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SOLID STATE DECOMPOSITION STUDY ON TETRAPEROXO SPECIES OF TRANSITION METALS. PART II. KINETICS OF ISOTHERMAL DECOMPOSITION OF $K_4[Ti(O_2)_4] \cdot 2H_2O$

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ABSTRACT

The isothermal decomposition of $K_4[Ti(O_2)_4] \cdot 2H_2O$ has been investigated using a constant volume apparatus in the temperature range 394–428 K to gain an insight into its kinetic features. The α–time plots are deceleratory in nature and kinetic obedience to the unimolecular decay law is observed for the initial stage of the decomposition. The contracting volume equation fits the latter part of the decomposition process well. Instantaneous nucleation has been attributed to two factors, namely the loss of lattice water preceding the peroxide decomposition, thereby generating defects and also the strain imposed by four peroxide rings. The activation energies are 61.9 and 44 kJ mol^{-1}.

INTRODUCTION

Solid state thermal decomposition studies on tetraperoxo complexes of transition metals are limited to a few elements only, i.e., Nb, Ta and Cr [1,2]. The results obtained on niobium and tantalum species encouraged the authors to extend their studies to Gr IVA elements. The present communication reports the kinetics of the isothermal decomposition of potassium tetraperoxo titanate (IV), $K_4[Ti(O_2)_4] \cdot 2H_2O$. This study constitutes the second set of results on tetraperoxo species reported from this laboratory.

EXPERIMENTAL

Potassium tetraperoxo titanate (IV), $K_4[Ti(O_2)_4] \cdot 2H_2O$ was prepared by the Schwartz and Giese method [3]. The constituents of the dried solid were analysed and examined by IR. The relevant data are given in Table 1.

The percentage weight loss (26.2%) observed in the TG agrees well with the combined amount of peroxy oxygen content (O_A) and lattice water. The decomposition is represented by the following equation

$$K_4[Ti(O_2)_4] \cdot 2H_2O_{(s)} \rightarrow K_4TiO_{4(s)} + 2O_2(g) + 2H_2O(\text{condensed})$$

TABLE 1

Elemental and IR analysis of $K_4[Ti(O_2)_4]\cdot 2H_2O$

	Chemical composition (%)				% Weight loss on heating [a]	Characteristic vibrational bands, (C–O)
	K	Ti	$O_A(\frac{1}{2}O_2^{2-})$	H_2O		
Experimental	43.2	12.4	17.1	9.3	26.2	850
Calculated	42.4	13	17.4	9.7	27.1	870

[a] TG study.

The stable solid obtained by thermal decomposition is tetraoxotitanate. This decomposition is irreversible and no melting of the solid is observed. The dried sample was sieved through a 250 μm mesh sieve without grinding and used for the kinetic studies. The kinetics of the decomposition was studied using the constant volume apparatus (accumulatory system) following the procedure outlined in our earlier publications [4–7]. The water vapour evolved was condensed in a liquid air trap as in our previous studies [8].

RESULTS

The isothermal decomposition of $K_4[Ti(O_2)_4]2H_2O$ was studied in the temperature range 394–427.5 K. The fractional decomposition α vs. time plots (Fig. 1) show that the decomposition reaction is deceleratory. The

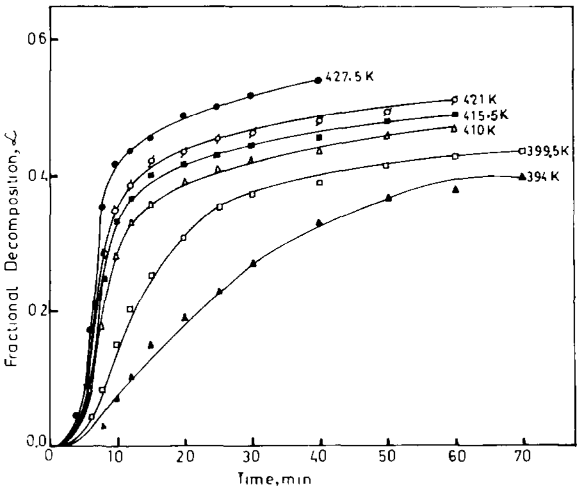

Fig. 1. Isothermal decompositon of $K_4[Ti(O_2)_4]\cdot 2H_2O$.

