SOLID STATE DECOMPOSITION STUDIES OF FLUOROPEROXO SPECIES OF TRANSITION METALS
VIII: PHOTODECOMPOSITION OF $Rb_3Zr_2(O_2)_2F_7 \cdot H_2O$ AND $Cs_3Zr_2(O_2)_2F_7 \cdot 2H_2O$

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Summary

The kinetics of photodecomposition of the solids $Rb_3Zr_2(O_2)_2F_7 \cdot H_2O$ and $Cs_3Zr_2(O_2)_2F_7 \cdot 2H_2O$ were studied under vacuum as a function of both intensity and temperature by measuring the pressure of the oxygen evolved with a McLeod gauge. Similar to other fluoroperoxozirconates the photolysis kinetics of these compounds are deceleratory throughout the decomposition reaction. The pressure–time curves are parabolic and the data fit the rate equation $p = kt^{1/2}$. Also the rate of photodecomposition is a linear function of the intensity, indicating a monoexcitation process for the photolysis. The probable mechanism of photodecomposition can be visualized as the interaction of peroxo groups in excited states at special sites:

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

$$O_2{}^{2-} + (O_2{}^{2-})^* \rightarrow O_2 + 2O^{2-}$$
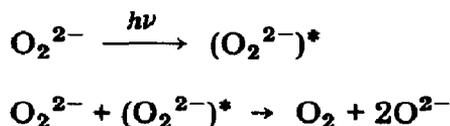
1. Introduction

Work is in progress in this laboratory on the kinetics of thermal and photochemical decomposition of fluoroperoxo species of transition metals [1 - 6]. Results on the photodecomposition of solid fluoroperoxozirconate species of alkali metals, *i.e.* $M_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ (M ≡ K⁺, Rb⁺, Cs⁺), have been reported [5]. The photolysis of potassium fluoroperoxozirconate ($K_3Zr_2(O_2)_2F_7 \cdot 2H_2O$) has been reported elsewhere [6].

In this work results on the photodecomposition of the solids $Rb_3Zr_2(O_2)_2F_7 \cdot H_2O$ and $Cs_3Zr_2(O_2)_2F_7 \cdot 2H_2O$ are presented and are discussed; the salient features observed for other fluoroperoxozirconates are also considered.

2. Experimental

The compounds were prepared by the method reported in ref. 2 and were characterized by analysis, IR and X-ray powder diffraction studies. For decomposition studies the compounds were ground as described previously [5, 6] in an agate mortar until the powder passed through a 150 μm mesh wire sieve. Each powdered sample (50 mg) was evenly spread in the photolysis cell which was connected to a constant-volume system. The high vacuum system, the UV source, the photolysis cell and other experimental details were the same as those described previously [5, 6].

The diffuse reflectance spectra of the compounds were recorded on a Unicam SP-700 spectrophotometer and are presented in Fig. 1 together with that of the potassium analogue.
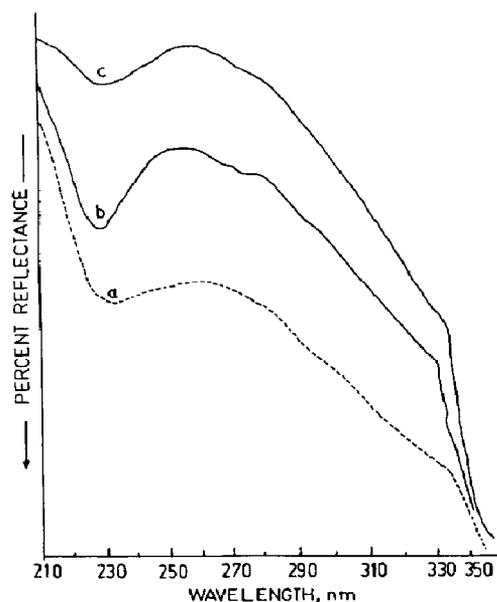

Fig. 1. Diffuse reflectance spectra of the compounds $M_3Zr_2(O_2)_2F_7 \cdot xH_2O$ ($M \equiv K^+$, Rb^+, Cs^+): curve a, $K_3Zr_2(O_2)_2F_7 \cdot 2H_2O$; curve b, $Rb_3Zr_2(O_2)_2F_7 \cdot H_2O$; curve c, $Cs_3Zr_2(O_2)_2F_7 \cdot 2H_2O$.

