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# Effect of metal oxide additives on the thermal decomposition kinetics of potassium metaperiodate

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**Abstract** The effect of additives (CuO, $MnO_2$ and $TiO_2$) on the thermal decomposition kinetics of potassium metaperiodate ($KIO_4$) to potassium iodate ($KIO_3$) has been studied in air by thermogravimetry under isothermal conditions. Irrespective of whether p- or n-type, the metal oxides show only a little or no influence on the rate of the decomposition except for the small decrease when the oxide concentration is as high as 10 wt%. The rate law for the decomposition of $KIO_4$ (Prout–Tompkins model) remained unaffected by the additives.

**Keywords** Isothermal decomposition kinetics · $KIO_4$ · Metal oxide additives—CuO, $MnO_2$ and $TiO_2$

## Introduction

Solid state reactions are generally complex since they are very sensitive to the history of the solid. A number of factors associated with mechanical, chemical and radiation treatments are found to influence the reactivity of solids. Reactivity of solids is greatly modified by pre-treatments and the nature of influence of the pre-treatments provides valuable information on the elementary steps and thereby on the mechanism and control of solid-state reactions [1, 2]. Thermogravimetric analysis (TG) has been used to obtain thermal stability parameters of solids [3–6]. The broad objectives of the present investigation are to study the importance of imperfections on the decomposition kinetics of potassium periodate ($KIO_4$), by altering the defect concentrations either by doping or by prior mechanical and/or thermal treatments of the lattice and thereby throw some light on the topochemistry and the decomposition mechanism of solids.

We have reported the effects of pre-treatments on the thermal reactivity of several high-energy solids such as halates and perhalates [7–13] that throw light on the mechanism of their decomposition. Thermal decomposition of halates and perhalates, which occupy an important place in modern solid-state chemistry, is extremely sensitive to the presence of impurities, additives, etc., and more data of this kind are desirable.

According to thermoanalytical studies, $KIO_4$ decomposes in two steps [14, 15]. At about 570 K, $KIO_4$ decomposes with heat evolution to potassium iodate ($KIO_3$) and oxygen. The decomposition of $KIO_3$ to KI takes place in the range 780–800 K. In the thermal decomposition of $KIO_4$ it has not been proved possible to identify the six valent iodine compound, $K_2IO_4$, analogous to the compounds, $M_2IO_4$, formed in the decomposition of lithium and sodium periodates. We have studied the effects of several pre-treatments on the kinetics and mechanism of the thermal decomposition of $KIO_4$. We observed that $KIO_4$ decomposes via Prout–Tompkins mechanism. Our earlier investigations [9, 12] showed that the isothermal decomposition of $KIO_4$ follows Prout–Tompkins kinetics at all temperatures studied and we proposed that the probable rate determining step in the thermal decomposition of $KIO_4$ is the transfer of an electron from the periodate anion to the potassium cation rather than the rupture of I–O bond or the diffusion of cations/anions.

In continuation of our investigations on the thermal behaviour of periodates of alkali metals [8, 9, 12, 13] in this paper we report the effect of metal oxide, such as cupric oxide (CuO), manganese oxide ($MnO_2$) and titanium

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dioxide ($TiO_2$), additives on the isothermal decomposition kinetics of $KIO_4$ to $KIO_3$ at 570 K. CuO is a black solid having molar mass of 79.545 with an ionic structure. It melts above 1474 K with some loss of oxygen. CuO has application as a p-type semiconductor, because it has a narrow band gap of 1.2 eV [16]. $MnO_2$ is a blackish brown solid having molar mass of 86.937. It is stable up to its melting point, 808 K, above which it decomposes. It is used extensively as an oxidizing agent in organic synthesis. The effectiveness of the reagent depends on the method of preparation, a problem that is typical for other heterogeneous reagents where surface area, among other variables, is significant [17]. $MnO_2$ is also used as a catalyst in the laboratory preparation of oxygen from potassium chlorate, a classical experiment of elementary chemistry classes. Manganese dioxide also catalyses the decomposition of hydrogen peroxide to oxygen and water. $TiO_2$ is a white solid having a molar mass of 79.870. It melts at 2143 K and boils at 3245 K. Titanium dioxide is the most widely used white pigment because of its brightness and very high refractive index ($\eta = 2.4$). It is also used as a semi-conductor [18].

