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SOME STUDIES ON THALLIUM OXALATES. II. THERMAL DECOMPOSITION OF POTASSIUM BISOXALATO DIAQUOTHALLATE(III) DIHYDRATE

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ABSTRACT

Potassium bisoxalato diaquothallate(III) dihydrate is obtained by precipitating thallium(III) with oxalic acid from slightly acidic (HNO_3 or H_2SO_4) solutions in the presence of potassium ions. The thermal decomposition behaviour of the complex is studied using the techniques of TG, DTA and DTG. The solid complex salt and the intermediate products of its thermal decomposition are characterised using IR absorption spectra, microscopic observations, electrical conductivity measurements and X-ray diffraction data.

INTRODUCTION

Potassium thallium(III) oxalate is known to crystallise as the trihydrate [1—3]. It was suggested that in this complex compound the "thallium(III) may be probably in the octahedral valence state suggesting the probable structural formula to be $K[Tl(C_2O_4)_2(H_2O)_2] \cdot H_2O$" [4]. The authors' results on the thermal decomposition behaviour of the complex, and characterisation of the complex and the intermediate product of its thermal decomposition are now presented. For this purpose the authors have used IR absorption, X-ray diffraction, microscopic observations and electrical conductivity measurements.

EXPERIMENTAL

The details of TG, DTG and DTA measurements; IR; microscopic observations, electrical conductivity measurements and X-ray diffraction studies are as described in our earlier communication [5].

Preparation and analysis of the complex

The complex is prepared using the conditions reported earlier [6,7] and the compound obtained is filtered through an IG 4 sintered glass crucible, washed with minimum quantities of wash liquid (containing 0.125 M nitric acid and 0.15 M potassium nitrate or 0.0625 M sulphuric acid and 0.075 M potassium sulphate) and finally with acidified water (with nitric or sulphuric

TABLE 1

Chemical analysis

Constituent	Original complex	Intermediate
Potassium (%)	7.92 (calc.)	11.80 (calc.)
Thallium (%)	41.43	61.56
Oxalate (%)	35.77	26.56
Water (%)	14.49	

acid) and dried under vacuum over silica gel.

The thallium and oxalate contents of the original complex and of the intermediate are found [8] to be in the ratio of 1 : 2 and 1 : 1, respectively. The ratio of potassium and thallium in the intermediate and hence in the original complex is found to be 1 : 1 by difference. The presence of the carbonate in the final product after heating is confirmed by the usual acid test. The water content in the original complex is computed, by difference, to be four moles per atom of thallium. This observation is in agreement with the thermal decomposition data recorded now and calculated by the methods suggested earlier [9]. The data in Table 1 suggest the structural formula of the original complex to be $K[Tl(C_2O_4)_2(H_2O)_2] \cdot 2\,H_2O$ which is further supported by the results of the following studies.

RESULTS AND DISCUSSION

Thermal decomposition of the complex

It is clear from the pyrolysis curve (Fig. 1) that the continuous loss from 50 to 150°C corresponds to the dehydration (four molecules of water) and redox decomposition of thallic oxalate to thallous oxalate with loss of one mole of oxalate. In the DTG curve there are three peaks indicating the stepwise loss in weight between 50 and 150°C. The peak at 105°C may be due to the loss of the lattice water which is followed by the loss of the coordinated water and the oxalate at 130 and 140°C, respectively. In the DTA curve the broad endothermic peak with a $\Delta T_{\min}$ at 105°C, the endothermic shoulder at 140°C and a sharp exothermic peak with a $\Delta T_{\max}$ at 150°C indicate the loss of lattice water, coordinated water and oxalate (due to redox decomposition of thallic oxalate to thallous oxalate), respectively. A small and broad exothermic peak with $\Delta T_{\max}$ at 60°C, where the crystalline compound appeared to crumble to a powder may be due to some sort of a structural change in the compound in the solid state. Polymorphic changes in the thallium salts of fatty acids are known [10]. The present authors' observations on the electrical conductivity of the compound also showed variation in behaviour at this temperature.

