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SOLID STATE DECOMPOSITION STUDIES ON TETRAPEROXO SPECIES OF TRANSITION METALS. KINETICS OF THE ISOTHERMAL DECOMPOSITION OF $K_3Nb(O_2)_4$ AND $K_3Ta(O_2)_4$

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ABSTRACT

The kinetics of the isothermal decomposition of $K_3Nb(O_2)_4$ and $K_3Ta(O_2)_4$ have been investigated using a constant volume apparatus in the temperature ranges 428–451 and 416–464 K, respectively. The α–time plots for both these solids are predominantly deceleratory in nature. They obey the unimolecular decay law $-\log(1-\alpha) = kt$ over a long period of time. Facile nucleation has been attributed to two factors, namely the fine size of the crystallites of the reactants and the strain imposed by four peroxide rings. The activation energies for $K_3Nb(O_2)_4$ and $K_3Ta(O_2)_4$ are 126.53 and 95.86 kJ mole^{-1}, respectively.

INTRODUCTION

Work is in progress in this laboratory on the solid state decomposition studies of the fluoroperoxo species of the transition elements [1–11]. The encouraging results obtained on these solids prompted the authors to extend the studies to the tetraperoxo complexes of the transition elements.

The present communication forms part of the same series of extended investigations and reports the kinetics of the isothermal decomposition of two tetraperoxo complexes, viz. (i) $K_3Nb(O_2)_4$, Potassium tetraperoxoniobate(V), hereafter referred to as solid "A" and (ii) $K_3Ta(O_2)_4$, potassium tetrapeoroxotantalate(V), hereafter referred to as solid "B".

This study constitutes the first set of results on tetraperoxo species in the solid state.

EXPERIMENTAL

The compound potassium tetraperoxoniobate(V), $K_3Nb(O_2)_4$, (solid A) was prepared by the method reported by Vuletic and Djordjevic [12]. The dried solid was test analysed for its constituents and examined by IR spectra. The relevant data are given in Table 1.

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TABLE 1

Elemental and IR analysis of $K_3Nb(O_2)_4$

	Chemical composition (%)			%weight loss on heating [a]	Characteristic vibrational bands (cm^{-1})
	K	Nb	$O_A(\frac{1}{2}O_2^{2-})$		
Experimental	34.5	27.6	18.9	19.0	815, ν(O–O)
Calculated	34.6	27.5	18.95	18.95	

[a] TG study.

A TG study of the sample shows that the decomposition starts around 423 K. The percentage loss in weight (19.0%) observed in TG agrees well with the peroxy oxygen content (O_A value) only. The decomposition is represented as

$$K_3Nb(O_2)_4(s) \rightarrow K_3NbO_4(s) + 2\ O_2(g) \tag{1}$$

The compound potassium tetraperoxotantalate(V), $K_3Ta(O_2)_4$, (solid B) was prepared by the method reported in Brauer's monograph [13]. The dried solid was test analysed for its constituents and examined by IR spectra. The relavant data are given in Table 2.

The percentage loss in weight (15.0%) observed in TG is attributed to the peroxy oxygen content only. The decomposition is represented as

$$K_3Ta(O_2)_4(s) \rightarrow K_3TaO_4(s) + 2\ O_2(g) \tag{2}$$

It is of relevance to mention here that both these solids are not associated with lattice water and the only moieties undergoing decomposition are the peroxo groups. The stable solids obtained by thermal decomposition are

TABLE 2

Elemental and IR analysis of $K_3Ta(O_2)_4$

	Chemical composition (%)			% weight loss on heating [a]	Characteristic vibrational bands (cm^{-1})
	K	Ta	$O_A(\frac{1}{2}O_2^{2-})$		
Experimental	27.6	42.6	14.9	15.0	810, ν(O–O)
Calculated	27.5	42.5	15.0	15.0	

[a] TG study.

tetraoxo metallates. These decompositions are irreversible, exothermic and no melting of the solids is observed.

