SOLID STATE DECOMPOSITION STUDIES OF FLUOROPEROXO SPECIES OF TRANSITION METALS
VII: PHOTODECOMPOSITION OF $M_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ (M = K^+, Rb^+ AND Cs^+)

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Summary

The kinetics of photodecomposition of the solid compounds $M_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ (M = K^+, Rb^+ and Cs^+) were studied under vacuum as a function of both intensity and temperature. The pressure of the oxygen evolved was measured with a constant volume apparatus fitted with a McLeod gauge. All the pressure–time curves obtained are parabolic and the data fit the rate equation $p = kt^{1/2}$. For all three solid compounds the rate of decomposition is linearly dependent on intensity, indicating a monoexcitation process for the photolysis. The activation energies deduced from Arrhenius plots are 0.93, 1.38 and 0.82 kcal mol^{-1} for the potassium, rubidium and caesium species respectively.

1. Introduction

Because of various experimental difficulties, the solid state photochemistry of inorganic compounds is still in the developmental stage [1, 2]. Most of the photochemical investigations of coordination compounds have been carried out in solution [3 - 6] and only a few solid state studies have been reported [7, 8]. There is no data in the literature on the solid state photodecomposition of peroxo compounds of the transition metals. We have investigated the thermal and photodecomposition of peroxo compounds of transition metals and some of the results of these studies have been published [9 - 12].

In this work results on the photodecomposition of the solid compounds $M_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ (M = K^+, Rb^+ and Cs^+) are presented and discussed.

2. Experimental

2.1. Sample preparation

The compounds were prepared according to the method described by Santhamma [13]. A known amount of zirconium oxychloride was dissolved

in 100 ml of a 1:1 mixture of water and methanol. About 30 ml of 30% H_2O_2 was added to this solution with stirring. This was followed by the slow addition of the respective alkali metal fluoride in an appropriate quantity to maintain the zirconium-to-fluoride mole ratio at 1:3. (Rubidium fluoride was prepared by reacting the carbonate with hydrofluoric acid.) The white solid obtained was filtered, and was washed well with a 1:1 mixture of water and methanol and finally with acetone. The compound was ground and dried over phosphorus pentoxide. The compositions of these dried solids were checked by analysis, by IR spectroscopy and with X-ray powder photographs. To keep uniformity in the nature of the starting material the samples were homogenized by sieving, using a mesh size smaller than 150 μm.

2.2. Equipment

A high vacuum constant volume system containing a photolysis cell with a transparent quartz window was used. The sample was spread evenly in the photolysis cell. A liquid air trap was used during the photodecomposition studies. Prior to each photolysis run the system was evacuated to a pressure of 10^{-6} Torr and, after studying the initial dark rate, the system was again evacuated to this pressure. The pressure of the oxygen evolved during photolysis was measured using a McLeod gauge. In the photolysis studies 150 mg of the potassium and 50 mg of the rubidium and the caesium fluoro-peroxozirconates were used.

A high pressure mercury arc lamp (HPK 125, Phillips Holland) was used for the photolysis; this lamp emits strong background radiation in the UV and visible regions in addition to the principal lines which have strong emissions at 253.7, 265.3, 313.0 and 365.5 nm. Actinometry by potassium tri-soxalatoferrate(III) trihydrate was carried out in order to determine the incident intensity. The lamp was allowed to warm up for 15 min before use and its full spectrum was used for the photodecomposition studies.

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

The diffuse reflectance spectra were recorded on a Unicam SP 700 UV–visible spectrophotometer and are shown in Fig. 1.