3. Results

3.1. $Rb_3Zr_2(O_2)_2F_7 \cdot H_2O$

Pressure–time (p–t) and p versus $t^{1/2}$ plots of the photodecomposition of $Rb_3Zr_2(O_2)_2F_7 \cdot H_2O$ at various intensities and constant temperature (25 °C) are presented in Fig. 2. It should be noticed that the rate of photolysis is a linear function of the intensity (Fig. 3). The photolysis was also carried out at various temperatures (5 - 45 °C) and a constant intensity of 21.27 $\times$ 10^{15} quanta s^{-1} cm^{-2}; the p–t and p versus $t^{1/2}$ plots are shown in Fig. 4.
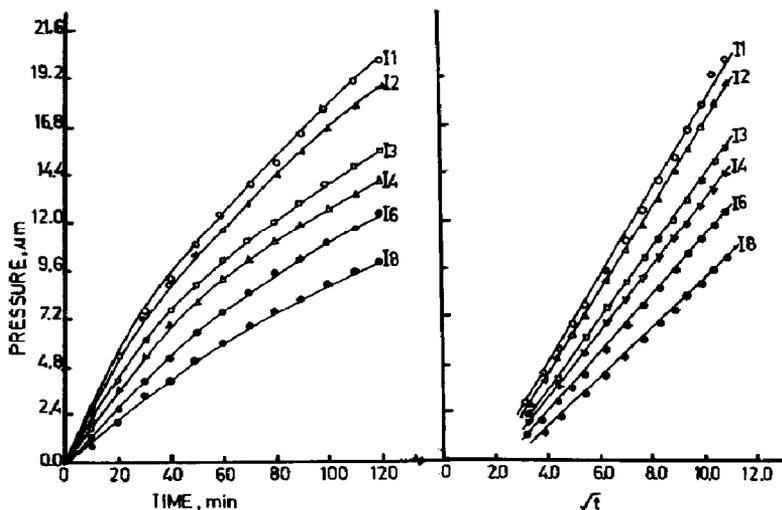
Fig. 2. Photodecomposition of $Rb_3Zr_2(O_2)_2F_7 \cdot H_2O$ at various intensities (quanta s^{-1} cm^{-2}) and a constant temperature of 25 °C: $I_1 = 22.25 \times 10^{15}$; $I_2 = 21.27 \times 10^{15}$; $I_3 = 19.09 \times 10^{15}$; $I_4 = 17.23 \times 10^{15}$; $I_6 = 14.24 \times 10^{15}$; $I_8 = 11.96 \times 10^{15}$.
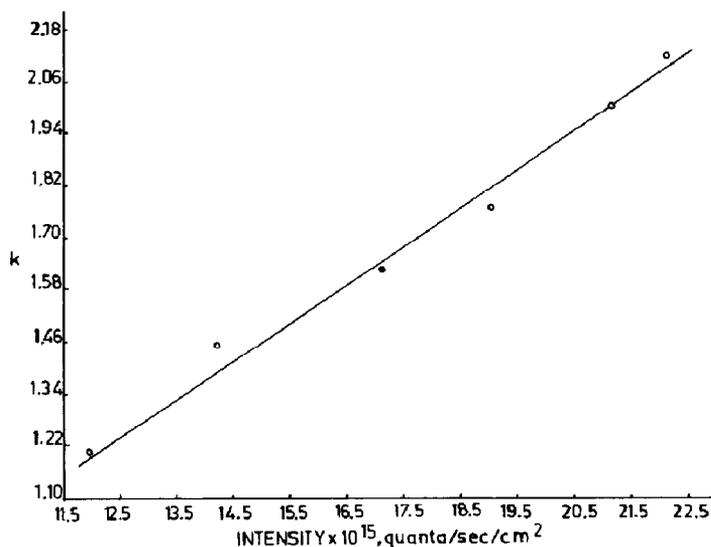

Fig. 3. The dependence of the rate constant k for $Rb_3Zr_2(O_2)_2F_7 \cdot H_2O$ on the intensity.

The activation energy for the process obtained from the Arrhenius plot is 5.4 kJ mol^{-1}.

