Effects of dopants on the isothermal decomposition kinetics of potassium metaperiodate

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Abstract

The isothermal decomposition of potassium metaperiodate (KIO_4) has been studied as a function of concentration of the dopants chloride, sulphate and barium, by thermogravimetry (TG) in the temperature range 560–580 K. The decomposition data for both pure and doped KIO_4 were found to be best described by the Prout–Tompkins (PT) equation. As the dopant concentration increases, the rate of decomposition remains unaffected with chloride, increases approximately linearly with sulphate and passes through a maximum with barium. However, doping did not change the activation energy of the reaction. The results favour an electron-transfer mechanism for the decomposition. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Kinetics of solid-state reactions is greatly modified by pre-treatments such as doping, pre-compression, pre-heating, etc. A knowledge of such effects provides a deep insight not only into the topochemistry but also into the mechanism and control of these reactions. With this view, we have taken up a systematic study of the effects of pre-treatments on the thermal behaviour of several technologically important high energy solids such as halates and perhalates, and have reported some results [1–5].

Halates and perhalates occupy an important place in modern solid-state chemistry. One particularly important property of these compounds is their thermal decomposition, which is extremely sensitive to the presence of impurities, additives, etc. Periodates form an important class of compounds of the above type. Relatively little is known of their thermal stability,

particularly in the presence of impurities, and more data of this kind are, therefore, desirable. In continuation of our investigations on the thermal behaviour of periodates of alkali metals [2,3], in this paper, we report the effect of the anion dopants chloride and sulphate, and the cation dopant barium on the isothermal decomposition kinetics of potassium metaperiodate (KIO_4) in the temperature range 560–580 K.

2. Experimental

Only AnalaR or "proanalysi" grade reagents were used. A saturated solution of KIO_4 in distilled water (2.5 g/100 ml) was prepared at 340 K and allowed to attain equilibrium at room temperature. The clear solution was decanted into a crystallizing dish, placed in a hot air oven maintained at 325 ± 2 K and allowed to undergo slow evaporation. The resulting crystals were removed, washed with acetone, dried and ground gently using a mortar and pestle to fix the particle size in the range 150–170 μm. Samples doped at four

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different concentrations, viz., 10^{-4}, 10^{-3}, 10^{-2} and 10^{-1} mol% were prepared by following the above procedure for an aqueous solution containing definite proportions of KIO_4 and dopant. KCl, K_2SO_4 and $BaCl_2 \cdot 2H_2O$ were used for doping Cl^-, SO_4^{2-} and Ba^{2+}, respectively. All the samples were stored over anhydrous calcium chloride in a vacuum desiccator. Like earlier workers [6–8], the actual concentrations of the dopant present were not determined. The concentrations mentioned in this paper refer to the solutions from which they were crystallized.

The thermogravimetric (TG) measurements in static air were carried out on a manual thermobalance which employed a sensitive quartz spring (sensitivity: 36.1 cm g^{-1}). The experimental set-up was similar to that of Hooley [9]. A tubular furnace was used for the purpose of heating. The temperature of the furnace was measured with an accuracy of ± 1 K by using a calibrated chromel–alumel themocouple connected to a Century (INDIA) temperature indicator controller (model CT 806 T) in combination with two variable transformers, a voltmeter and a relay system [10]. An INCO (INDIA) make Cathetometer with a sensitivity of 0.01 mm was used to measure the contraction of the spring balance. The sample size used for each analysis

was 50 mg and the crucible used was of platinum. The fraction of solid decomposed (α) was measured as a function of time (t) at five different temperatures (T), viz., 560, 565, 570, 575 and 580 K. Comparative runs were always made using samples of same age and particle size.

3. Results

The results of the decomposition of pure KIO_4 at different temperatures are presented in Fig. 1(A) in the form of α–t curves. The decomposition proceeds through three stages: (i) an initial rapid evolution of gas up to $\alpha \cong 0.006$, followed by an induction period, (ii) an acceleratory period up to $\alpha = 0.50$, and (iii) the final decay stage. The initial gas evolution is so rapid that it was not possible to determine the kinetics and energetics of the process.

