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KINETICS OF SOLID-STATE DECOMPOSITION OF $K_2[VO(O_2)_2F]$ BY A TG STUDY

J.K. GHOSH and G.V. JERE

Department of Chemistry, Indian Institute of Technology, Hauz Khas,
New Delhi-110 016 (India)

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ABSTRACT

The thermal decomposition of $K_2[VO(O_2)_2F]$ was studied by TG at constant temperature as well as at linearly-rising temperature. The thermal decomposition is regulated by random nucleation and the two-dimensional growth mechanism of the nuclei (Avrami–Erofee'v law). The kinetic parameters obtained at three heating rates (6, 8 and 10 °C min^{-1}) are in good agreement; however, the values of kinetic parameters estimated isothermally are smaller than those estimated dynamically.

INTRODUCTION

Solid state isothermal (accumulatory) and photochemical decomposition studies on fluoroperoxo and tetraperoxo species of transition metals have been reported from this laboratory [1–10]. During these investigations, it has been noticed that solid systems, which are not associated with water molecules, could also be subjected to non-isothermal studies to investigate their kinetic features. Although solid $K_2[VO(O_2)_2F]$ is a typical coordination compound with a large formula weight, the only moiety undergoing decomposition is the peroxo group. Hence, this system serves as a nearly-ideal system for kinetic study.

The debate about the merits of isothermal and non-isothermal methods employed for solid-state decompositions to investigate the kinetic features [11–15] prompted the authors to subject the fluoroperoxo complex $K_2[VO(O_2)_2F]$ to TG study. This study constitutes the second set of TG results on fluoroperoxo species reported from this laboratory.

EXPERIMENTAL

The title solid was prepared by the literature method [16]. The dried solid was analysed for some of its constituents and examined by IR spectroscopy. The relevant data are presented in Table 1.

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TABLE 1

Analysis of $K_2[VO(O_2)_2F]$[potassium oxofluorodiperoxo vanadate(V)]

	V	O_A	F	Characteristic vibrational bands (cm^{-1})	
Found (%)	22.6	13.6	8.1	ν(O–O)	ν(V–F)
Calculated (%)	22.3	14.0	8.3	900, 800	475

The percentage loss in weight observed in the TG study agrees with the peroxy oxygen content (O_A) only. The decomposition is represented as

$$K_2[VO(O_2)_2F]_{(s)} \rightarrow K_2VO_3F_{(s)} + O_{2(g)}$$

The decomposition reaction is exothermic and irreversible, and no melting is observed. It falls in the category $A_{(s)} \rightarrow B_{(s)} + C_{(g)}$. For the kinetic study, the dried pristine solid was sieved through a 250 mμ standard mesh, without being subjected to initial grinding.

Non-isothermal TG traces were obtained at three heating rates (6, 8 and 10 °C min^{-1}) in a static air atmosphere using STA-781 (Stanton-Redcroft, U.K.). Using the same apparatus and experimental arrangement, a set of isothermal TG traces was obtained for the title solid in the temperature range 473–523 K.

RESULTS

Non-isothermal

In order to obtain reliable kinetic parameters from the rising-temperature method, three different heating rates (6, 8 and 10 °C min^{-1}) were employed while keeping uniform particle size (250 mμ) and using a small mass (~ 7 mg) of the solid for TG study. Figure 1 shows a typical TG trace for the decomposition of $K_2[VO(O_2)_2F]$. Before attempting kinetic analysis using TG curves, the literature procedure to establish n, the reaction order, by an isothermal run (percentage weight loss α vs. time) at 523 K (which is in the range of the non-isothermal experiment), was followed using the Avrami–Erofee'v relation

$$g(\alpha) = -\log(1-\alpha)^{1/n} = kt$$

for $n = 1$, 2 and 3 (Fig. 2). It can be seen from Fig. 2 that good linear relationship is observed with $n = 2$.