The product obtained after thermal decomposition at 150°C is stable from 150 to 250°C and decomposes further from 250 to 440°C to give a mixture of potassium carbonate, thallous oxide and thallic oxide in the mole

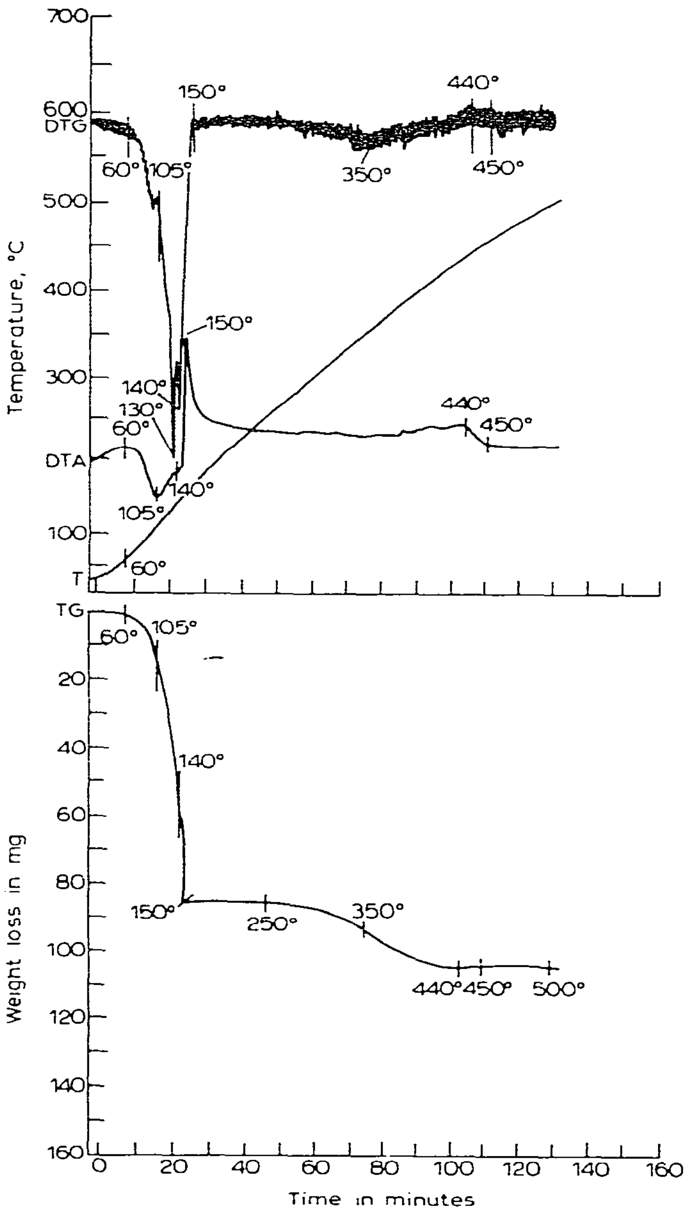

Fig. 1. TG, DTG and DTA curves of potassium bisoxalato diaquothallate(III) dihydrate.

ratio 4 : 1 : 3. This product is stable up to 500°C. A broad peak in DTG around 350°C (Fig. 1) corresponds to the above decomposition. A very broad exothermic peak around this region in DTA with ΔT_{max} at 440°C is obviously due to the decomposition and subsequent oxidation of the products.

The results are summarised in Tables 2 and 3. From these results the stepwise thermal decomposition of the complex may be given as

$$8\ K[Tl(C_2O_4)_2(H_2O)_2]\ 2\ H_2O \xrightarrow{\sim 105^\circ C} 8\ K[Tl(C_2O_4)_2(H_2O)_2] + 16\ H_2O$$

(1)

$$8\ K[Tl(C_2O_4)_2(H_2O)_2] \xrightarrow{\sim 140^\circ C} 8\ K[Tl(C_2O_4)_2] + 16\ H_2O$$

(2)

TABLE 2

Thermogravimetric data of potassium bisoxalato thallate (III)

