SOLID STATE DECOMPOSITION STUDIES ON FLUOROPEROXO SPECIES OF TRANSITION METALS. PART XII. KINETICS OF ISOTHERMAL DECOMPOSITION OF $K_2VO(O_2)_2F$ AND $K_3Nb(O_2)_2F_4$

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(Received 10 March 1982)

ABSTRACT

The kinetics of the isothermal decomposition of $K_2VO(O_2)_2F$ and $K_3Nb(O_2)_2F_4$ have been investigated in the temperature range 432–463 K using a constant volume apparatus. The α–time plots for both these solids are sigmoidal in nature. The kinetic obedience to the Avrami–Erofe'ev equation ($n = 2$) is observed for the initial stage of the decomposition. The contracting volume equation fits well for the deceleratory region. The activation energies are 108 and 53 kJ mole^{-1} for $K_2VO(O_2)_2F$, and 163 and 120 kJ mole^{-1} for $K_3Nb(O_2)_2F_4$. The effect of grinding on the latter solid shows deceleratory α–time curves. The decomposition of the ground sample is best described by the unimolecular decay and contracting volume equations. The change in reactivity also confirms the topochemical nature of solid state decompositions. In addition to this, the absence of lattice water in these two solids may also be responsible for the appearance of induction and acceleratory regions in pristine solids, in contrast to hydrated fluoroperoxozirconates, wherein the dehydration step precedes peroxide decomposition leading to facile nucleation and the totally deceleratory nature of isothermal decomposition (α-time) curves.

INTRODUCTION

Boldyrev [1] states that the control of the chemical reactivity of solids is one of the important current problems of solid state chemistry. To achieve this, first of all detailed kinetic data on decomposition study is essential. It is a matter of common knowledge that peroxy compounds have a wide range of practical applications due to their oxidizing power [2–4]. It is also evident from the recent monograph on reactions in the solid state [5] that there is very little work on the decomposition kinetics of solid inorganic peroxides

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and peroxo complexes of transition metals (coordination compounds).

In view of this the authors are continuing their studies on solid state thermal and photochemical decomposition of fluoroperoxo complexes of transition elements [6–10], on an elementwise basis to find out the generalities, trends, and differences, if any, by changing the cation, anion or the nature of peroxide linkage. The present paper forms part of the same series of extended investigations and reports the kinetics of isothermal decomposition of two diperoxo complexes:

(i) $K_2VO(O_2)_2F$, potassium oxofluorodiperoxovanadate(V), (referred to as solid A); and

(ii) $K_3Nb(O_2)_2F_4$, potassium tetrafluorodiperoxoniobate(V), (referred to as solid B).

EXPERIMENTAL

Potassium oxofluorodiperoxovanadate(V), $K_2VO(O_2)_2F$ (solid A), was prepared by the method reported earlier [11]. The dried solid was test analyzed for its constituents and examined by IR spectra. The relevant data are given in Table 1.

TGA study of the sample shows that the decomposition starts around 423 K. The percentage loss in weight (13.7) observed tallies with the peroxy oxygen content (O_A value) only. The decomposition is represented as

$$K_2VO(O_2)_2F(s) \rightarrow K_2VO_3F(s) + O_2(g) \tag{1}$$
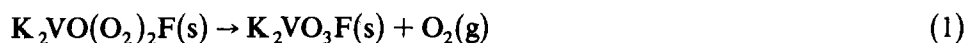
Potassium tetrafluorodiperoxoniobate(V), $K_3Nb(O_2)_2F_4$ (solid B), was prepared by the method reported by Vuletić and Djordjević [12]. The dried solid was again test analyzed for niobium, active oxygen (O_A), and fluorine using standard methods. It was also examined by IR and the experimental data are given in Table 2.
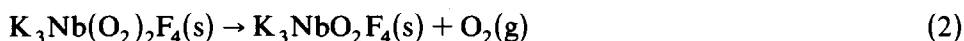
TABLE 1

Analysis of potassium oxofluorodiperoxovanadate(V)

