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KINETICS OF THERMAL DECOMPOSITION OF SULPHATE-DOPED POTASSIUM METAPERIODATE

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ABSTRACT

The effect of sulphate dopant on the thermal decomposition kinetics of potassium metaperiodate (KIO_4) has been studied by isothermal thermogravimetric analysis in the temperature range 580–600 K. Doping enhances the decomposition rate and the effect increases linearly with increasing dopant concentration. The decomposition process was found to the best described by the Prout–Tompkins equation. The activation energies (E) for pure and 1×10^{-4}, 1×10^{-3}, 1×10^{-2} and 1×10^{-1} mol% sulphate-doped KIO_4 are, respectively, 239.7, 229.2, 218.4, 212.5 and 209.5 kJ mol^{-1}. Doping did not affect the E values significantly.

INTRODUCTION

Halogen oxyacids and their salts occupy an important place in modern solid-state chemistry. One particularly interesting property of these types of compounds is their decomposition which is extremely sensitive to the presence of impurities, additives, etc. Periodates are an important class of compounds of the above type. Although a considerable amount of work has been reported on different solid systems, no detailed work appears to have been published on the thermal decomposition kinetics of periodates.

As part of our investigations on the thermal behaviour of periodates of alkali metals [1], in this paper we report the isothermal decomposition kinetics of pure and 1×10^{-4}, 1×10^{-3}, 1×10^{-2} and 1×10^{-1} mol% sulphate-doped potassium metaperiodate (KIO_4) in the temperature range 580–600 K, where the samples decompose at a measurable rate.

EXPERIMENTAL

Only AnalaR or "proanalysi" grade reagents were used. A saturated solution of KIO_4 in distilled water was prepared at 340 K and allowed to

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attain equilibrium at room temperature. The clear liquid was decanted into a crystallising dish, placed in a hot air oven maintained at 325 K and allowed to undergo slow evaporation over a period of days. The resulting crystals were dried and the particle size was fixed in the range 200–240 BSS mesh. Doped samples were prepared by following the above procedure for an aqueous solution containing definite proportions of KIO_4 and K_2SO_4. As in earlier papers [2–4], the actual concentration of the dopant present was not determined. The concentrations mentioned in this paper refer to the solutions from which they were crystallised. All samples were stored over anhydrous calcium chloride in a vacuum desiccator.

The thermogravimetric (TG) measurements in static air were carried out on a manual thermobalance with employed a sensitive quartz spring (sensitivity, 36.1 cm g^{-1}). The experimental set-up was similar to that of Hooley [5]. The sample size was 50 mg and the crucible used was of platinum. The temperatures were measured using a calibrated chromel–alumel thermocouple connected to a Century (India) temperature-indicator controller (model CT 806T) with an accuracy of $\pm 0.5°$.

The numerical analyses of the TG data were achieved using a program written in Microsoft BASIC for an IBM computer using DOS 4.00.

THEORETICAL

The integrated form of the kinetic equation for isothermal decompositions can be written

$$g(\alpha) = kt \tag{1}$$

where α is the fraction decomposed at time t, $g(\alpha)$ is the function of α dependent on the mechanism of decomposition and k is the rate constant. The least squares method (LSM) can be applied to eqn. (1) for selecting the best form of $g(\alpha)$ and thus the best value of k. But it has been shown [6] that the relationship of the form

$$g(\alpha) = kt + b \tag{2}$$

where b is an adjustable parameter, is more appropriate for the selection of $g(\alpha)$ by the LSM.

The usual LSM assumes constant variation of the dependent variable, in our case $g(\alpha)$. This assumption fails when the $g(\alpha)$ contains a logarithmic term, because using a logarithmic function tends to compress the high values while expanding the low values. This defect can be remedied by using weighted LSM. Several authors [6–8] have reported that the best fit of their experimental and calculated data was obtained using weighted LSM. The weights used most often are the inverse of the deviation of the dependent variable [9]. It has been shown [6] that the deviation, S_α^2 of the variable α is equal to $1 + \alpha^2$. Transforming α into $g(\alpha)$, one should also correspondingly transform S_α^2 into $S_{g(\alpha)}^2$. The deviation of $g(\alpha)$ is calculated from the transformed formula

$$S_{g(\alpha)}^2 = S_\alpha^2 \left(\frac{g(\alpha)}{\partial \alpha} \right)^2 \tag{3}$$