The α–t data in the range $\alpha = 0.05$–0.95 (range I) were fitted to various solid-state kinetic equations using the method of weighted least squares as described earlier [3]. The Prout–Tompkins (PT) equation [11], $\ln[\alpha/(1-\alpha)] = kt$, which is the simplest case of the description of an autocatalytic reaction [12], gave the best fits at all the temperatures studied. We
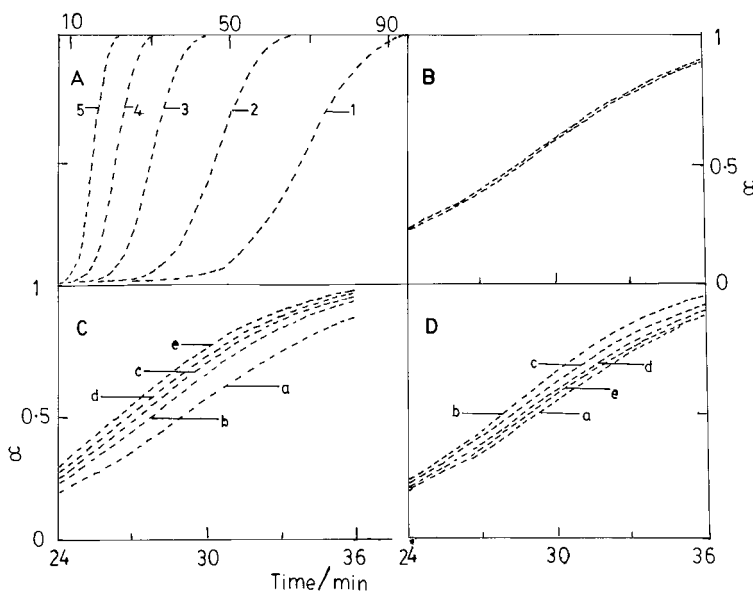

Fig. 1. Typical α–t plots for the thermal decomposition of (A) pure KIO_4 at five temperatures (1.560, 2.565, 3.570, 4.575 and 5.580 K), (B) Cl^-, (C) SO_4^{2-} and (D) Ba^{2+} doped KIO_4 at 570 K. Dopant concentrations (mol%) — a: Nil; b: 10^{-4}; c: 10^{-3}; d: 10^{-2}; e: 10^{-1}. In B curves a, b, c, d and e overlap in between the lines shown.

have also fitted the α–t data corresponding to the acceleratory region ($\alpha=0.05$–0.50; range II) and decay region ($\alpha=0.50$–0.95; range III) separately to the kinetic equations and found that the acceleratory stage gave the best fit with PT equation itself whereas the decay stage fitted better to the contracting square (CS) equation [13].

The decomposition of chloride-, sulphate- and barium-doped samples of KIO_4 was also studied in the temperature range 560–580 K and typical α–t curves (at 570 K) are shown in Fig. 1(B)–(D). Doping did not change the basic shape (sigmoid) of the α–t plots and the decomposition proceeded through the three stages mentioned in the case of pure KIO_4 obeying the same rate laws mentioned above for different ranges of decomposition.

The values of rate constants (k) at various temperatures for different ranges of the decomposition of pure and doped samples of KIO_4 (calculated by the method of weighted least squares) are given in Tables 1–3. The results show that the rate of decomposition is enhanced by the anion dopant sulphate, while the rate was unaffected by chloride. The cation dopant barium behaves differently from the anion dopant in that the rate passes through a maximum as the concentration increases. Fig. 2 illuminates these effects.

Table 1

Values of rate constant (k) for the whole range (I: $\alpha=0.05$–0.95), acceleratory stage (II: $\alpha=0.05$–0.50) and decay stage (III: $\alpha=0.50$–0.95) of the decomposition of pure and chloride doped KIO_4 at different temperatures

Temperature (K)	Dopant concentration (mol%)	$k\times10^3$ $(s^{-1})^a$		
		I	II	III
560	0	2.0924	1.8726	0.4220
	10^{-1}	2.0481	1.9120	0.4217
	10^{-2}	2.0524	1.9299	0.4219
565	0	2.9309	2.7498	0.6058
	10^{-4}	2.8128	2.5794	0.6008
	10^{-2}	2.8329	2.6466	0.5950
570	0	4.5308	4.4097	0.8609
	10^{-4}	4.3443	4.1295	0.8708
	10^{-3}	4.3625	4.3173	0.8292
	10^{-2}	4.4146	4.2116	0.8831
	10^{-1}	4.5201	4.3411	0.8535
575	0	6.6256	6.5701	1.2026
	10^{-4}	6.6940	6.1561	1.2761
	10^{-2}	6.6919	6.7042	1.1536
580	0	9.3259	9.3882	1.6968
	10^{-4}	9.9974	9.9965	1.7600
	10^{-2}	9.9583	10.8536	1.6082