	Chemical analysis (%)				Characteristic vibrational bands (cm^{-1})	
	K	V	O_A	F	ν(O–O)	ν(V–F)
Found	34.6	22.5	13.5	8.2	900, 880	475
Calculated	34.3	22.3	14.0	8.3		

TABLE 2

Analysis of potassium tetrafluorodiperoxoniobate(V)

	Chemical analysis (%)			Characteristic vibrational bands (cm^{-1})	
	Nb	O_A	F	ν(O–O)	ν(Nb–F)
Found	27.1	8.9	22.4	890, 870	590
Calculated	26.6	9.1	21.7		

The 9.0% weight loss observed in TGA is attributable to the peroxy oxygen content only [12]. The decomposition is given as

$$K_3Nb(O_2)_2F_4(s) \rightarrow K_3NbO_2F_4(s) + O_2(g) \qquad (2)$$

It is relevant to mention here that both these solids are not associated with lattice water at all [11,12] and the only moieties undergoing decomposition are the peroxo groups. The stable solids obtained by thermal decomposition are oxofluoro derivatives. These decompositions are irreversible and exothermic and no melting of the solids is observed.

For the kinetic studies, the dried pristine solids were sieved through a 250 μm mesh sieve without being subject to initial grinding. Isothermal decomposition studies were carried out in appropriate temperature ranges for each solid by the constant volume apparatus (accumulatory system) following the procedure described previously [6–10].

RESULTS

K₂VO(O₂)₂F (solid A)

The α-time plots of this solid for its isothermal decomposition studies in the temperature range 432.5–460 K are given in Fig. 1. They are sigmoidal in nature with initial induction and acceleratory regions followed by a decay period, at all temperatures. The initial stage of the decomposition is best described by the Avrami–Erofe'ev equation with a value of $n = 2$, i.e., $[-\log(1 - \alpha)]^{1/2} = k_1 t$ (Fig. 2). The activation energy of the process, deduced from an Arrhenius plot (Fig. 2 inset) is 108 kJ mole^{-1}. The subsequent stage of the decomposition obeys the contracting volume equation, i.e. $1 - (1 - \alpha)^{1/3} = k_2 t$ (Fig. 3), and the activation energy for this stage comes out to be 53 kJ mole^{-1} (Fig. 3 inset).
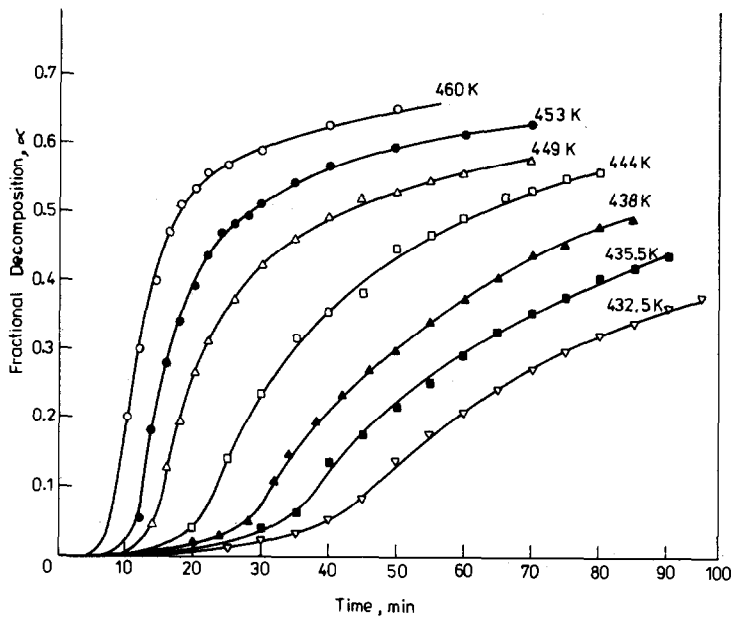
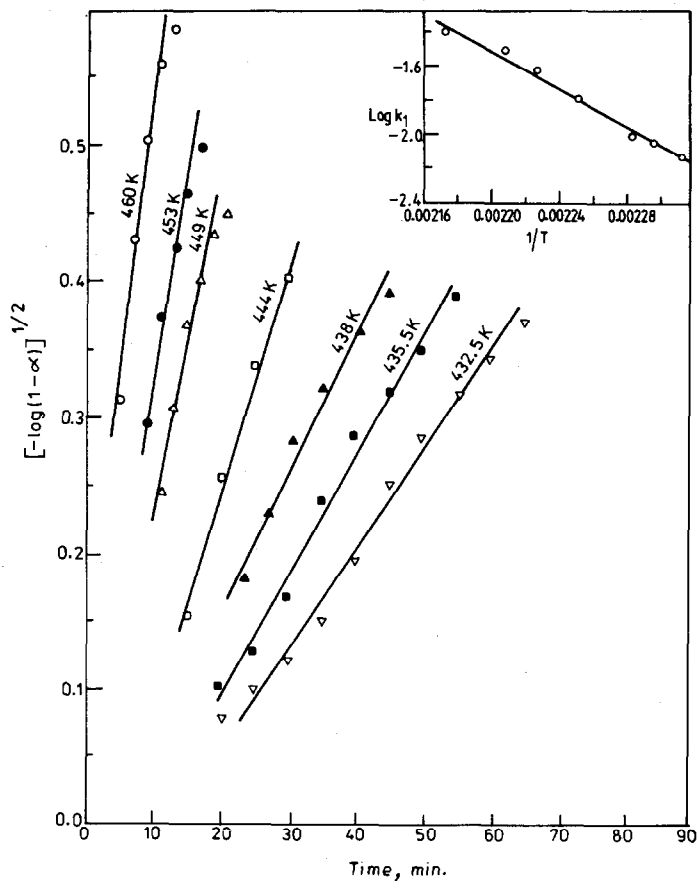Fig. 1. Isothermal decomposition of $K_2VO(O_2)_2F$.

