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Note

SOLID STATE DECOMPOSITION STUDIES ON FLUOROPEROXO SPECIES OF TRANSITION METALS. PART X. KINETICS OF THE ISOTHERMAL DECOMPOSITION OF $K_3TiO_2F_5$

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Work is in progress in this laboratory on solid state thermal and photochemical decomposition studies on fluoroperoxo species of transition elements [1—7]. The present communication reports the kinetics of the isothermal decomposition of potassium pentafluoroperoxotitanate(IV), $K_3TiO_2F_5$.

EXPERIMENTAL

Potassium pentafluoroperoxotitanate(IV), $K_3TiO_2F_5$, reported earlier in the literature was prepared using a slightly modified method [8]. The analytical data, as percentage values, of a representative sample are

calculated:	K, 40.1%; Ti, 16.4%; O_A, 5.5%; F, 32.5%
found:	K, 40.0%; Ti, 16.2%; O_A, 5.2%; F, 32.2%

The IR bands of the present compound are characteristic of $K_3TiO_2F_5$, as reported by Griffith [8].

The TGA curve shows the commencement of decomposition around 455 K and a flat plateau is observed after 540 K. The loss in weight in this temperature range is due to the active oxygen only and the decomposition is represented as

$$K_3TiO_2F_{5\,(s)} \xrightarrow{\text{Thermal energy}} \underset{\text{Potassium oxopentafluorotitanate (IV)}}{K_3TiOF_{5\,(s)}} + \tfrac{1}{2}\,O_{2\,(g)}$$

which falls into the category of

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

For the kinetic studies, the dried solid sample was sieved through a 250 μm mesh wire sieve without grinding. The constant volume equipment and the experimental procedure remained the same as reported earlier [1—5].

RESULTS AND DISCUSSION

The decomposition of $K_3TiO_2F_5$ was carried out under isothermal conditions in the temperature range 463—532 K. The fractional decomposition, α, was plotted against time (Fig. 1). The minimum and maximum values of α obtained in this temperature range are 0.18 and 0.53, respectively. It is seen from α—t curves that the decomposition reaction is predominantly deceleratory in nature except in the first 6—8 min, which might include short induction and acceleratory regions. But this region is too small for detailed kinetic analysis.

The initial stage of the deceleratory reaction follows the unimolecular decay law (Fig. 2), which is obeyed for a longer period at lower temperatures. The activation energy, deduced from the Arrhenius plot (Fig. 3), is 54 kJ mole^{-1}. The later part of the decomposition reaction fits into the contracting sphere equation (Fig. 4). The activation energy for this region is 48 kJ mole^{-1} (Fig. 5). The basis of kinetic obedience of these two equations in the case of fluoroperoxo compounds has been discussed earlier [1—5].

It is interesting to note that, unlike the compounds studied previously in this series [1—5], potassium pentafluoroperoxotitanate(IV) has no water of hydration. The slightly delayed appearance of deceleratory regions in the α—t curves (6—8 min) may be due to the absence of lattice-held water in the present compound. It has been observed by the authors that fluoroperoxo compounds, containing lattice water, show the deceleratory mode of decomposition almost from the onset of the decomposition reaction [1—5].

As in other fluoroperoxo species, potassium pentafluoroperoxo-

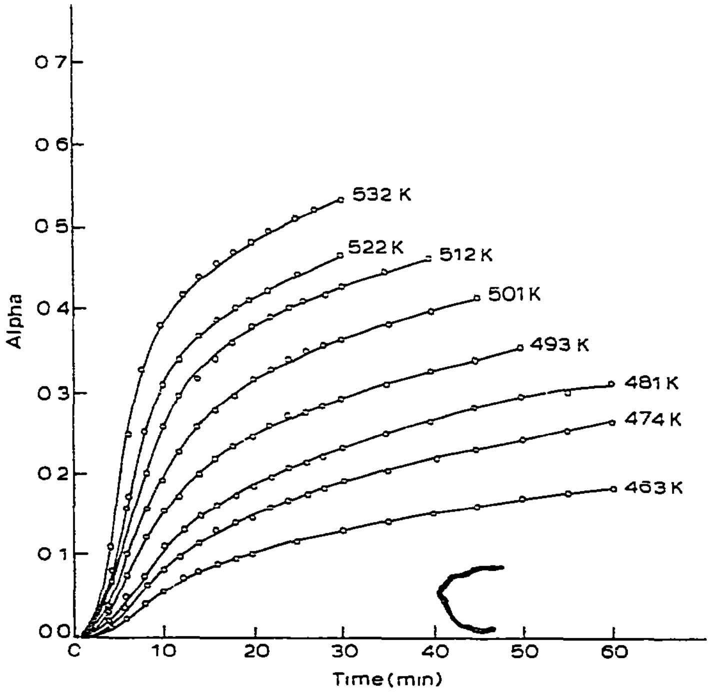


Fig. 1. Thermal decomposition curves for $K_3TiO_2F_5$.

