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SOLID-STATE DECOMPOSITION STUDIES ON FLUOROPEROXO SPECIES OF TRANSITION METALS. PART XIII. KINETICS OF ISOTHERMAL DECOMPOSITION OF $K_2[V_2O_3(O_2)_2F_2]$ AND $K_3[Ta(O_2)_2F_4]$

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ABSTRACT

The kinetics of isothermal decomposition of $K_2[V_2O_3(O_2)_2F_2]$ and $K_3[Ta(O_2)_2F_4]$ have been investigated in the temperature range 413–493 K using a constant volume apparatus. The α vs. time plots for both these solids are sigmoidal in nature. The kinetics obey the Avrami–Erofeev equation ($n = 2$) for the initial stage of the decomposition. The contracting volume equation fits well for the deceleratory region. The activation energies are 164.8 and 105.4 kJ mol^{-1} for $K_2[V_2O_3(O_2)_2F_2]$, and 85.2 and 76.6 kJ mol^{-1} for $K_3[Ta(O_2)_2F_4]$.

The absence of lattice water in these two solids may be responsible for the appearance of a short induction, followed by an acceleratory region in pristine solids, in contrast to hydrated fluoroperoxo zirconates, wherein the dehydration step preceding peroxide decomposition leads to facile nucleation and a deceleratory nature of decomposition.

The kinetic characteristics of the decomposition of fluoroperoxo species so far studied are summarized and discussed.

INTRODUCTION

The thermal decomposition of solids is still an important field of solid-state chemistry with vast technical applications, as is seen from the special monographs, and also the periodical national and international conferences on this subject [1–5]. The understanding and control of the chemical reactivity of solids are the main objects in undertaking decomposition studies [6,7]. Detailed kinetic data are essential and constitute the first step.

It is well known that peroxy compounds have a wide range of practical applications due to their oxidizing power [8–10]. From the recent monographs on decompositions in the solid state [1,2] and the proceedings of national and international conferences on thermal analysis, it is clear that little work has been done on the decomposition kinetics of solid inorganic peroxides and peroxocomplexes of transition metals. The authors are continuing their studies on solid-state thermal and photochemical decompositions of fluoroperoxo complexes of transition elements [11–16] because, in

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addition to their ability to release active oxygen, fluoroperoxo complexes give stable oxide fluorides and oxofluorometallates of transition elements on thermal decomposition, which are useful as solid-state materials [17–22].

The present paper forms part of the same series of extended investigations and reports on the kinetics of isothermal decomposition of: (i) $K_2[V_2O_3(O_2)_2F_2]$, potassium oxofluoroperoxovandate(V) referred to as solid A; and (ii) $K_3[Ta(O_2)_2F_4]$, potassium tetrafluorodiperoxo tantalate(V) referred to as solid B. The kinetic features of isothermal decomposition of solid fluoroperoxo complexes investigated so far are summarized and discussed in this communication.

EXPERIMENTAL

Solid A, was prepared by the method reported in the literature [23], dried and analysed for some of its constituents and examined by IR spectroscopy (Table 1).

The percentage weight loss (9.8%) observed in TG tallies with the peroxy oxygen content (O_A) only. The decomposition is represented as

$$K_2[V_2O_3(O_2)_2F_2](s) \rightarrow K_2V_2O_5F_2(s) + O_2(g) \qquad (1)$$

Solid B was prepared by the method reported by Vuletić and Djordjević [24]. The dried solid was again analysed for some of its constituents by standard methods and examined by IR spectroscopy (Table 2).

The 6.5% weight loss observed in TG is attributable to the peroxy oxygen content only (O_A). The decomposition is given as

$$K_3[Ta(O_2)_2F_4](s) \rightarrow K_3TaO_2F_4(s) + O_2(g) \qquad (2)$$

It is relevant to mention here that neither of these solids are associated with lattice water [23,24], and the only moieties undergoing decomposition are the peroxy groups. The stable solids obtained by thermal decomposition are oxofluoro derivatives and have been well characterized [17]. These decompositions are irreversible, 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 initial grinding. Isothermal decom-

TABLE 1

Analysis of solid A

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

TABLE 2

Analysis of solid B

	Ta	O_A	F	Characteristic vibrational bands (cm^{-1})	
Found (%)	40.1	6.5	17.5	ν(O–O)	ν(Ta–F)
Calcd. (%)	41.2	7.3	17.3	870, 856	450

position studies were carried out in appropriate temperature ranges for each solid by the constant-volume apparatus (accumulatory system) under 10^{-6} torr pressure, following the procedure described previously [11–16]. Carrying out the experiments in vacuum eliminates the possibility of reverse reactions, if any, and thus the results are a direct consequence of the thermal decomposition of the substance studied [25].