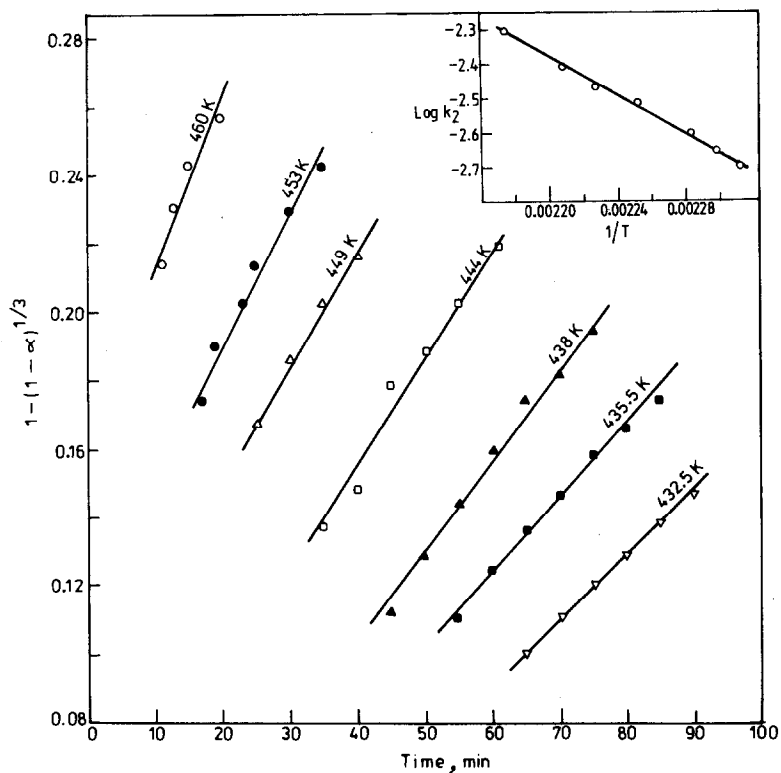Fig. 2. Plot of the Avrami–Erofe'ev equation ($n=2$) for the decomposition of $K_2VO(O_2)_2F$.

