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KINETICS OF SOLID STATE DECOMPOSITION OF $K_2[V_2O_3(O_2)_2F_2]$: A TG STUDY

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ABSTRACT

The thermal decomposition of $K_2[V_2O_3(O_2)_2F_2]$ was studied by TG at linearly increasing temperatures and also at constant temperature. The thermal decomposition is governed by random nucleation and the two-dimensional growth mechanism of the nuclei (the 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 kinetic parameters obtained isothermally are smaller than those obtained dynamically.

INTRODUCTION

In earlier publications we have reported solid-state isothermal (accumulatory) and photochemical decomposition of fluoroperoxo and tetraperoxo species of transition metals [1–9]. It has been observed that some of the systems we have studied, without water molecules, could also be subjected to non-isothermal studies for kinetic investigations. The philosophy of non-isothermal kinetics [10] and its parallels with that of isothermal kinetics [11–14] prompted us to subject the fluoroperoxo compound $K_2[V_2O_3(O_2)_2F_2]$ to TG study in order to improve our understanding of its kinetic features. The interesting results obtained are reported in this paper.

EXPERIMENTAL

The title solid was prepared by the literature method [15]. The dried solid was analysed for some of its constituents and examined by means of IR spectroscopy. The relevant data are presented in Table 1.

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

$$K_2[V_2O_3(O_2)_2F_2](s) \rightarrow K_2V_2O_5F_2(s) + O_2(g)$$

TABLE 1

Analysis of $K_2[V_2O_3(O_2)_2F_2]$ [potassium oxofluoroperoxovanadate(V)]

	V	O_A	F	Characteristic vibrational bands (cm^{-1})	
Found (%)	31.5	9.8	11.8	ν(O–O)	ν(V–F)
Calculated (%)	30.9	9.7	11.5	890	430

This decomposition reaction is exothermic and irreversible, and no melting is observed; it falls in the reaction category

$$A(s) \rightarrow B(s) + C(g)$$

For kinetic study, the dried clean solid was sieved through a 250 μm standard mesh, without subjecting it 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 an STA-781 device (Stanton-Redcroft, U.K.). Using the same apparatus and experimental arrangement, a set of isothermal TG traces was also obtained for the title solid in the temperature range 468–538 K.

RESULTS

Non-isothermal

In order to obtain reliable kinetic parameters from the increasing temperature method, three different heating rates (6, 8 and 10 °C min^{-1}) were employed, keeping a uniform particle size (250 μm) and using only a small mass (~ 7 mg) of the solid for the TG study. Figure 1 shows the typical TG trace for the decomposition of the title solid. Before doing kinetic analysis on the basis of the TG curves, the literature procedure of establishing the reaction order n by an isothermal run vs. time at 538 K, which is in the range covered in the non-isothermal experiments, was analysed using the Avrami–Erofee'v relation

$$g(\alpha) = -\log(1-\alpha)^{1/n} = Kt \qquad n = 1, 2, 3$$

It can be seen from Fig. 2 that a good linear relationship is observed with $n = 2$.

The method of Coats and Redfern [16] for evaluating the kinetic parameters of a dynamic run is one of the most reliable [17–19] known. The following equation is used:

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

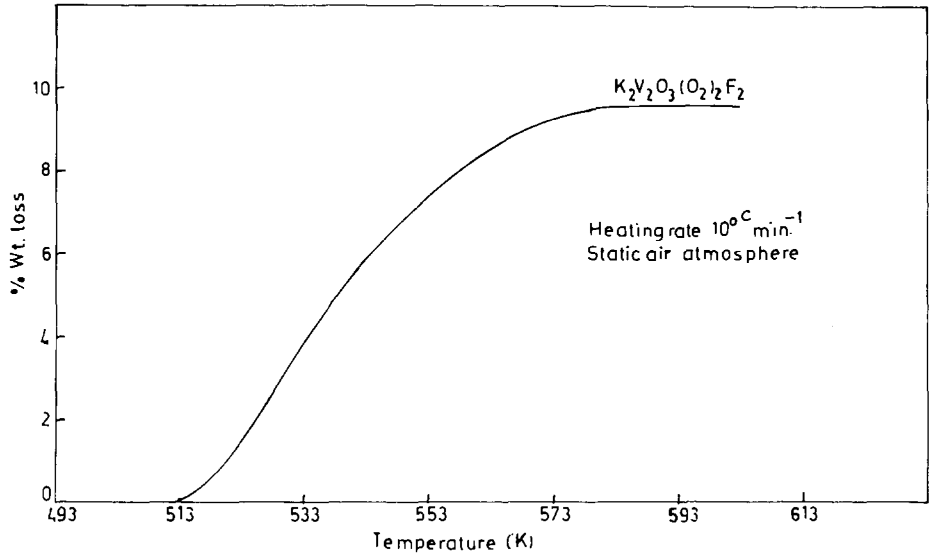

Fig. 1. Thermogravimetric curve for the decomposition of $K_2V_2O_3(O_2)_2F_2$.