and the following is used as weights (w) for the calculation of correlation coefficient (r) and slope

$$w = 1/S_{g(\alpha)}^2 \tag{4}$$

From the literature [10,11], it can be found, however, that r alone is not a good criterion for selecting the proper $g(\alpha)$ function. Rozycki and Maciejewski [6] have shown that the criterion involving the conformity of α_{exp} (the experimental value of α at time t) and α_{calc} (value of α at time t calculated on the basis of the equation $g(\alpha) = kt + b$) can be used successfully for the selection of the $g(\alpha)$ function best describing the experimental data, and they used the following expression for this purpose

$$R = \frac{1}{n} \sum_{i=1}^{n} \left(\alpha_{\text{calc},i} - \alpha_{\text{exp},i}\right)^2 \tag{5}$$

where n is the number of experimental values. According to the above authors, the $g(\alpha)$ function best describing the experimental data will be the one for which the value of R is minimum. In this paper we have used the values of both r and R to select the proper $g(\alpha)$ function.

RESULTS AND DISCUSSION

The results of the isothermal decomposition of pure and doped KIO_4 are presented in Figs. 1 and 2. Doping does not change the basic shape (sigmoid) of the α–t plots. The decomposition proceeds mainly through three stages: an initial gas evolution upto $\alpha \approx 0.01$; an acceleratory period upto $\alpha = 0.5$; and 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 (from $\alpha = 0.1$ to 0.9) for the pure and doped samples were fitted to various solid-state kinetic equations and the values of r and R were computed using weighted LSM. The various functions, $g(\alpha)$, and weights, w, employed for this purpose are given in Table 1. We have computed the values of r and R for these functions at five different temperatures (580, 585, 590, 595 and 600 K) for the pure and all of the doped samples. The values of r and R for pure and two doped (1×10^{-3} and 1×10^{-1} mol% K_2SO_4) samples at 590 K are given in Table 2. Similar results were obtained for all the other doped samples and temperatures. The Prout–Tompkins

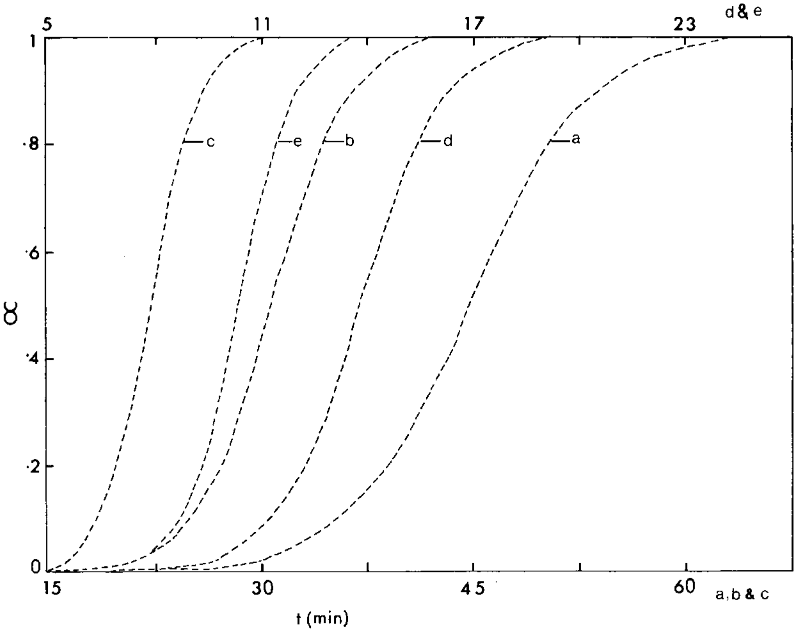

Fig. 1. $\alpha - t$ plots for the thermal decomposition of pure KIO_4 at: a, 580; b, 585; c, 590; d, 595; and e, 600 K.

