Thermochimica Acta, 136 (1988) 73–80
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

KINETICS OF SOLID STATE DECOMPOSITION OF $K_3[Nb(O_2)_4]$ AND $K_3[Ta(O_2)_4]$: A THERMOGRAVIMETRIC STUDY

J.K. GHOSH and G.V. JERE

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

(Received 15 January 1988)

ABSTRACT

The thermal decomposition of $K_3[Nb(O_2)_4]$ and $K_3[Ta(O_2)_4]$ has been studied by TG at linearly rising temperature and also at constant temperatures. For both these solids the thermal decompositions are governed by unimolecular decay law in the entire range of temperature investigated. The kinetic parameters obtained under isothermal conditions are smaller than those obtained under dynamic conditions.

INTRODUCTION

Work is in progress in this laboratory on solid state isothermal (accumulatory) and photochemical decomposition studies on fluoroperoxo and tetraperoxo species of transition metals [1–10]. During these investigations, it has been noticed that solid systems, which are not associated with water molecules, could be subjected to non-isothermal studies also, for understanding their kinetic features. Although the title solids are typical coordination compounds with large molecular formulations, the only moiety undergoing decomposition is the peroxo group. Hence, these systems serve ideally for kinetic studies.

The debate about the merits and demerits of both isothermal as well as non-isothermal methods employed for solid state decompositions to understand the kinetic features [11–15], prompted the authors to subject the tetraperoxo complexes, $K_3[Nb(O_2)_4]$ and $K_3[Ta(O_2)_4]$ to TG study. The first set of results of TG study on tetraperoxo complexes are reported in this communication.

EXPERIMENTAL

The title solids were prepared by literature methods [16,17]. The dried solids were test checked for some of their constituents and examined by IR

0040-6031/88/$03.50

TABLE 1
Analysis of $K_3[Nb(O_2)_4]$ (potassium tetraperoxo niobate(V)) and $K_3[Ta(O_2)_4]$ (potassium tetraperoxo tantalate(V))

	$K_3[Nb(O_2)_4]$			Characteristic vibrational bands (cm^{-1})	$K_3[Ta(O_2)_4]$			Characteristic vibrational bands (cm^{-1})
	K	Nb	O_A		K	Ta	O_A	
Found (%)	34.8	27.6	18.3		27.8	42.6	14.4	
Calculated (%)	34.6	27.5	18.95	815, ν(O–O)	27.5	42.5	15.0	810, ν(O–O)

spectroscopy. The relevant data are presented in Table 1. In both these solids the percentage loss in weight observed in the TG study tallies with the peroxy oxygen content (O_A) only. The decompositions are represented as

$$K_3[Nb(O_2)_4]_{(s)} \rightarrow K_3NbO_{4(s)} + 2O_2(g) \tag{1}$$

$$K_3[Ta(O_2)_4]_{(s)} \rightarrow K_3TaO_{4(s)} + 2O_2(g) \tag{2}$$

The decomposition reactions (1) and (2) are irreversible and exothermic and no melting of the solids is observed so they fall into the category $A_{(s)} \rightarrow B_{(s)} + C_{(g)}$.

Non-isothermal TG traces were obtained at three heating rates (6, 10, 20 °C min^{-1}) in static air atmosphere using STA-781 (Stanton-Redcroft, U.K.). Using the same apparatus and experimental arrangement, sets of isothermal TG traces were obtained for the title solids, in the temperature range 453–478 K and 448–468 K, respectively.

RESULTS

Non-isothermal

In order to obtain reliable kinetic parameters from the rising temperature method (TG study), three different heating rates (6, 10, 20 °C min^{-1}) are employed, taking a small mass (~ 7 mg) of both the solids. Figure 1 shows typical "TG" traces for the decompositions of the title solids.

The Coats and Redfern method [18] for evaluating kinetic parameters of a dynamic run is one of the commonly employed methods [19–21].