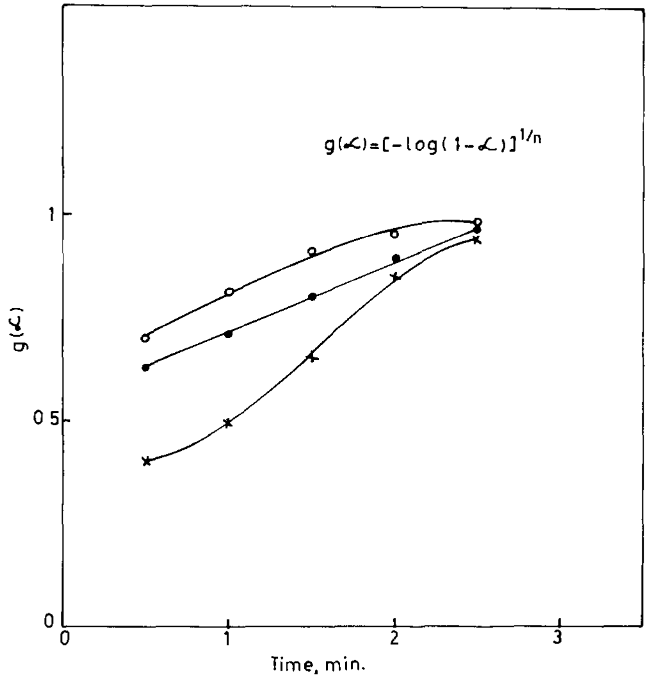

Fig. 2. Plots of $g(\alpha)$vs. time for the isothermal decomposition of $K_2V_2O_3(O_2)_2F_2$ in static air at 538 K.

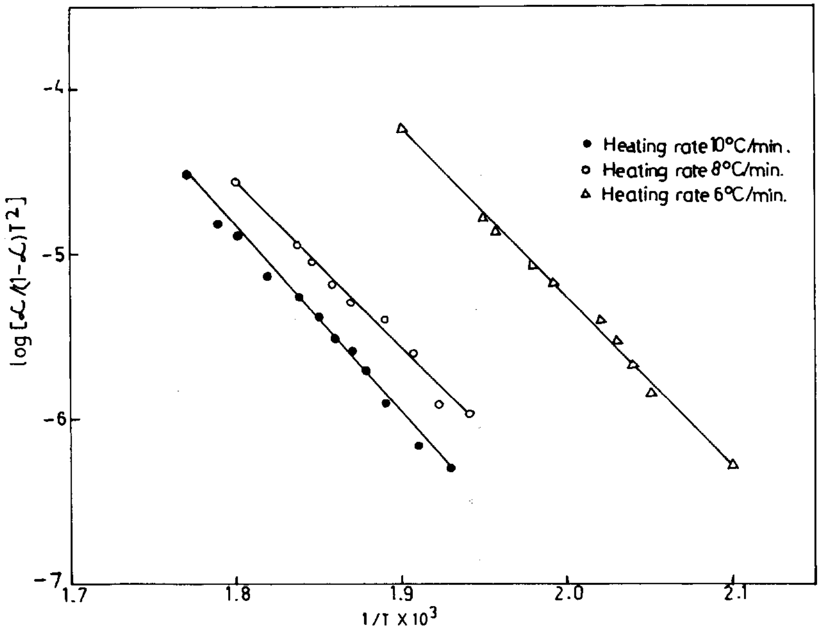

Fig. 3. Plots of log $[\alpha/(1-\alpha)T^2]$ vs. temperature for the decomposition of $K_2V_2O_3(O_2)_2F_2$ at different heating rates (the Coats and Redfern method).

where T is the absolute temperature, 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 the slopes and intercepts, respectively, of these plots for three heating rates and they are listed in Table 2.