3. Results

The pressure–time data for the oxygen evolved during the photodecompositions were obtained by measuring the oxygen pressure over the sample as a function of time. Duplicate sets of measurements carried out in some experiments showed excellent reproducibility for powdered samples. However, pelleted samples presented some difficulties. No dark rate was observed during the photodecomposition of these solids. Also there was no noticeable change in the colour of the samples.
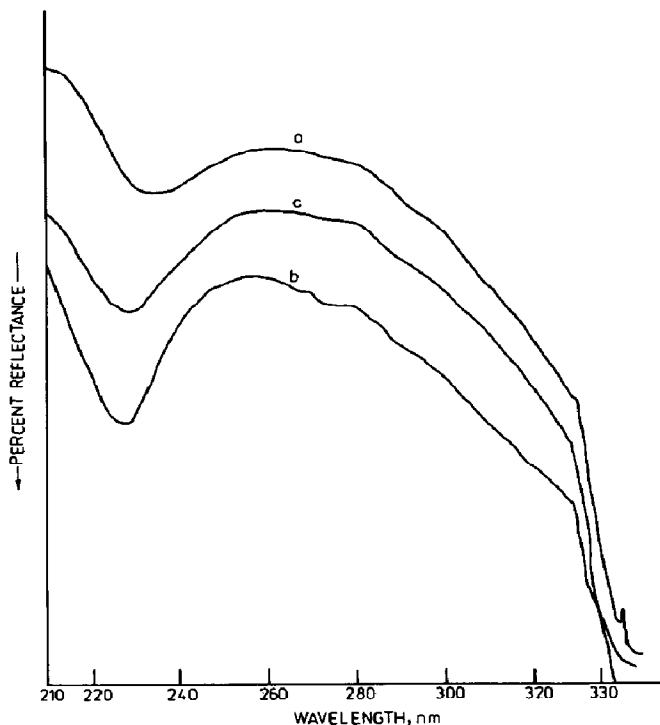
Fig. 1. Diffuse reflectance spectra of the compounds $M_2Zr_2(O_2)_2F_6 \cdot 2H_2O$: curve a, $M = K^+$; curve b, $M = Rb^+$, curve c, $M = Cs^+$.

3.1. $K_2Zr_2(O_2)_2F_6 \cdot 2H_2O$

Pressure–time data for the photodecomposition of $K_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ at different intensities and constant temperature (25 °C) are presented in Fig. 2. The photolysis was also carried out at a constant intensity of 21.27×10^{15} quanta s^{-1} cm^{-2} and different temperatures in the range 10 - 50 °C; the results are plotted in Fig. 3. The pressure–time curves in Figs. 2 and 3 are parabolic and fit the rate equation $p = kt^{1/2}$. Plots of p versus $t^{1/2}$ are linear and are given in Figs. 4 and 5. Figure 6 shows that the rate of photolysis is a linear function of intensity. The activation energy deduced from an Arrhenius plot is 0.93 kcal mol^{-1}.