RESULTS

$K_2[V_2O_3(O_2)_2F_2]$ (solid A)

The α vs. time plots of this solid for its isothermal decomposition in the temperature range 413.5–452 K are given in Fig. 1. They are sigmoidal in

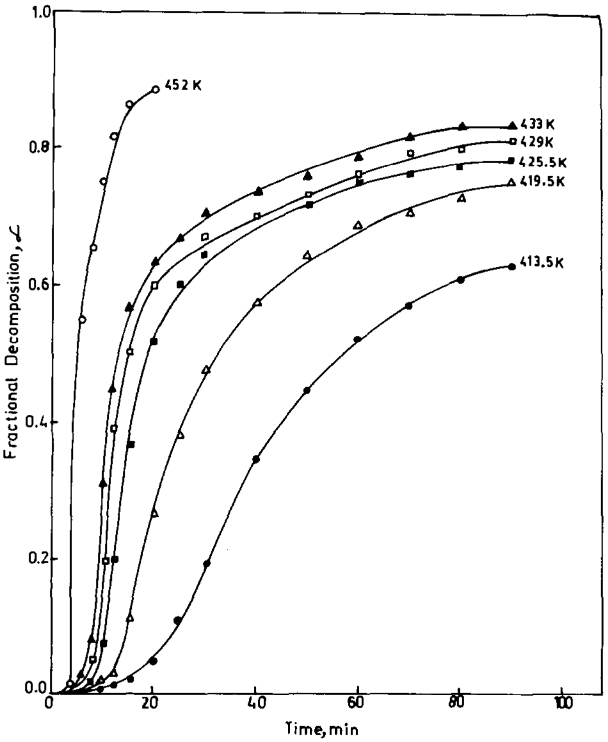


Fig. 1. Isothermal decomposition of $K_2V_2O_3(O_2)_2F_2$.

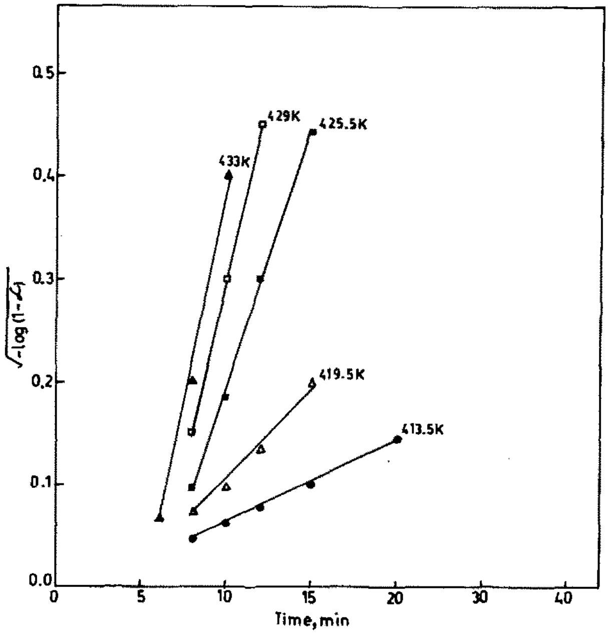


Fig. 2. Plots of the Avrami–Erofeev equation for the decomposition of $K_2V_2O_3(O_2)_2F_2$.

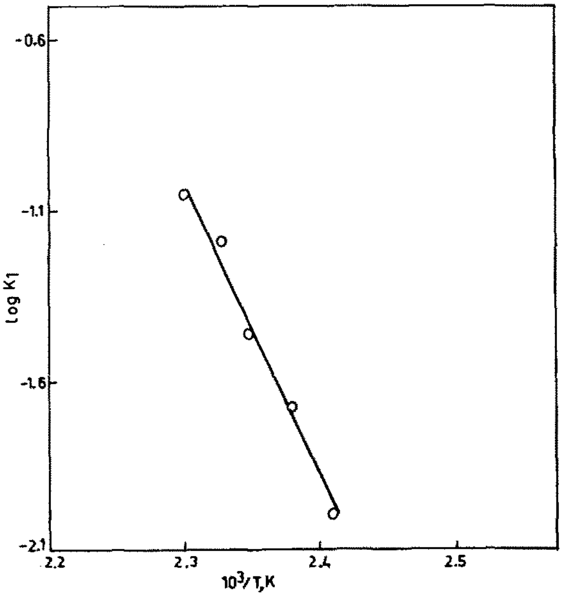


Fig. 3. Arrhenius plot of the Avrami–Erofeev equation rate constants of $K_2V_2O_3(O_2)_2F_4$. Correlation coefficient > 0.99.