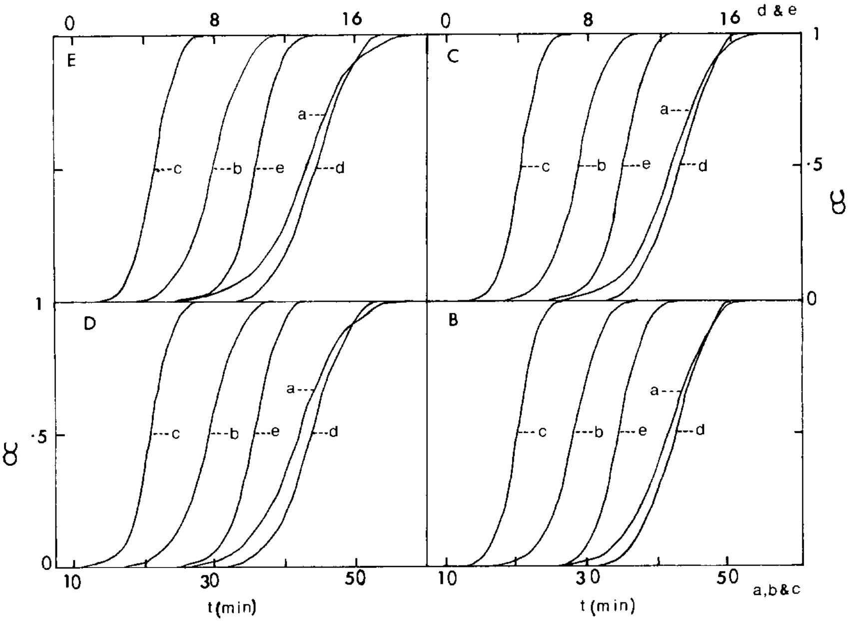

Fig. 2. $\alpha - t$ plots for the thermal decomposition of sulphate-doped KIO_4 at: a, 580; b, 585; c, 590; d, 595; and e, 600 K: $B = 1 \times 10^{-1}$, $C = 1 \times 10^{-2}$, $D = 1 \times 10^{-3}$ and $E = 1 \times 10^{-4}$ mol% sulphate-doped KIO_4.

TABLE 1

Kinetic functions and weights used in the present paper

Function number	Function $[g(\alpha)]$	Mechanism	$w(1+\alpha^2)$
1	$\alpha^{1/2}$	Power law	4α
2	$\alpha^{1/3}$	Power law	$9\alpha^{4/3}$
3	$\alpha^{1/4}$	Power law	$16\alpha^{3/2}$
4	$-\ln(1-\alpha)$	First-order	$(1-\alpha)^2$
5	$1/(1-\alpha)-1$	Second-order	$(1-\alpha)^4$
6	α^2	One-dimensional diffusion	$1/4\alpha^2$
7	$(1-\alpha)\ln(1-\alpha)+\alpha$	Two-dimensional diffusion	$[-\ln(1-\alpha)]^{-2}$
8	$[1-(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion (Jander eqn.)	$9(1-\alpha)^{4/3}/4[1-(1-\alpha)^{1/3}]^2$
9	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	Three-dimensional diffusion (Ginstling and Brounstein eqn.)	$[3(1-\alpha)^{-1/3}-1]^2/4$
10	$1-(1-\alpha)^{1/2}$	Contracting area	$4(1-\alpha)$
11	$1-(1-\alpha)^{1/3}$	Contracting volume	$9(1-\alpha)^{4/3}$
12	$[-\ln(1-\alpha)]^{1/1.5}$	Avrami–Erofeev	$9(1-\alpha)^2[-\ln(1-\alpha)]^{2/3}/4$
13	$[-\ln(1-\alpha)]^{1/2}$	Avrami–Erofeev	$4(1-\alpha)^2[-\ln(1-\alpha)]$
14	$[-\ln(1-\alpha)]^{1/3}$	Avrami–Erofeev	$\{3(1-\alpha)[-\ln(1-\alpha)]^{-2/3}\}^2$
15	$[-\ln(1-\alpha)]^{1/4}$	Avrami–Erofeev	$16(1-\alpha)^2[-\ln(1-\alpha)]^{3/2}$
16	$\ln[\alpha/(1-\alpha)]$	Prout–Tompkins	$[\alpha(1-\alpha)]^2$

equation [12], $\ln(\alpha/1-\alpha)=kt$, which is the simplest case of the description of an autocatalytic reaction where the reaction velocity is a function of both the amount of the reactant and the product [13], gave the best fits, i.e. maximum r value and minimum R value, for both pure and all the doped samples at all temperatures studied. Accordingly, the values of the rate constant k at different temperatures were evaluated for these samples using weighted LSM and are listed in Table 3 along with the corresponding values of r and R. The activation energies (E) obtained from the Arrhenius plots (Fig. 3) for pure and 1×10^{-4}, 1×10^{-3}, 1×10^{-2} and 1×10^{-1} mol% sulphate-doped KIO_4 are, respectively, 239.7, 229.2, 218.4, 212.5 and 209.5 kJ mol^{-1}.