Wt. of the complex taken (mg)	Step no.	Temp. (°C)		Loss in wt of the complex (mg)		Reaction involved
		Starting	Ending	Obs.	Calc.	
260	I	50	150	85	84.66	$8\ K[Tl(C_2O_4)_2] \cdot 4\ H_2O \rightarrow 4\ K_2C_2O_4 + 4\ Tl_2C_2O_4 + 32\ H_2O + 16\ CO_2$
	II	250	440	20	19.40	$4\ K_2C_2O_4 + 4\ Tl_2C_2O_4 \rightarrow 4\ K_2CO_3 + Tl_2O + 3\ Tl_2O_3 + 4\ CO_2 + 8\ CO$
	Overall	50	440	105	104.60	$8\ K[Tl(C_2O_4)_2] \cdot 4\ H_2O \rightarrow 4\ K_2CO_3 + Tl_2O + 3\ Tl_2O_3 + 32\ H_2O + 20\ CO_2 + 8\ CO$

TABLE 3

DTG and DTA data of potassium bisoxalato thallate(III)

	Reaction	Peak		
		Temperature (°C)	Nature	Type
DTG	Dehydration	105	Loss	Very sharp
	Redox decomposition	135	Loss	Sharp
	Decomposition and partial oxidation	350	Loss	Broad
DTA	Dehydration	105	Endothermic	Broad
	Redox decomposition	150	Exothermic	Sharp
	Decomposition and partial oxidation	440	Exothermic	Broad

$$8\ K[Tl(C_2O_4)_2] \xrightarrow{\sim 150^\circ C} [8\ KTlC_2O_4 + 16\ CO_2] \text{ or } [4\ K_2C_2O_4 + 4\ Tl_2C_2O_4 + 16\ CO_2]$$

(3)

$$8\ KTlC_2O_4 \text{ or } 4\ Tl_2C_2O_4 + 4\ K_2C_2O_4 \xrightarrow{250-440^\circ C} 4\ K_2CO_3 + Tl_2O + 3\ Tl_2O_3 + 12\ CO_2$$

(4)

From Fig. 1 it is not possible to know whether the intermediate formed at 150°C, by heating the complex, is a binary salt $KTlC_2O_4$ or an equimolar mixture of $K_2C_2O_4$ and $Tl_2C_2O_4$. The results of the separate thermograms of $K_2C_2O_4 \cdot H_2O$, $Tl_2C_2O_4$ and a mixture of the two in 1 : 1 mole ratio are given along with those obtained for the intermediate product in Table 4. From Table 4 it is evident that the intermediate product is probably an equimolar mixture and not a single compound, as the nature of the thermal decomposition of the synthetic mixture is identical with that of the intermediate product.

In an attempt to isolate the complex with the coordinated water and without the lattice water (at the end of the first stage of decomposition) an isothermal decomposition of the complex is carried out at 105°C. It has been observed by the authors that the compound is found to lose both forms of water at this temperature followed by the redox decomposition. This observation suggests that the two forms of water in the solid complex must have been intimately connected probably through hydrogen bonds, and that the stability of the complex itself appears to be dependent upon the presence of the coordinated water.

IR absorption spectra

The IR absorption spectrum of potassium bisoxalato thallate(III) is shown in Fig. 2(a). A sharp and very broad peak at 3480 cm^{-1} and a broad and very strong peak at 3370 cm^{-1} correspond to the asymmetric and symmetric stretching modes of vibration of H—O—H [11] and a very broad and strong peak at 1600 cm^{-1} corresponding to the bending modes of vibration of water shows the presence of water in general, while a very sharp and strong peak at 800 cm^{-1} and a broad and weak absorption at 610 cm^{-1} indicate the coordi-

TABLE 4

Comparison of thermal decomposition temperatures observed

Compound	Dehydration (°C)	Decomposition (°C) to		Oxidation of Tl(I) to Tl(III) (°C)
		Carbonate	Oxide	
$K_2C_2O_4 \cdot H_2O$	100—130	550—620	—	—
$Tl_2C_2O_4$	—	—	290—340 Tl_2O	380—420 $Tl_2O + nTl_2O_3$
$K_2C_2O_4 \cdot H_2O + Tl_2C_2O_4$ (equimolar mixture)	100—135		260—440 (decomposition and oxidation) $K_2CO_3 + \frac{1}{4}(Tl_2O + 3\ Tl_2O_3)$	
$KTlC_2O_4$ obtained by heating $K[Tl(C_2O_4)_2]4\ H_2O$			250—440 (decomposition and oxidation) $K_2CO_3 + \frac{1}{4}(Tl_2O + 3\ Tl_2O_3)$	