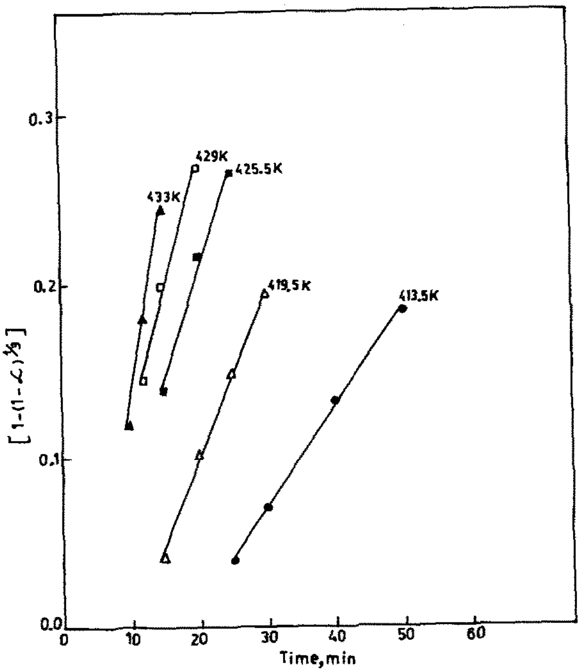


Fig. 4. Plots of contracting volume equation for the decomposition of $K_2V_2O_3(O_2)_2F_4$.

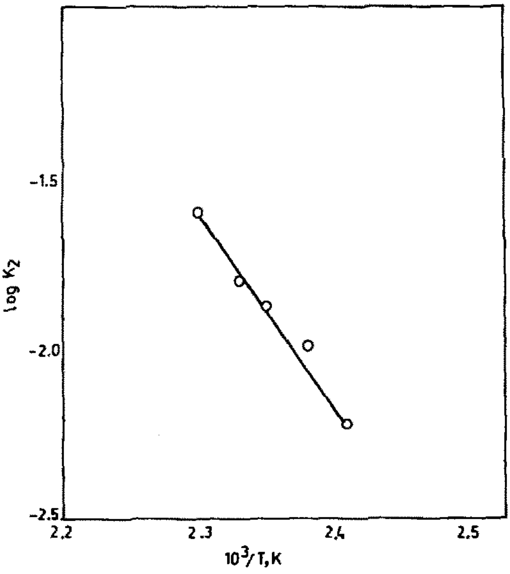


Fig. 5. Arrhenius plot of the contracting volume equation rate constants of $K_2V_2O_3(O_2)_2F_2$. Correlation coefficient > 0.98.

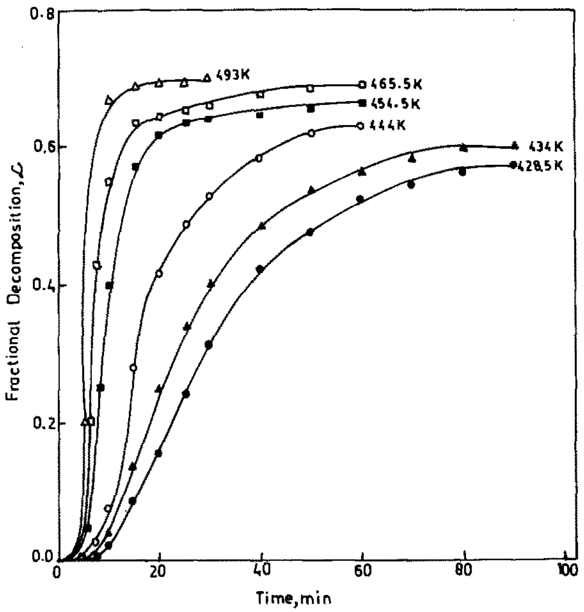


Fig. 6. Isothermal decomposition of $K_3Ta(O_2)_2F_4$.