It can be seen that the decomposition rate increases with an increase in the dopant concentration. However, the activation energy of the process was not significantly changed by doping. This implies that doping does not affect the basic mechanism of the decomposition.

TABLE 2

Values of R and r computed for various solid-state kinetic functions for pure and 1×10^{-3} and 1×10^{-1} mol% sulphate-doped KIO_4 at 590 K

Function number	Pure KIO_4		KIO_4 doped with 1×10^{-3} mol% K_2SO_4		KIO_4 doped with 1×10^{-1} mol% K_2SO_4	
	R	r	R	r	R	r
1	1.7210×10^{-3}	0.9844	1.8103×10^{-3}	0.9833	1.6752×10^{-3}	0.9847
2	2.5097×10^{-3}	0.9748	2.6104×10^{-3}	0.9735	2.4549×10^{-3}	0.9753
3	2.9545×10^{-3}	0.9692	3.0588×10^{-3}	0.9678	2.8937×10^{-3}	0.9697
4	5.2717×10^{-3}	0.9450	5.1863×10^{-3}	0.9449	5.1124×10^{-3}	0.9466
5	1.6623×10^{-2}	0.8716	1.6588×10^{-2}	0.8700	1.6315×10^{-2}	0.8735
6	8.9514×10^{-3}	0.9054	8.8662×10^{-3}	0.9057	1.6843×10^{-3}	0.9080
7	1.1021×10^{-2}	0.8391	1.2104×10^{-2}	0.8390	1.1965×10^{-2}	0.8424
8	2.6569×10^{-2}	0.7746	2.6521×10^{-2}	0.7741	2.6015×10^{-2}	0.7783
9	2.4865×10^{-2}	0.9559	2.5104×10^{-2}	0.9574	2.5086×10^{-2}	0.9561
10	1.7143×10^{-15}	0.9791	1.7143×10^{-15}	0.9794	1.7143×10^{-15}	0.9802
11	2.7660×10^{-3}	0.9690	2.6995×10^{-3}	0.9692	2.6552×10^{-3}	0.9702
12	3.0702×10^{-2}	0.9832	3.0710×10^{-2}	0.9835	3.0652×10^{-2}	0.9841
13	8.9249×10^{-2}	0.9941	8.9309×10^{-2}	0.9943	8.9325×10^{-2}	0.9946
14	2.0242×10^{-1}	0.9991	2.0257×10^{-1}	0.9989	2.0260×10^{-1}	0.9993
15	2.6539×10^{-1}	0.9994	2.6551×10^{-1}	0.9990	2.6551×10^{-1}	0.9995
16	4.5248×10^{-6}	0.9999	1.4166×10^{-5}	0.9998	1.7637×10^{-6}	0.9999

Mechanism of decomposition

In the temperature range studied, the products of the decomposition of pure and doped KIO_4 as determined by chemical and IR analyses are iodate and oxygen

$$2KIO_4 \rightarrow 2KIO_3 + O_2 \tag{6}$$

The weight loss data also agree very well with the above equation. The rate-determining step in reaction (6) may be one or more of the following steps

$$K^+ + IO_4^- \rightarrow K^{\bullet} + IO_4^{\bullet} \text{ (electron transfer)} \tag{7}$$

$$IO_4^{\bullet} \rightarrow IO_3^{\bullet} + O^{\bullet} \tag{8}$$

$$K^{\bullet} + IO_3^{\bullet} \rightarrow KIO_3 \tag{9}$$

$$O^{\bullet} + O^{\bullet} \rightarrow O_2 \text{ (diffusion)} \tag{10}$$

The free radical reactions (8) and (9) may be assumed to be very fast so that they may not be controlling the rates. As the present data do not fit any of the diffusion equations (7–10 in Table 1), it seems unlikely that the diffusion of the product gas (oxygen) is the rate-determining step. Thus, the most probable step controlling the rate of decomposition of KIO_4 is the transfer

