the complex. There is also an endothermic peak at 216.7 °C corresponding to the formation of the unstable intermediate, which is

Table 1
Summary of the thermal decomposition of the potassium salt

| Weight of compound (mg) | Step number | Temperature | | Loss in weight | | Possible decomposition product (intermediate) |
|---|---|---|---|---|---|---|
| | | Starting (°C) | Ending (°C) | Observed (%) | Calculated (%) | |
| 11.0 | 1 | 30.0 | 106.0 | 8.32 | 7.14 | $K_2[UO_2(O_2)C_2O_4]$ |
| | 2 | 106.0 | 248.2 | 19.95 | 15.87 | $K_2CO_3 \cdot UO_3$ |
| | 3 | 248.2 | 746.2 | 24.49 | 24.60 | $K_2UO_4$ |

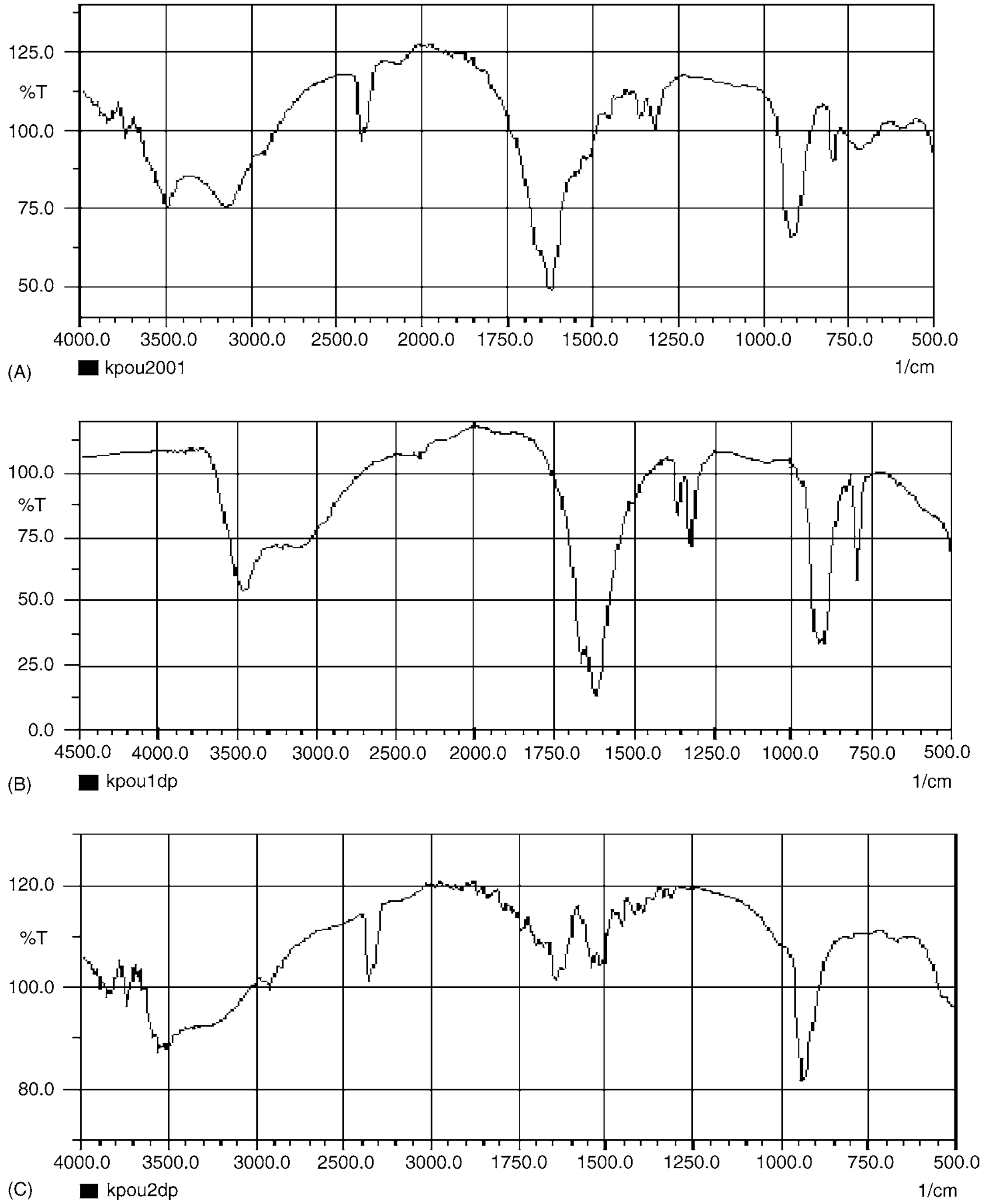

Fig. 2. (A) Infrared spectrum of potassium dioxodiaquaperoxyoxalatouranate(VI). (B) Infrared spectrum of potassium dioxodiaquaperoxyoxalatouranate(VI) after heating to 120 °C. (C) Infrared spectrum of potassium dioxodiaquaperoxyoxalatouranate(VI) after heating to 220 °C.

Table 2
Infra red absorption data of potassium dioxoperoxyoxalatouranate(VI) and the decomposition products

| Complex | | | Band assignment |
|---|---|---|---|
| Original ($cm^{-1}$) | Heated at 120 °C ($cm^{-1}$) | Heated at 220 °C ($cm^{-1}$) | |
| 3487 m, s | 3475 sp, s | | $\nu_{as,s}$ (H–O–H) |
| 1628 sp, s | 1635 sp, s | | $\nu_a$ (C=O) + $\delta$ (H–O–H) |
| 1365 m | 1375 m | | |
| 1323 m | 1325 s | | $\nu_s$ (C=O) + $\delta$ (O–C=O) |
| | | 1660 m | |
| | | 1550 m | $\nu_s$ (C–O) due to $CO_3{}^{2-}$ |
| | | 1420 w | |
| 922 sp, s | 925 sp, s | 950 sp, s | $\nu$ (U=O) |
| 802 m | 800 m, sp | | Coordinated water |
| 721 w | | | $\nu$ (O–O) |
| 604 w | | | $\nu$ (U–$O_2$) |

b: broad, m: medium, s: strong, sp: sharp, sh: shoulder, w: weak.

possibly a mixture of potassium carbonate and uranium trioxide.