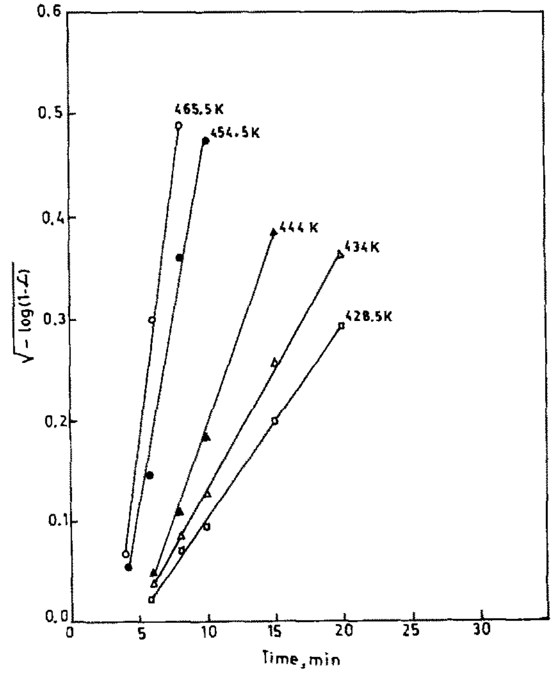


Fig. 7. Plots of the Avrami–Erofeev equation for the decomposition of $K_3Ta(O_2)_2F_4$.

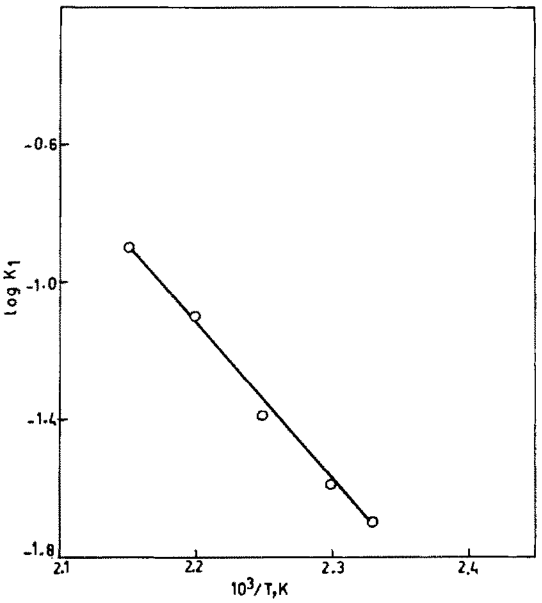


Fig. 8. Arhenius plot of the Avrami–Erofeev equation rate constants of $K_3Ta(O_2)_2F_4$. Correlation coefficient > 0.99.

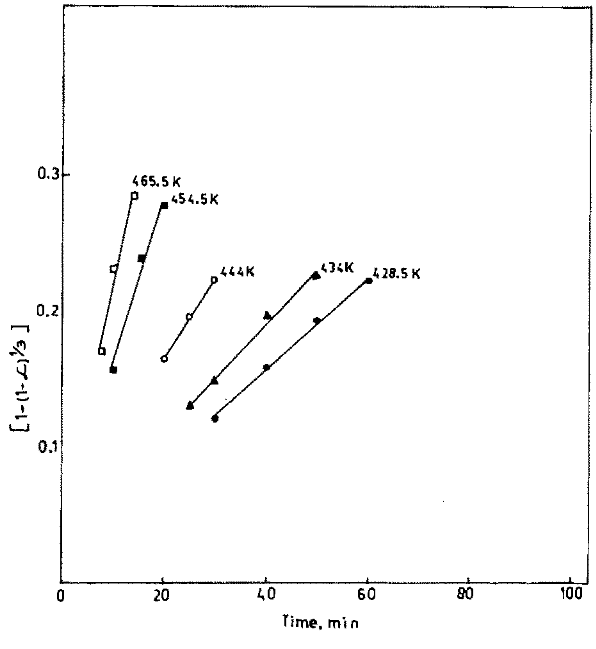


Fig. 9. Plots of contracting volume equation for the decomposition of $K_3Ta(O_2)_2F_4$.