Fig. 3. Plot of the contracting volume equation for the decomposition of $K_2VO(O_2)_2F$.

$K_3Nb(O_2)_2F_4$ (solid B)

The results of isothermal decomposition studies in the temperature range 440–463 K for solid B are presented in Figs. 4–6. It is seen from Fig. 4 that the α–time plots for solid B also show typical sigmoidal nature. They exhibit a short induction period, an acceleratory region followed by a deceleratory region.

The acceleratory region follows the Avrami–Erofe'ev equation with $n = 2$ (Fig. 5) and the Arrhenius plot gives a value of 163 kJ mole^{-1} for the activation energy of this stage of decomposition. The later part of the reaction follows the contracting volume equation (Fig. 6). Activation energy for this process is 120 kJ mole^{-1}.
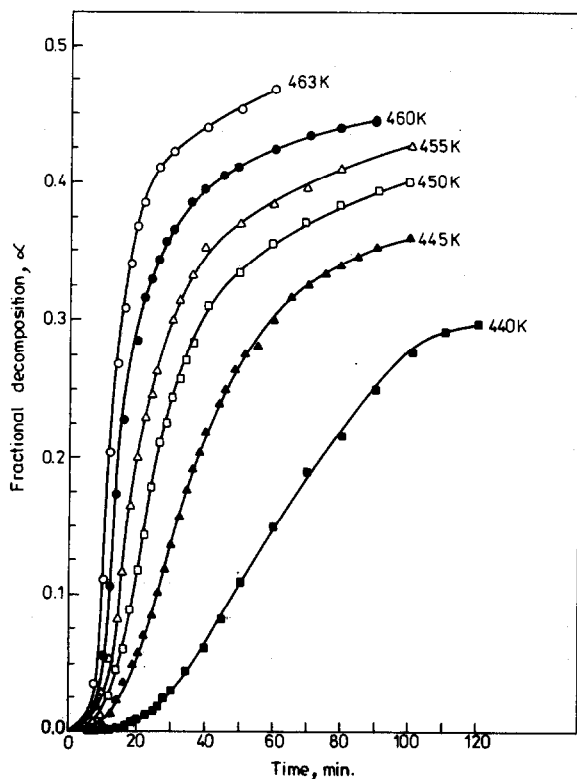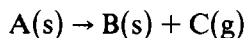
Fig. 4. Isothermal decomposition of $K_3Nb(O_2)_2F_4$.

DISCUSSION

$K_2VO(O_2)_2F$ and $K_3Nb(O_2)_2F_4$ are interesting species of fluoroperoxo complexes of vanadium and niobium. They are typical coordination compounds [11,12]. The two anions, which undergo decomposition are $[VO(O_2)_2F]^{2-}$ and $[Nb(O_2)_2F_4]^{3-}$. The only moieties undergoing decomposition in these anions are the two peroxo groups (-O-O-), which are triangularly linked and bidentate in nature [11,12]. The decomposition
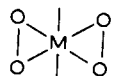
reactions (1) and (2) are exothermic, irreversible and no melting is observed. They fall in the category of