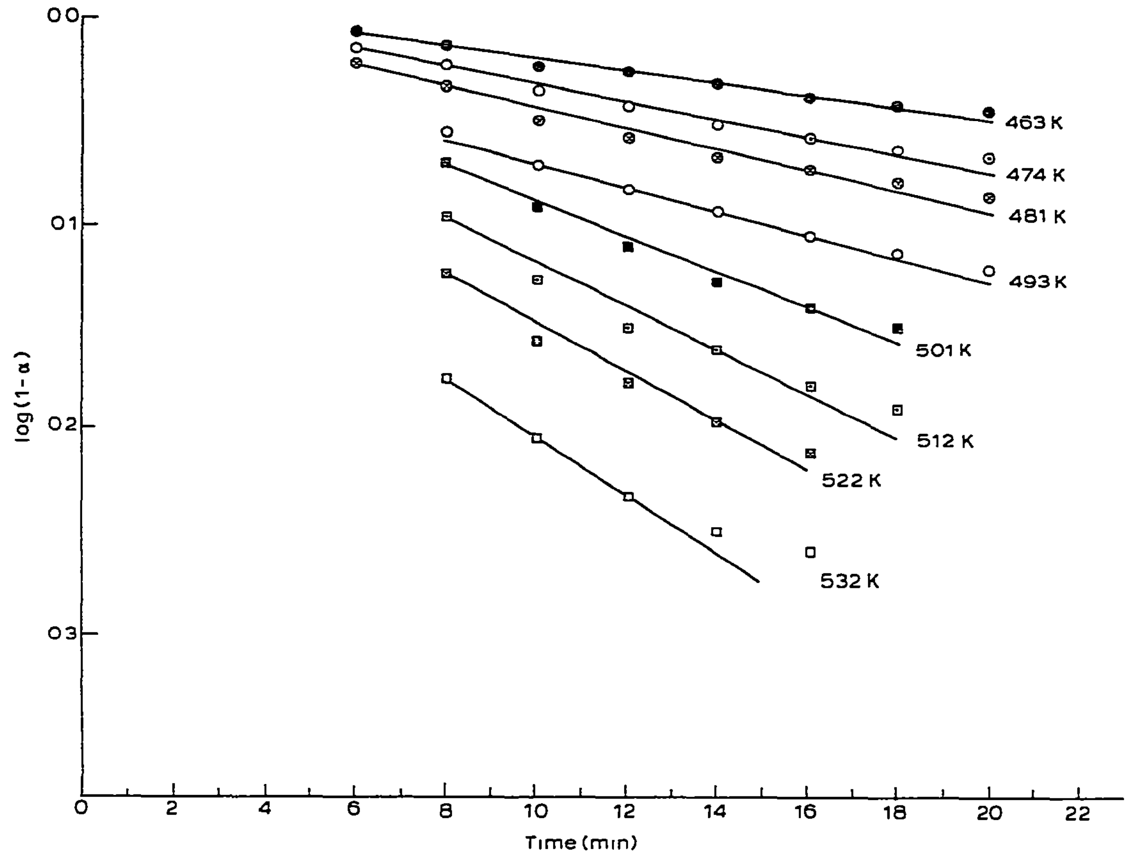


Fig. 2. Plot of unimolecular decay equation, $\log(1-\alpha)$ vs. time for $K_3TiO_2F_5$.

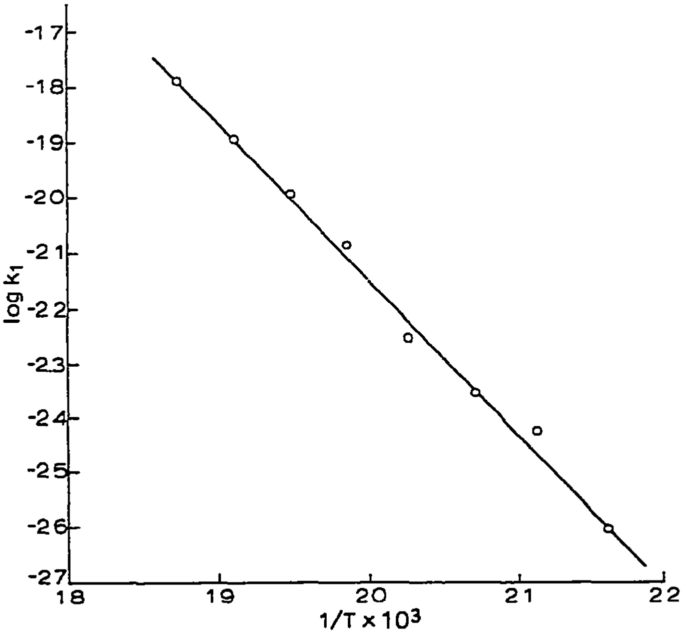


Fig. 3. Arrhenius plot of the unimolecular decay law rate constants, $\log k_1$ vs. $1/T \times 10^3$.