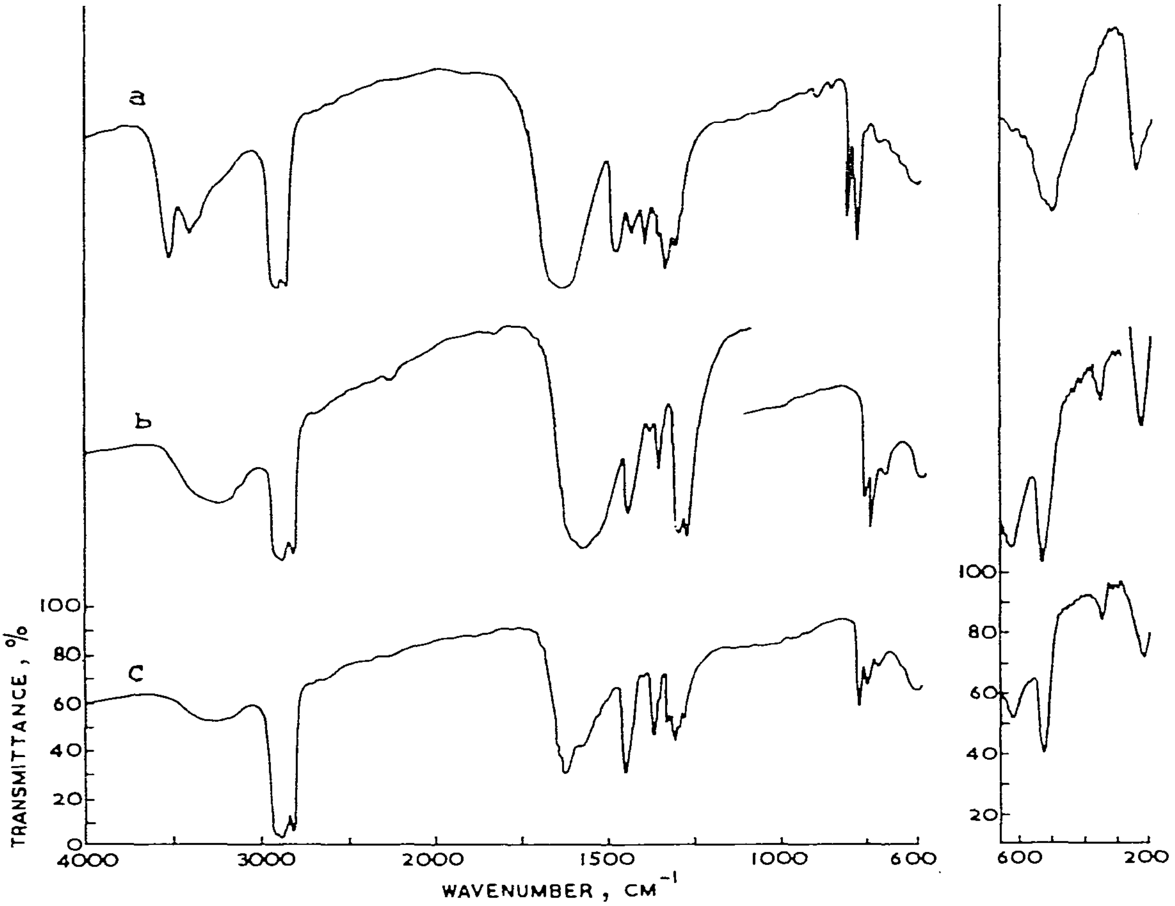

Fig. 2. Infrared absorption spectra of (a) the complex, (b) a mixture of potassium oxalate monohydrate and thallous oxalate in 1 : 1 molar ratio and (c) the product obtained after heating the complex to 170°C and cooling.

nated [12] and crystal water [12], respectively, in the complex.

The spectrum of the complex in Fig. 2(a), and that of an equimolar mixture of potassium oxalate monohydrate and thallous oxalate in Fig. 2(b), are compared with the spectrum of thallous oxalate already reported [5]. From the Figs. it is evident that sharp and strong absorption peaks of the mixture of potassium oxalate monohydrate and thallous oxalate corresponding to the bending modes of vibration of O=C=O at 770, 752 and 748 cm^{-1} are shifted towards the higher frequencies, 800, 785 and 770 cm^{-1} in the complex. This shift suggests the increase of covalence of the metal—oxygen bond in the complex [13]. Similar shifts of the peaks at 525 and 225 cm^{-1} in the case of the complex also suggest that the bonding in the complex might be somewhat different from those in simple salts by being more covalent in nature.