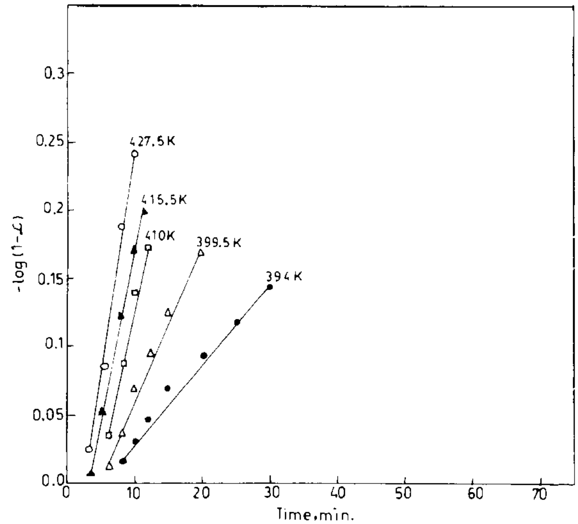

Fig. 2. Plots of the unimolecular decay law for the decomposition of $K_4[Ti(O_2)_4]\cdot 2H_2O$.

induction and acceleratory regions are practically absent at all the temperatures studied. The α–time data for the initial part of the decomposition reaction fit the unimolecular decay law, i.e., $-\log(1-\alpha) = K_1 t$ (Fig. 2). The activation energy of the process, deduced from an Arrhenius plot (Fig. 3) is

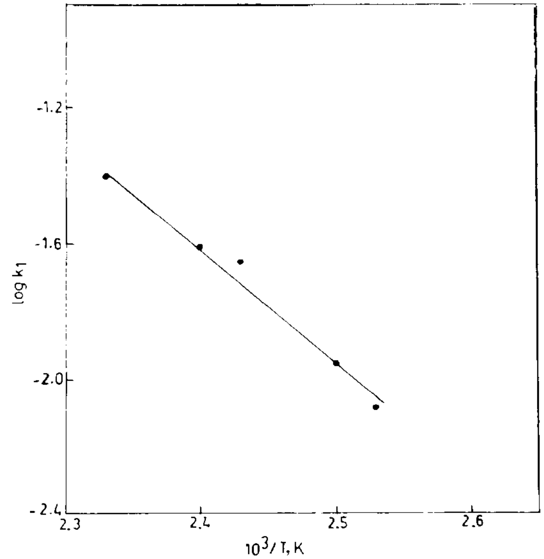

Fig. 3. Arrhenius plot of unimolecular decay constants of $K_4[Ti(O_2)_4]\cdot 2H_2O$. Correlation coefficient $(-\gamma) \rightarrow 0.99$.

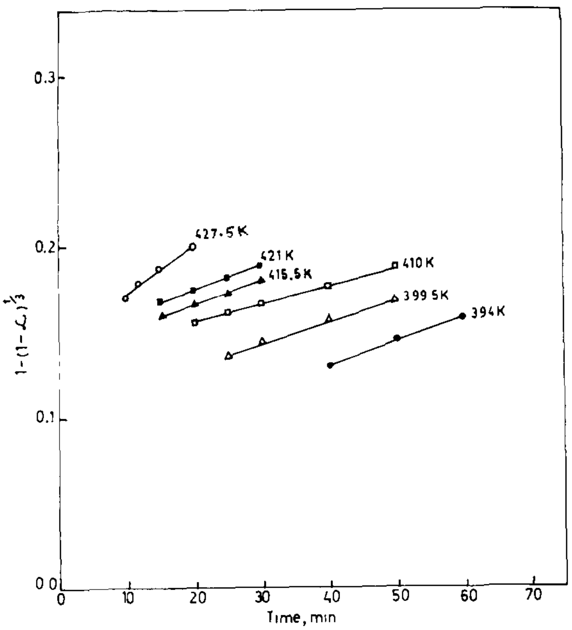

Fig. 4. Plots of the contracting volume equation for the decomposition of $K_4[Ti(O_2)_4]\cdot 2H_2O$.