3.2. $Rb_2Zr_2(O_2)_2F_6 \cdot 2H_2O$

The pressure–time data for $Rb_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ at different intensities and constant temperature (25 °C) are presented in Fig. 7, and at constant intensity and different temperatures (5 - 45 °C) in Fig. 8. These data were analysed using the rate equation $p = kt^{1/2}$ and linear plots of p versus $t^{1/2}$ are presented in Figs. 9 and 10. The rate of photodecomposition is linearly dependent on intensity (Fig. 11). The activation energy is 1.38 kcal mol^{-1}.
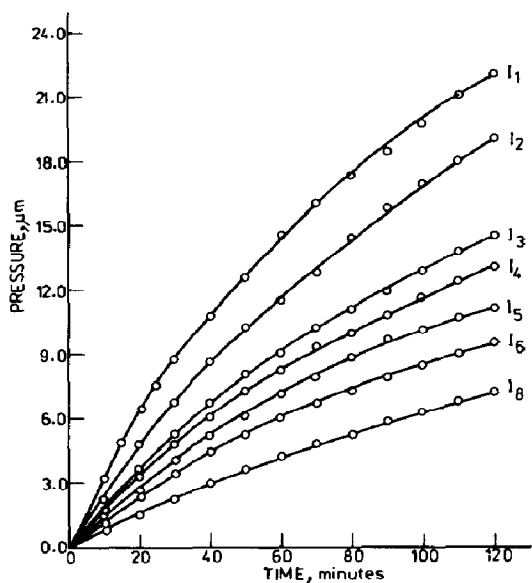
Fig. 2. Pressure–time plots for the photodecomposition of $K_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ at different intensities and constant temperature (25 °C).
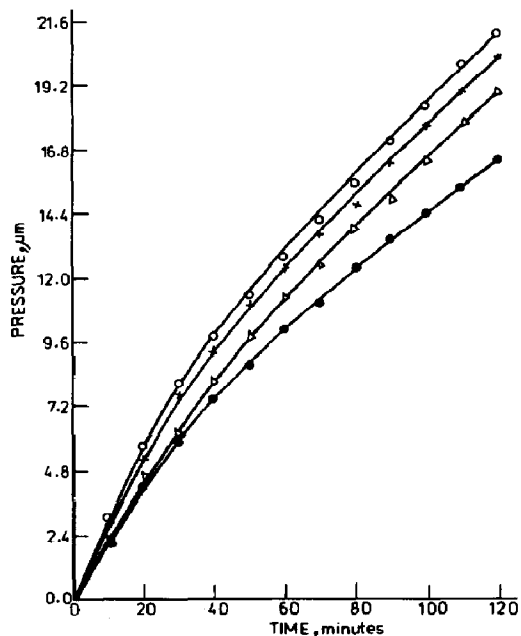
Fig. 3. Pressure–time plots for the photodecomposition of $K_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ at different temperatures and constant intensity: ●, 10 °C; △, 30 °C; ×, 40 °C; ○, 50 °C.
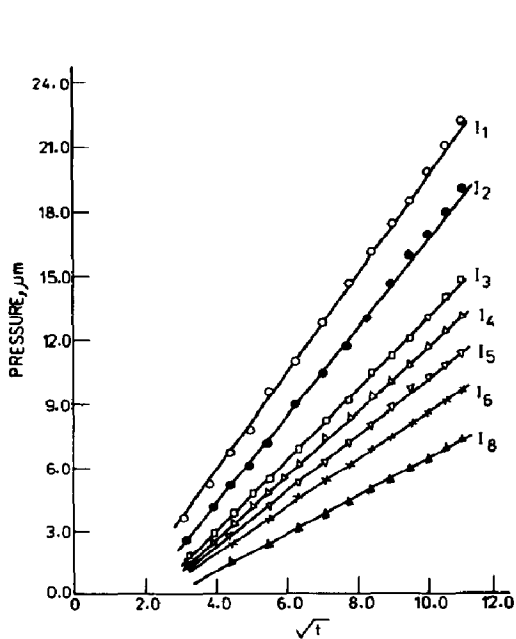

