

Solid State Decomposition Studies on Fluoroperoxo Species of Transition Metals. IV. Photodecomposition of $K_3Zr_2(O_2)_2F_7 \cdot 2H_2O$

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The kinetics of photodecomposition of solid $K_3Zr_2(O_2)_2F_7 \cdot 2H_2O$ have been studied under vacuum as a function of intensity and temperature by measuring the evolved oxygen with the help of a McLeod Gauge. Pressure-time curves are parabolic in nature and the data fit the empirical equation $p = kt^{1/2}$. The rate of photodecomposition is a linear function of intensity. The activation energy determined from an Arrhenius plot, in the temperature range 15-55°C, of the title compound is 2.15 kcal mole⁻¹ (9.00 kJ mole⁻¹).

Introduction

The study of the photochemistry of solids is still mainly at the phenomenological stage due to several intrinsic difficulties involved (1). The solids which have been subjected to detailed photodecomposition studies are azides (2, 3), perchlorates (4), bromates (5), permanganates (6), etc. Among the coordination compounds, trioxalatometallates, i.e., ferrate (7), cobaltate (8), and manganate (9, 10) have been studied. This area remains totally unexplored for solid peroxo compounds of transition elements. Work has been going on in this laboratory on the synthetic aspects of peroxide chemistry of transition elements (11-14) and also on solid state decomposition studies, both thermal and photochemical, on azides, hydroxyazides (15), and fluoroperoxo species of transition elements (16-18). The results of thermal decomposition of fluoroperoxo zirconate

species have been communicated elsewhere for publication (17, 18).

In the present communication, results of photodecomposition of solid $K_3Zr_2(O_2)_2F_7 \cdot 2H_2O$ are presented and discussed.

Experimental

The title compound was prepared as reported by Santhamma and Jere (14). It was characterized by analysis, ir, and X-ray powder diffraction studies. For photodecomposition, the compound was ground in an agate mortar until the powdered mass passed through a 150- μ m-mesh wire sieve. Samples of 150 mg were evenly distributed in the photolysis cell having a transparent quartz window for irradiation. The cell is connected to a constant volume system (3.2 liters). Prior to each photolysis run the system was evacuated to a pressure of 10⁻⁶ Torr. After studying the initial dark rate,

the system was again evacuated to the same pressure. The pressure of the oxygen produced during photodecomposition was measured with the help of a McLeod Gauge capable of measuring pressure up to 10^{-1} Torr ($100 \mu\text{m Hg}$).

The source of uv light used was a high-pressure mercury lamp (HPK 125, Phillips, Holland) which emits strong background radiation in the near-uv and visible region in addition to the principal lines having strong emissions at 365.5, 313.0, 265.3, and 253.7 nm. An accurate determination of intensity of light emitted by the source (in terms of quanta/sec/cm²) was achieved by actinometry of the lamp by potassium trisoxalatoferate(III)trihydrate. The lamp was allowed to warm up for 15 min before use and its full spectrum was used for photodecomposition studies.

Different intensities were obtained by varying the distance of the uv lamp from the sample and desired temperature by surrounding the photolysis cell by a jacket-bath connected to a cryostat (MK 70).

The diffuse reflectance spectrum of the

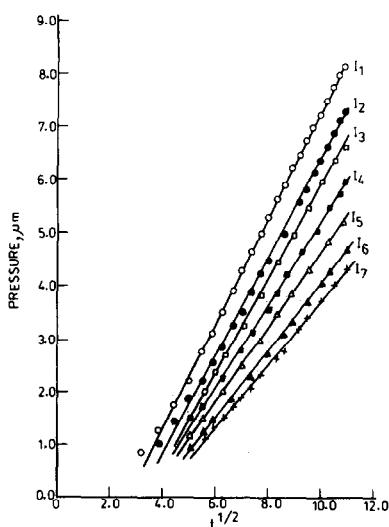


FIG. 1. p vs $t^{1/2}$ plots for photolysis of $\text{K}_3\text{Zr}_2(\text{O}_2)_2\text{F}_7 \cdot 2\text{H}_2\text{O}$, at different intensities and constant temperature, 25°C .