61.9 kJ mol^{-1}. The subsequent stage of the decomposition obeys the contracting volume equation, i.e., $1-(1-\alpha)^{1/3}=K_2t$ (Fig. 4), and the activation energy for this stage is 44 kJ mol^{-1} (Fig. 5).

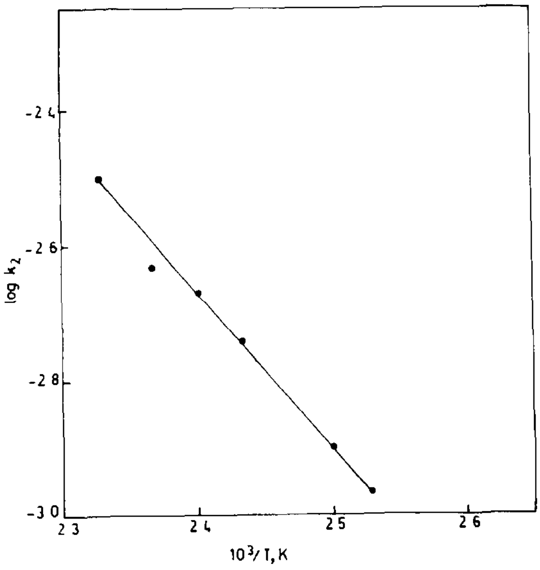

Fig. 5. Arrhenius plot of contracting volume rate constants of $K_4[Ti(O_2)_4]\cdot 2H_2O$. Correlation coefficient $(-\gamma)\rightarrow 0.99$.

DISCUSSION

The title solid is a typical coordination compound. In the anion $[Ti(O_2)_4]^{4-}$, titanium is surrounded by four peroxo groups which are triangularly linked and bidentate in nature, like $[Nb(O_2)_4]^{3-}$, $[Ta(O_2)_4]^{3-}$ and $[Cr(O_2)_4]^{3-}$ [1,2]. Such a configuration constitutes a highly strained ring system around the metal atom and is readily susceptible to decomposition [1,2].

It is seen from the kinetic analysis of $K_4[Ti(O_2)_4] \cdot 2H_2O$ that the unimolecular decay law governs the initial part of the reaction and that the subsequent stage of the reaction obeys the contracting volume equation.

Water, which is held within a lattice system in $K_4[Ti(O_2)_4] \cdot 2H_2O$ is lost before the peroxide decomposition, generating defects in the solid. This feature has also been observed in the decomposition of fluoroperoxozirconates [9,10].

Hence, it is probably that the dehydration step preceding the peroxide decomposition, plays an important role in the instantaneous nucleation and the consequent kinetic obedience to the unimolecular decay law in the initial part of the decomposition.

The application of the contracting sphere equation to the later part of the decomposition reaction shows that the reaction on the surface is complete and the reaction interface has begun penetrating the bulk of the solid.

It is interesting to note that the decomposition of $K_3Nb(O_2)_4$ and $K_3Ta(O_2)_4$ obey the unimolecular decay law over a long period of time. Facile nucleation in these two solids has been attributed to the fine size of the crystallites and also the strain imposed by four peroxide rings [1]. The kinetics of the decomposition of $K_3Cr(O_2)_4$ are also governed by the first-order equation for autocatalytic reactions [2].

These exploratory results show that tetraperoxo complexes of transition metals undergo uniform thermal decomposition and are amenable to kinetic investigation.

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