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Note

SOLID STATE DECOMPOSITION STUDIES ON FLUOROPEROXO SPECIES OF TRANSITION METALS. PART IX. KINETICS OF ISOTHERMAL DECOMPOSITION OF $K_2NbO_2F_5 \cdot H_2O$

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Studies on the solid state thermal and photochemical decomposition of fluoroperoxozirconates have been reported in this series [1—4]. This paper describes the kinetics of isothermal decomposition of potassium pentafluoroperoxoniobate (V) monohydrate, $K_2NbO_2F_5 \cdot H_2O$.

EXPERIMENTAL

The compound, $K_2NbO_2F_5 \cdot H_2O$, was prepared by heating 1 g of niobium pentoxide (Fisons) with 20 ml of 40% hydrofluoric acid (BDH) on a water bath until it dissolved. The solution was cooled and 15 ml of 30% hydrogen peroxide (BDH) were added. A stoichiometric amount of potassium hydroxide was dissolved in a minimum quantity of water, added to the above solution and cooled. The compound was precipitated by adding an excess of alcohol, filtered, washed with alcohol and ether and dried over phosphorus pentoxide.

The compound was analysed for potassium as potassium tetraphenyl boron, niobium by tannin, active oxygen by permanganate titration, and fluoride using an ion-selective electrode (Orion 94-09). Analysis showed the presence of 23.9% K, 29.9% Nb, 5.3% O_A, 30.5% F (calculated for $K_2NbO_2F_5 \cdot H_2O$: 24.7% K, 29.4% Nb, 5.1% O_A and 30.1% F). The compound was subjected to TGA, IR and laser Raman spectral studies. The conductivity of the aqueous solutions showed the presence of a 2 : 1 electrolyte.

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 a constant volume equipment evacuated to a pressure of 10^{-6} Torr. The equipment and procedure used was the same as described previously [1—3]. The water vapour evolved was condensed in a liquid air trap.

RESULTS AND DISCUSSION

The isothermal decomposition of $K_2NbO_2F_5 \cdot H_2O$ was studied in the temperature range 463—523 K. The fractional decomposition α vs. time

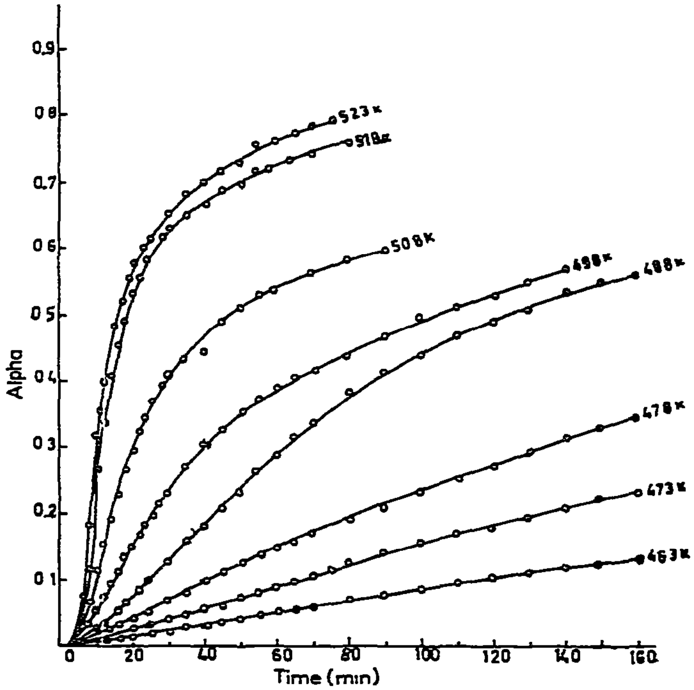


Fig. 1. Thermal decomposition curves for $K_2NbO_2F_5 \cdot H_2O$.