Coats and Redfern's method [17] of evaluating kinetic parameters of a dynamic run is one of the most reliable methods [18–20]. The following equation is used

$$\log g(\alpha)/T^2 = \log\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right) - \frac{E}{2.3RT}$$

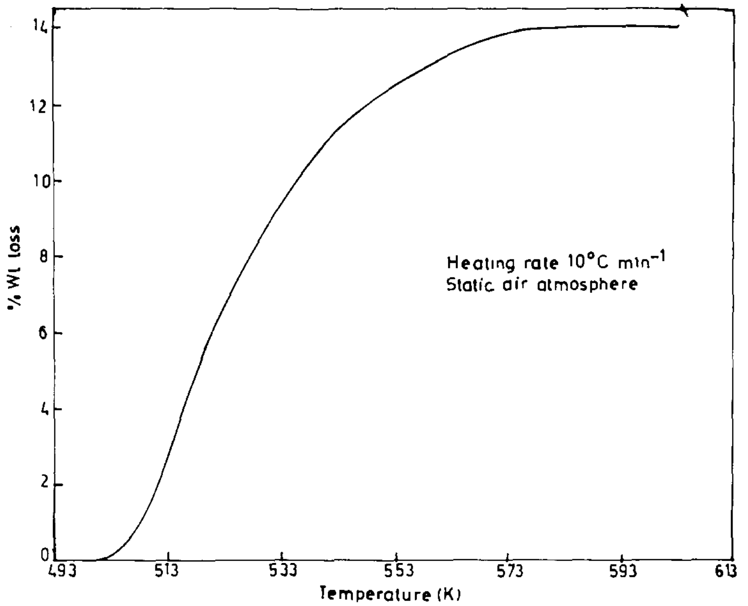

Fig. 1. Thermogravimetric curve for the decomposition for $K_2[VO(O_2)_2F]$.

where T is the absolute temperature, E is the activation energy, A is the frequency factor, R is the gas constant, β is the linear heating rate and $g(\alpha) = \alpha/(1-\alpha)$ for $n = 2$. Hence, log $\alpha/(1-\alpha)T^2$ was plotted against $1/T$ (Fig. 3). Activation energies and frequency factors were calculated from slopes and intercepts, respectively, of these plots at the three heating rates and are listed in Table 2.

Isothermal

The α vs. time plots for isothermal TG are given in Fig. 4. The initial part obeys the Avrami–Erofee'v equation, $-\log(1-\alpha)^{1/2} = k_1 t$ (Fig. 5). The later part obeys a contracting-cube equation, $1-(1-\alpha)^{1/3}$ (Fig. 6). The kinetic parameters are obtained by the method of least-squares for these processes and are listed in Table 3. For sake of comparison and ready

TABLE 2

Kinetic parameters derived from TG at different heating rates in the α range 0.1–0.9

Heating rate (°C min^{-1})	E (kJ mol^{-1})	log A (s^{-1})
6	182.6	16.8
8	183.6	16.6
10	181.0	15.7

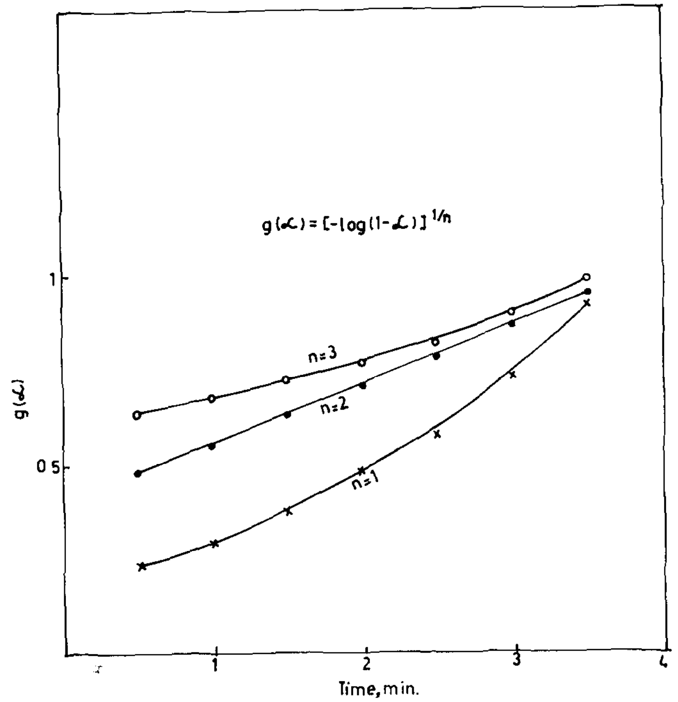

Fig. 2. Plots of g(α) vs. time for the isothermal decomposition of $K_2[VO(O_2)_2F]$ in static air at 523 K.