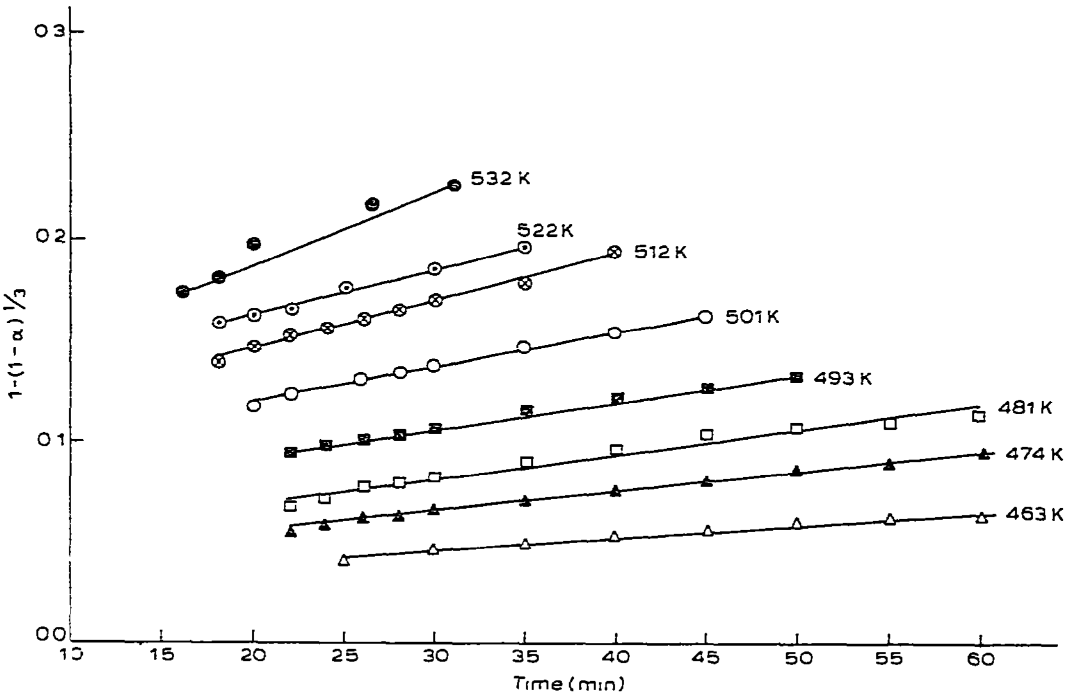
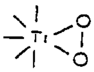


Fig. 4. Plot of the contracting sphere equation, $1-(1-\alpha)^{1/3}$ vs time for $K_3TiO_2F_5$.

titanate(IV) also posesses the strained metal—peroxide ring system



It is, therefore, quite probable that here also the first step is the rupture of the metal—peroxide bond [4,5]. This is then followed by the lattice rearrangement leading to the evolution of oxygen and the formation of potassium oxopentafluorotitanate(IV).

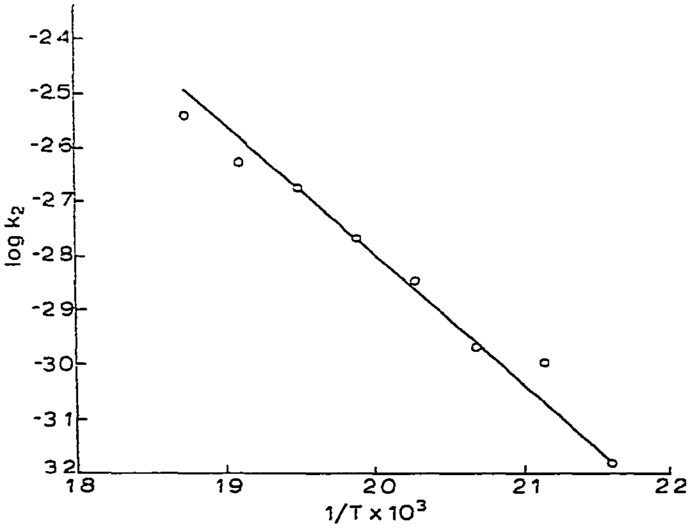


Fig. 5. Arrhenius plot of the contracting sphere rate constants, log k_2 vs. $1/T \times 10^3$.

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