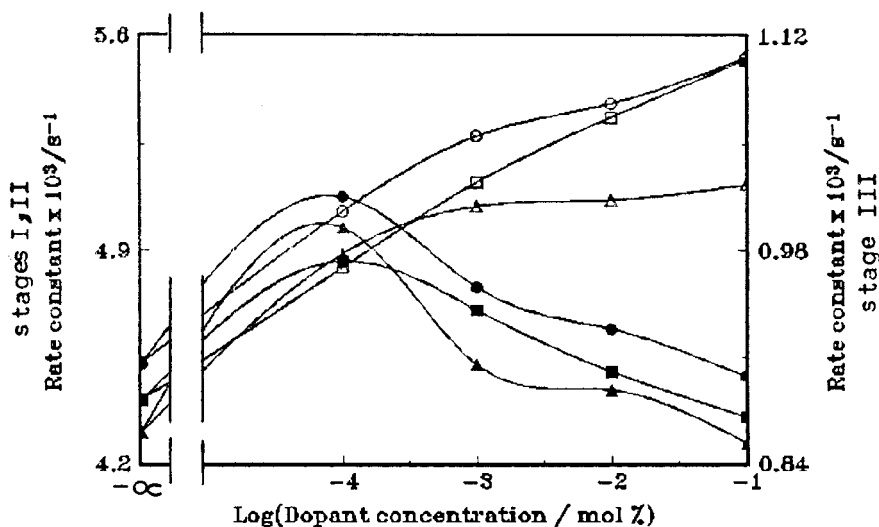^{a} Calculated from the best fitting equations, viz., PT for ranges I and II, and CS equation for range III.

Fig. 2. Plots of rate constant versus dopant concentration for the thermal decomposition of SO_4^{2-} doped KIO_4 at 570 K. Whole range (I) ($\bigcirc$), acceleratory stage (II) ($\square$), deceleratory stage (III) ($\triangle$). Solid symbols correspond to Ba^{2+} doped samples.

Table 2

Values of rate constant (k) for the whole range (I: α=0.05–0.95), acceleratory stage (II: α=0.05–0.50) and decay stage (III: α=0.50–0.95) of the decomposition of pure and sulphate doped KIO_4 at different temperatures

Temperature (K)	Dopant concentration (mol%)	$k \times 10^3$ (s^{-1})[a]		
		I	II	III
560	0	2.0924	1.8726	0.4220
	10^{-4}	2.1946	2.0543	0.4484
	10^{-3}	2.2770	2.1427	0.4582
	10^{-2}	2.3376	2.2176	0.4649
	10^{-1}	2.3839	2.2828	0.4691
565	0	2.9309	2.7498	0.6058
	10^{-4}	3. 1925	2.9180	0.6755
	10^{-3}	3.3593	3.1188	0.6933
	10^{-2}	3.4391	3.2042	0.7100
	10^{-1}	3.5393	3.3193	0.7242
570	0	4.5308	4.4097	0.8609
	10^{-4}	5.0292	4.8440	0.9778
	10^{-3}	5.2734	5.1243	1.0094
	10^{-2}	5.3804	5.3340	1.0134
	10^{-1}	5.5300	5.5235	1.0237
575	0	6.6256	6.5701	1.2026
	10^{-4}	6.9557	6.7923	1.3372
	10^{-3}	7.3448	7.2449	1.3813
	10^{-2}	7.5761	7.5532	1.4116
	10^{-1}	7.5493	7.9643	1.3192
580	0	9.3259	9.3882	1.6968
	10^{-4}	11.3140	10.8750	2.1794
	10^{-3}	11.7560	11.5360	2.2906
	10^{-2}	12.0550	11.7530	2.3455
	10^{-1}	12.4150	12.1880	2.3918

[a] Calculated from the best fitting equations, viz., PT for ranges I and II, and CS for range III.