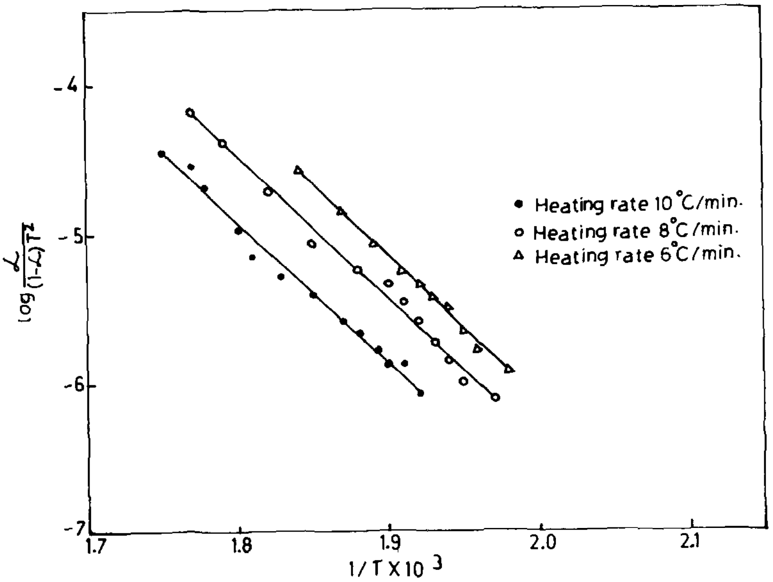

Fig. 3. Plots of $\log[\alpha/(1-\alpha)T^2]$ vs. reciprocal temperature for the decomposition of $K_2[VO(O_2)_2F]$ at different heating rates (Coats and Redfern method).

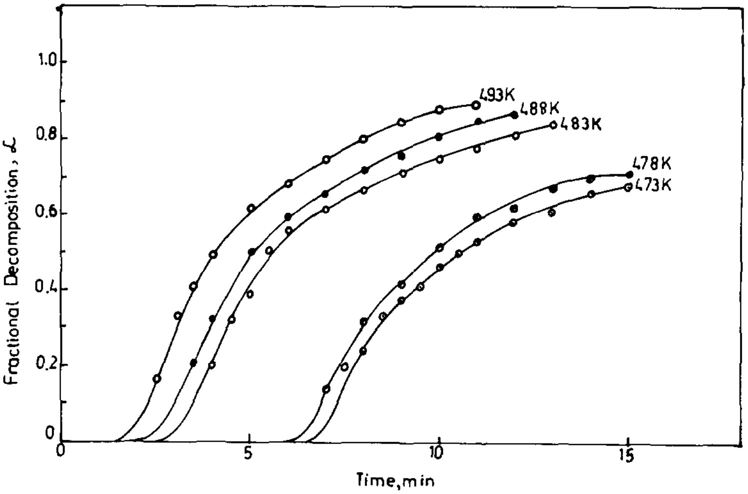

Fig. 4. Isothermal thermogravimetric decomposition of $K_2[VO(O_2)_2F]$.

reference, the activation energies for this solid reported by our earlier study [21] using an accumulatory system with vacuum of 10^{-6} torr are also given in Table 3 and discussed.

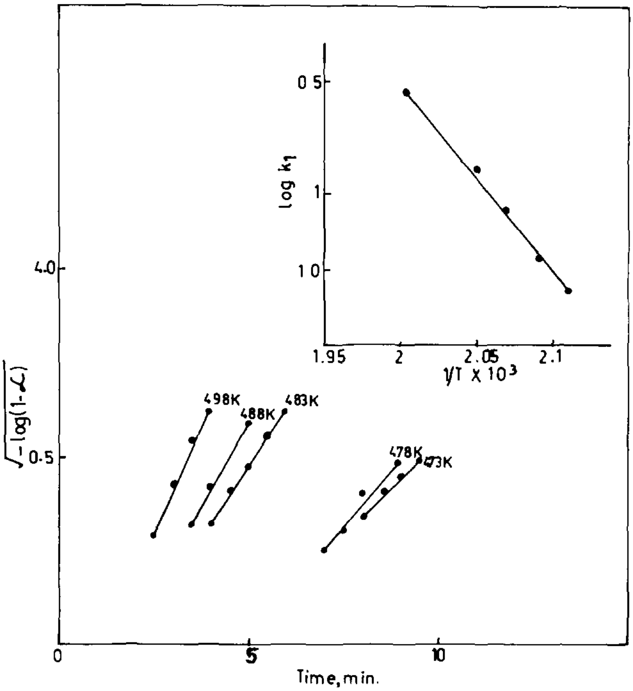

Fig. 5. Plots of the Avrami–Erofee'v equation for the decomposition of $K_2[VO(O_2)_2F]$. The insert shows the Arrhenius plot.