### 3.2. Infrared spectra of potassium dioxodiaquaperoxyoxalatouranate(VI)

The IR spectra of potassium dioxodiaquaperoxyoxalatouranate(VI) and the products obtained by heating the complexes at 120° and 220 °C and cooling to room temperature are given in Fig. 2A-C, respectively. The data obtained from the IR spectra is given in Table 2. As in the ammonium complex [19] the spectra of this complex also show distinctly strong and sharp absorption bands at 922 $cm^{-1}$ which may be assigned [20–24] to the $\nu$U=O (trans-linked O=U=O), and that at 721 $cm^{-1}$ to the $\nu$O–O (the peroxy modes) and at 604 $cm^{-1}$ to the $\nu$U–$O_2$ bond. This spectrum also indicates a peroxide in which the $O_2{}^{2-}$ group is bonded to the $UO_2{}^{2+}$ center, in a triangular bidentate ($C_{2v}$) manner[7-11]. The IR modes due to the coordinated $C_2O_4{}^{2-}$ ligand (at 1628 $cm^{-1}$) also show the presence of a chelated oxalato group [25,26]. The $\nu$H–O–H band at 3487 $cm^{-1}$ and the δH–O–H at 1628 $cm^{-1}$ along with an absorption at 802 $cm^{-1}$ in the IR spectra of the compound suggests the presence of coordinated water [25,27,28].

There is a similarity in the spectra of the original complex and the first decomposition product owing to the fact that only water is removed from the former. The difference in the shape of the bands at around 3500 and 1600 $cm^{-1}$ regions clearly indicates this. On the other hand, the spectrum of the second decomposition product shows that some of the characteristic bands of the original complex and the first decomposition product are missing. In particular the lack of significant peaks in the lower frequency region (~600 $cm^{-1}$), to the vibrational stretching modes of the –O–O– and the U–$O_2$ linkages, suggests that the original complex has undergone step-wise decompositions. In addition, the peaks appearing at 1660, 1550 and 1420 $cm^{-1}$ may be attributed to the presence of carbonate. However, the band assigned to the $\nu$ (U=O) appears to be more intense in both decomposition products as compared to the original complex indicating possible transformations of the uranium-oxygen linkage. The broad bands in the range of 3500–3000 $cm^{-1}$ for the second decomposition product may be due to absorption of moisture from atmospheric air.