## Experimental

All the chemicals used were of AnalaR grade reagents of E Merck. Pure sample of $KIO_4$ was prepared by the method described earlier [12]. Mixtures of $KIO_4$ with oxides such as CuO, $MnO_2$ and $TiO_2$ were prepared with oxide concentrations 0.5, 1, 2, 5 and 10 wt%. The particle size of both the components was fixed in the range 90–106 μ. The thermogravimetric measurements in static air were carried out on a manual thermobalance fabricated in this laboratory [9, 12], the upgraded version of that used by Hooley [19].

The major problem [20] of the isothermal experiment is that a sample requires some time to reach the experimental temperature. During this period of non-isothermal heating, the sample undergoes some transformations that are likely to affect the results of the following kinetic analysis. The situation is especially aggravated by the fact that under isothermal conditions, a typical solid-state process has its maximum reaction rate at the beginning of the transformation. So we fabricated a thermobalance particularly for isothermal studies, in which loading of the sample is possible at anytime after attaining the desired constant temperature. This will avoid the effect of pre-heating, usually observed in common TG instruments. The operational characteristics of the thermobalance are: accuracy; balance: $\pm 1 \times 10^{-5}$ g, temperature: ±0.5 K, sample mass: $5 \times 10^{-2}$ g, particle size: 90–106 μ and crucible: platinum. The fraction of solid decomposed ($\alpha$) was measured as a function of time ($t$) at 570 K for initially mixed metal oxide samples of $KIO_4$ at different concentrations.

## Results and discussion

The $\alpha$–$t$ curves for the decomposition of pure $KIO_4$ and the results of its thermal decomposition kinetics were reported earlier [12]. Similar curves were obtained for all metal oxide mixed samples of $KIO_4$. The $\alpha$–$t$ data were fitted to various solid state kinetic equations available in the literature (Table 1) using the method of weighted least squares as described earlier [9]. In all cases the Prout–Tompkins equation [21], $\ln[\alpha/(1-\alpha)] = kt$, which is the simplest case of an autocatalytic reaction [22], gave the best fits for all metal oxide mixed samples studied. Additives did not change the basic shape (sigmoid) of the $\alpha$–$t$ plots and the decomposition proceeded through the same way as that of pure $KIO_4$ (Figs. 1, 2, 3).

The values of rate constant ($k$) for the thermal decomposition of pure and metal oxide mixed samples of $KIO_4$ are given in Table 2. Surprisingly the metal oxides show a little or no influence on the rate of decomposition except the small decrease of rate when the oxide concentration is as high as 10 wt%. We note that none of these metal oxides alters the reaction model (Prout–Tompkins) of the decomposition process.

Philips and Taylor [23] studied the kinetics of thermal decomposition of $KIO_4$ to $KIO_3$ in vacuum by measuring the pressure of oxygen evolved as a function of time and they observed a four-stage process. The last two stages, which contribute more than 99.9% of the decomposition, were best represented by the Prout–Tompkins and the

**Table 1** Different reaction models used to describe the reaction kinetics

| S1. no. | Reaction model | Function/g(α) |
|---|---|---|
| 1 | Power law | $\alpha^{1/4}$ |
| 2 | Power law | $\alpha^{1/3}$ |
| 3 | Power law | $\alpha^{1/2}$ |
| 4 | Power law | $\alpha^{3/2}$ |
| 5 | One-dimensional diffusion | $\alpha^2$ |
| 6 | Mampel (first order) | $-\ln(1-\alpha)$ |
| 7 | Avrami–Erofeev | $[-\ln(1-\alpha)]^{1/4}$ |
| 8 | Avrami–Erofeev | $[-\ln(1-\alpha)]^{1/3}$ |
| 9 | Avrami–Erofeev | $[-\ln(1-\alpha)]^{1/2}$ |
| 10 | Three-dimensional diffusion | $[1-(1-\alpha)1/3]^2$ |
| 11 | Contracting sphere | $1-(1-\alpha)^{1/3}$ |
| 12 | Contracting cylinder | $1-(1-\alpha)^{1/2}$ |
| 13 | Second order | $(1-\alpha)^{-1}-1$ |
| 14 | Prout–Tompkins | $\ln[\alpha/(1-\alpha)]$ |