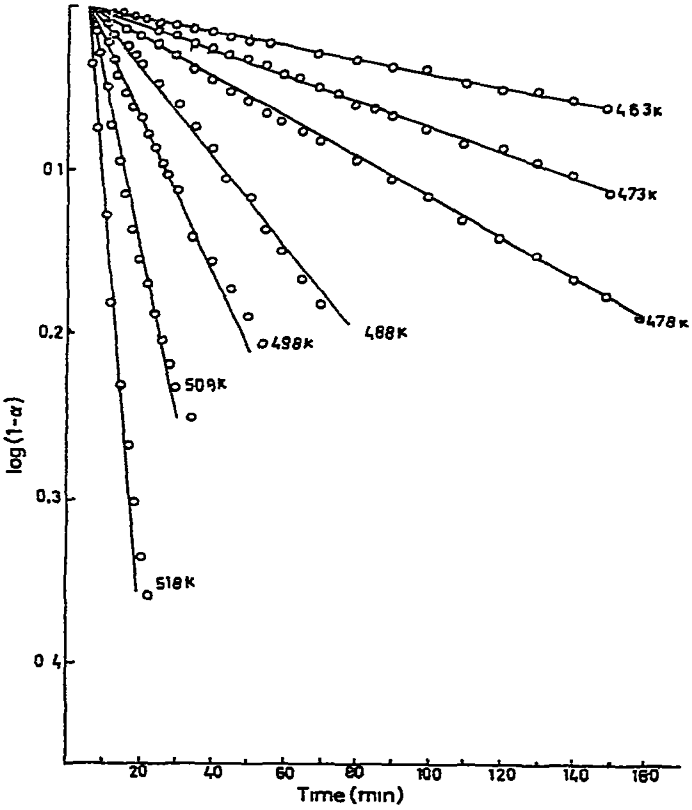


Fig. 2. Plot of the unimolecular decay equation, $\log(1-\alpha)$ vs. time for $K_2NbO_2F_5 \cdot H_2O$.

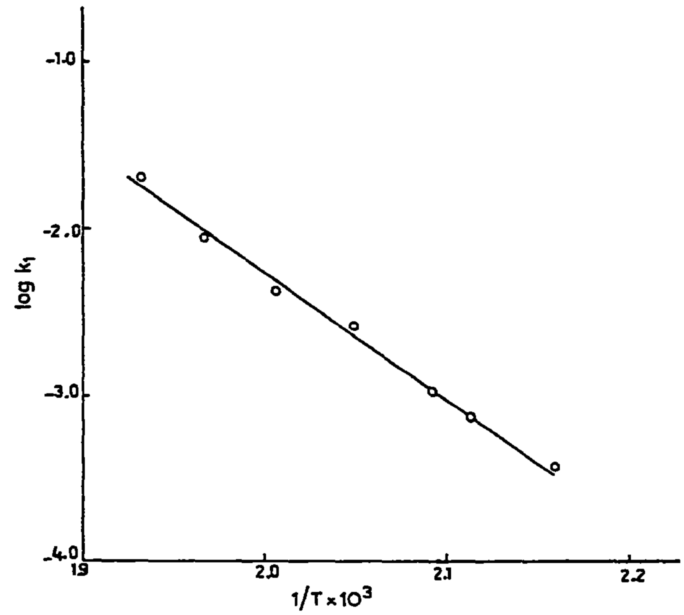


Fig. 3. Arrhenius plot of the unimolecular decay law rate constants, log k_1 vs. $1/T \times 10^3$.

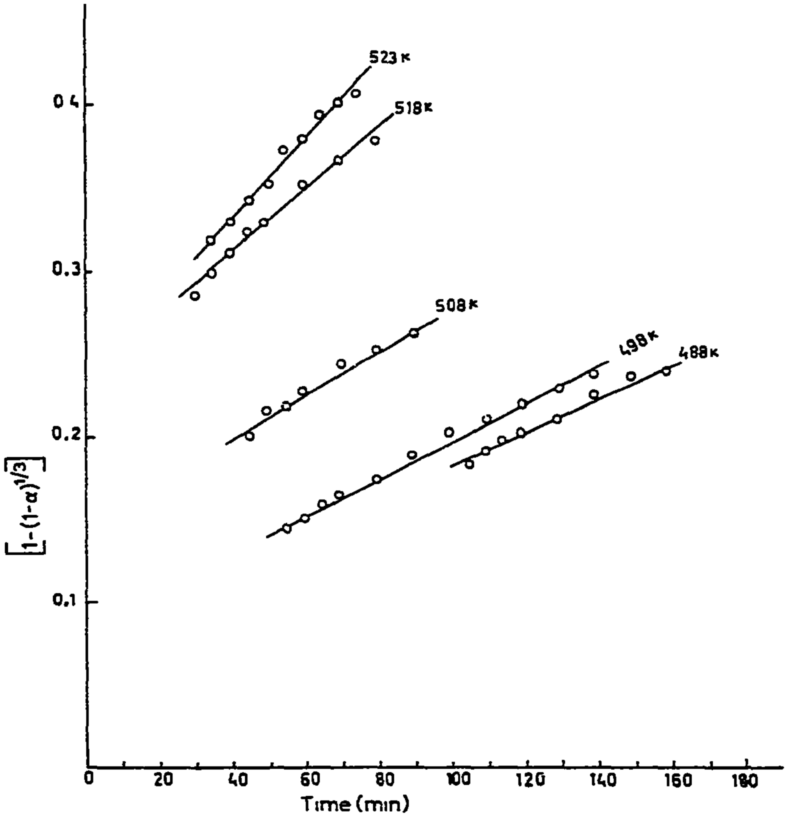


Fig. 4. Plot of the contracting sphere equation, $1-(1-\alpha)^{1/3}$ vs. time for $K_2NbO_2F_5 \cdot H_2O$.