3.2. $Cs_3Zr_2(O_2)_2F_7 \cdot 2H_2O$

The photodecomposition of $Cs_3Zr_2(O_2)_2F_7 \cdot 2H_2O$ was carried out at various intensities and a constant temperature of 25 °C (Fig. 5) and also at various temperatures (5 - 45 °C) and a constant intensity of 21.27×10^{15} quanta s^{-1} cm^{-2} (Fig. 6). Here again the rate of photolysis was found to be
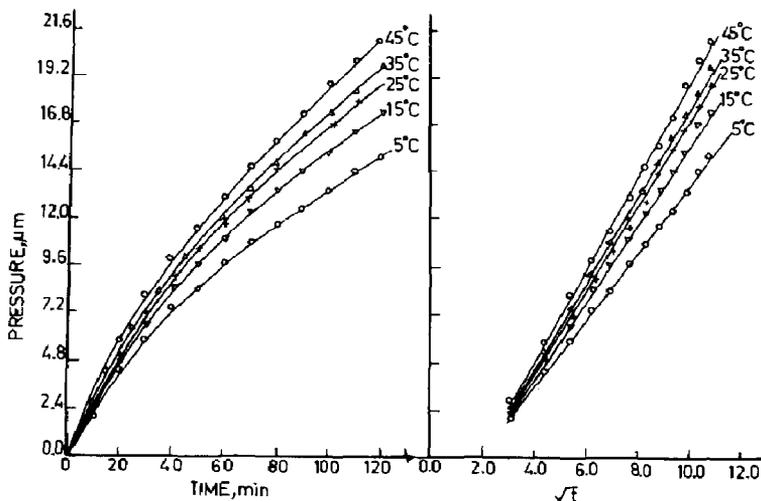
Fig. 4. Photodecomposition of $Rb_3Zr_2(O_2)_2F_7 \cdot H_2O$ at various temperatures and a constant intensity of 21.27×10^{15} quanta s^{-1} cm^{-2}.
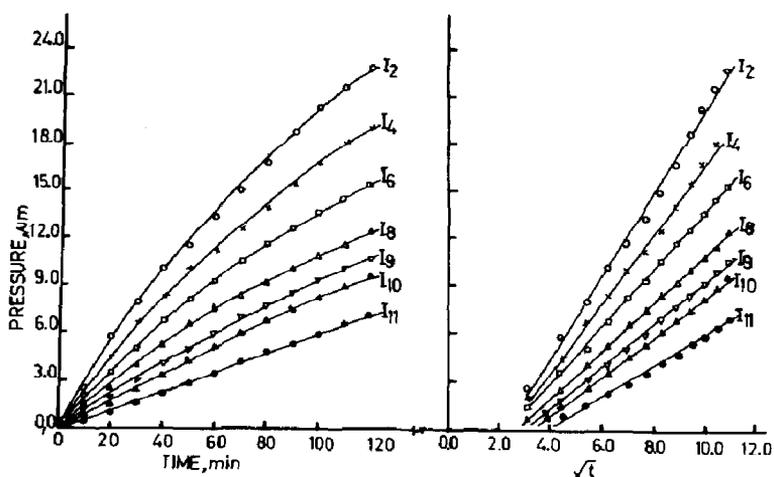
Fig. 5. Photodecomposition of $Cs_3Zr_2(O_2)_2F_7 \cdot 2H_2O$ at various intensities (quanta s^{-1} cm^{-2}) and a constant temperature of 25 °C: $I_2 = 21.27 \times 10^{15}$; $I_4 = 17.23 \times 10^{15}$; $I_6 = 14.24 \times 10^{15}$; $I_8 = 11.96 \times 10^{15}$; $I_9 = 10.19 \times 10^{15}$; $I_{10} = 8.79 \times 10^{15}$; $I_{11} = 6.73 \times 10^{15}$.

linearly dependent on the intensity (Fig. 7). The activation energy for the process is 9.6 kJ mol^{-1}.

4. Discussion

The $p-t$ curves for the photolysis of these compounds are parabolic in nature, i.e. the photolysis kinetics are deceleratory throughout and the maximum rate occurs at the onset of the decomposition reaction. The decrease in the photolysis rate with time may have been caused by the slow consumption of special sites which are present initially and which aid the