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

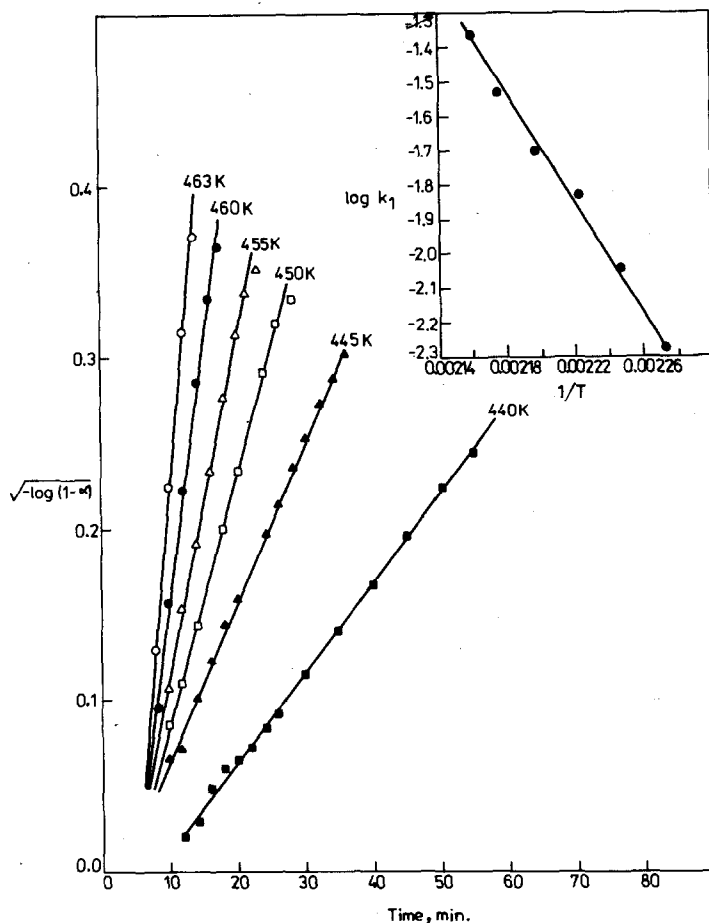which is explained in terms of the well-known mechanism involving nuclea-

Fig. 5. Plot of the Avrami–Erofe'ev equation ($n = 2$) for the decomposition of $K_3Nb(O_2)_2F_4$.

tion and growth of the product phase [5]. The α–time plots of both the solids are sigmoidal in nature (Figs. 1 and 4). The data could not be fitted into a single rate law over the entire range of the reaction.

The initial stages of the decomposition are best described by Avrami–Erofe'ev equation with $n = 2$. This kinetic obedience implies that the solids undergo decomposition by random nucleation followed by two-dimensional growth of nuclei [5]. The later stage of decomposition in both the solids studied here, governed by the contracting sphere equation, indicates that the surface has undergone complete decomposition and the interface is advancing towards the centre of the particle. It has been pointed out by Brown et al. [5] that the α–time curves characteristic of the later part of a reaction,
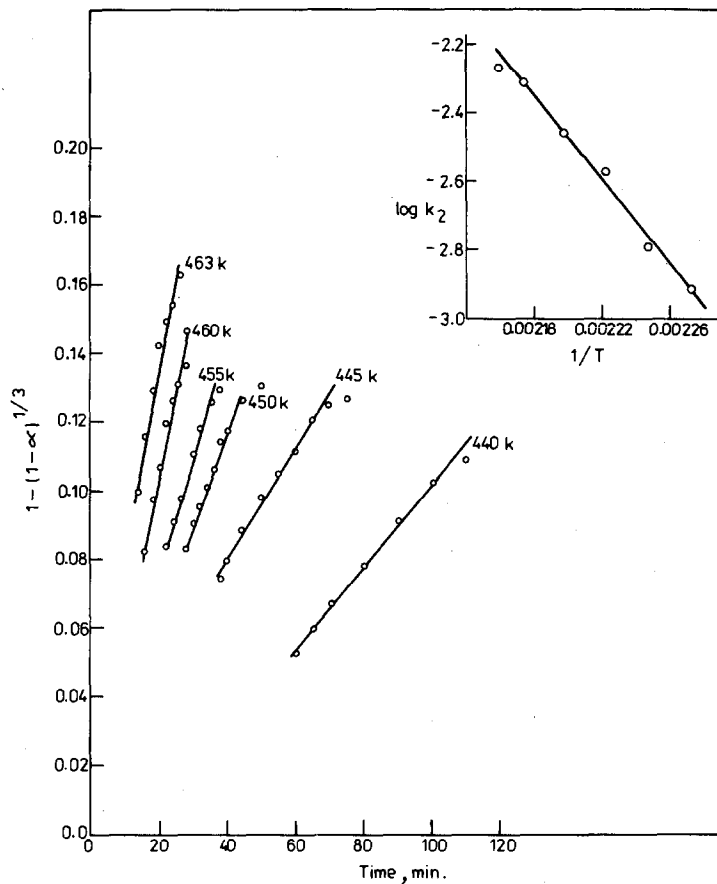
Fig. 6. Plot of the contracting volume equation for the decomposition of $K_3Nb(O_2)_2F_4$.

initially obeying the Avrami–Erofe'ev equation, are deceleratory in nature and difficult to analyse completely.

