

SOME STUDIES ON THALLIUM OXALATES

XI. Calculation of activation energies for the thermal decomposition reactions of thallium oxalates*

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Two methods (the Horowitz–Metzger and the Dharwadkar–Karkhanavala) for calculating the apparent activation energies of different thallium(I) oxalates were compared. The Dharwadkar–Karkhanavala method gave consistent values.

During the past twenty years, non-isothermal techniques have been used to study the kinetics of solid-state decomposition reaction [1]. With these methods, the reaction kinetics could be studied from a single thermal curve. Though there are certain advantages to these methods, the results obtained are not very consistent [2–6], due to the variation in the experimental parameters.

Dharwadkar and Karkhanavala [6] have studied the effects of variations in experimental parameters such as sample size and heating rate on the activation energy of dehydration of calcium oxalate monohydrate of uniform particle size, using the Horowitz and Metzger equation [7]. They have also studied the applicability and accuracy of equations proposed by different authors. However, there appears to be no theoretical explanation for the observed variations. Hence, the method of calculation was analysed and a modified equation was given by Dharwadkar and Karkhanavala [8].

$$E^+ = \text{slope} \times (T_f - T_i) \cdot 100 \times RT_i^2$$

where T_i = temperature of initiation of the reaction, T_f = temperature of completion of the reaction. The modified equation is reported to give constant values of E^+ , which are independent of the heating rate and sample size.

The present authors have used both the Horowitz and Metzger equation and that modified by Dharwadkar and Karkhanavala for the calculation of activation energies, and the results are compared.

The TG curves already reported [9–13] have been utilized to calculate the activation energies for the various stages of thermal decomposition of $\text{Ti}_2\text{C}_2\text{O}_4$, TiHC_2O_4 , $\text{TiH}_3(\text{C}_2\text{O}_4)_2 \cdot 2 \text{H}_2\text{O}$, $\text{Ti}^{\text{III}}[(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3 \text{H}_2\text{O}$ and $\text{Py}_3[\text{Ti}(\text{C}_2\text{O}_4)_3]$. The results are summarized in Table 1.

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Table 1 Activation energies for the thermal decomposition of thallium oxalates. Heating rate = 4°C/min; furnace atmosphere = atmospheric air

Compound	Decomposition reaction	Activation energy, kJ/mol using equation	
		I	II
Thallium(I) oxalate (~ 600 mg)	$Tl_2C_2O_4 \longrightarrow Tl_2O$	286.3	222.6
Thallium(I) monohydro oxalate (~ 350 mg)	$TlHC_2O_4 \longrightarrow 1/2(Tl_2C_2O_4)$	159.5	88.2
	$Tl_2C_2O_4 \longrightarrow Tl_2O$	171.9	110.6
Thallium(I) trihydro dioxalato dihydrate (~ 350 mg)	$TlH_3(C_2O_4)_2 \cdot 2 H_2O \longrightarrow TlH_3(C_2O_4)_2$	99.9	87.8
	$TlH_3(C_2O_4)_2 \longrightarrow TlHC_2O_4$	182.3	85.6
	$TlHC_2O_4 \longrightarrow 1/2 (Tl_2C_2O_4)$	138.5	82.7
	$Tl_2C_2O_4 \longrightarrow Tl_2O$	232.4	108.8
Thallium(I) bisoxalato diaquo thallate(III) trihydrate (~ 350 mg)	$Tl[Tl(C_2O_4)_2(H_2O)_2] \cdot 3 H_2O \longrightarrow Tl_2C_2O_4$	100.8	39.63
	$Tl_2C_2O_4 \longrightarrow Tl_2O$	150.0	107.0
Pyridinium trisoxalato thallate(III) (~ 300 mg)	$Py_3[Tl(C_2O_4)_3] \longrightarrow Py_3[Tl(C_2O_4)_2]$	179.7	59.3
	$Py_3[Tl(C_2O_4)_2] \longrightarrow Py_2HTl(C_2O_4)_2$	77.6	52.3
	$Py_2HTl(C_2O_4)_2 \longrightarrow 1/2 (Tl_2C_2O_4)$	96.9	62.28
	$Tl_2C_2O_4 \longrightarrow Tl_2O$	181.1	108.7

I Horowitz and Metzger

II Dharwadkar and Karkhanavala

From the results in Table 1 it is clear that the activation energies calculated using the Horowitz and Metzger equation for the decomposition of separate samples of thallium(I) oxalate obtained from different sources (as intermediate decomposition products of different thallium oxalates) are not constant. However, when the activation energies are calculated using the equation modified by Dharwadkar and Karkhanavala, the results are consistent and the activation energy is ~ 109 kJ/mole. In the case of the decomposition of recrystallized thallium(I) oxalate (from water), the calculated activation energy deviates very much from the value obtained from the other samples. This is due in all probability to the difference in fineness of the samples involved. The samples of thallium(I) oxalate obtained as intermediate products of decomposition will contain particles which are ultramicroscopic in size (as the decomposition takes place at a molecular level) and several orders smaller than the particles of the powdered sample. This may be one of the reasons for the observed difference in the activation energies obtained for the two samples.

In the case of the thermal decomposition of thallium(I) monohydro oxalate (unlike the case of thallium(I) oxalate), the activation energies calculated for the recrystallized sample and for the sample obtained as an intermediate decomposition product are almost equal. Visual observation during heating of thallium(I) monohydro oxalate showed that the compound melts at 200°. On continued heating (below the temperature of decomposition of thallium(I) oxalate) it solidifies. Unlike the case of thallium(I) oxalate, the activation energies for the recrystallized (from water) and the intermediate thallium(I) monohydro oxalates coincide, since they decompose from the liquid state. In conclusion, it can be stated that the effects of experimental variables are averaged out by the modified equation.

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