Fig. 4. Plots of p vs. $t^{1/2}$ for $K_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ at different intensities and constant temperature (25 °C).
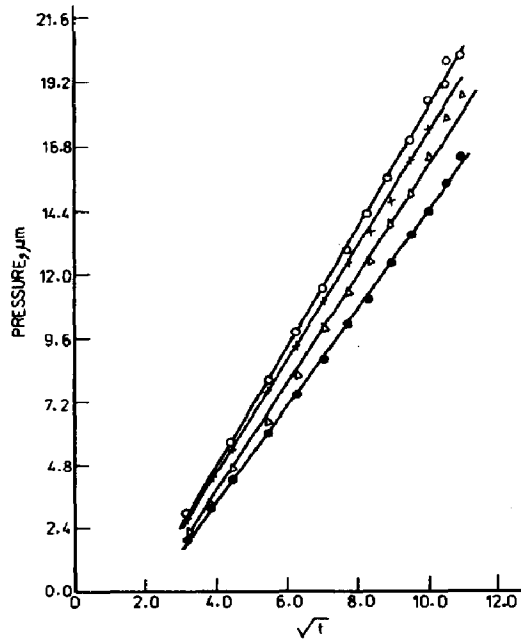
Fig. 5. Plots of p vs. $t^{1/2}$ for $K_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ at different temperatures and constant intensity $(21.27 \times 10^{15}$ quanta s^{-1} cm$^{-2})$: ●, 10 °C; △, 30 °C; ×, 40 °C; ○, 50 °C.
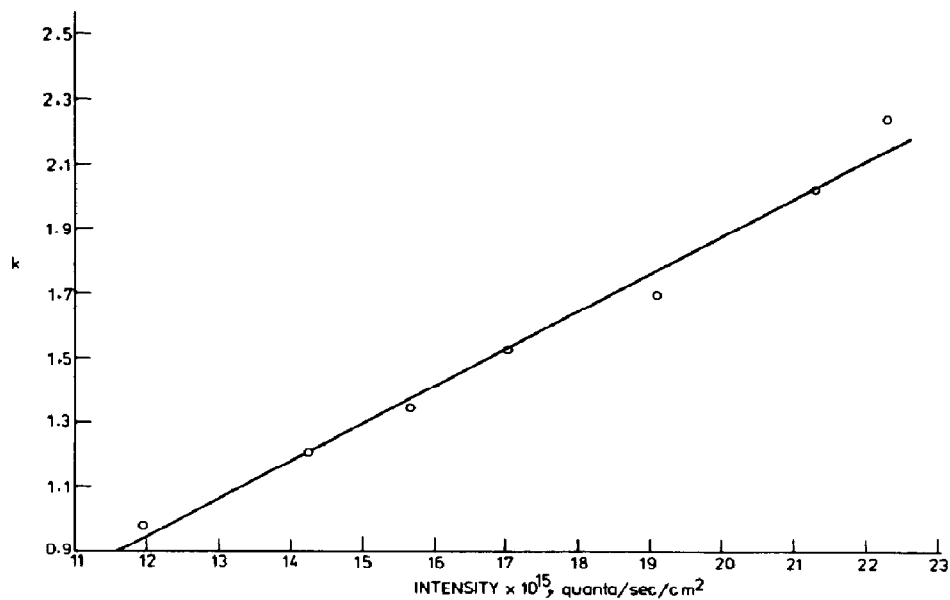
Fig. 6. The dependence of the rate constant k on the intensity for $K_2Zr_2(O_2)_2F_6 \cdot 2H_2O$.
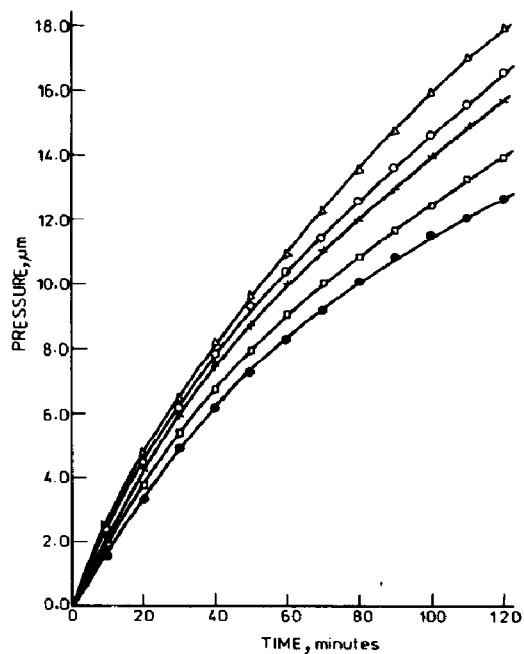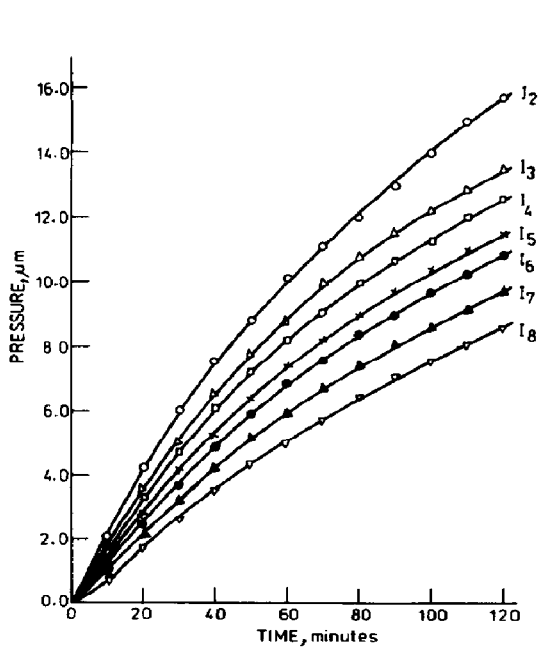
Fig. 7. Pressure–time plots for the photodecomposition of $Rb_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ at different intensities and constant temperature (25 °C).