The following equation is used

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

where, T is the absolute temperature, E and A are activation energy and

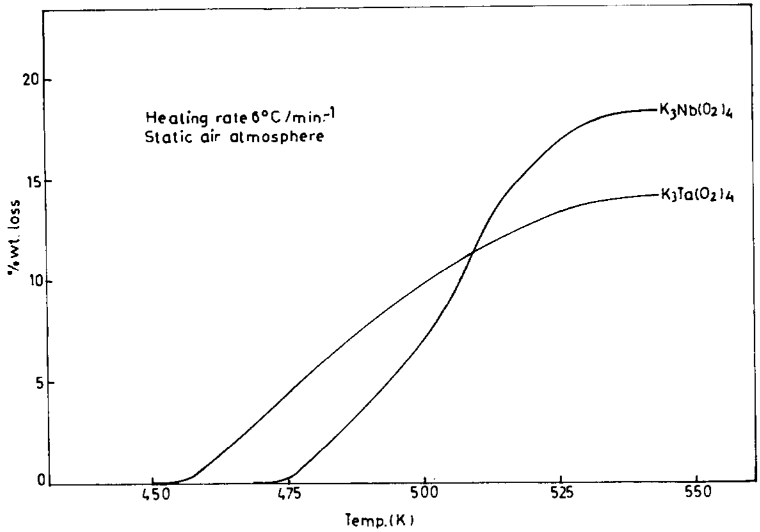

Fig. 1. Thermogravimetric curve for the decomposition of $K_3Nb(O_2)_4$ and $K_3Ta(O_2)_4$.

frequency factor, respectively, R is the gas constant, β is the linear heating rate and

$$g(\alpha) = \left[\frac{1-(1-\alpha)^{1-n}}{(1-n)}\right]$$

where, α is the fractional decomposition and n is the reaction order.

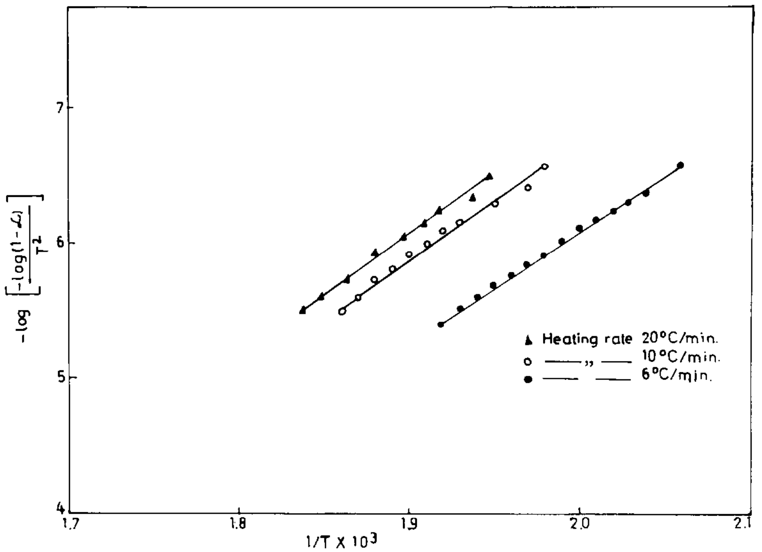

Fig. 2. Plots of $-\log[-\log(1-\alpha)/T^2]$ vs. temp. for the decompostion of $K_3Nb(O_2)_4$ at different heating rates (Coats and Redfern [18] method).

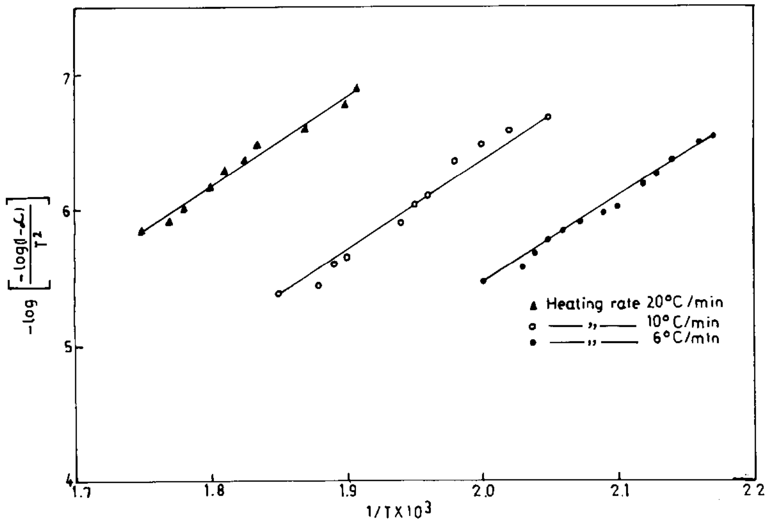

Fig. 3. Plots of $-\log[-\log(1-\alpha)/T^2]$ vs. temp. for the decomposition of $K_3Ta(O_2)_4$ at different heating rates (Coats and Redfern [18] method).