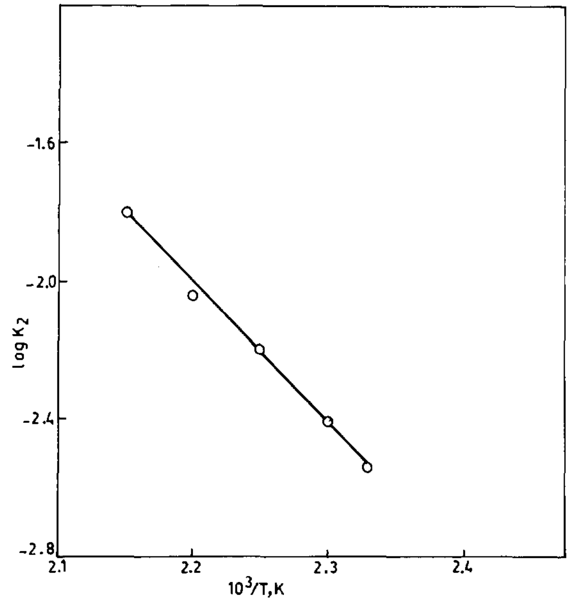


Fig. 10. Arrhenius plot of the contracting volume equation rate constants of $K_3Ta(O_2)_2F_4$. Correlation coefficient > 0.99.

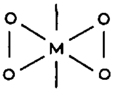
nature with very short induction periods, and the acceleratory region is followed by a decay period at all temperatures. The initial stage of the decomposition (acceleratory region) is best described by the Avrami–Erofeev equation with a value of $n = 2$, i.e. $-\log(1-\alpha)^{1/2} = k_1t$ (Fig. 2). The activation energy of the process, deduced from an Arrhenius plot (Fig. 3) is 164.8 kJ mol^{-1}. The subsequent decomposition obeys the contracting volume equation, i.e. $1-(1-\alpha)^{1/3} = k_2t$ (Fig. 4), and the activation energy for this stage comes out to be 105.4 kJ mol^{-1} (Fig. 5).

$K_3[Ta(O_2)_2F_4]$ *(solid B)*

The results of isothermal decomposition studies in the temperature range 428.5–493 K for solid B are presented in Figs. 6–10. It is seen from Fig. 6 that the α vs. time plots for solid B also show typical sigmoidal nature. They exhibit a short induction period, an acceleratory region, followed by a decceleratory region. The acceleratory region follows the Avrami–Erofeev equation with $n = 2$ (Fig. 7) and the Arrhenius plot gives a value of 85.2 kJ mol^{-1} for the activation energy of this stage of decomposition (Fig. 8). The later part of the reaction follows the contracting volume equation (Fig. 9). The activation energy for this process is 76.6 kJ mol^{-1} (Fig. 10).

DISCUSSION

$K_2[V_2O_3(O_2)_2F_2]$ and $K_3[Ta(O_2)_2F_4]$ are interesting species of fluoroperoxo complexes of vanadium and tantalum. They are typical coordination compounds [23,24]. The two anions, which undergo decomposition are $[V_2O_3(O_2)_2F_2]^{2-}$ and $[Ta(O_2)_2F_4]^{3-}$. The only moieties undergoing decomposition in these solids are the two peroxo groups (–O–O–), which are triangularly linked and bidentate in nature [23,26], forming strained ring systems.



The decomposition reactions (1) and (2) are exothermic and irreversible. No melting is observed. They fall in the category of A(s) → B(s) + C(g). This decomposition is explained in terms of the well-known mechanism involving nucleation and growth of the product phase [1,27,28]. The α vs. time plots of both solids are sigmoidal in nature (Figs. 1 and 6). 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 the Avrami–Erofeev equation with $n = 2$. This kinetic behaviour implies that the solids undergo decomposition by random nucleation followed by two-dimensional growth of nuclei [1,27,28]. The later stage of decomposition in both the solids is governed by the contracting cube equation. This 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. [1,27,28] that the α vs. time curves characteristic of the later part of a reaction, initially obeying the Avrami–Erofeev equation, are deceleratory in nature and difficult to analyse completely.

As expected, the E_a values for the surface processes are higher than those of the reactions occurring in the bulk of the solid [1,27,28], e.g. solid A, 164.8 and 105.4 kJ mol^{-1}, and solid B, 85.2 and 76.6 kJ mol^{-1}.

As discussed in detail in our earlier publications, the probable first step in the decomposition of the present solids is again the breaking of the metal peroxide bonds, thereby releasing the strain of the system. After cleavage, lattice rearrangement will occur with the evolution of oxygen and the formation of oxofluorovandate(V) and tantalate(V).

Isothermal solid state decomposition of fluoroperoxo complexes have been investigated in this laboratory on an exploratory basis to understand their feasibility for decomposition studies, kinetic features and mechanism of oxygen evolution.