The title solids, being obtained in the form of very fine crystallites [13], were subjected to isothermal decomposition studies without any pretreatment. The present investigations were carried out in the appropriate temperature range for each solid, by the constant volume apparatus (accumulatory system) following the procedure described in our earlier publications [1–11].

RESULTS

Solid A, $K_3Nb(O_2)_4$

The α–time plots for the isothermal decomposition of this solid in the temperature range 428–451 K are given in Fig. 1. They show that the

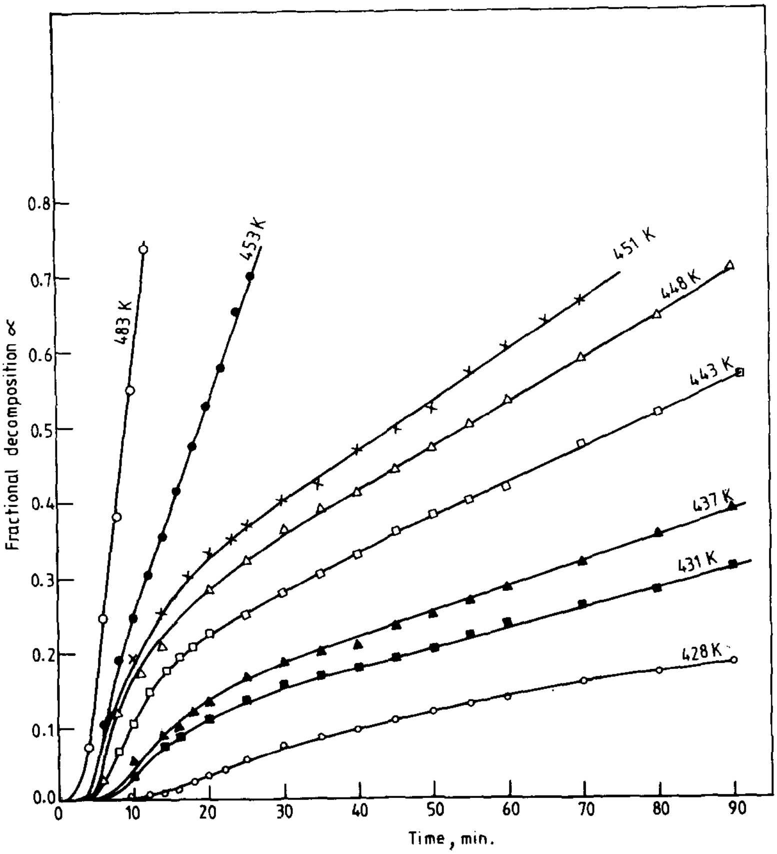

Fig. 1. Isothermal decomposition of $K_3Nb(O_2)_4$.