For a number of assumed values of n, $\log[1-(1-\alpha)^{1-n}/T^2(1-n)]$ versus $1/T \times 10^3$ is plotted and the correct value of n for a given thermal decomposition reaction gives a straight line. It is seen from Figs. 2 and 3 that linear plots are obtained for $n = 1$. Activation energies and frequency factors were calculated from slopes and intercepts respectively, of these plots for the three heating rates and are listed in Table 2.

Isothermal

The α versus time plots for both the solids are given in Figs. 4 and 5. It is seen from these figures that the mode of decomposition of $K_3[Nb(O_2)_4]$ and $K_3[Ta(O_2)_4]$ is predominantly deceleratory in nature. The reaction in each case obeys the unimolecular decay law, i.e. the plot of $-\log(1-\alpha)$ versus

TABLE 2
Kinetic parameters derived from TG at different heating rates in the α range 0.1–0.9

Sample	Heating rate (°C min^{-1})	E(kJ mol^{-1})	log A (s^{-1})
$K_3Nb(O_2)_4$	6	148.4	13.4
	10	153.1	13.5
	20	160.5	13.2
$K_3Ta(O_2)_4$	6	119.1	10.9
	10	121.3	10.3
	20	123.2	9.5

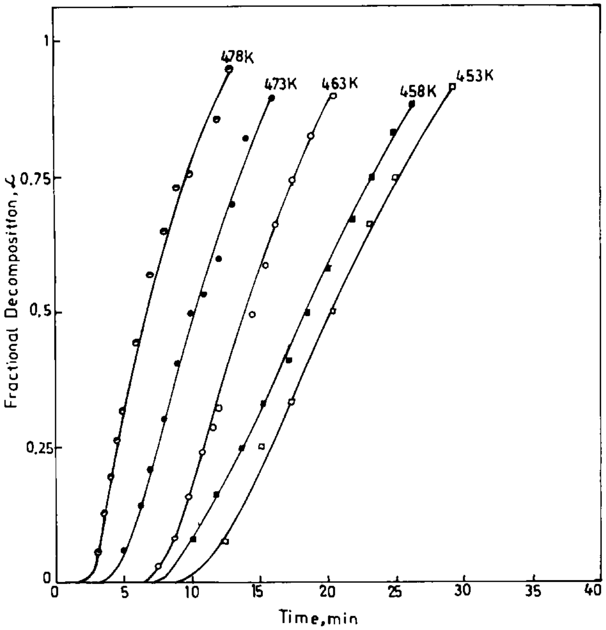

Fig. 4. Isothermal thermogravimetric decompositon of $K_3Nb(O_2)_4$.

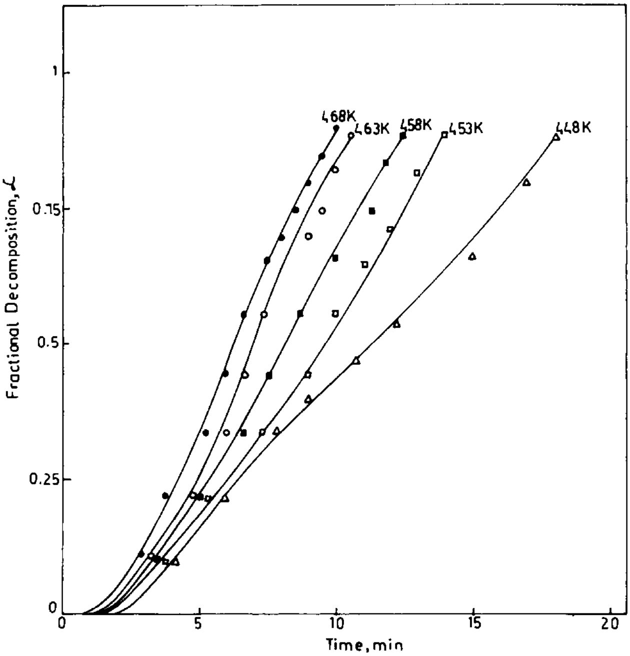

Fig. 5. Isothermal thermogravimetric decomposition of $K_3Ta(O_2)_4$.