Table 3

Values of rate constant (k) for the whole range (I: α=0.05–0.95), acceleratory stage (II: α=0.05–0.50) and decay stage (III: α=0.50–0.95) of the decomposition of pure and barium doped KIO_4 at different temperatures

Temperature (K)	Dopant concentration (mol%)	$k \times 10^3$ (s^{-1})[a]		
		I	II	III
560	0	2.0924	1.8726	0.4220
	10^{-4}	2.2094	2.0521	0.4501
	10^{-3}	2.1065	1.9539	0.4393
	10^{-2}	2.0691	1.9108	0.4306
	10^{-1}	2.0439	1.8716	0.4213
565	0	2.9309	2.7498	0.6058
	10^{-4}	3.2071	2.9472	0.6721
	10^{-3}	2.7935	2.5028	06290
	10^{-2}	2.7021	2.4279	0.6009
	10^{-1}	2.9341	2.7480	0.6082
570	0	4.5308	4.4097	0.8609
	10^{-4}	5.0771	4.8649	0.9951
	10^{-3}	4.7795	4.7055	0.9056
	10^{-2}	4.6431	4.5049	0.8887
	10^{-1}	4.4878	4.3555	0.8538
575	0	6.6256	6.5701	1.2026
	10^{-4}	7.1090	6.5911	1.3234
	10^{-3}	6.7352	6.7571	1.2410
	10^{-2}	6.5536	6.4221	1.2123
	10^{-1}	6.7271	6.4762	1.2296
580	0	9.3259	9.3882	1.6968
	10^{-4}	11.3420	10.6224	2.2734
	10^{-3}	10.3496	10.6224	1.8385
	10^{-2}	9.9343	10.6224	1.6495
	10^{-1}	10.3957	10.5748	1.8579

[a] Calculated from the best fitting equations, viz., PT for ranges I and II, and CS for range III.

Using the rate constant–temperature data for pure and doped samples (Tables 1–3), the values of activation energy (E), and pre-exponential factor (A) were calculated from the Arrhenius plots by the method of weighted least squares and are given in Table 4. The table also includes the values of correlation coefficient (r). We note that none of these dopants alters the activation energy of the decomposition process.

4. Discussion

4.1. Decomposition of pure KIO_4

The kinetics of thermal decomposition of KIO_4 to KIO_3 in vacuum was studied by Phillips and Taylor [14] by measuring the pressure of oxygen evolved as a function of time and they observed a four stage process. The initial two stages were very small amounting only to α=0.006. The third stage which was acceleratory in character, proceeded up to α=0.50 and was then followed by the final decay stage. They observed that the last two stages were best represented by the PT and the contracting cube equations, respectively, with an E value of 191 kJ mol^{-1} for both these stages. Since the E values agreed closely with the heat of the process,

$$KIO_4 \rightarrow KIO_3 + O, \quad \Delta H = -208 \, \text{kJ mol}^{-1}$$
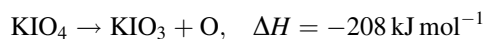
they suggested that the primary chemical act (i.e., the

Table 4
Values of activation energy (E), pre-exponential factor (A) and correlation coefficient (r) of the Arrhenius plots for the thermal decomposition of pure and chloride-, sulphate- and barium-doped KIO_4[a]

Dopant	Dopant concentration (mol%)	E (kJ mol^{-1})			$\ln A$ (s^{-1})			$-r$		
		Range I	Range II	Range III	Range I	Range II	Range III	Range I	Range II	Range III
Nil	0	209.01	221.35	187.54	38.69	41.26	32.51	0.9998	0.9997	1.0005
Cl^-	10^{-4}	218.21	225.70	195.20	40.62	42.15	34.15	0.9988	0.9971	1.0001
	10^{-2}	217.17	238.79	180.55	40.41	44.54	31.02	0.9991	0.9972	0.9992
SO_4^{2-}	10^{-4}	219.34	225.93	207.79	40.97	42.28	36.92	0.9987	0.9986	0.9980
	10^{-3}	219.72	227.59	211.23	41.09	42.71	37.67	0.9993	0.9991	0.9978
	10^{-2}	219.97	226.67	212.06	41.18	42.55	37.86	0.9974	0.9991	0.9976
	10^{-1}	219.30	228.42	208.42	41.05	42.96	37.10	0.9984	0.9993	0.9916
Ba^{2+}	10^{-4}	219.85	221.23	212.02	41.08	41.31	37.81	0.9991	0.9981	0.9965
	10^{-3}	219.54	221.23	191.48	40.96	41.31	33.39	0.9968	0.9981	0.9999
	10^{-2}	217.46	237.92	183.23	40.47	44.75	31.60	0.9963	0.9932	0.9998
	10^{-1}	220.64	233.49	198.42	41.16	43.83	34.83	0.9997	0.9993	0.9995