Isothermal

The α vs. time plots for isothermal TG are given in Fig. 4. The initial part of the plots obeys the Avrami–Erofee'v equation, $-\log(1-\alpha)^{1/2} = k_1 t$

TABLE 2

Kinetic parameters from TG at different heating rates for the decomposition of $K_2V_2O_3(O_2)_2F_2$ in the α range 0.1–0.9

Heating rate (°C min^{-1})	E (kJ mol^{-1})	log A (s^{-1})
6	195.2	18.8
8	196.5	17.7
10	197.2	18.3

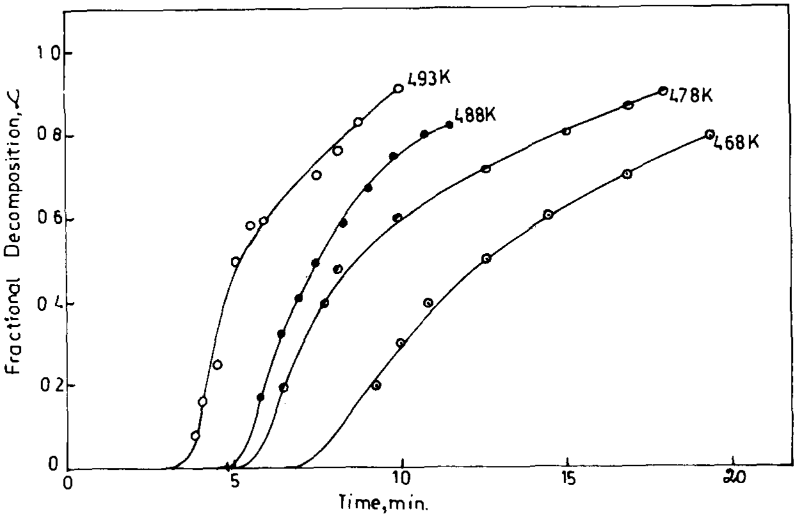

Fig. 4. Isothermal thermogravimetric decomposition of $K_2V_2O_3(O_2)_2F_2$.

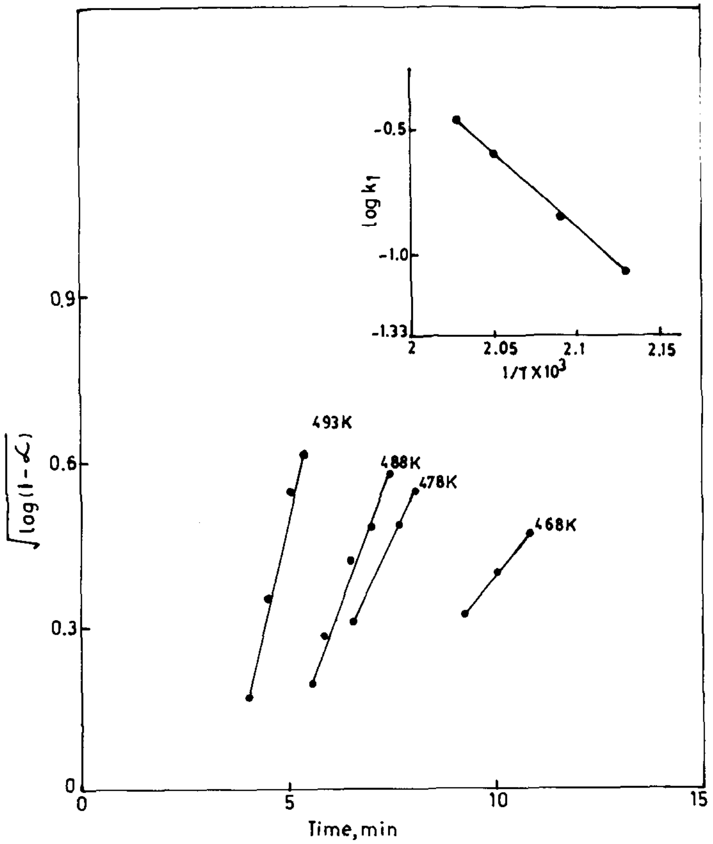

Fig. 5. Plots of the Avrami–Erofee'v equation for the decomposition of $K_2V_2O_3(O_2)_2F_2$ (inset: Arrhenius plot).