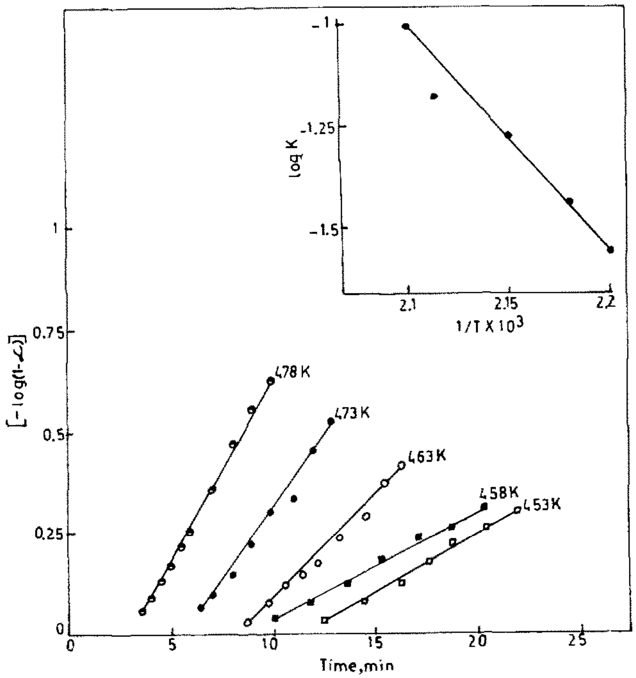

Fig. 6. Plots of unimolecular decay law for the decomposition of $K_3Nb(O_2)_4$. Inset, Arrhenius plot.

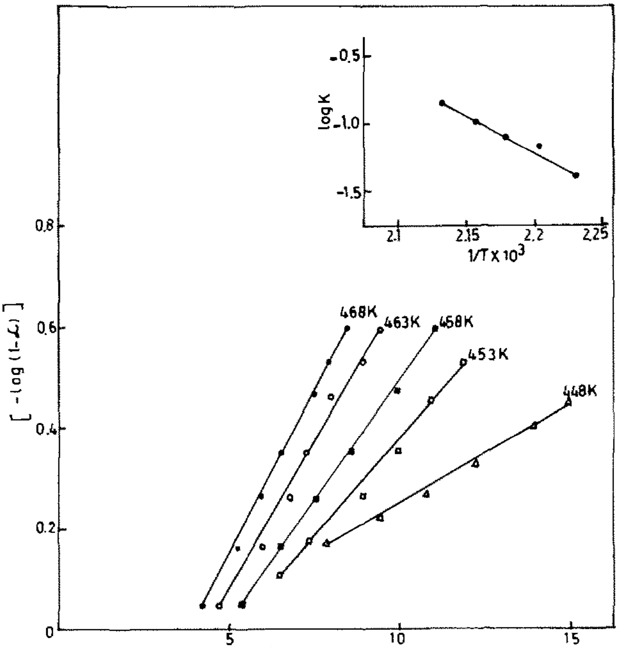

Fig. 7. Plots of unimolecular decay law for the decomposition of $K_3Ta(O_2)_4$. Inset, Arrhenius plot.

TABLE 3

Kinetic parameters derived from the Arrhenius plots by means of isothermal studies

Method	Sample	E (kJ mole^{-1})	log A (s^{-1})	$-r$
TG	$K_3Nb(O_2)_4$	103.8	8.57	0.99869
	$K_3Ta(O_2)_4$	93.4	8.06	0.99058
Accumulatory [22]	$K_3Nb(O_2)_4$	126.53	–	–
	$K_3Ta(O_2)_4$	95.86	–	–

time is linear over a long period of time (Figs. 6 and 7). The activation energies and frequency factors for the solids are deduced from the respective Arrhenius plots (inset Figs. 6 and 7) and are listed in Table 3. For the sake of comparison and ready reference, the activation energies for these solids reported by our earlier study [22] using an accumulatory system with vacuum of 10^{-6} Torr, are also given in Table 3 and discussed.