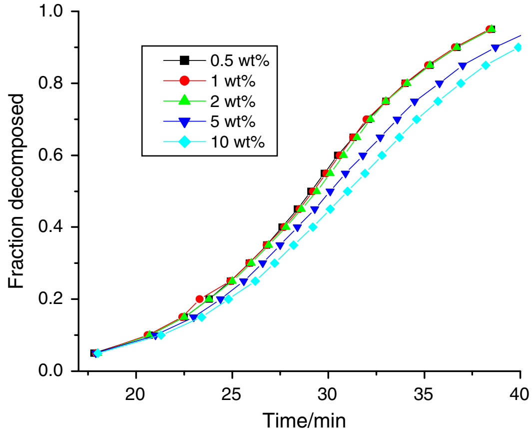

**Fig. 1** $\alpha$–$t$ Curves for the thermal decomposition of CuO mixed $KIO_4$ at 570 K

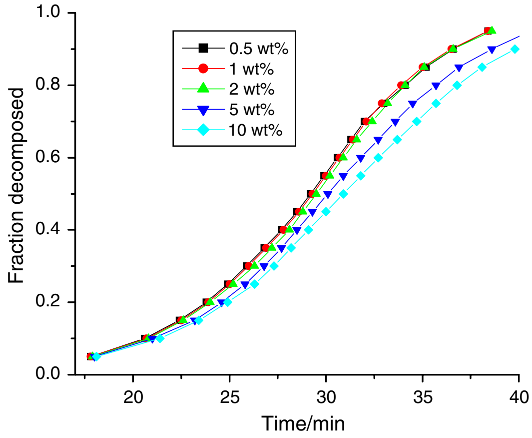

**Fig. 2** $\alpha$–$t$ Curves for the thermal decomposition of $MnO_2$ mixed $KIO_4$ at 570 K

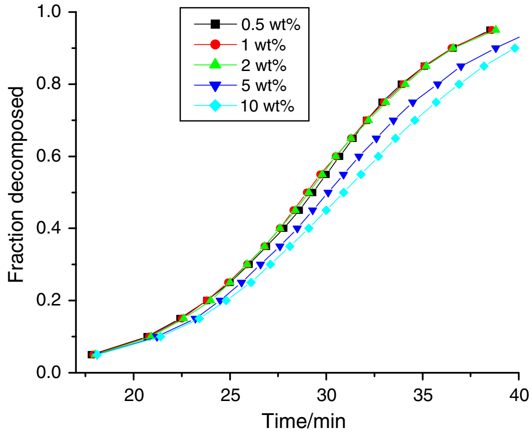

**Fig. 3** $\alpha$–$t$ Curves for the thermal decomposition of $TiO_2$ mixed $KIO_4$ at 570 K

**Table 2** Values of rate constant ($k$) for the thermal decomposition of pure and CuO, $TiO_2$ and $MnO_2$ mixed samples of $KIO_4$ at 570 K

| Oxide | Concentration/wt% | $k \times 10^3/s^{-1}$ |
|---|---|---|
| Nil | 0 | 4.5308 |
| CuO | 0.5 | 4.5311 |
| | 1.0 | 4.5245 |
| | 2.0 | 4.4895 |
| | 5.0 | 4.0818 |
| | 10.0 | 3.8459 |
| $TiO_2$ | 0.5 | 4.5156 |
| | 1.0 | 4.5702 |
| | 2.0 | 4.5520 |
| | 5.0 | 4.1719 |
| | 10.0 | 3.8824 |
| $MnO_2$ | 0.5 | 4.5426 |
| | 1.0 | 4.5603 |
| | 2.0 | 4.5650 |
| | 5.0 | 4.1405 |
| | 10.0 | 3.8468 |

contracting cube equations, respectively with an $E$ value of 191 kJ $mol^{-1}$ for both stages. As the heat of the decomposition process ($\Delta H = -208$ kJ $mol^{-1}$) is almost equal to the above value, they proposed that the rupture of I–O bond determines the rate of the decomposition of $KIO_4$ to $KIO_3$. Our earlier investigations [8, 12] showed that the isothermal decomposition of $KIO_4$ follows Prout–Tompkins kinetics with an $E$ value of 209 kJ $mol^{-1}$. On the light of the results we proposed that the probable step in the thermal decomposition of $KIO_4$ is the transfer of an electron from the periodate anion to the potassium cation rather than the rupture of I–O bond or the diffusion of cations/anions.