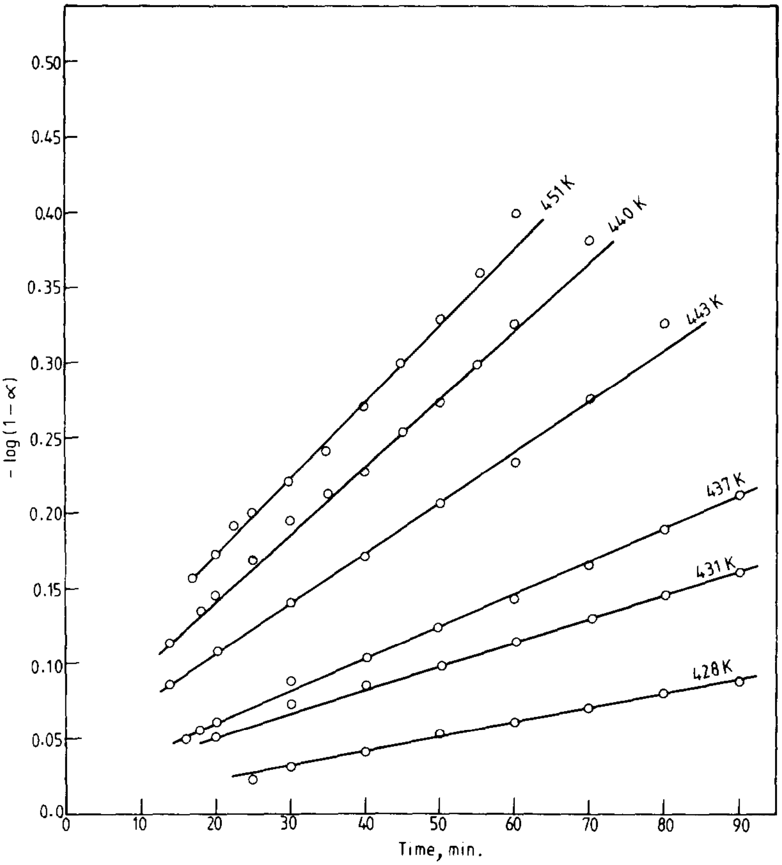

Fig. 2. Plots of the unimolecular decay law for the decomposition of $K_3Nb(O_2)_4$.

decomposition is predominantly deceleratory in nature. It is seen that short induction and acceleratory regions are observed for a period of about 10–12 min at the lowest temperature investigated (428 K). This goes on diminishing as the temperature increases (Fig. 1). The maximum value of α obtained is 0.7. The reaction obeys the unimolecular decay law, i.e. the plot of $-\log(1 - \alpha)$ vs. time is linear over a long period of time (Fig. 2). The activation energy deduced from the Arrhenius plot (Fig. 3) is 126.53 kJ mole^{-1}.

Solid B, $K_3Ta(O_2)_4$

The results of isothermal decomposition studies in the temperature range 416–464 K for solid B are presented in Figs. 4–6. It is seen from Fig. 4 that the α–time plots for the decomposition of solid B are predominantly

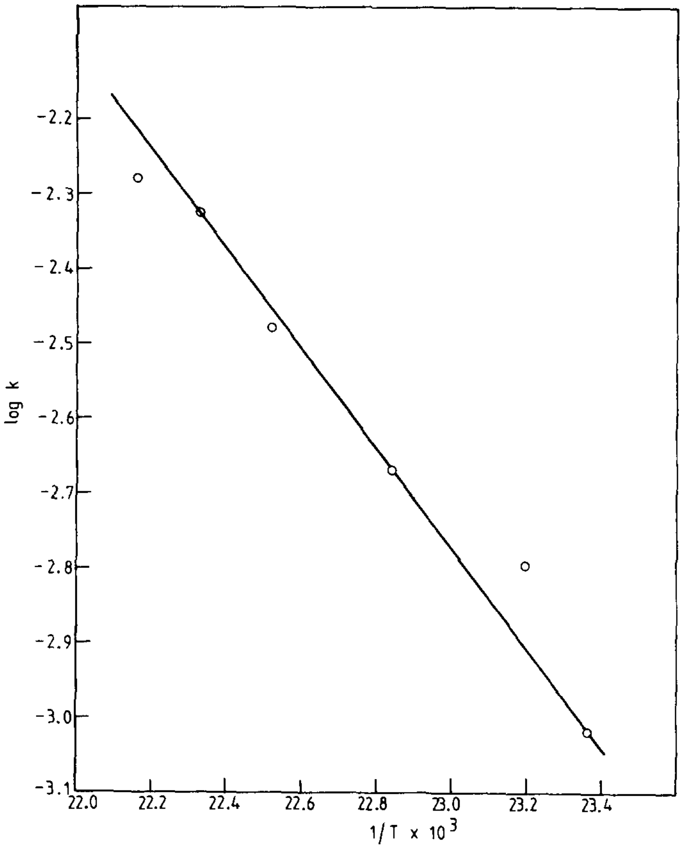

Fig. 3. Arrhenius plot of the unimolecular decay rate constants of $K_3Nb(O_2)_4$.

