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SOLID-STATE DECOMPOSITION STUDIES ON FLUOROPEROXO SPECIES OF TRANSITION METALS PART II

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The kinetics of isothermal decomposition of solid $K_2Zr_2(O_2)_2F_6 \cdot 2\,H_2O$ have been studied in the temperature range 100–226° under vacuum. The fractional decomposition α has been determined by measuring the pressure of evolved oxygen during pyrolysis with the help of a McLeod gauge. The α values ranged from 0.05 to 0.62. The α *vs.* t data showed that the kinetics are deceleratory throughout the course of the reaction. The initial part of the decomposition reaction could be best described by a unimolecular decay law, while the later stages obey contracting volume kinetics. The activation energies have been determined and the respective values for the above stages are 13.6 and 6.9 kcal $\cdot$ mole^{-1}.

Kinetic studies on solid-state decompositions have been attracting attention for a long time [1–4]. Recently, this topic was reviewed by Tompkins [5] and by Galwey [6] in two independent monographs on solid-state chemistry. It is seen from the literature survey that very little work has been done on inorganic peroxy salts, which have diverse utility in the textile, polymer, food, cosmetic, etc. industries, due to the oxygen content, which can readily be released on heating or chemically. Only a few solids, such as Li_2O_2, Na_2O_2, CaO_2 and BaO_2 [7]; $Rb_2CO_3 \cdot 3\,H_2O_2$ and $Cs_2CO_3 \cdot 3\,H_2O_2$ [8]; and $Na_2C_2O_6$ and $K_2C_2O_6$ [9] have been studied by isotopic distribution measurement of the oxygen evolved. Hence, a well-founded mechanism of liberation of active oxygen from the solid peroxy compounds during thermal decomposition is yet to be worked out. Kinetic study, though not sufficient in itself, is the first important step in this direction.

Work has been going on in this laboratory on the decomposition of zinc azides [10] and also the preparative aspects of the peroxide chemistry of transition elements [11–16]. This initiated the authors to subject the newly synthesized potassium fluoroperoxozirconate, $K_2Zr_2(O_2)_2F_6 \cdot 2\,H_2O$, to an exploratory decomposition study, as several other peroxo compounds present their own difficulties for such investigations. The compound was studied under isothermal conditions. This is preferred over non-isothermal methods, because it is assumed that at constant temperature the shape of the curve representing α as a function of time depends only on the mechanism of the reaction, whereas under dynamic conditions it depends upon numerous physicochemical factors and on the experimental conditions [17–19]. Further it is common practice to evaluate activation energy by the Arrhenius equation. However, there is some evidence [20–21] that this may show some shortcomings when applied to the reactivity of solids.

In this communication, results on the solid-state decomposition of $K_2Zr_2(O_2)_2F_6 \cdot 2\,H_2O$ under isothermal conditions are presented and discussed.

Experimental

Sample preparation

Solid potassium fluoroperoxozirconate, $K_2Zr_2(O_2)_2F_6 \cdot 2\,H_2O$, was prepared by the method reported by Santhamma and Jere [16]. The white solid was ground and finally dried over phosphorus pentoxide and analyzed. The sample was homogenized by sieving below 150 μ mesh.

Equipment

The conventional setup of the apparatus containing constant-volume vessel and McLeod gauge was used. Initially the apparatus and the sample (5–8 mg) was evacuated to a pressure of 10^{-6} mm Hg with the help of a mercury diffusion pump backed by a rotary pump for ten to twelve hours. Degassing rate was studied and again the system was evacuated, for one hour. After isolation of the system from the pump, the sample was heated in an electronically controlled furnace maintained at the desired temperature within $\pm 0.25°$. The condensable vapours were removed by using a liquid nitrogen trap. The fractional decomposition α was determined by measuring the pressure of oxygen evolved at different time intervals with the help of the McLeod gauge.