Fig. 8. Pressure–time plots for the photodecomposition of $Rb_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ at different temperatures and constant intensity: •, 5 °C; □, 15 °C; ×, 25 °C; ○, 35 °C; △, 45 °C.
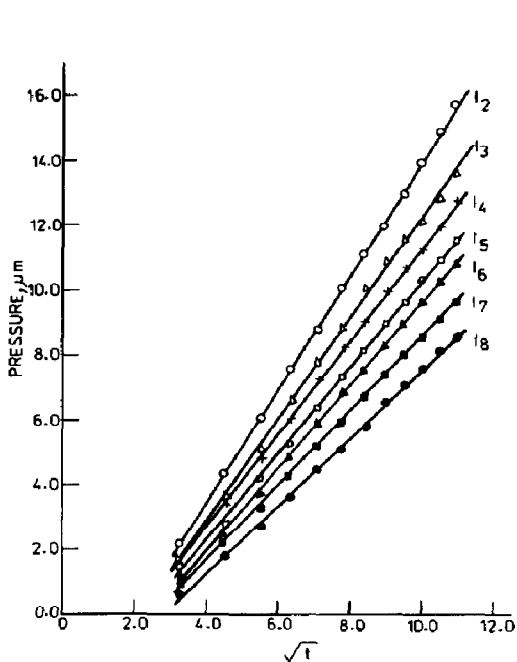
Fig. 9. Plots of p vs. $t^{1/2}$ for $Rb_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ at different intensities and constant temperature (25 °C).
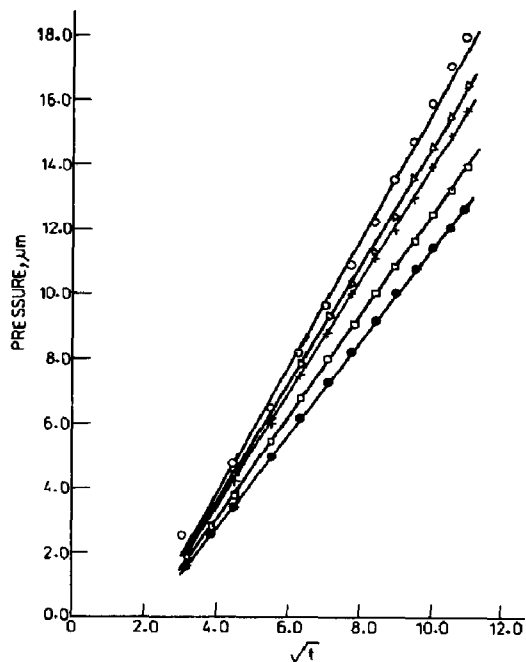
Fig. 10. Plots of p vs. $t^{1/2}$ for $Rb_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ at different temperatures and constant intensity: •, 5 °C; □, 15 °C; ×, 25 °C; △, 35 °C; ○, 45 °C.
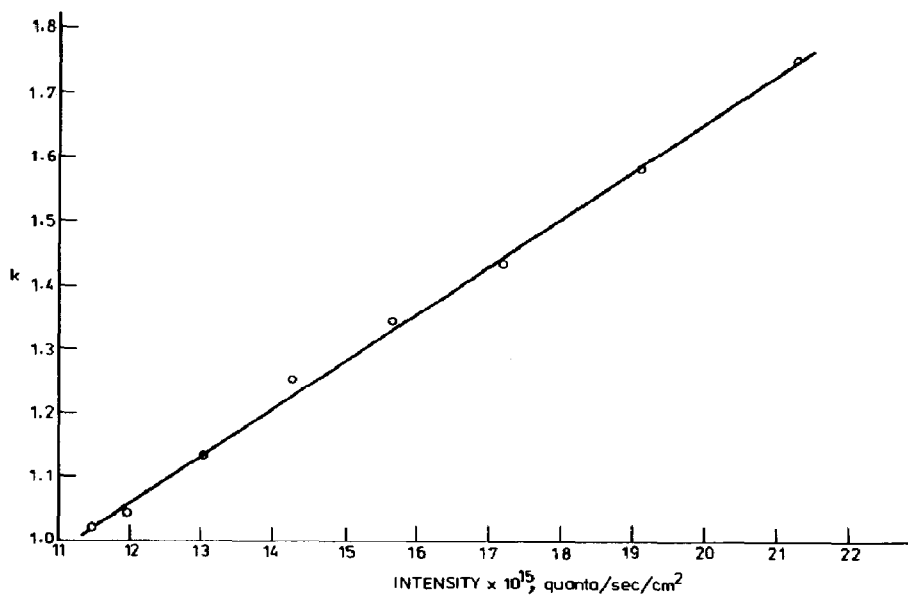
Fig. 11. The dependence of the rate constant k on the intensity for $Rb_2Zr_2(O_2)_2F_6 \cdot 2H_2O$.