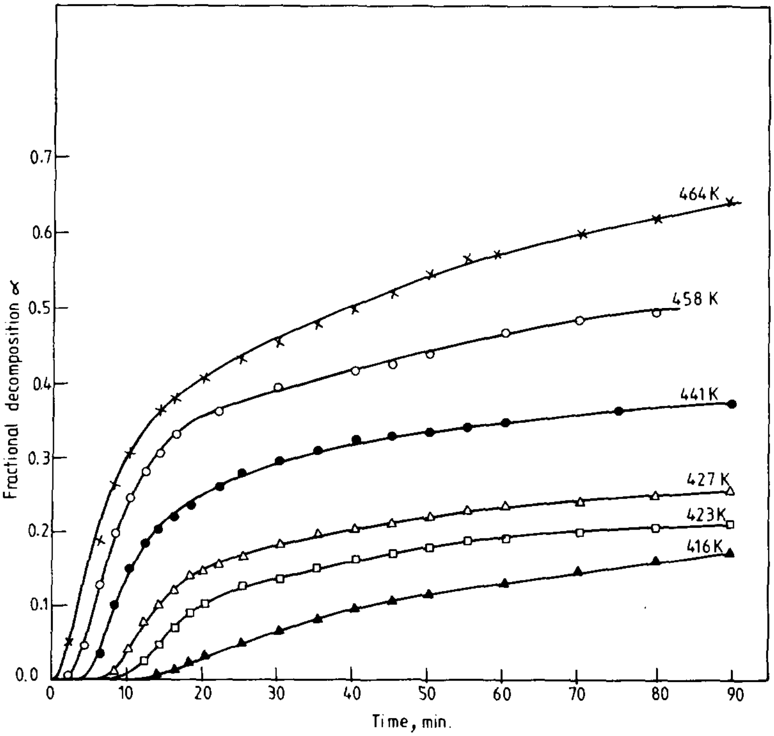

Fig. 4. Isothermal decomposition of $K_3Ta(O_2)_4$.

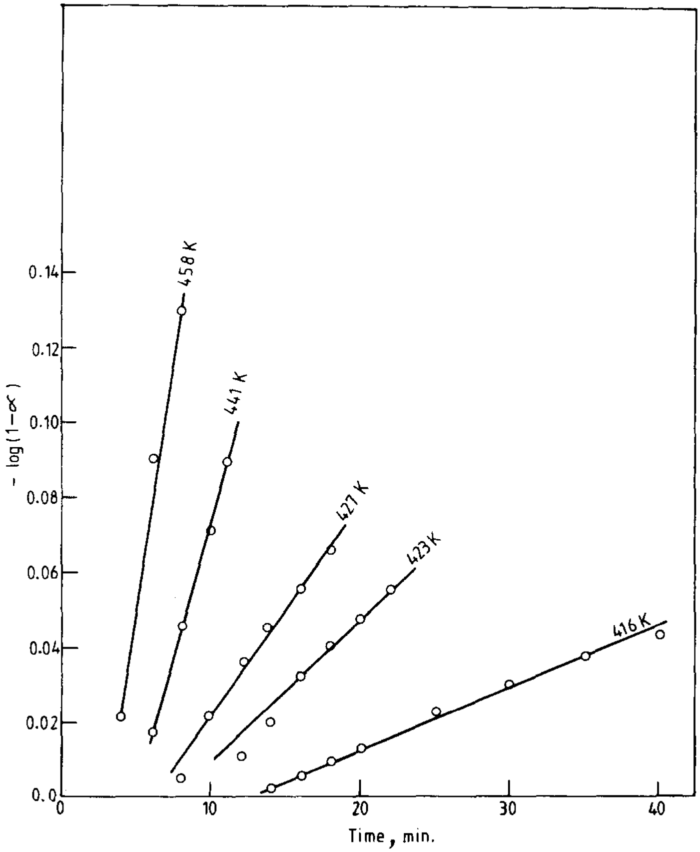

Fig. 5. Plots of the unimolecular decay law for the decomposition of $K_3Ta(O_2)_4$.