The experimental results obtained so far are listed in Table 3. The following features are to be noted:

(1) The solids can be grouped into two categories, i.e. those containing water of hydration and those without it. The peroxo group (–O–O–) is

TABLE 3

Experimental results

No.	Compound	Temp. (K)	Rate equation	Activation energy (kJ mol^{-1})
1	$K_3Zr_2(O_2)_2F_7 \cdot 2H_2O$	399–536	A *	41
			and	29
2	$Rb_3Zr_2(O_2)_2F_7 \cdot 2H_2O$	394–473	B *	55
				41
3	$Cs_3Zr_2(O_2)_2F_7 \cdot H_2O$	374–474	A *	60
			and	46
4	$K_2Zr_2(O_2)_2F_6 \cdot 2H_2O$	373–499	B *	57
				29
5	$Rb_2Zr_2(O_2)_2F_6 \cdot 2H_2O$	388–475	A *	59
			and	46
6	$Cs_2Zr_2(O_2)_2F_6 \cdot 2H_2O$	374–492	B *	54
				47
7	$K_2Nb(O_2)F_5 \cdot H_2O$	463–523	A *	146
			and	63
8	$K_2Ta(O_2)F_5 \cdot H_2O$	528–553	B *	120
				90
9	$K_3Nb(O_2)_2F_4$	440–468	C *	163
			and	120
10	$K_2VO(O_2)_2F$	432–460	B *	108
				53
11	$K_2V_2O_3(O_2)_2F_2$	413–452	C *	164.8
			and	105.4
12	$K_3Ta(O_2)_2F_4$	428–493	B *	85.2
				76.6

A * = Unimolecular decay law, $-\log(1-\alpha) = kt$.
B * = Contracting cube equation, $1-(1-\alpha)^{1/3} = kt$.
C * = Avrami–Erofeev equation, $-\log(1-\alpha)^{1/2} = kt$.

triangularly linked bidentate in nature in all these solids, and constitutes a highly strained ring system. The metal–fluorine bond is strong.

(2) They are all suitable for kinetic studies, as they undergo neat decompositions and α vs. time plots are found to be sigmoidal in shape.

(3) In the case of the solids containing water of hydration, the unimolecular decay law satisfactorily describes the initial part of the decomposition. This has been attributed to facile nucleation due to the dehydration step, preceding the peroxide decomposition.

(4) In the case of the remaining solids, i.e. without water molecules, the Avrami–Erofeev equation governs the initial part of the decomposition,

indicating random nucleation followed by two-dimensional growth of the nuclei.

(5) The subsequent stage of decomposition of all these solids obeys the contracting cube equation. This kinetic behaviour is due to the fact that the surface is completely transformed into the product and the interface progresses in the direction of the centre of the crystal. The reaction is deceleratory since the interface progressively decreases.

(6) The activation energy for "surface processes" is higher than that of "interface processes" (Table 3).

(7) The first stage of peroxide decomposition for all these solids, is the breaking of the metal–peroxide bond, thus releasing the strain in the system. After cleavage of the metal–peroxide bond, an extensive lattice rearrangement may take place with the evolution of oxygen and formation of oxofluorometallate.

(8) The solids undergo photolysis on UV radiation from a high-pressure mercury lamp. This study, complementary to thermal decomposition, is useful in understanding the mechanisms of the reactions.

(9) These solids are typical coordination compounds, and those without water molecules serve as near ideal systems for understanding the kinetic behaviour and the reactivity of coordination compounds. In a large majority of coordination compounds, the complexity of the ligands severely limits their kinetic studies.

We are yet to arrive at the actual mechanism of evolution of oxygen, the probable one being that postulated earlier [15,16]:

$$O_2^{2-} \xrightarrow{h\nu} (O_2^{2-})^*$$

$$(O_2^{2-})^* + (O_2^{2-}) \rightarrow O_2 + 2O^{2-}$$

Information on primary steps is difficult to obtain.

The stable decomposition products of all these solids are oxofluorometallates. Our studies have shown that thermal decomposition provides a new, convenient and versatile route for the synthesis of oxide fluorides and oxofluorometallates [17]. These solids attract attention due to their technical applications. Further work is in progress on these solids in this laboratory.

It is thus seen from the present studies that fluoroperoxo species of transition elements constitute an interesting set of solids amenable for a variety of studies.

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