It has been shown by Galwey and co-workers [5,13] that charge transfer is the first step in the decomposition of ionic solids, but in the case of coordination compounds, the first step may be the bond rupture. It is, therefore, probable that the first step in the decomposition of the two anions is the breaking of the strained metal peroxide bonds, which would release the strain in the system. After the cleavage, lattice rearrangement may occur with the evolution of oxygen and the formation of oxofluorovanadate and niobate.

It has been pointed out previously [6–8] that the Arrhenius parameters for heterogeneous rate processes are not necessarily associated with a single rate limiting step [5,14], and caution has to be exercised in using these data.

However, as expected, the E_A values for the surface processes are higher than that of the reactions occurring in the bulk of the solid [5], e.g., solid A, 108 and 53 kJ mole^{-1} and for solid B, 163 and 120 kJ mole^{-1}.

Effect of grinding

It is well known that the method of preparation of the solid and its pretreatment prior to the reaction greatly influence its reactivity [5]. Grinding or other such treatment may increase the number or extent of imperfections and thus alter the reactivity [5]. This feature was studied with $K_3Nb(O_2)_2F_4$. It was ground in an agate mortar, sieved through 150 μm mesh and its decomposition studied at 438, 445 and 458 K. The α–time plots are given in Fig. 7, which show the absence of induction and acceleratory regions and the reaction is deceleratory throughout. The initial part of the α–time data fits into the unimolecular decay equation (Fig. 8), and the later part obeys contracting volume equation (Fig. 9). This alteration of kinetic behaviour of $K_3Nb(O_2)_2F_4$ shows that the grinding has created imperfec-
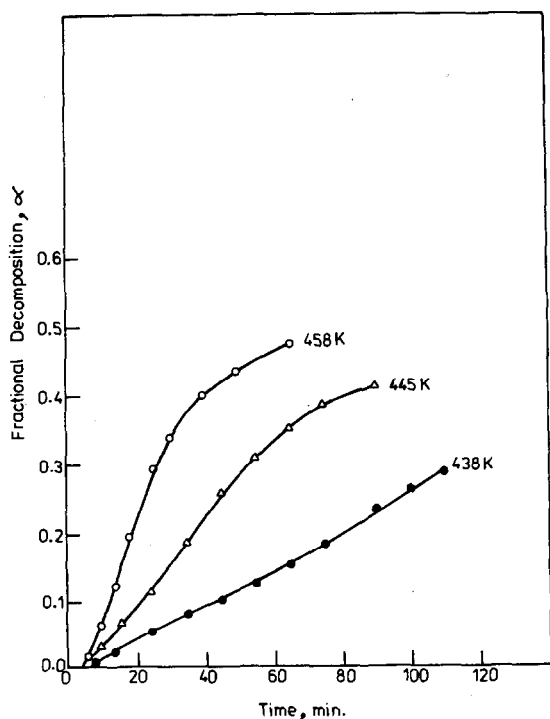

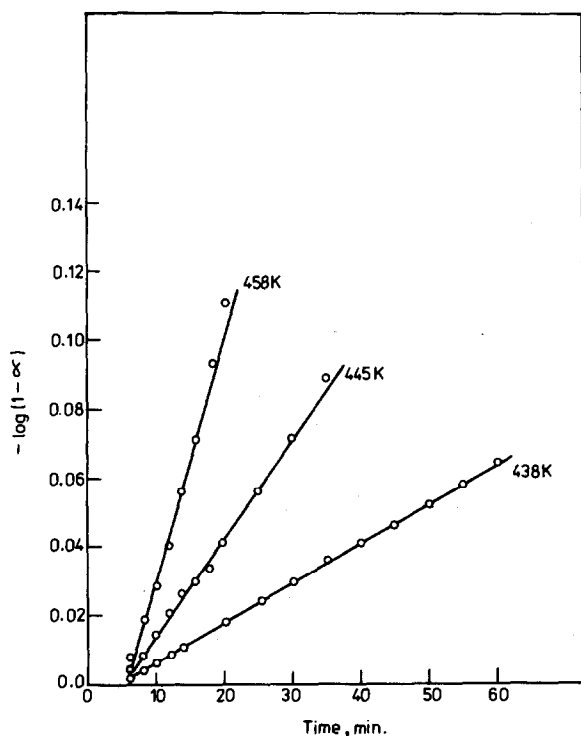Fig. 7. Isothermal decomposition of a ground sample of $K_3Nb(O_2)_2F_4$.