Fig. 6. Photodecomposition of $Cs_3Zr_2(O_2)_2F_7 \cdot 2H_2O$ at various temperatures and a constant intensity of 21.27×10^{15} quanta s^{-1} cm^{-2}.
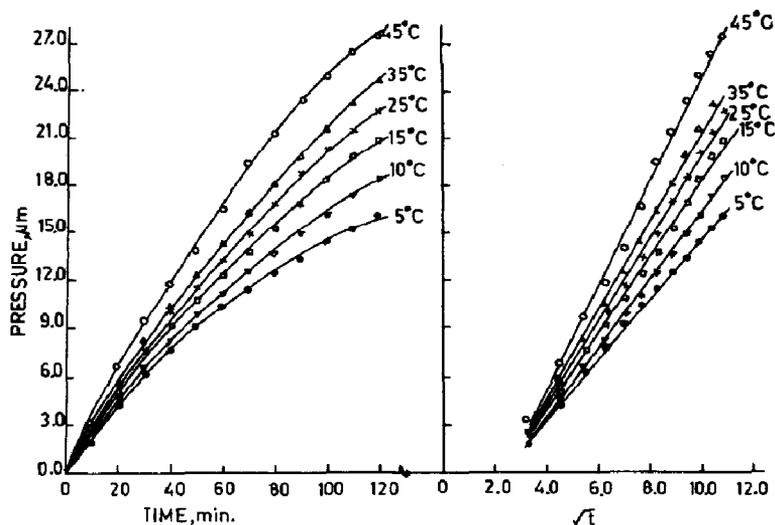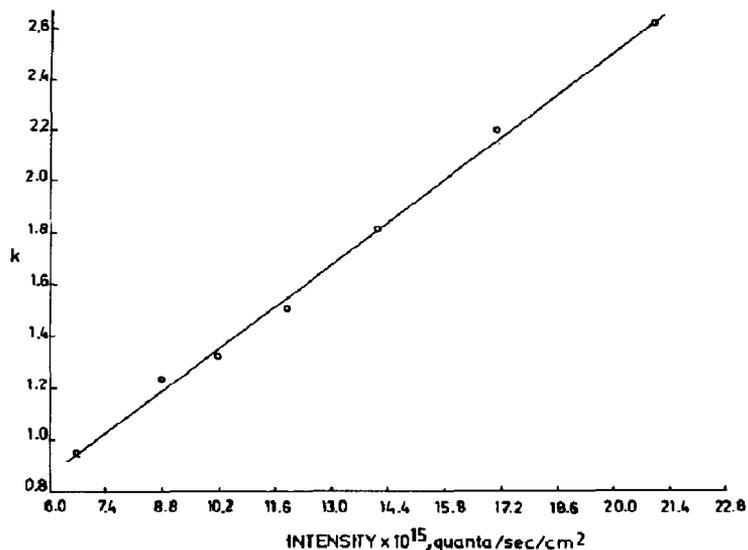

Fig. 7. The dependence of the rate constant k for $Cs_3Zr_2(O_2)_2F_7 \cdot 2H_2O$ on the intensity.

photodecomposition. This viewpoint is not new and the role of solid state defects and electronic processes in the initiation and growth of nuclei in photodecomposition has been extensively discussed by Jacobs and Tompkins [7], Young [8, 9] and Levy and Herley [10, 11]. Further, it is noticed that the kinetic data fit the rate equation $p = kt^{1/2}$ which describes the simple parabolic relationship between the pressure of oxygen evolved from peroxide photolysis and the duration of the irradiation. Similar equations have been employed by Prout and Lownds [12] for the deceleratory mode of the photolysis of potassium permanganate, by Morantz *et al.* [13] for the photolysis of polycrystalline lead bromide and by Yoganarasimhan and Sood

[14] for the photolysis of zinc azide. The rate of photolysis is a linear function of the intensity (Figs. 3 and 7) which indicates that the decomposition involves a monoexcitation process. It is of interest to note that similar features have been observed in the photolysis kinetics of other fluoroperoxozirconates [5, 6].

It may therefore be inferred from the close similarity in the photolysis behaviour of these fluoroperoxozirconates (all six solids) that the photoexcitation process and the subsequent steps leading to the evolution of oxygen appear to be the same in all cases. Unlike thermal activation, photochemical activation is selective in nature [15]. Also it is important to note that the only photoexcitable moiety in these fluoroperoxozirconates is the peroxo group which is linked triangularly to the zirconium and is bidentate in nature [16]:

$$\underset{O}{\overset{O}{\underset{/\,|\,\backslash}{\overset{\backslash\,|\,/}{Zr}}}}$$

Since the photolysis involves a monoexcitation process, it is the interaction of peroxo groups in the excited state at special sites which must account for the evolution of oxygen and the formation of the oxide ion which is retained in the lattice. This may be visualized as

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

$$O_2{}^{2-} + (O_2{}^{2-})^* \rightarrow O_2 + 2O^{2-}$$
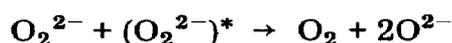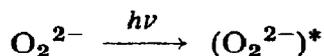
Somewhat similar ideas have been proposed by Poznyak *et al.* [17] for the photolysis of frozen aqueous solutions (77 K) of potassium tetraperoxochromate, which was investigated using electron paramagnetic resonance and optical absorption spectroscopy. As photoconductivity could not be observed in the fluoroperoxozirconates, this interaction might occur through exciton formation [5].

Other interesting and common features noticed in the photochemical decomposition of these fluoroperoxozirconates are now summarized.

(1) The broad absorption band in the range 230 - 280 nm, attributable to the peroxo group, is observed in all these solids.

(2) The absence of a dark rate shows that the entities induced by the photolysis are either relatively stable or decay extremely rapidly, resulting in a thermally stable product.

(3) The lattice-held water remains unaffected and the $p-t$ data are highly reproducible with powdered samples.

(4) No change in colour was observed after photolysis, ruling out the possibility of the reduction of zirconium(IV) to zirconium(III) [5].

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