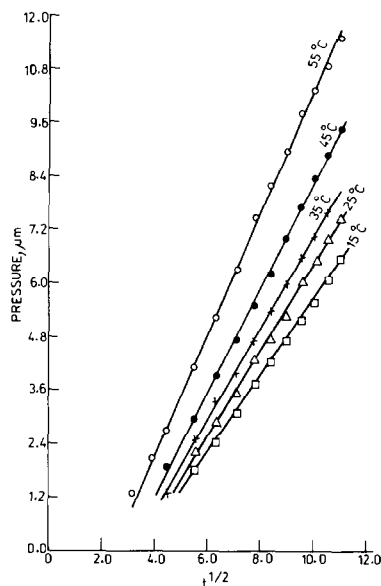


FIG. 2. p vs $t^{1/2}$ plots for photolysis of $\text{K}_3\text{Zr}_2(\text{O}_2)_2\text{F}_7 \cdot 2\text{H}_2\text{O}$ at different temperatures and constant intensity.

sample was recorded on a Unicam SP 700 spectrophotometer.

Results

The pressure-time data of the evolved oxygen were obtained by measuring the

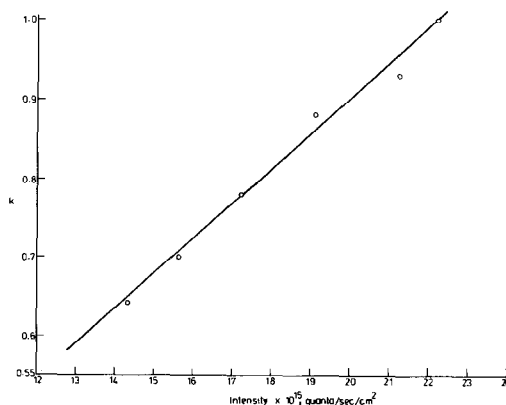


FIG. 3. Plot to show the dependence of "k" on intensity for $\text{K}_3\text{Zr}_2(\text{O}_2)_2\text{F}_7 \cdot 2\text{H}_2\text{O}$.

oxygen pressure over the sample as a function of time. Duplicate sets of measurements at the same intensity and temperature have yielded highly reproducible pressure-time data in the case of the powdered samples, whereas in the case of pellets some difficulties were encountered. Experiments were also carried out with and without a liquid air trap in the vacuum system keeping other conditions the same to find out the behavior of lattice-held water. No significant change in pressure-time data was observed.

The "*p**t*" data of photodecomposition of the title compound at different intensities and constant temperature (25°C), and at different temperatures (15 to 55°C) and constant intensity of 21.27×10^{15} quanta/sec/cm², were analyzed using the rate equation, $p = kt^{1/2}$. The plots of *p* vs *t*^{1/2} are linear in both sets of experiments (Figs. 1 and 2). The dependence of the rate of photolysis on intensity was determined by plotting "*k*" vs "*I*" (Fig. 3). It is found that "*k*" is a linear function of intensity. The Arrhenius plot of photolysis of the title compound yields an energy of activation of 2.15 kcal mole⁻¹ (9.00 kJ mole⁻¹).

No dark rate was present and also no color change in the compound was noticed.

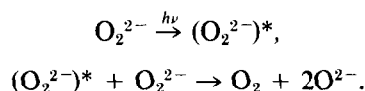
Discussion

Since the present study is the first of its kind on peroxo compounds of transition elements, it has to be of an exploratory nature, examining the feasibility of the system and summarizing some salient observations.

Though the molecular formulation of the species, $K_3Zr_2(O_2)_2F_7 \cdot 2H_2O$, looks big, the group which undergoes photoexcitation and subsequent decomposition is the peroxo group, which gives a measurable oxygen pressure. The primary process during photolysis is the absorption of radiation by the peroxide. It is seen, from the dif-

fused reflectance spectrum of the above compound, that a broad absorption band occurs in the range of 240–270 nm and a long-wavelength tail of this absorption extending up to 330 nm. The evolved oxygen does not affect the stable reactant matrix or the photodecomposition process. Further it has been observed that lattice water held by the compound remains unaffected during photolysis, unlike that in thermal decomposition (16).

The decrease of the photolytic rate with time, as seen by the parabolic nature of *p*-*t* data, may have been caused by the gradual consumption of special sites initially present which are helpful for the photodecomposition reaction. It is seen from Fig. 3 that rate of photodecomposition is a linear function of intensity. This indicates that single excitation is needed for peroxide decomposition. This may be tentatively visualized as below:



It is thus seen from the present study that the title compound is amenable for photodecomposition investigations. Work is in progress with similar solid species on an elementwise basis.

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