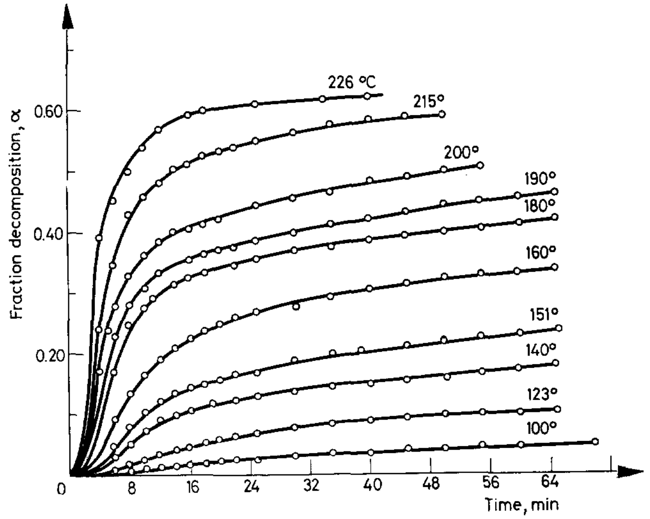


Fig. 1. Thermal decomposition of potassium fluoroperoxozirconate, $K_2Zr_2(O_2)_2F_62\,H_2O$, at different temperatures

Results

The isothermal decomposition of the compound was carried out in the temperature range 100–226°. The primary kinetic data (α *vs.* time) thus obtained are presented in Fig. 1, which shows that there is no induction period and acceleratory region as generally observed in a solid decomposition in which one of the products is a gaseous species, i.e. a characteristic sigmoidal decomposition curve. At all temperatures the compound decomposes with maximum rate at the beginning of decomposition, the rate subsequently decreasing with increasing degree of decomposition, i.e. the reaction is deceleratory throughout its course. The minimum and maximum values of α in this temperature range are 0.05 and 0.62, respectively.

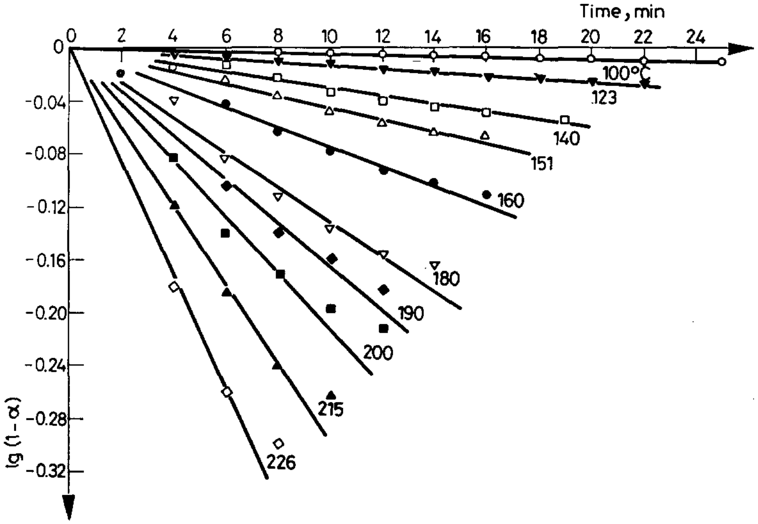


Fig. 2. Plot of log (1 — α) *vs.* *t*, unimolecular decay law, for potassium fluoroperoxozirconate, $K_2Zr_2(O_2)_2F_6 \cdot 2\,H_2O$

The applicability of equations commonly used to describe the thermal decomposition of solids was investigated. The kinetic data could not be fitted to a single rate equation over the entire decomposition range. The initial part of the decomposition could best be described by an unimolecular decay law, i.e. log $(1-\alpha)$ *vs.* *t* is linear. It is also observed that the rate equation holds good for a longer period at lower temperatures than at higher temperatures (Fig. 2). The rate constants k_1 were determined at different temperatures from the slopes of these lines. The activation energy (*Ea*) was determined from the Arrhenius plot (Fig. 3). The value is 13.6 kcal $\cdot$ mole^{-1}. The later stages of the decomposition could best be described by contracting volume kinetics, i.e. $1-(1-\alpha)^{1/3}$ *vs.* *t* is linear (Fig. 4). Similarly, the rate constants k_2 at various temperatures, and the corresponding activation energy, were determined. The value is 6.9 kcal mole^{-1} (Fig. 5).