[a] Range I: $\alpha=0.05$–0.95; Range II: $\alpha=0.05$–0.50; Range III: $\alpha=0.50$–0.95.

rate determining step) in the decomposition is the rupture of I–O bond. They also pointed out that the autocatalytic stage does not involve a diffusion chain proposed by Hill [15]. No other kinetic studies on KIO_4 are available in the literature.

In the present investigation, we found that the PT equation gave the best fit for the overall decomposition ($\alpha=0.05$–0.95) at all the temperatures studied, with an E value of 209 kJ mol^{-1}. The acceleratory and decay stages were also analysed separately. Although the acceleratory period was best described by PT equation itself with an E value of 221 kJ mol^{-1}, the decay stage was best represented by contracting area equation with an E value of 188 kJ mol^{-1} (Table 4). This suggests that up to $\alpha=0.50$, the solid decomposes according to PT model involving nucleation, branching and termination of nuclei. However, when the extent of decomposition exceeds 50%, the process of branching becomes insignificant and the kinetics is governed by the movement of the interface, which has developed well by this time, in two dimensions towards the interior of the solid with a deceleratory rate. Since in the decay region the interface advances in a two-dimensional manner, it is likely that in the acceleratory region too the nuclei grow in plate-like form. Thus, we suggest that KIO_4 decomposes in accordance with PT model with two-dimensional nucleus growth up to 50% decomposition, and further decomposition proceeds according to contracting area law.

Such a description of reaction kinetics using different rate laws for different ranges of α is not unusual in solid-state reactions. For instance, as mentioned above, Phillips and Taylor [14] used PT equation to describe the acceleratory region of the decomposition of KIO_4 (as we did) and the contracting cube equation for the decay stage. The acceleratory stage in the decomposition of lithium perchlorate [16] followed PT rate law, whereas the decay stage followed the monomolecular model. Similarly, both the acceleratory and decay regions of the decomposition of sodium perchlorate [17,18] and of potassium bromate [19] were well described by the PT relation with separate rate constants.

4.2. On the mechanism of the decomposition

Thermal decomposition reactions can be broadly classified into two groups [20]. The first group includes reactions in which the chemical bond is broken as a result of localized process and the second group covers reactions in which charges are transferred in the crystal lattice by the movement of electrons, protons or the lattice forming cations or anions. Thus, the possible rate-controlling steps in the thermal decomposition of KIO_4 are the following:

1. Thermal breakdown of the periodate anion by the rupture of the I–O bond.

2. Electron-transfer from the periodate anion to the potassium cation.
3. Migration of cation and/or anion through the lattice.

A bond breaking mechanism was suggested by Phillips and Taylor [14] for the decomposition of this solid, based on the agreement between the dissociation energy of I–O bond and the experimental activation energy. However, more evidence is essential to rule out the other two possibilities. Effects of pre-treatments can provide useful information in identifying the most probable mechanism.

The rate law and the activation energy of the decomposition remain unaltered by doping (see Tables 1–4). This suggests that the basic mechanism of the decomposition is not affected by doping, the only effect being a modification in the concentration of active sites.

Being monovalent like IO_4^-, doping KIO_4 with chloride does not cause any change in the concentration of anion/cation vacancies and thus this impurity can influence the decomposition of KIO_4 only through its size difference. The present results (see Fig. 2) show that the rate is not significantly affected by chloride impurity; similar results were reported for chloride doped barium azide [8].