3.3. $Cs_2Zr_2(O_2)_2F_6 \cdot 2H_2O$

The pressure–time data for $Cs_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ as a function of intensity and of temperature are presented in Figs. 12 and 13 respectively. The rate equation $p = kt^{1/2}$ is applicable and linear plots of p versus $t^{1/2}$ are presented in Figs. 14 and 15. The rate of photolysis is linearly dependent on intensity (Fig. 16) and the activation energy is 0.82 kcal mol^{-1}.
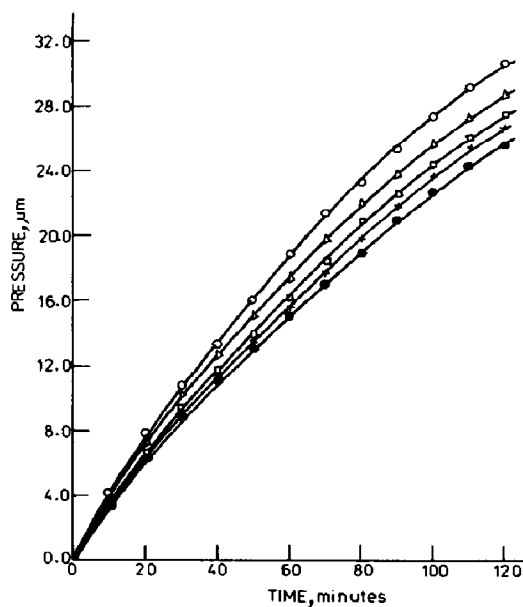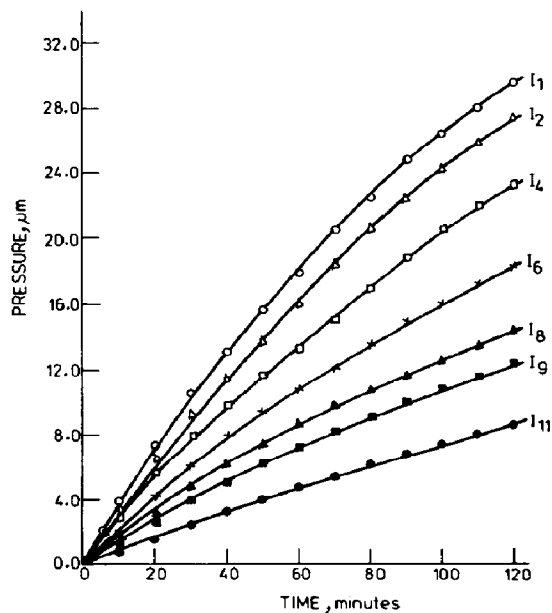
Fig. 12. Pressure–time plots for the photodecomposition of $Cs_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ at different intensities and constant temperature (25 °C).