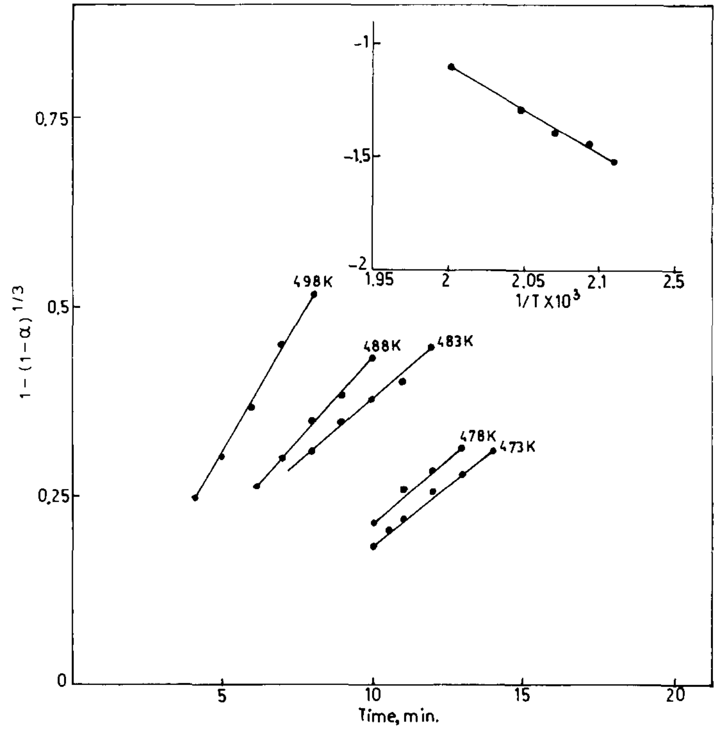

Fig. 6. Plots of the contracting-volume equation for the decomposition of $K_2[VO(O_2)_2F]$. The insert shows the Arrhenius plot.

TABLE 3

Kinetic parameters derived from the Arrhenius plots by means of isothermal TG study in the α range 0.1–0.9

Method	E (kJ mol^{-1})	log A (s^{-1})	$-r$
TG	102.3	8.5	0.99692
	61.2	3.4	0.99744
Accumulatory [21]	108	–	–
	53		

DISCUSSION

The title solid has been subjected to TG study under isothermal and non-isothermal conditions to investigate the kinetic features of its decomposition. The solid undergoes neat decomposition. It is generally accepted that the reaction mechanism can be elucidated from the isothermal methods, whereas non-isothermal methods present some intrinsic difficulties [22], in addition to the heterogeneous nature of decomposition. It is precisely to understand these complexities that the authors subjected the solid to the present TG study.

General observations on kinetic features of $K_2[VO(O_2)_2F]$

Isothermal

It is interesting to note that the Avrami–Erofee'v equation with $n = 2$ is obeyed in the initial part of the decomposition, followed by a contracting-cube equation in both the isothermal studies (accumulatory [21] and TG), thereby showing a similar mechanism of decomposition. Hence, kinetic obedience to the Avrami–Erofee'v equation, ($n = 2$) indicates that the solid undergoes decomposition by random nucleation followed by two-dimensional growth of the nuclei [23].

The E values obtained by two isothermal methods are in good agreement (Table 3). This small difference in the activation energies is to be expected since one set of results is obtained under vacuum and the other in static air conditions.

Non-isothermal

Close agreement is seen in the kinetic parameters obtained using the three heating rates, which demonstrates internal consistency (Table 2). It is worth mentioning here that the kinetic parameters obtained from dynamic TG are considerably larger than those from the isothermal methods (Tables 2 and 3). This experimental finding is similar to the ones observed by Tanaka et al. [15] and also to those of House and coworkers [24–25], who attributed the difference in kinetic parameters to the change in the dynamic decomposition mechanism or the kinetic compensation effect. The observed difference in the kinetic parameters of the title solid may be tentatively attributed to similar factors. Further work is in progress with other fluoroperoxo and tetraperoxo species of transition metals to understand their kinetic features in a general way.

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