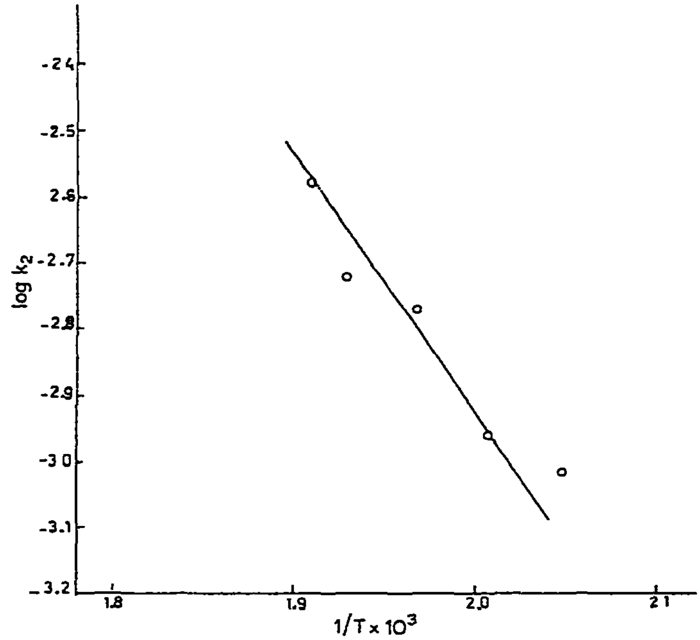


Fig. 5. Arrhenius plot of the contracting sphere rate constants, log k_2 vs. $1/T \times 10^3$.

plots (Fig. 1) show that the decomposition reaction is deceleratory. The induction and acceleratory regions are practically absent at all the temperatures studied. At 523 K, the highest temperature studied, most of the decomposition was over by 80 min at a value of α about 0.8. At 463 K, the lowest temperature studied, the value of α was about 0.1 even at 160 min.

The α—time data for the initial part of the decomposition reaction fit the unimolecular decay law very well (Fig. 2). At the lower temperatures, the data fit for as long as the reaction was studied (160 min). The Arrhenius plot (Fig. 3) gives a value of 146 kJ mole^{-1} for the activation energy.

The α—time plots for the later part of the decomposition reaction fit the contracting sphere equation (Fig. 4). The activation energy for this process is found to be 63 kJ mole^{-1} from the Arrhenius plot (Fig. 5).

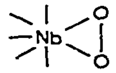
As in the case of fluoroperoxozirconates, the decomposition of potassium pentafluoroperoxoniobate monohydrate can be represented by the generalised equation

$$A_{(s)} \rightarrow B_{(s)} + C_{(g)}$$

$$K_2NbO_2F_5 \cdot H_2O_{(s)} \rightarrow K_2NbOF_{5(s)} + 1/2\ O_{2(g)} + H_2O \text{ (condensed)}$$

giving a stable oxofluoroniobate.

It has been observed by IR, laser Raman and other studies of this and related compounds that the peroxo group is triangularly linked and bidentate in nature [5—7]



which puts the system under some strain. It is therefore probable that the metal—peroxo bond cleaves first during decomposition of the peroxo group [2].

Water, which is lattice held, is lost before the onset of the peroxide decomposition. This feature has also been observed in the fluoroperoxozirconates [1—3]. In these cases, where dehydration precedes the peroxide decomposition, the mode of decomposition is seen to be deceleratory in nature with practically no induction or acceleratory regions. It is, however, of interest to mention here that $K_3Nb(O_2)_2F_4$, which has no water molecule in it, shows a typical sigmoidal behaviour with a large induction period [8]. Hence, it is probable that the dehydration step, preceding the peroxide decomposition, plays an important role in the instantaneous nucleation and the consequent application of the unimolecular decay law to the decomposition of these compounds.

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

Further studies on an element-wise basis of fluoroperoxo species of transition metals will help us in understanding the nature of decomposition of the peroxo group in these compounds.

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