Fig. 13. Pressure–time plots for the photodecomposition of $Cs_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ at different temperatures and constant intensity: ●, 5 °C; ×, 15 °C; □, 25 °C; △, 35 °C; ○, 45 °C.

4. Discussion

Because this investigation of the photolysis of $M_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ species in the solid state is the first of its kind on transition metal peroxo compounds, the results are somewhat preliminary in nature.

The close similarity of the experimental data of the solids should be noted. This indicates that the photoexcitation process leading to the evolution of oxygen is the same in all three, where the anionic part of the complex is unaltered. Unlike thermal activation, photochemical activation is selective in nature [2]. The only photoexcitable moiety in the compounds studied is the peroxo group; the lattice-held water remains unaffected during the photodecomposition.
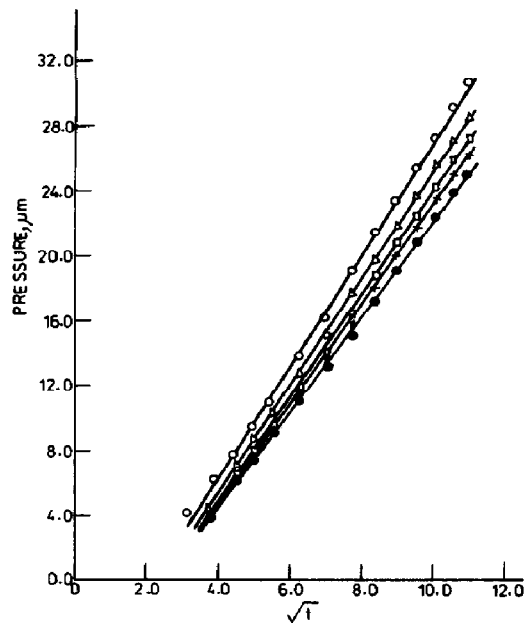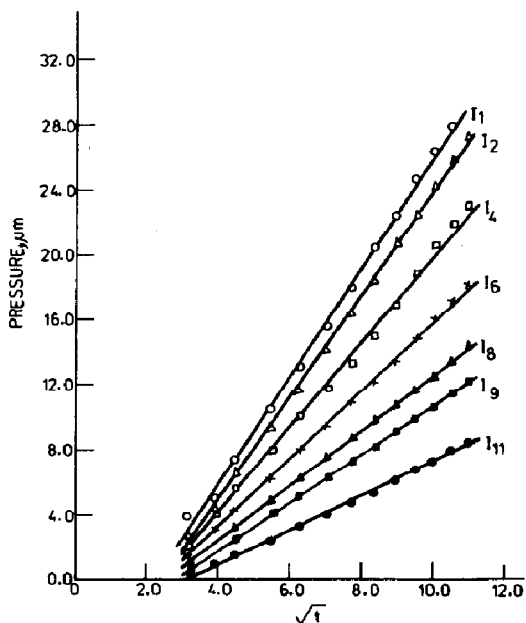
Fig. 14. Plots of p *vs.* $t^{1/2}$ for $Cs_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ at different intensities and constant temperature (25 °C).