The IR spectrum of the complex after heating at 170°C (and cooling to room temperature) is shown in Fig. 2(c) and is compared with that of a mixture of potassium oxalate monohydrate and thallous oxalate (Fig. 2b). All the prominent absorption peaks in both the Figs. are coincident, indicating the similarity of the heated product with the mixture. Hence, the intermediate product of thermal decomposition of the complex must be a mixture and not a single compound. The spectrum of the heated product after decomposition and cooling (Fig. 2c) also shows a peak corresponding to water. This is obviously due to the absorption of moisture by the anhydrous potassium oxalate in the heated product. (Preliminary observations indicate that both anhydrous potassium oxalate and the intermediate obtained at 150°C absorb moisture while thallous oxalate does not.)

Microscopic observations

Potassium bisoxalato thallate(III) occurs as colourless transparent irregular crystals with low birefringence. The lower refractive index is 1.596 ± 0.002

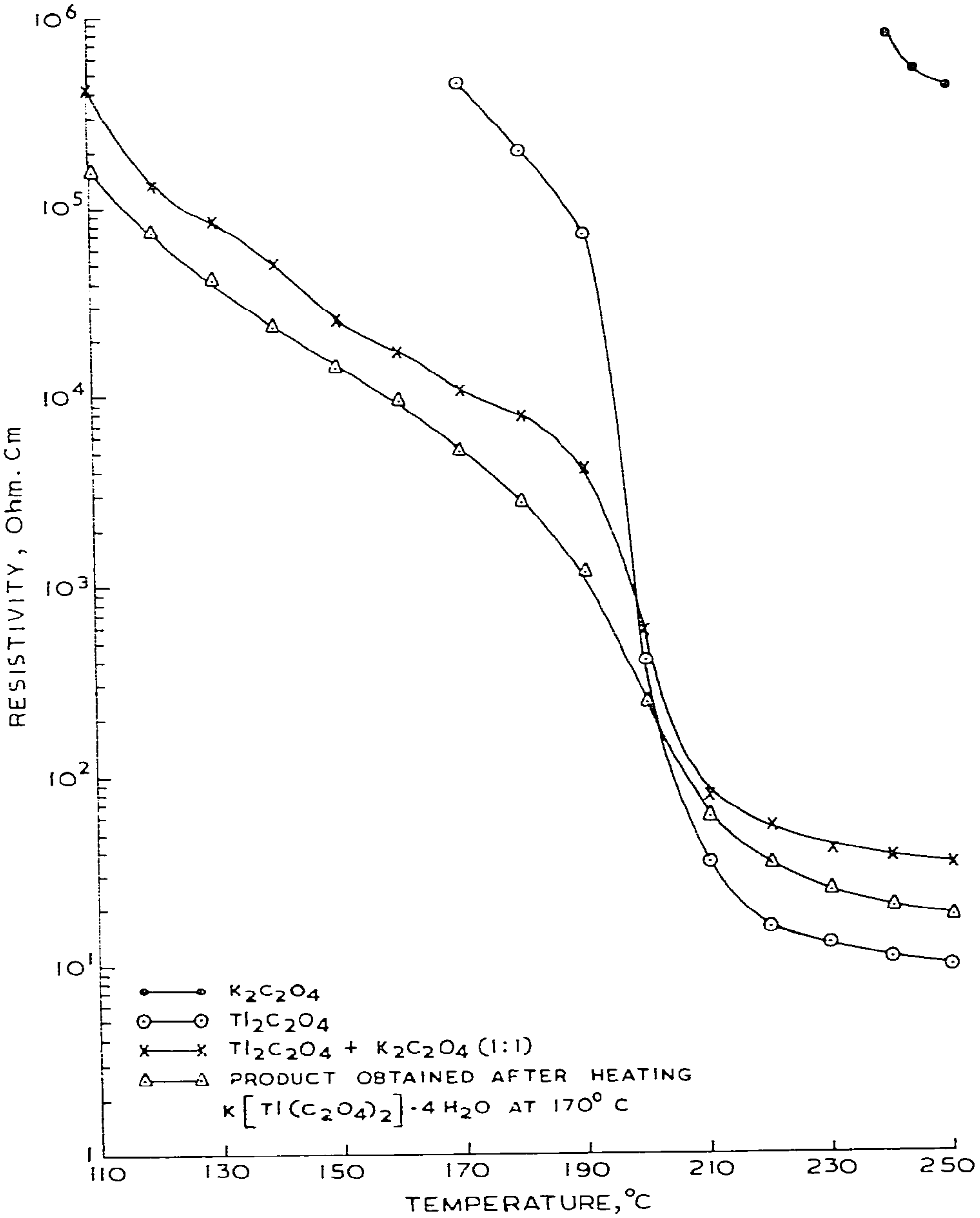

Fig. 3. Plot of electrical resistivity vs. temperature.

and the higher refractive index is 1.600 ± 0.002. The crystals developed from the aqueous solution of the product obtained by heating the complex at 170°C (intermediate 4) are observed under the microscope. These observations show the presence of separate thallous oxalate [5] and potassium oxalate crystals, suggesting the probability of the intermediate to be a mixture ($Tl_2C_2O_4$ and $K_2C_2O_4$).

Electrical conductivity measurements

The plots of resistance vs. temperature (rate of heating 5° min^{-1}) are obtained for thallous oxalate, potassium oxalate, a 1 : 1 mixture of potassium oxalate and thallous oxalate and the product of thermal decomposition of the complex at 170°C, by taking in the form of a pellet after grinding. The results are shown in Fig. 3. From Fig. 3 it is evident that the physical synthetic mixture of potassium oxalate and thallous oxalate and the product of decomposition of the complex at 170°C behave in the same manner, suggesting the intermediate 4 to be a mixture of potassium oxalate and thallous oxalate.