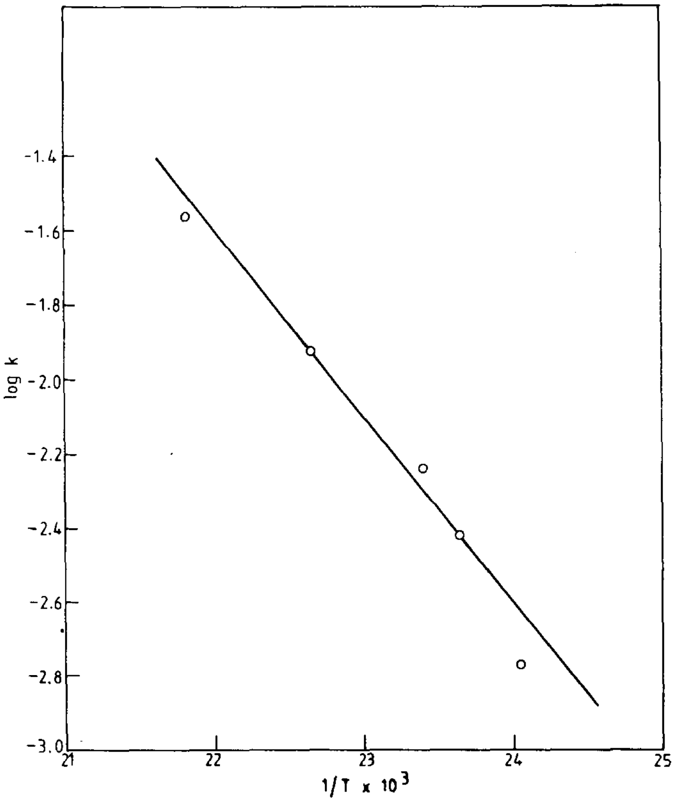

Fig. 6. Arrhenius plot of the unimolecular decay rate constants of $K_3Ta(O_2)_4$.

deceleratory in nature. They are similar to those of solid A. The maximum value of α obtained in this temperature range is 0.64. The plot of $-\log(1-\alpha)$ vs. time is linear (Fig. 5) and the activation energy deduced from the Arrhenius plot (Fig. 6) is 95.86 kJ mole^{-1}.

DISCUSSION

The title solids are typical coordination compounds. In the anions $[Nb(O_2)_4]^{3-}$ and $[Ta(O_2)_4]^{3-}$, niobium and tantalum are surrounded by four peroxo groups which are triangularly linked and bidentate in nature. The structure around the metal atom is dodecahedral and is similar to the tetraperoxo chromate $[Cr(O_2)_4]^{3-}$ ion [14]. The only moieties undergoing decomposition in the above anion are the peroxo groups, which on decomposition give out oxygen leaving behind a stable solid, potassium tetraoxo metallate(V). The decomposition reactions (1) and (2) fall in the category of

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

It is seen from the kinetic analysis of the isothermal decomposition studies of $K_3Nb(O_2)_4$ that the unimolecular decay law fits well and is obeyed over a long period of time in the temperature range 428–451 K, except for the initial few minutes.

The four triangularly linked bidentate peroxo groups in the anion $[Nb(O_2)_4]^{3-}$ constitute highly strained ring systems around the metal atom and are susceptible to ready decomposition.

Further, it is also important to note here that, during its preparation, $K_3Nb(O_2)_4$ separates in the form of very fine crystallites (very small particles). In his monograph, Brauer makes this important and specific observation for $K_3Nb(O_2)_4$ after describing its method of preparation [13].

These twin factors, i.e. fine size of the crystallites of the reactant and the strain imposed by four peroxide rings, may account for the facile nucleation. 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.

The decomposition kinetics behaviour of $K_3Ta(O_2)_4$ is similar to that of $K_3Nb(O_2)_4$.

It is probable in the present case that each individual anion in the assemblage may be nucleated with equal probability, thereby showing the kinetic obedience to the first-order equation [18]. Such kinetic behaviour has been reported earlier in the literature for sodium bromate [15], sodium azide [16], zinc azide and zinc hydroxyazide, etc. [17,18].

The present study shows that potassium tetraperoxoniobate(V),

$K_3Nb(O_2)_4$ and potassium tetraperoxotantalate(V), $K_3Ta(O_2)_4$, undergo neat thermal decomposition and are amenable for kinetic investigations.

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