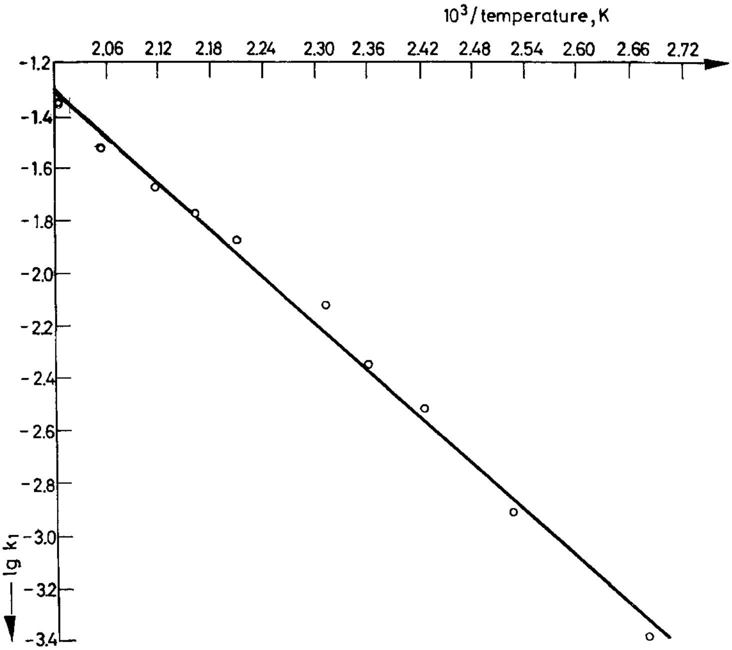


Fig. 3. Arrhenius plot of unimolecular decay law rate constants, i.e. log k_1 vs $\frac{1}{T} \cdot 10^2$, K

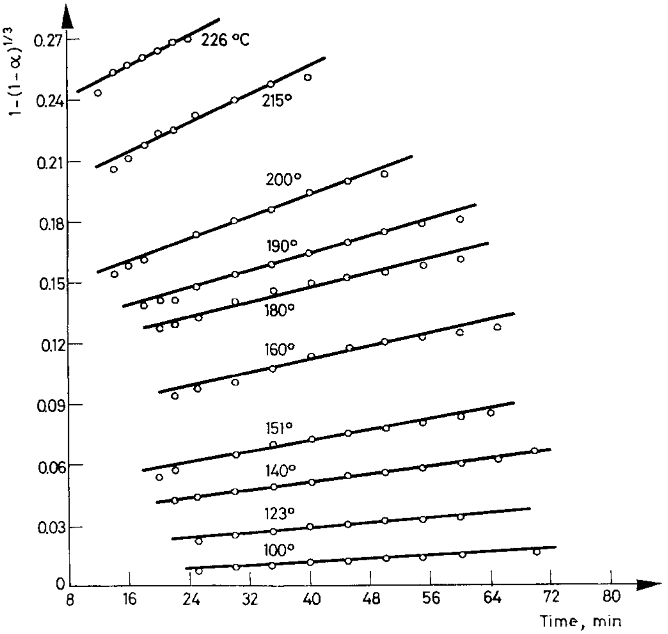


Fig. 4. Plot of $1 - (1 - \alpha)^{1/3}$ vs. t, contracting cube equation, for potassium fluoroperoxozirconate, $K_2Zr_2(O_2)_2F_6 \cdot 2\,H_2O$

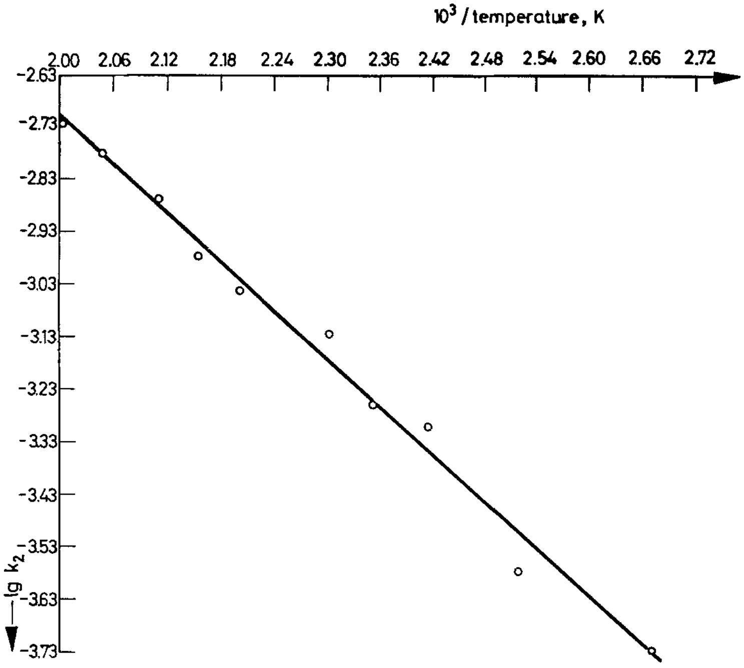


Fig. 5. Arrhenius plot of contracting cube rate constants, i.e. log k_2 *vs* $\frac{1}{T} \cdot 10^3$, K