Very few studies were reported in the literature on the thermal decomposition of $KIO_4$ in the presence of different additives. Solymosi [24] found that the preliminary mixing of the solid product, $KIO_3$ with $KIO_4$ caused practically no change in the course of the reaction. In both cases the decomposition was found to be autocatalytic, and the rate maximum appeared at about 50% conversion, independent of the temperature. However, substantial increase in the rate was caused by KI and NiO [24] without any essential change in the activation energy values. Furuichi et al. [25] from DTA experiments in static air, found no effect on the decomposition of $KIO_4$ by the addition of $\alpha$-$Al_2O_3$ or $\alpha$-$Fe_2O_3$ to $KIO_4$. The same authors from scanning electron microscopic (SEM) and X-ray studies [26] reported considerable differences in the decomposition behaviour of pure $KIO_4$ and $KIO_4$ mechanically mixed with $\alpha$-$Fe_2O_3$. Rudolf and Freeman [27] found that the p-type oxides ($Cr_2O_3$, $MnO_2$, CuO and NiO) effectively catalyse the decomposition of $KClO_4$. They explained the significance of the p-character of the oxides by the promotion of the electron-transfer process. $MnO_2$ exerts a large catalytic effect on the decomposition of ammonium perchlorate at

508 K [28]. While the decomposition of pure ammonium perchlorate is immeasurably slow below 473 K, in the presence of CuO it already begins at 453 K after an induction period of about 10–15 h. $TiO_2$ was found to be practically inactive in the decomposition of both orthorhombic and cubic ammonium perchlorate.

In this study we have examined the effect of mixing $KIO_4$ with metal oxides such as CuO and $MnO_2$ (p-type semiconductors) and $TiO_2$ (n-type semiconductor). In both CuO and $MnO_2$, the current carriers are holes and have a narrow band gap [16, 17]. On the other hand $TiO_2$ is an electronic semi-conductor in which the current carriers are free electrons [18]. None of these oxides influenced the decomposition of $KIO_4$ (at 570 K) up to a concentration of 2 wt%, above which these oxides desensitized the decomposition rather than catalyzing it. The extent of desensitization has gone up to ca. 15% when the oxide concentration is 10 wt%. The rate law of the decomposition remained unaffected by the additives, which implies that Prout–Tompkins model is still valid.

The influence of a heterophase additive in reactions involving charge transfer may be connected with the electrical properties of the additives. When a metal is placed in contact with a semiconductor a flow of electrons takes place across the boundary as long as there exists a difference between the free energies of the electrons in the two substances. In a similar fashion, when a solid (e.g. $KIO_4$) is placed in contact with a semiconducting additive (e.g. CuO) a contact potential difference arises at the interface between the solid and the additive. This contact potential depends on the work functions of electron from the solid and the additive, and may cause either an increase or decrease in the number of electrons in the contact layer. Semiconducting oxides for which the electron work functions are greater than that of the solid accept electrons from the contact layer and thus catalyse electron-transfer process occurring in the solid, where as additives with smaller electron work functions decelerate the electron transfer process. For instance, the thermolysis of $KMnO_4$, where the transfer of an electron from one $MnO_4^-$ to another to form stable $MnO_4^{2-}$ and unstable $MnO_4^{\bullet}$ is the rate determining step, is catalysed by semi conducting additives, for which the electron work function is greater than that for $KMnO_4$ and decelerated by additives with smaller electron work function [29]. Solymosi et al. [30, 31] have concluded that in the thermal decomposition of ammonium perchlorate, the most effective catalysts are the p-type semiconductors (e.g. CuO, NiO, CoO) while the n-type semiconductors are completely inactive.

In the thermolysis of $KIO_4$ we observed that both p- and n-type oxides, when present in high concentration, decelerate the decomposition. This suggests that the electron work functions of these oxides might be smaller than that of $KIO_4$ so that the oxides lack electron acceptor property with respect to $KIO_4$. Thus the electrons may flow from the oxide to $KIO_4$, which affects the electron transfer reaction adversely. The possibility of chemisorptions of the decomposition product, $O_2$, on the semiconductor surface can also lead to an inhibition of the decomposition process.

## Conclusions

The behaviour of mechanical mixtures of $KIO_4$ with n- and p-type semiconducting oxides suggests that the electron work functions of these oxides might be smaller than that of $KIO_4$ so that they lack electron acceptor property with respect to $KIO_4$ and thus fail to favour electron transfer process. More studies are, however, necessary to draw any correlation between electron work functions of the oxides and their effect on decomposition rate.

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