DISCUSSION

The solids undergo 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 of their own [23], in addition to the heterogeneous nature of decomposition. It is precisely to understand these complexities that the authors subjected the present solids to TG study.

General observations on kinetic features of $K_3[Nb(O_2)_4]$ and $K_3[Ta(O_2)_4]$

Isothermal

It is interesting to note that unimolecular decay law fits well and is obeyed over a long period of time in both the isothermal studies (accumulatory [22], TG), thereby showing a similar mechanism of decomposition. Kinetic obedience to unimolecular decay law indicates facile nucleation, attributed to the twin factors, fine size of the crystallites of the reactant [17] and the strain imposed by four peroxide rings. It is probable that the first step in the decomposition of the anion is the breaking of the metal–peroxide bonds, which would release the strain present in the system. After cleavage, lattice rearrangement may occur with the evolution of oxygen and the formation of potassium tetraoxoniobate(V), K_3NbO_4 and tetraoxotantalate(V), K_3TaO_4.

The E values obtained by the two isothermal methods are comparable, (126.53 and 103.8 kJ mol^{-1}; 95.86 and 93.4 kJ mol^{-1}) (Table 3) but the small differences in the activation energies are to be expected since one set of results is obtained under vacuum and others are in static air conditions.

Non-isothermal

Close agreement is seen in the kinetic parameters obtained with three heating rates, showing internal consistency (Table 2), but the kinetic parameters obtained from the dynamic TG are larger than those from the isothermal methods (Tables 2 and 3). Further work is in progress with other fluoroperoxo and tetraperoxo species of transition metals to understand their kinetic features in a generalized way.

ACKNOWLEDGEMENT

J.K.G. is grateful to the Indian Institute of Technology, Delhi, for a research fellowship.

REFERENCES

1 G.V. Jere and S.M. Kaushik, J. Therm. Anal., 18 (1980) 277.
2 G.V. Jere and S.M. Kaushik, Thermochim. Acta, 36 (1980) 307.
3 G.V. Jere and S.M. Kaushik, J. Photochem., 12 (1980) 275.
4 G.V. Jere and S.M. Kaushik, J. Solid State Chem., 33 (1980) 145.
5 G.V. Jere, M.K. Gupta, L. Surendra and S.M. Kaushik, Can. J. Chem., 60 (1982) 1891.
6 G.V. Jere, L. Surendra, S.M. Kaushik and M.K. Gupta, Thermochim. Acta, 43 (1981) 379.
7 J.K. Ghosh and G.V. Jere, J. Photochem. Photobiol. A, 40 (1987) 295.
8 J.K. Ghosh and G.V. Jere, Thermochim. Acta, 114 (1987) 347.
9 J.K. Ghosh and G.V. Jere, Thermochim. Acta, 117 (1987) 73.
10 J.K. Ghosh and G.V. Jere, Thermochim. Acta, 118 (1987) 229.
11 D.W. Johnson, Jr. and P.K. Gallagher, J. Phys. Chem., 76 (1972) 1474.
12 T.J.W. Bruijn, W.A. Dejong and P.J. Denberg, Thermochim. Acta, 45 (1981) 315.
13 T.B. Tang and M.M. Chaudhri, J. Therm. Anal., 18 (1980) 247.
14 S.R. Dharwadkar, M.S. Chandrasekharaih and M.D. Karkhanavala, Thermochim. Acta, 25 (1978) 372.
15 H.Tanaka and T. Sadamoto, Thermochim. Acta, 54 (1982) 273.
16 N. Vuletic and C. Djordjevic, J. Less-Common Met., 45 (1976) 85.
17 G. Brauer, Handbook of Preparative Inorganic Chemistry, Vol. 2, Academic Press, New York, 1965, p. 1325.
18 A.W. Coats and J.P. Redfern, Nature (Lond), 201 (1964) 68.
19 J. Zsako, J. Therm. Anal., 5 (1973) 239.
20 V.M. Gorbachev, J. Therm. Anal., 8 (1975) 349.
21 H. Tanaka, S. Ohshima, S. Ichiba and H. Negita, Thermochim. Acta, 48 (1981) 137.
22 G.V. Jere, L. Surendra and M.K. Gupta, Thermochim. Acta, 63 (1983) 229.
23 W.W. Wendlandt, Thermal Analysis, 3rd edn., Wiley-Interscience, New York, 1986.