Fig. 8. Plot of the unimolecular decay law for the decomposition of a ground sample of $K_3Nb(O_2)_2F_4$.

tions, which affect its nucleation process. This observation also shows the topochemical nature of the solid state decomposition process.

It has been observed by the authors that in the case of solids wherein the dehydration step precedes the peroxide decomposition, the dehydration step itself generates large defects in the solid leading to facile nucleation and their deceleratory nature of decompositions [6–8]. One of the probable reasons for the appearance of induction and acceleratory regions in the case of $K_2VO(O_2)_2F$ and $K_3Nb(O_2)_2F_4$ may be the absence of water molecules in them.

In a large majority of coordination compounds, the complexity of the ligands present in the anion increases the number of types of bond redistribution processes which are, in principle, possible within and between coordination spheres [5]. This puts a severe limitation on the interpretation of kinetic studies of solid coordination compounds. However, the present two solids serve as near-ideal systems for studying the kinetic behaviour and the reactivity of solid coordination compounds. Further, they also undergo near
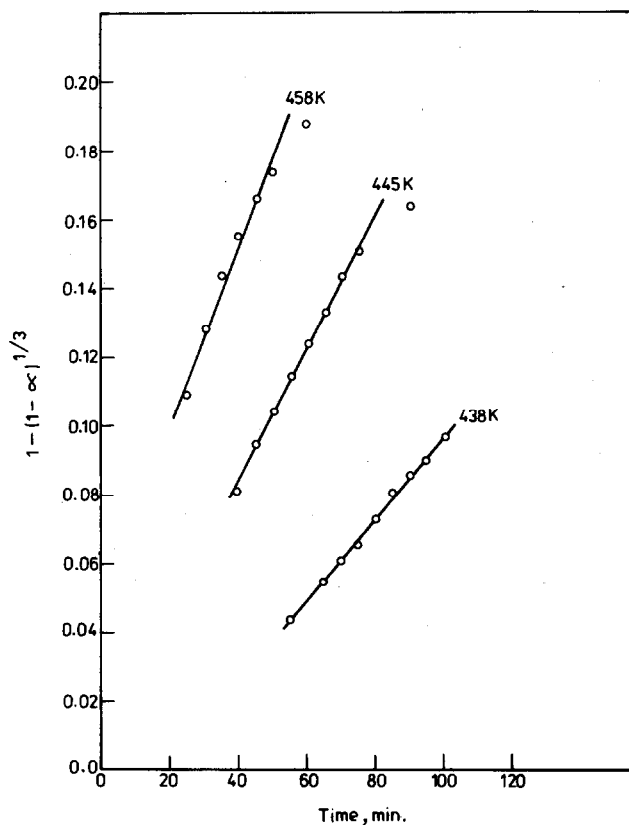
Fig. 9. Plot of the contracting volume equation for the decomposition of a ground sample of $K_3Nb(O_2)_2F_4$.

photolysis (unpublished results), on irradiation from a high pressure mercury lamp giving out oxygen. The photolysis studies have been complementary to thermal decompositions in elucidating the mechanisms of the reactions [9,10]. The authors' continuing interest in these systems also stems from the fact that fluoroperoxo complexes of transition elements serve as a convenient route for the synthesis of oxofluorometallates, which find wide applications as solid state materials [15–17].

ACKNOWLEDGEMENTS

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