The cation and anion vacancies and in Frenkel systems the associated interstitial ions and also the lattice impurities alter the frequency of the lattice vibrations in the region surrounding these defect centres. This contributes substantially in weakening the chemical bonds in the vicinity of the defects and thus increases reactivity of the solid. Therefore, on doping KIO_4 with either cation or anion will result in an increase in the rate of the thermal decomposition if the rupture of I–O bond determines the rate. SO_4^{2-} and Ba^{2+} doped KIO_4 samples do show an enhanced rate of decomposition, but only up to a dopant concentration of 10^{-4} mol% in the case of Ba^{2+} (see Fig. 2). At higher concentrations of Ba^{2+}, the rate decreases without a change in the activation energy, which suggests the operation of the same mechanism in the low as well as high dopant-concentration range. This fact cannot be easily explained in terms of the bond breaking mechanism.

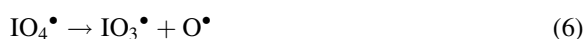A diffusion-controlled mechanism also appears to be unlikely on the following grounds. By virtue of its smaller size, the diffusion of K^+ through the ionic lattice is more probable than the diffusion of periodate anion. In a Schottky system, the diffusion of cations is enhanced by an increase in the number of cation vacancies, whereas in a Frenkel system, the diffusion is enhanced by an increase in the number of interstitial cations. If KIO_4 belongs to Schottky system, then a decrease in the concentration of cation vacancies would be caused by the dopant SO_4^{2-}, whereas an increase would be caused by Ba^{2+}. On the other hand, if KIO_4 has Frenkel structure, SO_4^{2-} would cause an increase, whereas Ba^{2+} a decrease, in the concentration of interstitial potassium ions. Thus, whatever be the defect structure of KIO_4, the dopants SO_4^{2-} and Ba^{2+} are expected to cause opposite effects on the thermal decomposition of KIO_4 if diffusion of K^+ ions determines the rate. In case the IO_4^- ions were the diffusing species, then also a similar opposite effect would be expected. Our present results (see Fig. 2) are contrary to this expectation suggesting that a diffusion-controlled mechanism is unlikely. This conclusion is supported by the observation that the rate of decomposition of KIO_4 was enhanced significantly on pre-compression (results not included here). A decrease in the rate is expected on pre-compression if ionic diffusion determines the rate [5].

The next possibility to be considered is an electron-transfer mechanism. The mechanism may be represented as follows:

$$K^+IO_4^- \rightarrow K^\bullet + IO_4^\bullet \quad \text{(electron-transfer)} \quad (1)$$

$$IO_4^\bullet \rightarrow IO_3^\bullet + O^\bullet \quad (2)$$

$$O^\bullet + O^\bullet \rightarrow O_2 \quad (3)$$

$$K^\bullet + IO_3^\bullet \rightarrow KIO_3 \quad (4)$$

Step (1) involves the transfer of an electron from the periodate anion to the potassium cation to form the free radicals $K^\bullet$ and $IO_4^\bullet$. As $IO_4^\bullet$ involves a one electron bond, it is very unstable and readily decomposes to give $O^\bullet$ and relatively stable $IO_3^\bullet$ [step (2)]. Two $O^\bullet$ species combine to give one oxygen molecule [step (3)]. In step (4), $IO_3^\bullet$ is stabilized by receiving an electron from $K^\bullet$ forming KIO_3. In the above scheme steps (2)–(4) are fast since they involve highly reactive species. The electron-transfer process, step (1), is the slowest and plays an important role in determining the rate. The present results support this mechanism as can be seen below.

Doping KIO_4 with sulphate introduces additional anion vacancies in the solid (charge balance requirement). Anion vacancies can capture electrons and thus function as electron traps (T) because of the localization of positive charge in their neighbourhood [3,7]. An anion vacancy traps an electron from the neighbouring periodate anion to produce $IO_4^{\bullet}$ which decomposes to $IO_3^{\bullet}$ and $O^{\bullet}$. The trapped electron is then transferred to K^+ to produce $K^{\bullet}$ which combines with $IO_3^{\bullet}$ to form KIO_3:

$$IO_4^- + T \rightarrow IO_4^{\bullet} \, Te \tag{5}$$

$$IO_4^{\bullet} \rightarrow IO_3^{\bullet} + O^{\bullet} \tag{6}$$

$$Te + K^+ \rightarrow K^{\bullet} + T \tag{7}$$

$$K^{\bullet} + IO_3^{\bullet} \rightarrow KIO_3 \tag{8}$$

Thus the anion vacancy acts as a bridge between the periodate anion and potassium cation facilitating the electron-transfer. When concentration of the dopant ion increases, the number of anion vacancies (i.e., T) also increases. Consequently, the rate of formation and growth of nuclei are promoted resulting in an enhanced rate of decomposition in proportion to the dopant level (Fig. 2).