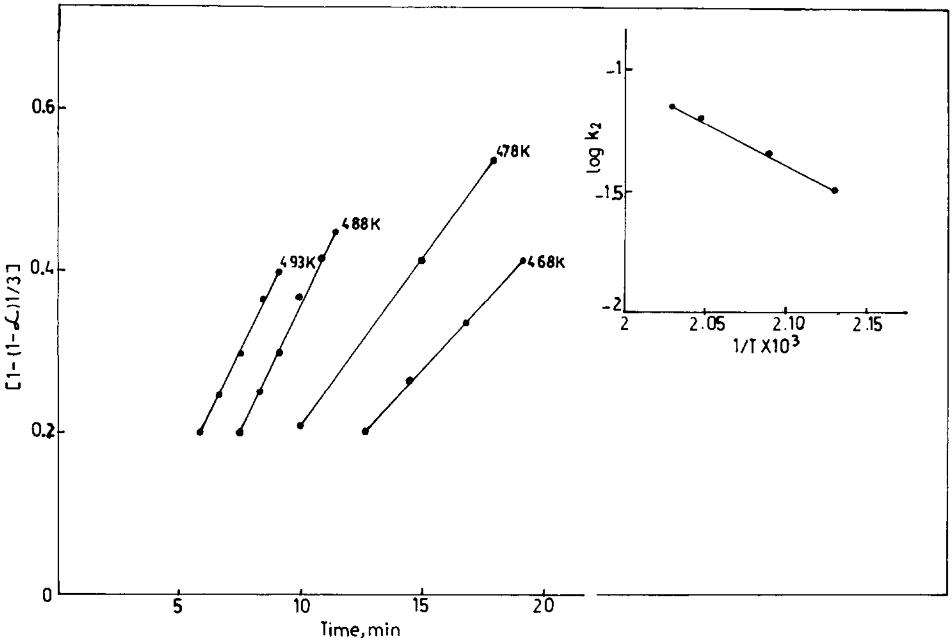

Fig. 6. Plots of the contracting-volume equation for the decomposition of $K_2V_2O_3(O_2)_2F_2$ (inset: Arrhenius plot).

(Fig. 5), while the later part obeys the contracting-cube equation, $1-(1-\alpha)^{1/3}=k_2t$ (Fig. 6). The kinetic parameters were obtained by the method of least squares for these processes and they are listed in Table 3. For the sake of comparison and easy reference, the activation energies for this solid, reported in our earlier publication [8] on the basis of work using an accumulatory system with a vacuum of 10^{-6} Torr, are also given in Table 3 and discussed below.

TABLE 3

Kinetic parameters derived from the Arrhenius plots for the decomposition of $K_2V_2O_3(O_2)_2F_2$ by means of isothermal studies

Method	E (kJ mol^{-1})	log A (s^{-1})	$-r$
TG			
Avrami–Erofee'v	110.9	9.7	0.99761
Contracting cube	63.0	3.8	0.99501
Accumulatory [8]	168 105	–	–

DISCUSSION

The solid undergoes straightforward decomposition. It is generally accepted that the reaction mechanism can be elucidated using isothermal methods, whereas non-isothermal methods present some intrinsic difficulties of their own [20], in addition to the heterogeneous decomposition involved. It was to investigate precisely these complexities that we subjected the title solid to TG study.

General observations on the kinetic features of $K_2[V_2O_3(O_2)_2F_2]$

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 contracting-cube equation dependence in both isothermal studies, the accumulatory method [8] and TG, indicating 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 [21].

The E_a values obtained by the two isothermal TG methods are 168 and 110.9 kJ mol^{-1} (Table 3). This difference is significant between the vacuum and the static air conditions. It may arise from structural elements or other factors, but it is difficult to account in a quantitative way for the difference. By and large, the order and magnitudes of the E_a values obtained are the same.

Non-isothermal

Close agreement is seen in the kinetic parameters obtained with three different heating rates, indicating internal consistency (Table 2). It is relevant to mention here that the kinetic parameters obtained from the dynamic TG are considerably larger than those obtained using the isothermal methods (Tables 2 and 3). This experimental finding is similar to those of Tanaka and Sadamoto [22] and also those of House and coworkers [23,24]. The difference in the kinetic parameters for the title solid may be tentatively attributed to the decomposition mechanism ($n = 2$).

Further work is in progress with other fluoroperoxo and tetraperoxo species of transition metals to improve our general understanding of their kinetic features under both static and dynamic conditions.

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