Fig. 15. Plots of p *vs.* $t^{1/2}$ for $Cs_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ at different temperatures and constant intensity: •, 5 °C; ×, 15 °C; □, 25 °C; △, 35 °C; ○, 45 °C.
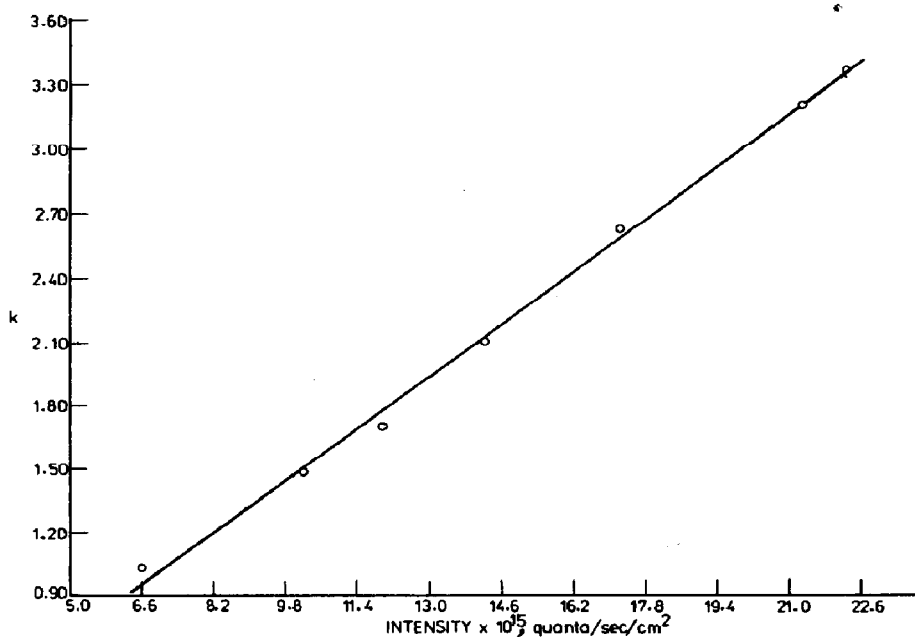
Fig. 16. The dependence of the rate constant k on the intensity for $Cs_2Zr_2(O_2)_2F_6 \cdot 2H_2O$.

The diffuse reflectance spectra for these solids (Fig. 1) show a broad absorption centred at about 260 nm. The long tail of the absorption extends up to 330 nm. The parabolic nature of the pressure—time curves indicates that there is a decrease in the photolytic rate with time. This can be explained in terms of special sites which aid the photodecomposition and which are slowly consumed during the photolysis. The rate of photolysis is linearly dependent on intensity, indicating that monoexcitation is required for peroxide decomposition in these solids, *i.e.*

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

$$O_2{}^{2-} + (O_2{}^{2-})* \longrightarrow O_2 + 2O^{2-}$$
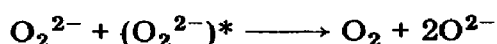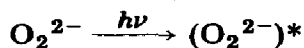
The chances of reducing the Zr(IV) to Zr(III) during the photodecomposition are very remote, in contrast with some other systems [14 - 16] where the metal ion does undergo a change in oxidation state. Therefore, it is primarily the interaction between peroxo groups which leads to the evolution of oxygen and to the formation of oxide ions which are held in the lattice of the product. The redox system could occur by exciton formation.

No attempt was made to calculate quantum yields in this work, since accurate quantum yield determinations for solid state photodecompositions are difficult to achieve. These reactions have their own inherent difficulties such as the heterogeneous nature of the reactions and absorption by photoproducts. Hence the quantum yields, if determined, will not be very accurate. Despite these limitations some efforts are being made to evaluate quantum yields [17 - 21].

This work has shown that the $M_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ compounds are amenable for photodecomposition investigations. Work is in progress on thermal and photodecomposition studies of fluoroperoxo species of titanium, niobium and tantalum.

Acknowledgment

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