TABLE 5

X-ray diffraction data, *d*(Å)

Potassium bisoxalato thallate (III)	The product obtained by heating the complex at 170°C	$Tl_2C_2O_4$	$K_2C_2O_4 \cdot H_2O$	$K_2C_2O_4$
7.081_x	6.450_1	6.511_2		
5.644_9		4.970_3		
4.396_4	4.311_2	4.311_2		4.310_1
4.004_2	3.789_3	3.802_3		
3.917_8	3.433_x	3.440_x		
3.507_5	3.361_7	3.278_6		
3.132_5	3.106_5	3.110_4	3.080_3	3.100_1
2.959_4	2.750_9	2.763_7	2.740_1	2.920_x
2.894_1	2.658_1	2.660_3		
2.818_3	2.515_2	2.522_2		
2.788_5	2.458_6		2.450_x	2.460_6
2.622_1	2.318_x	2.321_1	2.320_1	2.320_6
2.571_1	2.181_4	2.186_6		2.140_1
2.535_2	2.136_4	2.137_6		
2.344_2	2.034_4	2.010_2	2.020_2	
2.281_1	1.967_5	1.969_2		
2.249_1	1.868_4	1.863_4		
2.186_2	1.748_2	1.752_3		
2.164_1	1.662_2	1.675_2		
2.085_2	1.632_2	1.634_2		
	1.594_2	1.593_3		
	1.570_1	1.575_1		
	1.486_1	1.488_2		
	1.426_1	1.427_1		
	1.388_2	1.386_2		

X-ray diffraction data, d(Å)

Prominent peaks of the X-ray diffraction data of the complex, its heated product (obtained by heating the complex at 170°C and cooling to room temperature under laboratory conditions), thallous oxalate, potassium oxalate monohydrate and anhydrous potassium oxalate are given in Table 5. It is clear from Table 5 that the heated product contains free thallous oxalate and potassium oxalate monohydrate (and not anhydrous potassium oxalate). Prominent "*d*" values of the complex (7.081_x, 5.644_9 and 3.917_8) may be utilised to differentiate the potassium salt from the other salts [5,14] of bisoxalato thallate(III) ion.

All these results support the proposed structural formula for the complex as $K[Tl(C_2O_4)_2(H_2O)_2] \cdot 2\,H_2O$, and the proposed mechanism for its thermal decomposition.

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