Incorporation of Ba^{2+} into KIO_4 lattice generates cation vacancies and this results in a decrease in the number of anion vacancies. Thus, in the event of the validity of the electron-transfer mechanism, one would expect a continuous decrease in the rate on doping KIO_4 with Ba^{2+}. But the rate of decomposition is found to vary in a complex manner; the rate first increases reaching a maximum value around 10^{-4} mol% and then falls on further increase in the dopant level (Fig. 2). Since the activation energy of the decomposition remains unaffected by doping, it is not possible to visualize the reaction to take place via one mechanism at low dopant concentration (when the rate is elevated) and via another mechanism at high dopant concentration (when the rate is depressed). The situation can be resolved by considering the polarizing action of cation, Ba^{2+}. The polarizing power of a cation is proportional to Ze/R^2, where Z is its valency, R its radius and e the electronic charge. The high Z and small R values make the polarizing power of Ba^{2+} very high (ca. 11 times that of K^+). As anions are readily polarizable due to their diminished control of electron cloud by the nucleus, it is easy for Ba^{2+} to strongly polarize the periodate anion and even capture an electron from it. In other words, Ba^{2+} itself acts as an electron trap and promotes the decomposition according to the above scheme [steps (5)–(8)] where T stands for Ba^{2+} and Te for Ba^+. Thus, doping with Ba^{2+} results in two concurrent effects, viz. (i) enhancement of electron-transfer rate by the action of Ba^{2+} as electron traps, and (ii) suppression of the rate due to a decrease in the number of anion vacancies which are good electron traps. The enhancing effect predominates at low concentrations of Ba^{2+}, whereas suppression takes upper hand at high concentrations possibly because of the association of the positively charged Ba^{2+} with negatively charged cation vacancies ($\oplus$) and the consequent lowering of the effectiveness of the impurity ion as an electron trap. The situation may be represented as

$$Ba^{2+} + \oplus \rightleftharpoons \{Ba^{2+} \; \oplus\} \tag{9}$$
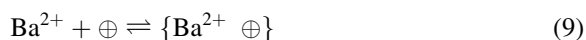
With respect to the normal occupancy of lattice sites, Ba^{2+} has a charge of $+1$ and $\oplus$ has -1, and hence the pair $\{Ba^{2+} \oplus\}$ is neutral. The dopant Ba^{2+} is thus rendered ineffective as electron trap by the association of the defects, and consequently, the inhibiting effect (due to the decrease in the concentration of anion vacancies) predominates. This type of electrostatic interaction of defects is more probable at high concentrations of the Ba^{2+} impurity and the cation vacancies, due to the high probability of occurrence of these defects in proximity to each other within the solid. This results in a steady decrease in the rate of decomposition as the concentration of Ba^{2+} increases, as is observed in this investigation (Fig. 2).

A similar association between SO_4^{2-} dopant and anion vacancies is not possible because interstitial diffusion of sulphate is unlikely due to its larger size. For the same reason, vacancy diffusion of SO_4^{2-} is also insignificant. It may be further noted that, because of the better proximity, the interaction of a cation dopant occupying an interstitial site with a cation vacancy, is stronger than the interaction of an anion dopant occupying a normal lattice site, with an anion vacancy. This means that deactivation of anion vacancies by their association with anion dopants is not significant in anion doped samples and therefore these samples show a normal increase in rate with dopant concentration.

We see from the above discussion that doping influences the rate of decomposition of KIO_4 greatly and in a complex manner, without, however, affecting the activation energy of the decomposition. Both the direction and magnitude of the rate are strongly dependent on the dopant concentration.

As found previously [1,4], this study emphasizes that extreme care should be taken in interpreting the effect of a dopant for elucidating the mechanism of decomposition.

Acknowledgements

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