Discussion

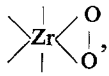
The shapes of α *vs.* t plots for the isothermal decomposition of the compound are reminiscent of the deceleratory kinetics observed in the case of sodium bromate [22] and sodium azide [23].

The kinetic course of a solid-state decomposition reaction is dominated by topochemical factors, and is described in terms of nucleation and growth of nuclei. Nucleation starts on the surface, because it contains a specific number of potential nucleus-forming sites of enhanced reactivity; these become germ nuclei on receipt of a critical quantity of energy, and are later transformed to active growth nuclei. The decomposition reaction of the present solid can be explained on the same lines. The initial part of the decomposition, obeying a unimolecular decay law, may be due to extremely rapid nucleation or instantaneous nucleation of the peroxide compound, followed by rapid surface growth [2]. By the time the surface is completely transformed into the product, a sufficient penetration of the reaction zone into the particle is also possible. The energy 13.6 kcal mole^{-1} may be attributed to several factors, such as nucleation, surface growth, penetration into the crystal, etc. The applicability of the contracting cube equation in the later stages of the decomposition reaction explains that the surface is transformed into the product and the interface progresses in the direction of the centre of the particle. The reaction is deceleratory since the interface progressively decreases.

It is rather premature to propose a definite mechanism for the decomposition reaction at this stage. Work is in progress in this laboratory on the thermal as well as the photodecomposition of solid peroxy compounds of transition elements; the results will be communicated in subsequent publications dealing with the probable mechanism of decomposition. However, some features of the present solid are indicated below.

The compound contains a triangularly-linked bidentate peroxo group [24], which constitutes a highly-strained system. On decomposition, the solid gives molecular oxygen, water and potassium oxofluorozirconate as shown below (TG study) [24]:

$$K_2Zr_2(O_2)_2F_6 \cdot 2\,H_2O(s) \rightarrow K_2Zr_2O_2F_6(s) + O_2(g) + 2\,H_2O(g)\ \text{(condensed)}$$

The strained ring configuration, , may be responsible for the low activation energies. So, probably at the beginning, there is a cleavage of metal–peroxide bonds, leading to an extensive lattice rearrangement, followed by the evolution of oxygen with the rupture of peroxide bonds (O – O).

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Zusammenfassung — Die Kinetik der isothermen Zersetzung von festen $K_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ wurde im Temperaturbereich von 100—226° im Vakuum untersucht. Die fraktionierte Zersetzung α wurde durch Messung des Druckes des während der Pyrolyse entwickelten Sauerstoffs mit einem McLeod-Manometer bestimmt. Die α-Werte variierten von 0.05 bis 0.62. Die α-t Daten zeigen, daß die Kinetik im Verlauf der Reaktion herabgesetzt wird. Der erste Teil der Zersetzungsreaktion konnte am besten durch ein unimolekulares Zerfallgesetzt beschrieben werden, während die späteren Phasen der Kinetik der Volumenkontraktion gehorchten. Die Aktivierungsenergien wurden berechnet und die entsprechenden Werte für obige Reaktionen ergaben sich 13.6 bzw. 6.9 Kcal mol^{-1}.

Резюме — Была изучена кинетика изотермического разложения в вакууме твердого соединения $K_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ в области температур 100—226°. Фракционированное разложение «α» было определено измерением давления кислорода, выделенного во время пиролиза, с чомощью маномера МакЛеода. Значения «α» изменялись от 0.05 до 0.62. Данные α—t показали, что кинетика замедляется в течении всего хода реакции. Начальная стадия реакции разложения наилучшим образом подчиняется мономолекулярному закону распада, в то время как последние стадии — кинетике сжатых объемов. Определены энергии активации, которые, соответственно, равны 13.6 и 6.9 ккал.моль$^{-1}$.