### 3.3. X-ray diffraction data

The X-ray diffraction data of potassium dioxodiaquaperoxyoxalatouranate(VI) and that of the product obtained after heating the original complex to 120 °C and cooling are given in Table 3 along with those of uranium(VI) oxalate and potassium oxalate for comparison. The figures in the table indicate the ‘d’ spacings while the subscripts indicate the relative intensity of the peaks with respect to the maximum intensity peak the value of which is taken as ‘X’. The data in the table clearly show that the heated product obtained at 120 °C is an individual

Table 3
X-ray diffraction data of potassium dioxodiaquaperoxyoxalatouranate(VI) and the products after heating it to 120 and 220 °C, compared with uranium(VI) oxalate and potassium oxalate

| $K^+$ complex | Complex heated to 120 °C | Complex heated to 220 °C | $UO_2C_2O_4$ | $K_2C_2O_4$ |
|---|---|---|---|---|
| $13.62_2$ | | $8.619_x$ | | |
| $7.843_6$ | $7.4122_2$ | $7.775_6$ | | |
| $5.926_x$ | | | | |
| $5.133_3$ | $5.0549_4$ | | | |
| $4.595_5$ | $4.4392_2$ | $4.745_5$ | $4.87_6$ | $4.310_1$ |
| $4.258_8$ | $4.1278_3$ | $4.136_7$ | $4.57_6$ | |
| $3.869_2$ | | | $4.46_x$ | |
| $3.641_3$ | | | | $3.100_1$ |
| $3.410_6$ | $3.2003_1$ | $1.872_8$ | | |
| $2.999_2$ | | | | $2.920_x$ |
| $2.836_3$ | | $2.774_4$ | | $2.460_6$ |
| $2.601_2$ | $2.5791_1$ | | | |
| $2.293_2$ | $2.4314_1$ | $2.268_4$ | | |
| $2.240_2$ | $2.3648_1$ | | | $2.320_6$ |
| $2.168_1$ | $2.7006_1$ | $2.107_8$ | | $2.140_1$ |
| $2.085_2$ | $2.0906_2$ | | | |
| $2.020_3$ | $2.0205_7$ | | | |
| $1.951_3$ | $1.9048_2$ | $1.917_5$ | | |
| $1.756_1$ | $1.7422_2$ | $1.699_5$ | | |
| $1.456_1$ | | $1.644_5$ | | |
| $1.382_2$ | $1.2888_x$ | $1.397_7$ | | |

compound, not a mixture of potassium and uranyl oxalates.

The complex was also heated to 220 °C and maintained at this temperature for half an hour and the product obtained in this manner was tested for the presence of carbonate by the usual acid test. The result of this test indicates the presence of carbonate in the product.

## 4. Conclusion

On the basis of the above thermal data the compound may be represented by the structural formula $K_2[UO_2(O_2)C_2O_4(H_2O)_2]$. The following step-wise thermal decomposition mechanism supports the ideas expressed.

$$\begin{aligned}&K_2[UO_2(O_2)C_2O_4(H_2O)_2]\\&\quad\xrightarrow{30\text{–}106\,^{\circ}C} K_2[UO_2(O_2)C_2O_4]\\&\quad\xrightarrow{106\text{–}248.2\,^{\circ}C} K_2CO_3\cdot UO_3 \xrightarrow{248.2\text{–}746.2\,^{\circ}C} K_2UO_4\end{aligned}$$

Overall

$$\begin{aligned}&K_2[UO_2(O_2)C_2O_4(H_2O)_2]\\&\quad\to K_2UO_4 + 2H_2O + 2CO_2\end{aligned}$$

Literature [29] shows that uranyl ion (a linear structure) has conventionally been assumed to be the centre of the complex, as it does not take part in the inner-sphere substitution reactions and remains unchanged. Besides, uranyl ion exhibits six coordination. Hence it can be concluded from the results of the above investigation that the complex has an octahedral structure with composition $K_2[UO_2(O_2)C_2O_4(H_2O)_2]$.

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