TABLE 3

Rate constants and the corresponding values of R and r at different temperatures

Sample no. [a]	Parameter	580 K	585 K	590 K	595 K	600 K
I	$k(s^{-1})$	4.0616×10^{-3}	6.3821×10^{-3}	9.7821×10^{-3}	1.4633×10^{-2}	2.1873×10^{-2}
	R	5.8873×10^{-6}	6.8583×10^{-6}	4.5248×10^{-6}	1.1401×10^{-5}	3.4166×10^{-5}
	r	0.9999	0.9999	0.9999	0.9998	0.9995
II	$k(s^{-1})$	4.9043×10^{-3}	7.3169×10^{-3}	1.0617×10^{-2}	1.5718×10^{-2}	2.3280×10^{-2}
	R	4.7488×10^{-6}	1.1401×10^{-5}	5.3696×10^{-6}	9.6422×10^{-6}	8.2641×10^{-6}
	r	0.9999	0.9998	0.9999	0.9998	0.9999
III	$k(s^{-1})$	5.2787×10^{-3}	7.6899×10^{-3}	1.1557×10^{-2}	1.6177×10^{-2}	2.3253×10^{-2}
	R	4.0886×10^{-6}	3.9136×10^{-6}	1.4166×10^{-5}	6.2222×10^{-6}	7.2420×10^{-6}
	r	0.9999	0.9999	0.9998	0.9999	0.9999
IV	$k(s^{-1})$	5.4787×10^{-3}	8.0397×10^{-3}	1.1527×10^{-2}	1.6788×10^{-2}	2.3614×10^{-2}
	R	1.9800×10^{-6}	4.6356×10^{-6}	6.1715×10^{-6}	5.1994×10^{-6}	1.7325×10^{-5}
	r	0.9999	0.9999	0.9999	0.9999	0.9996
V	$k(s^{-1})$	5.6400×10^{-3}	8.3066×10^{-3}	1.1909×10^{-2}	1.6838×10^{-2}	2.3923×10^{-2}
	R	5.1524×10^{-6}	1.0051×10^{-6}	1.7637×10^{-6}	4.0396×10^{-6}	7.7000×10^{-6}
	r	0.9999	0.9999	0.9999	0.9999	0.9999

[a] I = pure KIO_4, and II, III, IV and V are, respectively KIO_4, doped with 1×10^{-4}, 1×10^{-3}, 1×10^{-2} and 1×10^{-1} mol% K_2SO_4.

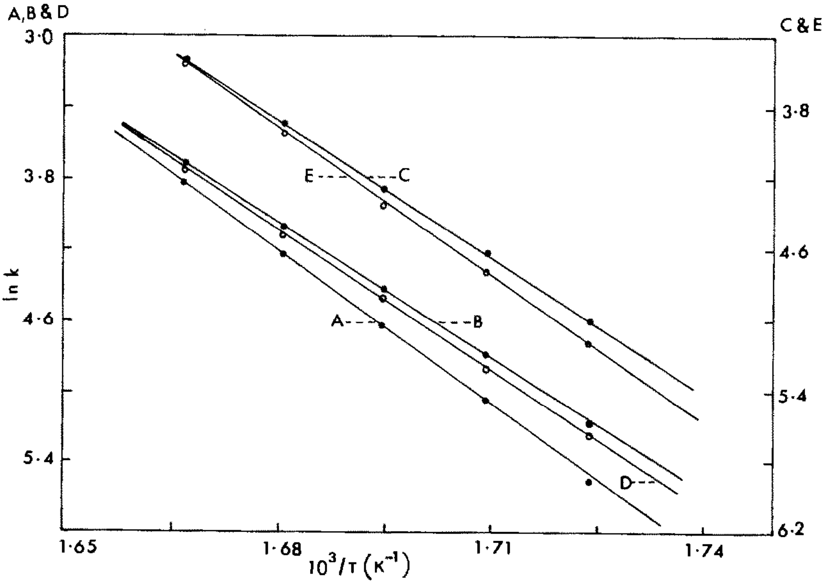

Fig. 3. Arrhenius plots for: A, pure KIO_4; B, 1×10^{-1}; C, 1×10^{-2}; D, 1×10^{-3}; and E, 1×10^{-4} mol% sulphate-doped KIO_4.

of an electron from IO_4^- to K^+ leading to the growth of nuclei via Prout–Tompkins kinetics, which visualise the nuclei as linear branching chains. Doping KIO_4 with SO_4^{2-} introduces additional anion vacancies in the solid (charge balance requirement). Anion vacancies are known to act as electron traps [2] and, hence, can act as potential nucleus-forming sites in electron transfer processes. This appears to be the reason for the observed enhancement in the rate of decomposition of doped KIO_4, in amount proportional to the dopant level.

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